UGCHE-103

Physical Chemistry-I

(Basic Physical Chemistry)

Uttar Pradesh Rajarshi Tandon
Open University

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BLOCK

1

PHYSICAL CHEMISTRY-I

NMDC-183

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Note: Symbols $^{\alpha}$ = Block-1 (Unit-01,02 and 03) and $^{\beta}$ = Block-2 (Unit-04,05 and 06)

ISBN :

Printed and Published by Dr. Arun Kumar Gupta Registrar, Uttar Pradesh Rajarshi Tandon Open University, 2021.

Printed By : K.C.Printing & Allied Works, Panchwati, Mathura -281003.

Unit : 1 MATHEMATICAL CONCEPTS AND COMPUTERS

Structure

INTRODUCTION

In this unit we discussed the Mathematical concepts and Computers. In first section Mathematical concepts we learn Logarithmic relations, Curve sketching, linear graphs and calculation of slopes; Differentiation of functions like f(x), ex, xn, sin x, log x; maxima and minima, Partial; Differentiation and reciprocity relations; Integration of some useful/relevant functions; Permutations and combinations and Factorials, Probability and Recreations. Were as in section Computers we learn General introduction to computers; Different components of a computer, hardware and software; Computer languages and Programming, operating systems; Use and application of different software in the Chemistry.

Objective

After studying this unit learner may be able to:

- Define elementary mathematic and methods for application in solving various studies of chemistry.
- General introduction to computers.
- Different components of a computer, hardware and software.
- Computer languages and Programming, operating systems
- Use and application of different software in the Chemistry

1.1 (A) MATHEMATICAL CONCEPTS

1.1.1 Logarithmic relations

Logarithms are the "opposite" of exponentials, just as subtraction is the opposite of addition and division is the opposite of multiplication. Logs "undo" exponentials. Technically speaking, logs are the inverses of exponentials

$y = b^x$ ....is equivalent to.............. $\log_b(y) = x$
(means the exact same thing as)

On the left-hand side above is the exponential statement "y = bx". On the right-hand side above, "logb(y)

Simply says **Logarithm**: If a is a positive real number, other than 1 and a^m = X, then we write:

$\mathbf{m = \log_a x}$ and we say that the value of log x to the base a is m.

Example:

(i) $10^3 = 1000 \Rightarrow \log_{10} 1000 = 3$

(ii) $2^{-3} = 1/8 \Rightarrow \log_2 1/8 = -3$

(iii) $3^4 = 81 \Rightarrow \log_3 81 = 4$

(iv) $(.1)^2 = .01 \Rightarrow \log_{(.1)} .01 = 2$.

II. Properties of Logarithms:

1. $\log_a(xy) = \log_a x + \log_a y$

2. $\log_a (x/y) = \log_a x - \log_a y$

3. $\log_x x=1$

4. $\log_a 1 = 0$

5. $\log_a(x^p)=p(\log_a x)$ 1

6. $\log_a x =1/\log_x a$

7. $\log_a x = \log_b x/\log_b a=\log\_x/\log a$.

Remember: When base is not mentioned, it is taken as 10.

I. **Common Logarithms:**

Logarithms to the base 10 are known as common logarithms.

II. The logarithm of a number contains two parts, namely *characteristic* and *mantissa.*

Characteristic: The integral part of the logarithm of a number is called its ***characteristic.***

Case I: When the number is greater than 1.

In this case, the characteristic is one less than the number of digits in the left of the decimal point in the given number.

Case II: When the number is less than 1.

In this case, the characteristic is one more than the number of zeros between the decimal point and the first significant digit of the number and it is negative.

Instead of - 1, - 2, etc. we write, $\bar{1}$ (one bar), $\bar{2}$ (two bar), etc.

Example:

Number	***Characteristic***	***Number***	***Characteristic***
348.25	2	0.6173	$\bar{1}$
46.583	1	0.03125	$\bar{2}$
9.2193	0	0.00125	$\bar{3}$

Mantissa: The decimal part of the logarithm of a number is known is its ***mantissa.*** For mantissa, we look through log table.

Solved Examples

1. Evaluate:

(1) $\mathbf{log}_3 27$

(2) $\mathbf{log}_7 (1/343)$

(3) $\mathbf{log}_{100(0.01)}$

SOLUTION:

(1) let $\log_{3} 27=3^{3}$ or n=3.

ie, $\log_{3} 27 = 3$.

(2) Let $\log_{7} (1\backslash 343) = n$.

Then ,$7^{n} =1/343$

$=1/7^{3}$

n = -3.

ie, $\log_{7}(1\backslash 343)= -3$.

(3) let $\log_{100}(0.01) = n$.

Then,. (100) = 0.01 = 1 /100=100^{-1} 0r n=-1

EX.2. Evaluate

(i) $\log_{7} 1=0$ (ii)$\log_{34} 34$ (iii)$36^{\log_{6} 4}$

solution:

i) we know that $\log_{a} 1=0$,so $\log_{7} 1=0$.

ii) we know that $\log_{a} a=1$,so $\log_{34} 34=0$.

iii) We know that $a^{\log_{6} x} =x$.

. now $36^{\log_{6} 4}=(6^{2})^{\log_{6} 4} =6^{\log_{6}(16)=16.}$

Ex.3. If $\log_{\sqrt{8}} x=3 (1/3)$, find the value of x.

$\log_{\sqrt{8}} x=10/3$,$x=(\sqrt{8})^{10/3}=(2^{3/2})^{10/3}=2^{(3/2*10/3)}=2^{5}=32$.

Ex.4: Evaluate: (i) $\log_{5}3*\log_{27} 25$ (ii) log 27 $-\log_{27} 9$

(i)$\log_{5}^{3} * \log_{27} 25$=(log 3/log 5)*(log 25/log 27)

=(log 3/log 5)*(log 5^{2}*log3^{3})

=(log 3/log 5)*(2log5/3log3)

=2/3

(ii)Let $\log_{9}27=n$

Then,

$9^{n} =27 \Leftrightarrow 3^{2n} =3^{3} \Leftrightarrow 2n=3 \Leftrightarrow n=3/2$

Again, let $\log_{27}9=m$

Then,

$27^{m} =9 \Leftrightarrow 3^{3m} =3^{2} \Leftrightarrow 3m=2 \Leftrightarrow m=2/3$

$\Rightarrow$ $\log_{9}27- \log_{27}9=(n-m)=(3/2-2/3)=5/6$

These are the things you should know from this lesson so far:

- The Relationship: "$log_b(x) = y$" means the same thing as "$b^y = x$".
- Logarithms are really exponents (powers); they're just written differently.
- $log_b(b) = 1$, for any base b, because $b^1 = b$.
- $log_b(1) = 0$, for any base b, because $b^0 = 1$.
- $log_b(a)$ is undefined if a is negative.
- $log_b(0)$ is undefined for any base b.
- $log_b(b^n) = n$, for any base b.

It is even possible that the "*ln*" notation is a mistake: A European mathematician once proposed abbreviating "*log*" as "*lg*" and then using a script "*l*" for the function, with, effectively, a little squiggle afterwards which was meant to indicate a subscripted italic "*g*". But in the graphic I've seen, the "*g*" looks much more like an "*n*". Some of the other proposed notations for the natural logarithm were even odder.

A logarithm can have any positive value as its base, but two log bases are more useful than the others. The base-10, or "common", log is popular for historical reasons, and is usually written as "$log(x)$". For instance, pH (the measure of a substance's acidity or alkalinity), decibels (the measure of sound intensity), and the Richter scale (the measure of earthquake intensity) all involve base-10 logs. If a log has no base written, you should generally (in algebra classes) assume that the base is 10.

1.1.2 CURVE SKETCHING, LINEAR GRAPHS AND CALCULATION OF SLOPES

Line-Graphs

This section comprises of question in which the data collected in a particular discipline are represented by specific points together by straight lines. The points are plotted on a two-dimensional plane taking one parameter on the horizontal axis and the other on the vertical axis. The candidate is required to analyse the given information and thereafter answer the given questions on the basis of the analysis of data.

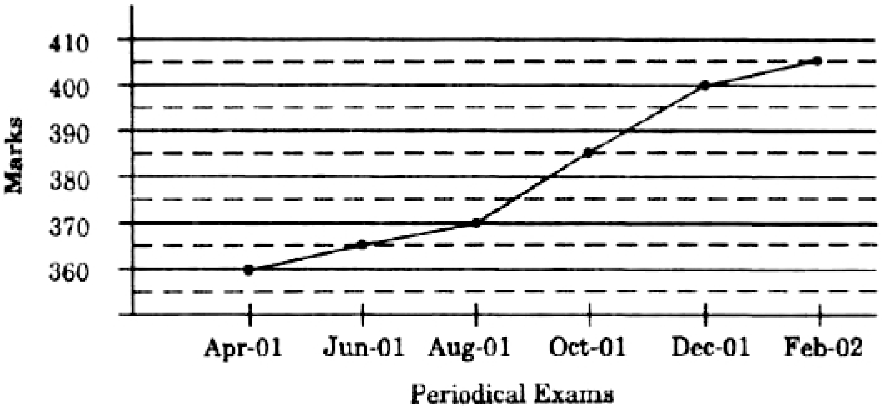
Solved Examples

Ex. 1. In a school the periodical examination are held every second month. In a session during Apr. 2001 – Mar. 2002, a student of Class IX appeared for each of the periodical exams. The aggregate marks obtained by him in each periodical exam are represented in the line-graph given below. Study the graph and answer the questions based on it.

Marks Obtained By A Student In Six Periodical Exams Held In

EVERY TWO MONTHS DURING THE YEAR IN THE SESSION 2001-02

Maximum Total Marks In each Periodical Exam = 500



1. **The total number of marks obtained in Feb. 02 is what percent of the total marks obtained in Apr. 01?**

   (a) 110% (b) 112.5% (c) 115% (d) 116.5% (e) 117.5%

2. **What are the average marks obtained by the student in all the periodical exams of during the session.**

   (a) 373 (b) 379 (c) 381 (d) 385 (e) 389

3. **what is the percentage of marks obtained by the student in the periodical exams of Aug. 01 and Oct. 01 taken together?**

   (a) 73.25% (b) 75.5% (c) 77% (d) 78.75% (e) 79.5%

4. **In which periodical exams there is a fall in percentage of marks as compared to the previous periodical exams?**

   (a) None (b) Jun. 01 (c) Oct. 01 (d) Feb. 01 (e) None of these

5. **In which periodical exams did the student obtain the highest percentage increase in marks over the previous periodical exams?**

   (a) Jun. 01 (b) Aug. 01 (c) Oct. 01 (d) Dec. 01 (e) Feb. 02

Sol. Here it is clear from the graph that the student obtained 360, 365, 370, 385, 400 and 405 marks in periodical exams held in Apr. 01, Jun. 01, Aug. 01, Oct. 01, Dec. 01 and Feb. 02 respectively.

1. (b) : Required percentage = [(405/360)*100] % = 112.5 %

2. (c) : Average marks obtained in all the periodical exams.

= (1/6)*[360+370+385+400+404] = 380.83 ≈ 381.

3. (d) : Required percentage = [(370+385)/(500+500) * 100] % = [(755/1000)*100]% =75.5%

4. (a) : As is clear from graph, the total marks obtained in periodical exams, go on increasing. Since, the maximum marks for all the periodical exams are same , it implies that the percentage of marks also goes on increasing. Thus, in none of the periodical exams, there is a fall in percentage of marks compared to the previous exam.

5. (c) : Percentage increases in marks in various periodical exams compared to the previous exams are:

For **Jun. 01** = [(365-360)/360 * 100] % = 1.39 %

For **Aug. 01** = [(370-365)/365 * 100] % = 1.37 %

For **Oct. 01** = [(385-370)/370 * 100] % = 4.05%

For **Dec. 01** = [(400-385)/385 * 100] % = 3.90 %

For **Feb. 02** = [(405-400)/400 * 100] % = 1.25 %

BAR GRAPHS

This section comprises of questions in which the data collected in a particular discipline are represented in the form of vertical or horizontal bars drawn by selecting a particular scale.one of the parameters is plotted on the horizontal axis and the other on the vertical axis . the candidate is required to understand the given information and thereafetr answer the given questions on the basis of data analysis.

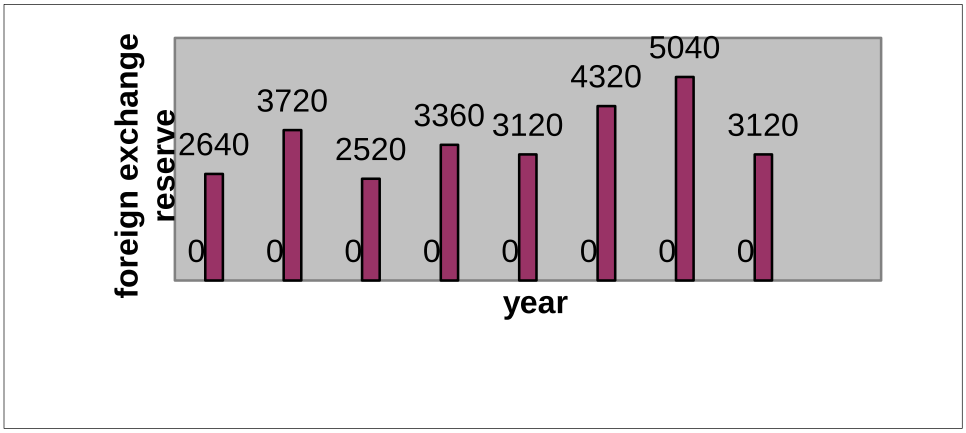
1. The bar graph given below shows the foreign exchange reserves of a country

(in million us$)

from 1991-92 to 1998-99 .answer the questions based on this graph.

FOREIGN EXCHANGE RESERVES OF A COUNTRY

(IN MILLION US $)



1. **The foreign exchange reserves in 1997-98 was how ,any times that in 1994-95?**

   (a) 0.7 (b) 1.2 (c) 1.4 (d) 1.5 (e) 1.8

2. **What was the percentage increase in the foreign exchange reserves in 1997-98 over 1993-94?**

   (a) 100 (b) 150 (c) 200 (d) 620 (e) 2520

3. **For which year,the percent increase of foreign exchange reserves over the previous year,is the highest?**

   (a) 1992-93 (b)1993-94 (c)1994-95 (d)1996-97

   (e) 1997-98

4. **The foreign exchange reserves in 1996-97 werw approximately what percent of the average foreign exchange reserves over the period under review?**

   (a) 95% (b) 110% (c) 115% (d) 125% (e)140%

5. **The ratio of the number of years,in which the foreign exchange reserves are above the average reserves ,to those in which the reserves are below the average reserves is :**

   (a) 2:6 (b)3:4 (c)3:5 (d)4:4 (e)5:3

Solutions

1 (d) : required ratio = 5040/3360 = 1.5

2 (a) : foreign exchange reserve in 1997-98=5040 million us $

foreign exchange reserves in 1993-94=2520 million us$

therefore increase=(5040-2520)=2520 million us $

therefore percentage increase=((2520/2520)*100)%=100%

3 (a) : there is an increase in foreign exchange reserves during the years 1992- 93,1994-951996-97,1997-98 as compared to previous year (as shown by bar graph)

the percentage increase in reserves during these years compared to previous year are

(1) for 1992-93 =[(3720-2640)/2640*100]% =40.91%

(2) for 1994-95=[(3360-2520)/2520*100]%=33.33%

(3) for 1996-97=[(4320-3120)/3120*100]%=38.46%

(4) for 1997-98=[(5040-4320)/4320*100]%=16.67%

Clearly, the percentage increase over previous year is highest for 1992-93.

4. (d) : Average foreign exchange reserves over the given period

= [_x (2640 + 3720 + 2520 + 3360 + 3120 + 4320 + 5040 + 3120)] million US $

= 3480 million US $.

Foreign exchange reserves in 1996-97 = 4320 million US $. . .

Required Percentage = x 100 % = 124.14% .. 125%.

3480 .

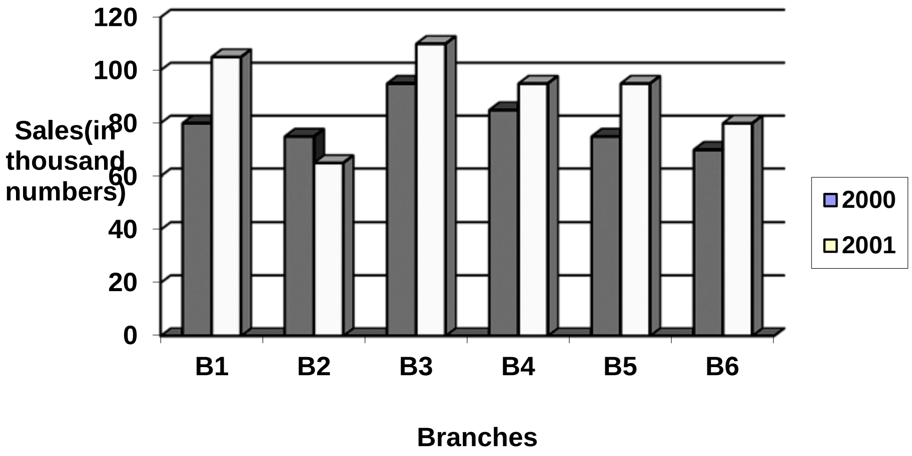
5. *(c)* : Average foreign exchange reserves over the given period = 3480 million US $.

The country had reserves above 3480 million US $ during the years 1992-93, 1996-97 and 1997-98 *i.e.*, for 3 years and below 3480 million US $ during the years 1991-92, 1993-94, 1994-95, 1995-96 and 1998-99 *i.e.*, for 5 years.

Hence, required ratio = 3 : 5.

Ex. 2. The bar-graph provided on next page gives the sales of books (in thousand numbers) from six branches of a publishing company during two consecutive years 2000 and 2001. Answer the questions based on this bar-graph:

Sales of books (in thousand numbers) from six branches-B1,B2,B3,B4,B5 and B6 of a publishing company in 2000 and 2001



1. **Total sales of branches b1,b3 and b5 together for both the years (in thousand numbers) is:**

   (a)250 (b) 310 (c) 435 (d)560 (e)585

2. **Total sales of branch b6 for both the years is what percent of the total sales of branch b3 for both the years?**

   (a) 68.54% (b)71.11% (c) 73.17% (d)75.55% (e)77.26%

3. **What is the average sale of all the branches (in thousand numbers) for the year 2000?**

   (a)73 (b)80 (c)83 (d)88 (e)96

4. **What is the ratio of the total sales of branch b2 for both years to the total sales of branch b4 for both years ?**

   (a)2:3 (b)3:5 (c)4:5 (d)5:7 (e)7:9

5. **What percent of the average sales of branchesn b1,b2 and b3 in 2001 is the average sales of branches b1,b3 and b6 in 2000?**

   (a)75% (b)77.5% (c)82.5% (d)85% (e)87.5%

Solutions:

1.(d) total sales of branches B1,B3 and B5 for both the years (in thousand numbers)=(80+105)+(95+110)+(75+95)=560

2(c) required percentage=[(70+80)/(95+110)*100]%=(150/205*100)%=73.17%

3(b)average sales of all the six branches (in thousand numbers) for the year 2000=1/6*(80+75+95+85+75+70)=80

4(e) required ratio=(75+65)/(85+95)=140/180=7/9

5(e)average sales(in thousand numbers of branches B1,B3,and B6 in 2000= 1/3*(80+95+70)=245/3

average sales(in thousand numbers of branches B1,B2,and B3 in 2001=1/3*(105+65+110)=280/3

therefore required percentage=[((245/3)/(280/3))*100]%=(245/280*100)%=87.5%

PIE-CHARTS

Important Facts and Formulae

The **pie-chart** or a **pie-graph** is a method of representing a given numerical data in the form of sectors of a circle.

The sectors of the circle are constructed in such a way that the area of each sector is proportional to the corresponding value of the component of the data.

From geometry, we know that the area of a circle is proportional to the central angle.

So, the central angle of each sector must be proportional to the corresponding value of the component.

Since the sum of all the central angle is 360°, we have

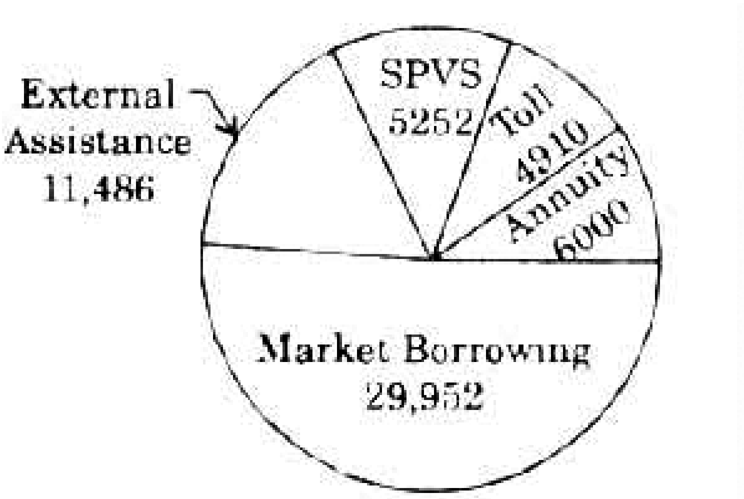
$$\text{Central angle of the component} = \left| \frac{\text{Value of the component}}{\text{Total value}} * 360 \right|^{\circ}$$

SOLVED EXAMPLES

The procedure of solving problems based on pie-charts will be clear from the following solved examples.

Example 1. The following pie-chart shows the sources of funds to be collected by the National Highways Authority of India (NHAI) for its Phase II projects. Study the pie-chart and answer the questions that follow.

SOURCES OF FUNDS TO BE ARRANGED BY NHAI FOR PHASE II PROJECTS (IN CRORES RS.)



Total funds to be arranged for Projects (Phase II) =Rs.57,600 crores.

1. Near about 20% of the funds are to be arranged through:

   (a) SPVS (b) External Assistance

   (c) Annuity (d) Market Borrowing

2. The central angle corresponding to Market Borrowing is:

   (a) 52° (b) 137.8°

   (c) 187.2° (d) 192.4°

3. The approximate ratio of the funds to be arranged through Toll and that through Market Borrowing is:

   (a) 2:9 (b) 1:6

   (c) 3:11 (d) 2:5

4. If NHAI could receive a total of Rs. 9695 crores as External Assistance, by what percent (approximately) should it increase the Market Borrowings to arrange for the shortage of funds ?

   (a) 4.5% (b) 7.5%

   (c) 6% (d) 8%

5. If the toll is to be collected through an outsourced agency by allowing a maximum 10% commission, how much amount should be permitted to be collected by the outsourced agency, so that the project is supported with Rs. 4910 crores ?

   (a) Rs.6213 crores (b) Rs. 5827 crores

   (c) Rs. 5401 crores (d) Rs. 5216 crores

Solution

1. (b) : 20% of the total funds to be arranged = Rs.(20% of 57600) crores
   = Rs.11520 crores Rs.11486 crores.
2. (c) : Central angle corresponding to Market Borrowing

   $$= \frac{29952}{57600} \times 360^\circ$$

   $$= 187.2^\circ$$

3. (b) : Required ratio = $\frac{4910}{29952} = \frac{1}{6.1} = \frac{1}{6}$

4. (c) : Shortage of funds arranged through External Assistance
   =Rs.(11486-9695) crores =Rs. 1791 crores.
   therefore, Increase required in Market Borrowings =Rs. 1791 crores.

   $$\text{Percentage increase required} = \left| \frac{1791}{29952} * 100 \right| \% = 5.98\ \% = 6\%$$

6. (c) : Amount permitted = (Funds required from Toll for projects of Phase II) + (10 % of these funds)
=Rs. 4910 crores + Rs. (10% of 4910) crores
=Rs. (4910 + 491) crores = Rs. 5401 crores.

1.1.6 Permutations and combinations

Important Facts and Formulae

Factorial Notation: Let n be a positive integer. Then, factorial n, denoted by n! is defined as:

n! = n (n-1) (n-2)........3.2.1.

Examples: (i) 5! = (5x 4 x 3 x 2 x 1) = 120; (ii) 4! = (4x3x2x1) = 24 etc.

We define, 0! = 1.

Permutations: The different arrangements of a given number of things by taking some or all at a time, are called permutations.

Ex. 1. All permutations (or arrangements) made with the letters a, b, c by taking two at a time are: **(ab, ba, ac, bc, cb).**

Ex. 2. All permutations made with the letters a,b,c, taking all at a time are:

(abc, acb, bca, cab, cba).

Number of Permutations: Number of all permutations of n things, taken r at a time, given by:

$$^{n}P_{r} = n(n-1)(n-2).....(n-r+1) = n!/(n-r)!$$

Examples: (i) $^{6}p_{2} = (6x5) = 30$. (ii) $^{7}p_{3} = (7x6x5) = 210$.

Cor. Number of all permutations of n things, taken all at a time = n!

An Important Result: If there are n objects of which p_1 are alike of one kind; p_2 are alike of another kind; p_3 are alike of third kind and so on and p_r are alike of rth kind, such that $(p_1+p_2+.......p_r) = n$.

Then, number of permutations of these n objects is:

$$n! \ / \ (p_1!).p_2!)......(p_r!)$$

Combinations: Each of the different groups or selections which can be formed by taking some or all of a number of objects, is called a combination.

Number of Combinations: The number of all combination of n things,

taken r at a time is:

$$^{n}C_{r} = n! / (r!)(n-r)! = n(n-1)(n-2).....\text{to r factors} / r!$$

Note that: $^{n}c_{r} = 1$ and $^{n}c_{0} = 1$.

An Important Result: $^{n}c_{r} = {}^{n}c_{(n-r)}$.

Example: (i) $^{11}c_{4} = (11x10x9x8)/(4x3x2x1) = 330$.

(ii) $^{16}c_{13} = {}^{16}c_{(16-13)} = 16x15x14/3! = 16x15x14/3x2x1 = 560$.

Self Assessment questions:

Q. 1. Suppose we want to select two out of three boys A, B, C. Then, possible selections are AB, BC and CA.

Note that AB and BA represent the same selection.

Q. 2. All the combinations formed by a, b, c, taking two at a time are **ab, bc, ca.**

Q. 3. The only combination that can be formed of three letters a, b, c taken all at a time is **abc.**

Q. 4. Various groups of 2 out of four presons A, B, C, D are:

AB, AC, AD, BC, BD, CD.

Q. 5. Note that ab and ba are two different permutations but they represent the same combination.

Self assessment questions with solutions:

Q. 1. Evaluate: 30!/28!

Sol. We have, 30!/28! = 30x29x(28!)/28! = (30x29) = 870.

Q. 2. Find the value of (i) $^{60}p_3$ (ii) $^{4}p_4$

Sol. (i) $^{60}p_3$ = 60!/(60-3)! = 60!/57! = 60x59x58x(57!)/57! = (60x59x58) = 205320.

(ii) $^{4}p_4$ = 4! = (4x3x2x1) = 24.

Q. 3. Find the vale of (i) $^{10}c_3$ (ii) $^{100}c_{98}$ (iii) $^{50}c_{50}$

Sol. (i) $^{10}c_3$ = 10x9x8/3! = 120.

(ii) $^{100}c_{98}$ = $^{100}c_{(100-98)}$ = 100x99/2! = 4950.

(iii) $^{50}c_{50}$ = 1. [$^{n}c_n$ = 1]

Q. 4. How many words can be formed by using all letters of the word “BIHAR”

Sol. The word BIHAR contains 5 different letters.

Required number of words = $^{5}p_5$ = 5! = (5x4x3x2x1) = 120.

Q. 5. How many words can be formed by using all letters of the word ‘DAUGHTER’ so that the vowels always come together?

Sol. Given word contains 8 different letters. When the vowels AUE are always together, we may suppose them to form an entity, treated as one letter.

Then, the letters to be arranged are DGNTR (AUE).

Then 6 letters to be arranged in $^{6}p_6$ = 6! = 720 ways.

The vowels in the group (AUE) may be arranged in 3! = 6 ways.

Required number of words = (720x6) = 4320.

1.2 (B) **COMPUTER**

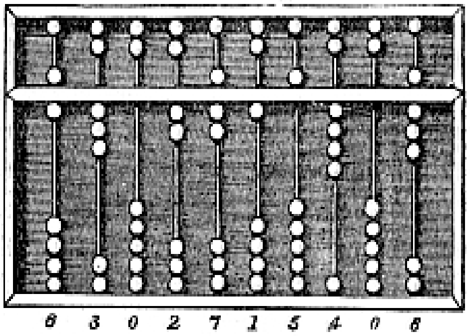
1.2.1 **General introduction to computers**

A computer is a multipurpose electronic device that can receive, store data (numbers, text, sound, image, animations, video, etc.) and process. They are used as tools in every part of society as school, university, shops, markets, transports, etc together with the Internet. They all need to work together for the computer to work; knowing how a computer works makes it easier to use a computer by being able to understand how a computer will respond. Nowadays Computers are complex; there are a lot of different components inside them and they all serve different purposes. A storage device is an apparatus for storing data and information. A basic computer consists of 4 components: an input device, a CPU, output devices, and memory. The data is inserted using an input device. The central processing unit (CPU) converts data to information. The information is put on an output device.

History

Pre-20th century, devices have been used to aid computation for thousands of years.The earliest counting device was probably a form of tally stick. Later record keeping aids throughout the Fertile Crescent included calculi (clay spheres, cones, etc.) which represented counts of items, probably livestock or grains, sealed in hollow unbaked clay containers. The use of counting rods is one example. The abacus was initially used for arithmetic tasks. The Roman abacus was developed from devices used in Babylonia as early as 2400 BC.

The Chinese Suanpan (the number represented on this abacus is 6,3,0,2,7,1,5,4,0,8)



Calculating instrument used for solving problems in proportion, trigonometry, multiplication and division and for various functions such as squares and cube roots was developed in the late 16th century.

First computing device

Charles Babbage, an English mechanical engineer, originated the concept of a programmable computer. Considered the "father of the computer", he conceptualized and invented the first mechanical computer in the early 19th century. After working on his revolutionary difference engine, designed to aid in navigational calculations.

Analog computers

During the first half of the 20th century, many scientific computing needs were met by increasingly sophisticated analog computers which used a direct mechanical or electrical model of the problem as a basis for computation. However, these were not programmable and generally lacked the versatility and accuracy of modern digital computers.

Digital computers

Early digital computers were electromechanical, electric switches group mechanical relays to perform the calculation. These devices had a low operating speed and were eventually superseded by much faster all-electric computers, originally using vacuum tubes. In the US, John Vincent Atanasoff and Clifford E. Berry of Iowa State University developed and tested the Atanasoff–Berry Computer (ABC) in 1942, the first "automatic electronic digital computer". This design was also all-electronic and used about 300 vacuum tubes, with capacitors fixed in a mechanically rotating drum for memory.

Modern computers

The principle of the modern computer was proposed by Alan Turing in 1936. He proved that such a machine is capable of computing anything that is computable by executing instructions/program stored on tape, allowing the machine to be programmable. The fundamental concept of Turing's design is the stored program, where all the instructions for computing are stored in memory.

Stored programs

Early computing machines had fixed programs. Changing its function required the re-wiring and re-structuring of the machine. With the proposal of the stored-program computer this changed. A stored-program computer includes by design an instruction set and can store in memory a set of instructions (a program) that details the computation.

In 1945, Turing joined the National Physical Laboratory and began work on developing an electronic stored-program digital computer. His 1945 report Electronic Calculator was the first specification for such a device. The Manchester Small-Scale Experimental Machine, nicknamed ***Baby***, was the world's first stored-program computer. It was built at the Victoria University of Manchester by Frederic C. Williams, Tom Kilburn and Geoff Tootill, and ran its first program on 21 June 1948.

Transistors

The bipolar transistor was invented in 1947. From 1955 onwards transistors replaced vacuum tubes in computer designs, giving rise to the "second generation" of computers.

Integrated circuits

The next great advance in computing power came with the advent of the integrated circuit. The idea of the integrated circuit was first conceived by a radar scientist working for the Royal Radar Establishment of the Ministry of Defence in Washington, D.C. on 7 May 1952. The first practical ICs were invented by Jack Kilby at Texas Instruments, Kilby recorded his initial ideas concerning the integrated circuit in July 1958, successfully demonstrated. This new development an explosion in the commercial and personal use of computers and led to the invention of the microprocessor.

Different components of a computer, hardware and software

Input devices

When unprocessed data is sent to the computer with the help of input devices, the data is processed and sent to output devices. The input devices may be hand-operated or automated. The act of processing is mainly regulated by the CPU. Some examples of hand-operated input devices are:

1. Computer keyboard
2. Digital camera
3. Digital video
4. Graphics tablet
5. Image scanner
6. Joystick
7. Microphone
8. Mouse
9. Overlay keyboard
10. Trackball
11. Touchscreen

Output devices

The means through which computer gives output are known as output devices. Some examples of output devices are:

1. Computer monitor
2. Printer
3. PC speaker
4. Projector
5. Sound card
6. Video card

Central processing unit (CPU)

The control unit, ALU, and registers are collectively known as a central processing unit (CPU). Early CPUs were composed of many separate components but since the mid-1970s CPUs have typically been constructed on a single integrated circuit called a microprocessor.

Arithmetic logic unit (ALU)

The ALU is capable of performing two classes of operations: arithmetic and logic.The set of arithmetic operations that a particular ALU supports may be limited to addition and subtraction, or might include multiplication, division, trigonometry functions such as sine, cosine, etc., and square roots. Some can only operate on whole numbers (integers) whilst others use floating point to represent real numbers, albeit with limited precision. However, any computer that is capable of performing just the simplest operations can be programmed to break down the more complex operations into simple steps that it can perform.

Memory

In almost all modern computers, each memory cell is set up to store binary numbers in groups of eight bits (called a byte). Each byte is able to represent 256 different numbers ($2^8 = 256$); either from 0 to 255 or −128 to +127. To store larger numbers, several consecutive bytes may be used (typically, two, four or eight). When negative numbers are required, they are usually stored in two's complement notation

Computer main memory comes in two principal varieties:

1. Random-access memory or RAM
2. Read-only memory or ROM

RAM can be read and written to anytime the CPU commands it, but ROM is preloaded with data and software that never changes, therefore the CPU can only read from it. ROM is typically used to store the computer's initial start-up instructions. In general, the contents of RAM are erased when the power to the computer is turned off, but ROM retains its data.

Software

Software refers to parts of the computer which do not have a material form, such as programs, data, protocols, etc. Software is that part of a computer system that consists of encoded information or computer instructions.

When software is stored in hardware that cannot easily be modified, such as with BIOS ROM in an IBM PC compatible computer, it is sometimes called "firmware".

Operating systems

BINARY NUMBERS AND ARITHMETIC

Converting Binary to Decimal

Numbers expressed with 2 symbols (0, 1) are called binary, or "base-2" numbers.

For example:

1 (one-digit-read: 1)

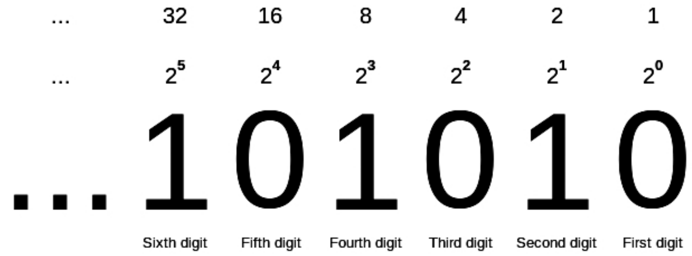
10 (two-digit-read: 1, 0)

100 (three-digit-read: 1,0,0)

1101 (four-digit-read: 1, 1, 0, 1)

etc.

In the Binary Numeral System, digits have a value specified, this value being equal with (base-number ^ 0, 1, 2, 3,…): (right to left)



Value of Digits in the Binary number system

First digit (base-number^0): 2^0 = 1

Second digit (base-number^1): 2^1 = 2

Third digit (base-number^2): 2^2 = 4

Fourth digit (base-number^3): 2^3 = 8

etc.

Converting Decimal to Binary

To convert decimal to binary

Divide the decimal number by 2

- If there IS a remainder the rightmost column will be a 1
- If there is NO remainder, the rightmost column will be a 0.

Then repeat the process, moving one column to the left each time until you have divided down to

Example

74/2 = 37 remainder 0 (Binary number = ??????0)
37/2 = 18 remainder 1 (Binary number = ?????10)
18/2 = 9 remainder 0 (Binary number = ????010)
9/2 = 4 remainder 1 (Binary number = ???1010)
4/2 = 2 remainder 0 (Binary number = ??01010)
2/2 = 1 remainder 0 (Binary number = ?001010)
The final result will always be 1 in the leftmost column (Binary number = 1001010)

1.2.5 USE AND APPLICATION OF DIFFERENT SOFTWARE IN THE CHEMISTRY

Now a day's computation and Information and Communication Technology **(ICT)** play a vital role in wellbeing of humanity but also upgrading status of the research. In the scientific advancement of Science, for accurate and frequent analysis of data is needed, which conducted with the help of computers and software's. Various disciplines of science subjects- Physics, Chemistry, Mathematics and Biology now become much multidiscipline subjects as specialized one such as Quantum Physics, Computational Physics, Bioinformatics, Computational biology, Computational Chemistry, Material Science, Biotechnology, etc.

Globally numbers organizations and units of scientific domain are using and producing number of softwares which are useful for more and more precise study. Some of the popular softwares /sites and web-interfaces are listed below in the subject-Chemistry:

A Program to Analyse and Visualize Atoms in Molecules

ACD/ChemSketch;

10.0-chemical drawing software;

Chem-DRAW

BKchem

AIM2000-A

Software Site

Alchemie

Program for visualization/animation of molecular vibrations

A molecular modeling, graphics, and drug design program

ALP-vibro

Atoms, Symbols and Equations- Unique interactive Chemistry teaching software which tests students as they learn. Starting from very basic principles, the program guides students through all the concepts required for understanding and writing chemical formulae and for balancing chemical equations; Avogadro.exe- to calculate Avogadro numbers; Balancing of Chemical Reactions when the Reactions are Unknown. a free chemical drawing program; Bohr.exe- to formulate **Bohr**'s theorem; **Bravais**.exe- to understand Bravais lattice and crystal systems; **ChemCalc** is a calculator that is more oriented towards chemical compositions in chemistry; **ChemDigiT** is a chemical calculator. No approximations made. All calculated variables show their exact values.

The algorithm used for calculations is based on a full set of equations describing acid/base and salt dissociation equlibrium solved with Newton–Raphson method; Chemistry assistant an expression calculator for fast calculation of molecular weight of compounds by simple entry of chemical formula. The program translates the texts with chemical element symbols or without them into a mathematical expression and calculates them; Chemical engineering software; Chemical Equation Expert Chemical Equation Expert is an integrated tool for chemistry professionals and students.

You'll find complicated work such as balancing chemical equations and related calculations, Balance complicated equations by one mouse click; **CHEMMOL** (V1.0) is a freeware program for the calculation of molecular masses and chemical analyses of compounds; **Chemspread** PRO chemistry spreadsheet calculcator - balances virtually any chemical equation and follows up with stoichiometry calculations as well as equillibrium calculations; Chemistry Experiment-Simulations and Conceptual Computer Animations; ChemToolBox is the swiss army knife of the lab worker, is a freeware which contains numerous scientific data very useful in a laboratory; **EniG** -Periodic table of the elements contains the basic data about the element in 7 languages.

The Molecular Workbench (MW) software offers interactive, visual simulations that have been widely used to teach and learn science and engineering at all levels of science education; **MoleView** 1 Display and view images of 3D molecules. View, render, and rotate 3D molecules. This will help to understand the chemicals formula of the chemical compound; Orbital Viewer-A program for drawing orbitals- **ORTEX** is a program for the study and display of crystal structures; Periodic Library Periodic Library is an interactive periodic table of the elements. But it is more than simply a computerized version of the standard periodic table. It takes full advantage of your computer's capabilities to give you an in-depth look at the elements that make up our earth, the solar system, the galaxy;

Periodic Table Classic v3.3 - The application contains all the elements of the Periodic Table along with images of the elements in their natural state, as well as lots of other information and interactive displays; Periodic Table of elements Download it for free, A very useful educational software for students, teachers and researchers of chemistry; Periodic Table XP Using Periodic Table XP, one can quickly determine a significant amount of information such as Atomic Weight, Oxidation State, Boiling Point, Melting Point, Density, Electron Configuration, Acid/Base Properties, Atomic Volume, Atomic Radius, etc. of an element; PovChem a chemical visualization and illustration program with a new graphic interface. It takes molecules in the PDB format, lets you to set up a picture with fine control over details of the illustration - colors, atom and bond radii, view orientation, etc;

REDOX V2.0-Oxidation and Reduction Reactions, a freeware program designed for evaluating and predicting oxidation and reduction reactions in aqueous systems. Just select an oxidant and a reductant and the program will give the user an overview of all the redox halfreactions that may play a role in the redox; Virtual Lab Simulation-The Virtual

Laboratory allows students to select from hundreds of standard reagents and manipulate them in a manner that resembles that of a real lab. It allows students to design and perform diverse experiments in acid-base chemistry, thermochemistry, solubility and redox chemistry.

ChemDraw Ultra 8.0- Drawing of Chemical reactions and mechanism. Demonstrating the Biological and chemical interactions; **Mercury** 2.3- To visualizing X-ray structure and their interactions, bonding and symmetry interpretation through 3D images; **WinGX** v1.80.05- To solve X-ray diffraction data to get precise data for interpretation of molecular structure of the compounds; **SHELXS-97** X-ray diffraction data to get precise data for interpretation of molecular structure of the compounds; **PLATON** X-ray diffraction data to get precise data for interpretation of molecular structures; Olex2 To visualizing X-ray structure and their interactions, bonding and symmetry interpretation through 3D images; ACD/Spectrus Processor interpret all analytical data in one common interface, including NMR, LC/GC/UV/MS, IR and more.

ChemDraw® Ultra

Chemical Structure Drawing Standard

© 1985-2003 CambridgeSoft Corporation
100 CambridgePark Drive
Cambridge, MA 02140 USA

CambridgeSoft

www.cambridgesoft.com

Mercury 4.1.0 (Build 235316)

Gain assistance with routine structure verification and access to spectral databases; Optical Techniques-Software Prediction, processing, and interpretation software for Infra-Red, Raman, UV, and other optical spectroscopy techniques; Chromatography Software-Process and analyze liquid and gas chromatography separations experiments, with the unique ability to assign structures to chromatographic peaks. Build applications databases to share expert knowledge throughout your department, or organization; Analytical Curve Software **ACD/Labs'-analytical** curve software offers efficient and effective ways to handle a large variety of analytical curve data such as kinetics, titrimetry, thermal analysis (DSC, TGA, DTA) and more. **R-software**- for statistical analysis; LeTeX- for thesis writing and for presentations; MS-Office word and Power Point Presentation- are very useful for writing and presenting research work.

Applications of software

Many more softwares are used in the study of chemistry and formulations of chemistry interpretation. Combine experimental data from NMR, GC/MS, LC/UV/MS, Chromatography, IR, Raman, X-Y, and other hyphenated data from most major instrument vendors in a uniform software environment. Processing and interpretation of analytical data range from applications for casual users with minimal experience, to software for use by spectroscopists, spectrometrists, separations scientists and others with expertise in their field of analytical chemistry.

To understand how these softwares help to interpredict chemistry see some of the software added works conducted.

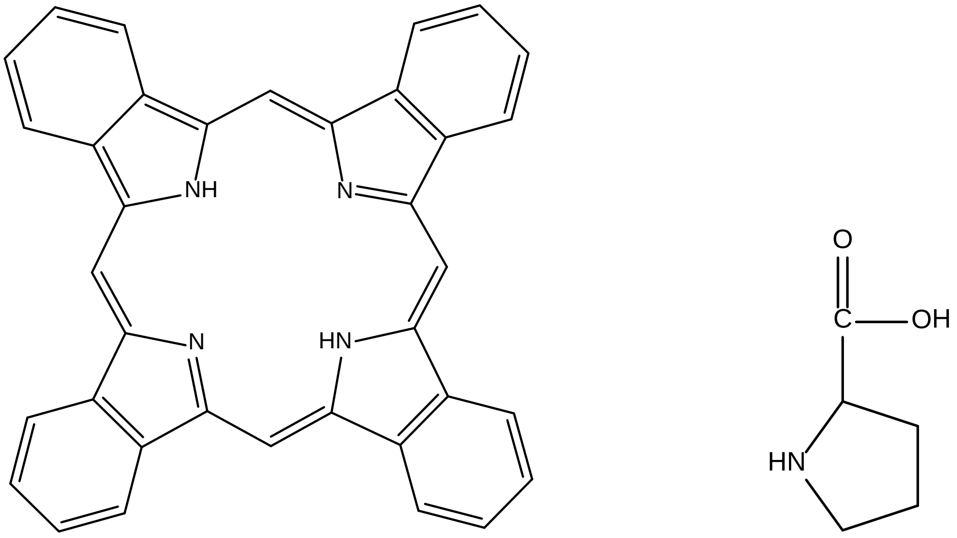
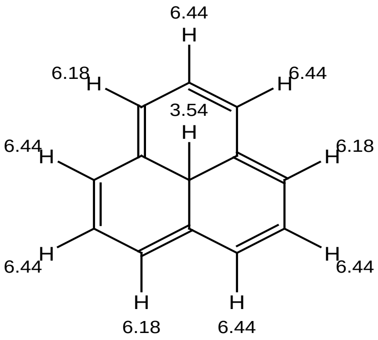


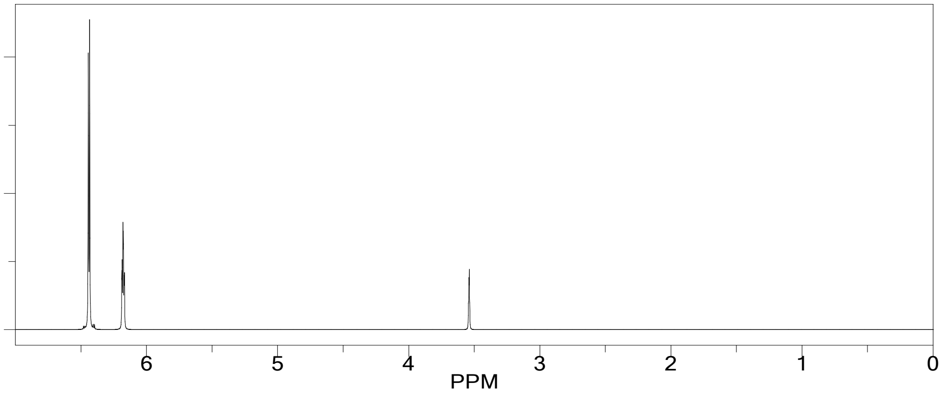
Figure 1 : Chemical Ligands drawing through Chem. Draw Ultra.

ChemDraw Ultra not only can help to drawing structures of molecules but also can give their spectroscopic analytic data with the reference one. Given figure below provide some information of amino acid compound (2-amino-3-(1H-imidazol-4-yl)propanoic acid) and their 1H and 14C-NMR spectra with their values in below Figures.

ChemNMR H-1 Estimation

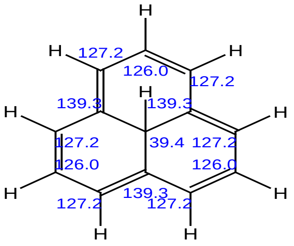


Estimation Quality: blue = good, magenta = medium, red = rough

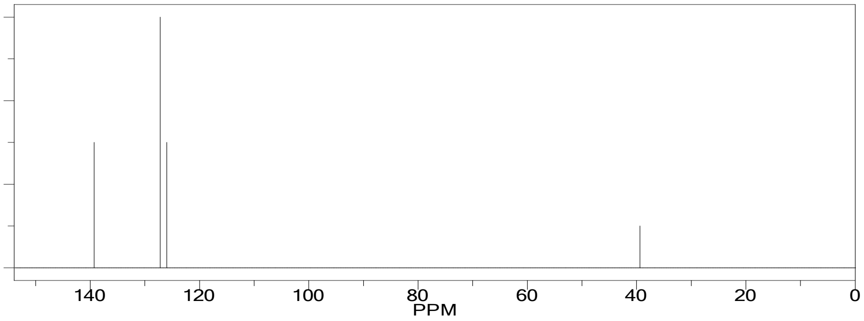


```
Protocol of the H-1 NMR Prediction:

Node     Shift    Base + Inc.   Comment (ppm rel. to TMS)

   H      3.54       1.50       methine
                     2.04       3 alpha -C=C
   H      6.44       5.25       1-ethylene
                     1.24       1 -C=C gem
                    -0.05       1 -C=C trans
   H      6.44       5.25       1-ethylene
                    -0.05       1 -C=C trans
                     1.24       1 -C=C gem
   H      6.18       5.25       1-ethylene
                     1.24       1 -C=C gem
                     0.02       1 -C=C cis
                    -0.33       1 -CC=C trans
   H      6.44       5.25       1-ethylene
                     1.24       1 -C=C gem
                    -0.05       1 -C=C trans
   H      6.44       5.25       1-ethylene
                    -0.05       1 -C=C trans
                     1.24       1 -C=C gem
   H      6.18       5.25       1-ethylene
                     1.24       1 -C=C gem
                     0.02       1 -C=C cis
                    -0.33       1 -CC=C trans
   H      6.44       5.25       1-ethylene
                     1.24       1 -C=C gem
                    -0.05       1 -C=C trans
   H      6.44       5.25       1-ethylene
                    -0.05       1 -C=C trans
                     1.24       1 -C=C gem
   H      6.18       5.25       1-ethylene
                     0.02       1 -C=C cis
                    -0.33       1 -CC=C trans
                     1.24       1 -C=C gem
```

ChemNMR C-13 Estimation



Estimation Quality: blue = good, magenta = medium, red = rough



```
Protocol of the C-13 NMR Prediction:

Node     Shift    Base + Inc.   Comment (ppm rel. to TMS)

  CH     127.2       123.3      1-ethylene
                      13.6      1 -C=C
                      -7.0      1 -C=C
                      -2.7      general corrections
  CH     126.0       123.3      1-ethylene
                      -7.0      1 -C=C
                      13.6      1 -C=C
                      -3.9      general corrections
  CH     127.2       123.3      1-ethylene
                      13.6      1 -C=C
                      -7.0      1 -C=C
                      -7.4      1 -C
                       4.7      general corrections
   C     139.3       123.3      1-ethylene
                      -7.0      1 -C=C
                      13.6      1 -C=C
                       9.4      1 -C
   C     139.3       123.3      1-ethylene
                      13.6      1 -C=C
                       9.4      1 -C
                      -7.0      1 -C=C
  CH     127.2       123.3      1-ethylene
                      13.6      1 -C=C
                      -7.0      1 -C=C
                      -2.7      general corrections
  CH     126.0       123.3      1-ethylene
                      -7.0      1 -C=C
                      13.6      1 -C=C
                      -3.9      general corrections
  CH     127.2       123.3      1-ethylene
                      13.6      1 -C=C
                      -7.0      1 -C=C
                      -7.4      1 -C
                       4.7      general corrections
   C     139.3       123.3      1-ethylene
                      -7.0      1 -C=C
                      13.6      1 -C=C
                       9.4      1 -C
  CH     127.2       123.3      1-ethylene
                      13.6      1 -C=C
                      -7.0      1 -C=C
                      -2.7      general corrections
  CH     126.0       123.3      1-ethylene
                      -7.0      1 -C=C
                      13.6      1 -C=C
                      -3.9      general corrections
  CH     127.2       123.3      1-ethylene
                      -7.0      1 -C=C
                      -7.4      1 -C
                      13.6      1 -C=C
                       4.7      general corrections
  CH      39.4        -2.3      aliphatic
                      58.5      3 alpha -C=C
                      20.7      3 beta -C=C
                     -37.5      general corrections
```

Figure 2

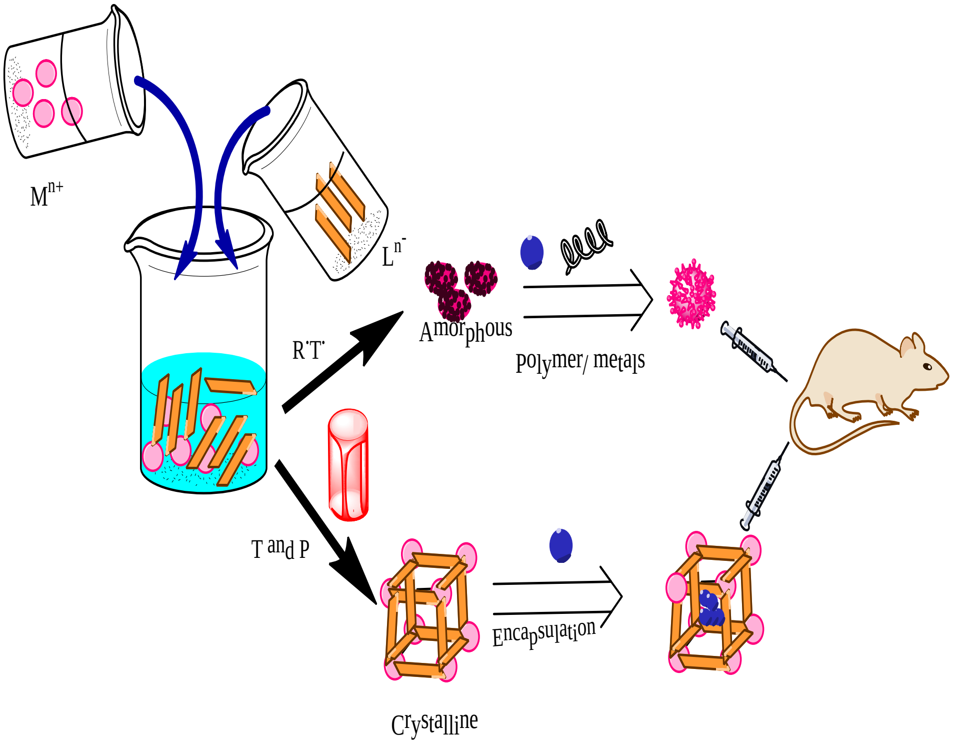


Figure 2: Showing reaction mechanism of formation of MOFs and their post synthetic treatment

with biological application Drawing by ChemBioDraw Ultra.

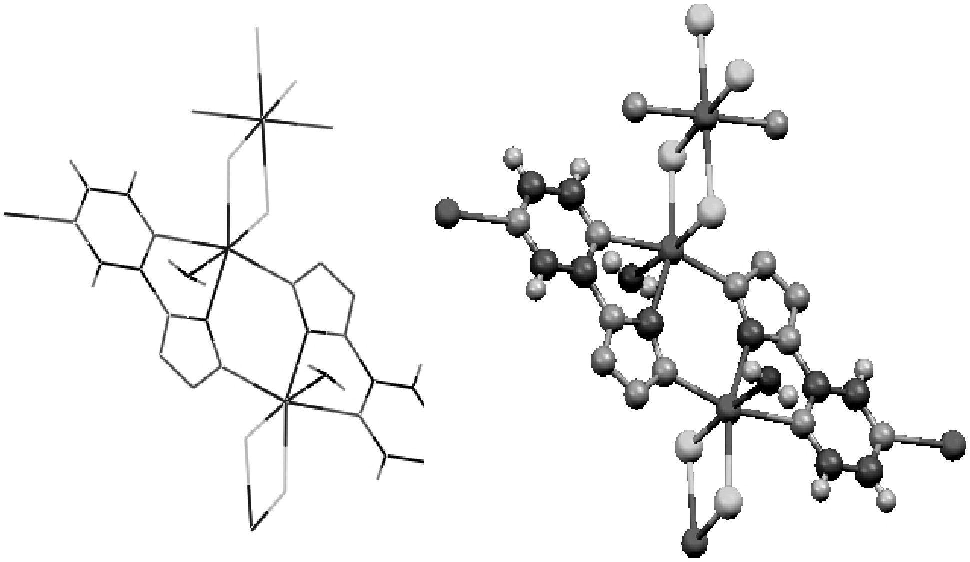


Figure 4: Single Crystal X-ray structure of a molecule wire frame and ball stick model through Mercury 2.3 Software were pink color ball (atom=Cd), green color ball (atom=Cl), Blue color ball (atom=N), Black color ball (atom=C), Red color ball (atom=O) and white color ball (atom=H)

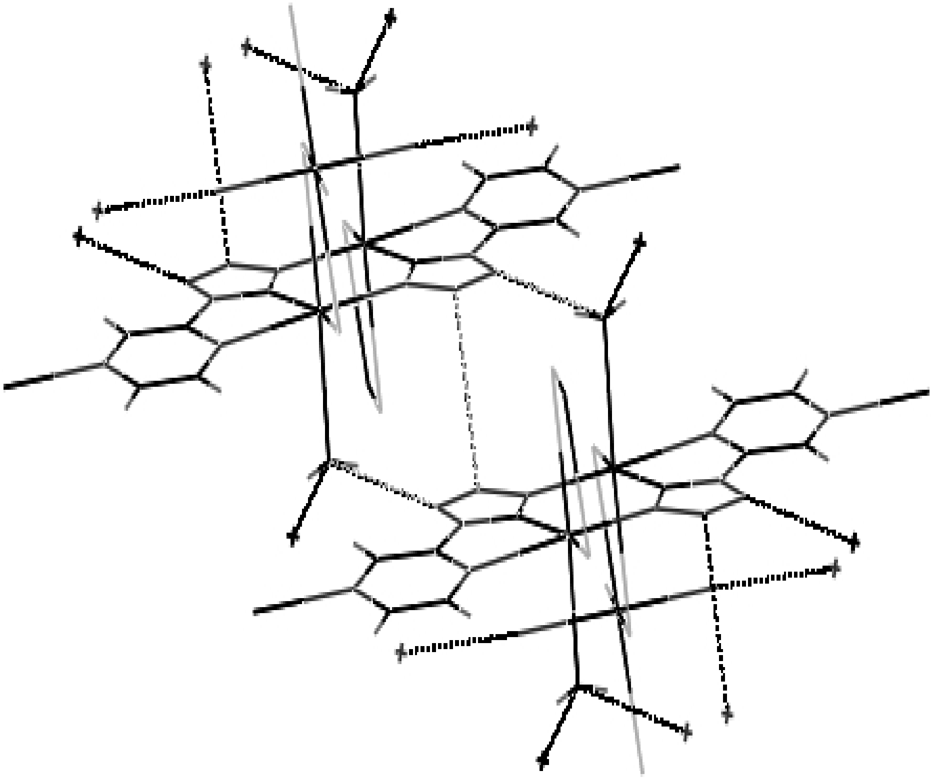


Figure 5: Single Crystal X-ray structure of a molecule wire frame through Mercury software showing intermolecular hydrogen bonding and interactions

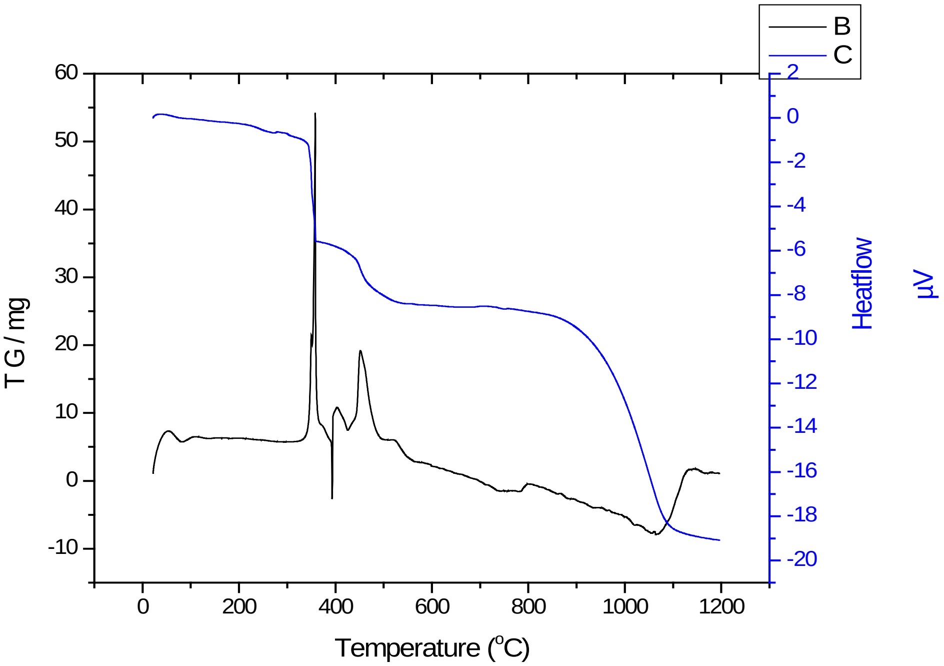


Figure 6: Thermal analysis of compound 1: TGA/DTA representation through Origin Software

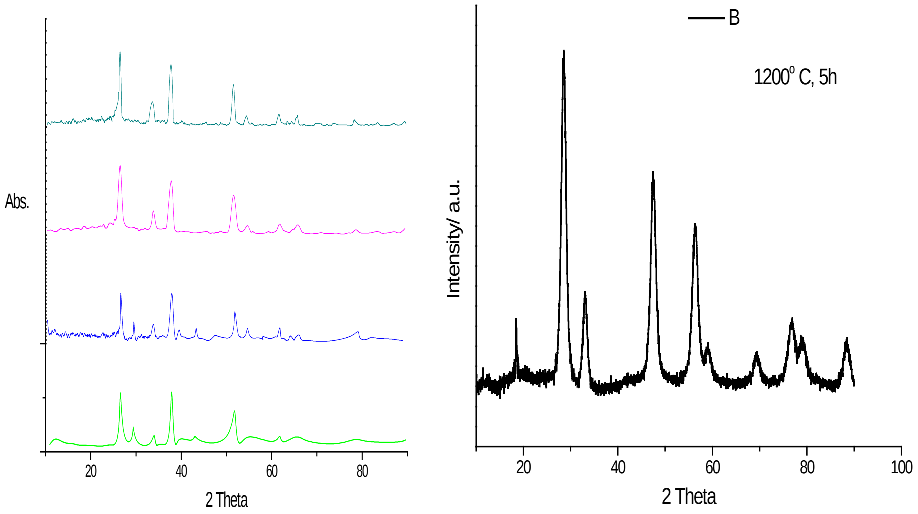


Figure 7: X-ray reflection data representation through Origin 6.1 Software

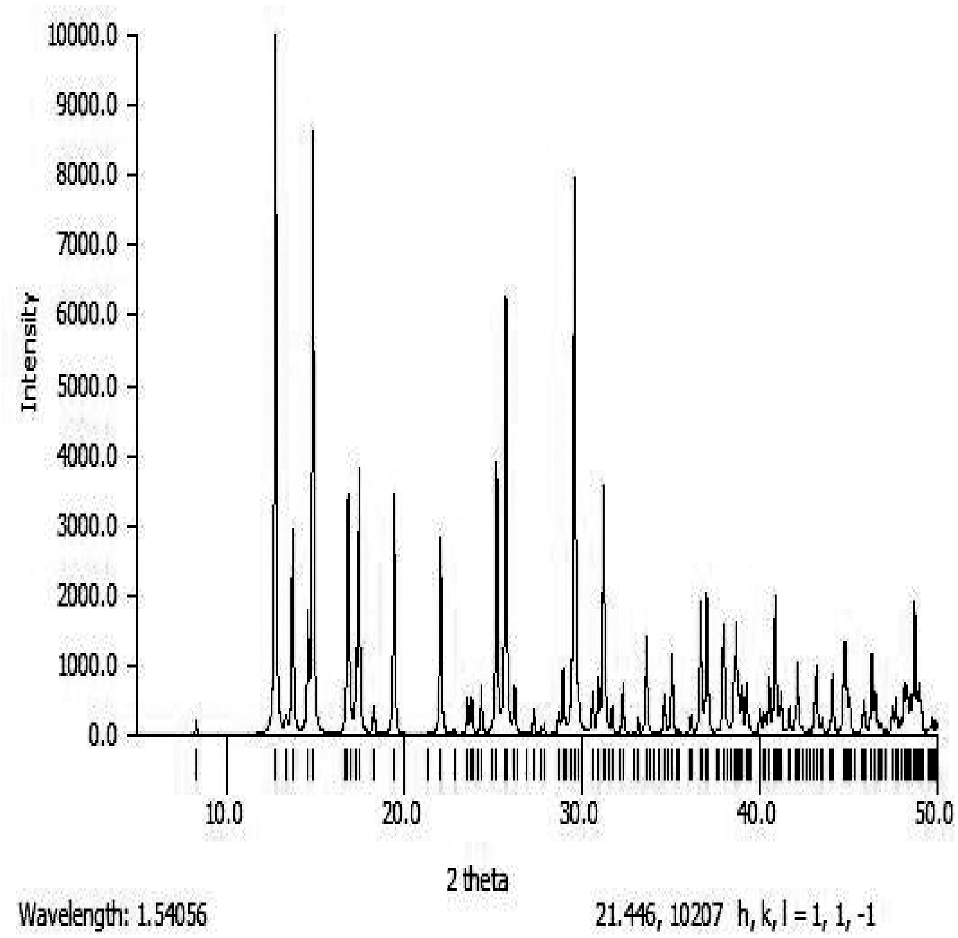
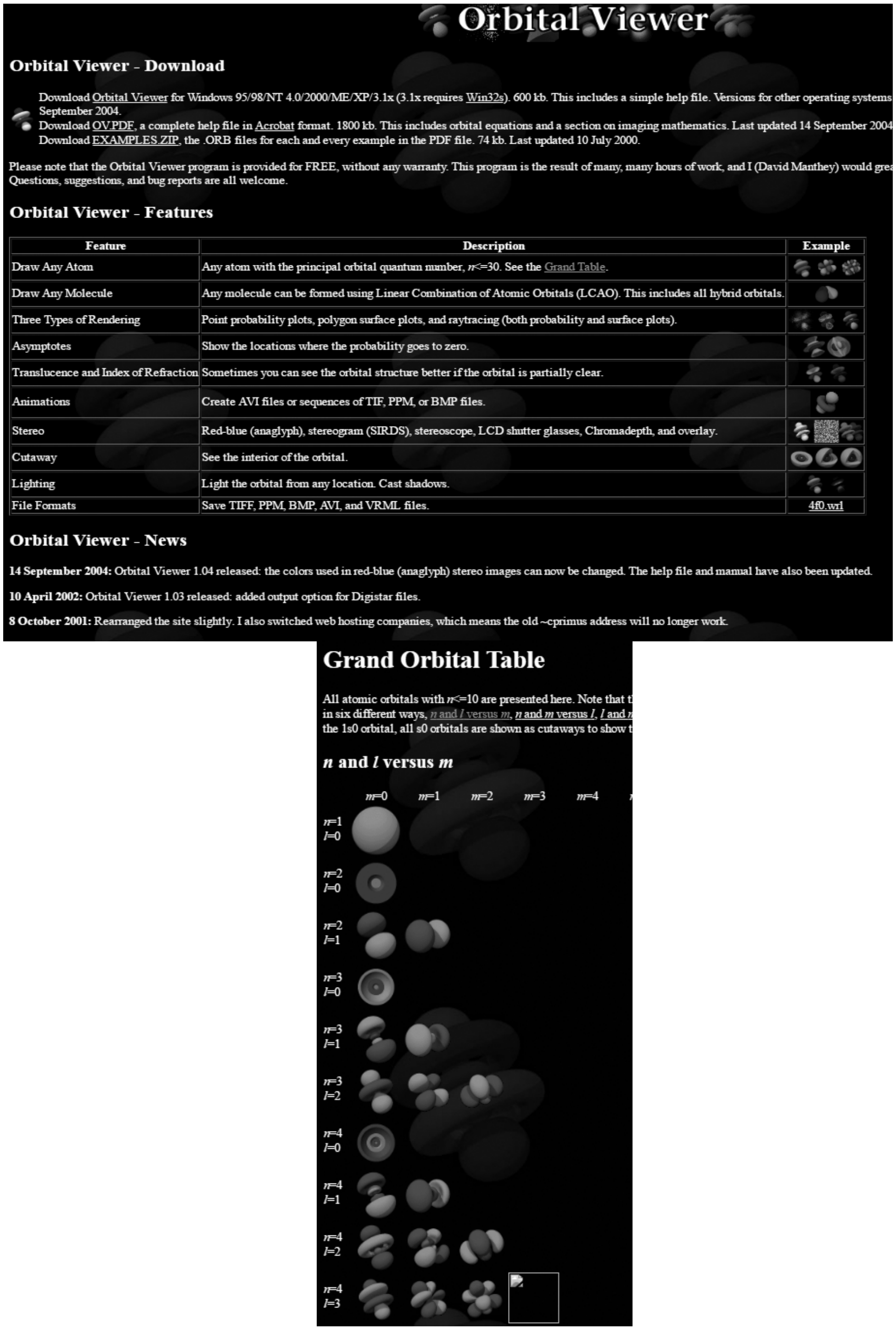


Figure 8: Simulated PXRD of compound 1: generated by Mercury software



Orbital Viewer

Orbital Viewer - Download

Download Orbital Viewer for Windows 95/98/NT 4.0/2000/ME/XP/3.1x (3.1x requires Win32s). 600 kb. This includes a simple help file. Versions for other operating systems
September 2004.
Download OV.PDF, a complete help file in Acrobat format. 1800 kb. This includes orbital equations and a section on imaging mathematics. Last updated 14 September 2004
Download EXAMPLES.ZIP, the .ORB files for each and every example in the PDF file. 74 kb. Last updated 10 July 2000.

Please note that the Orbital Viewer program is provided for FREE, without any warranty. This program is the result of many, many hours of work, and I (David Manthey) would grea
Questions, suggestions, and bug reports are all welcome.

Orbital Viewer - Features

Feature	Description	Example
Draw Any Atom	Any atom with the principal orbital quantum number, n<=30. See the Grand Table.	
Draw Any Molecule	Any molecule can be formed using Linear Combination of Atomic Orbitals (LCAO). This includes all hybrid orbitals.	
Three Types of Rendering	Point probability plots, polygon surface plots, and raytracing (both probability and surface plots).	
Asymptotes	Show the locations where the probability goes to zero.	
Translucence and Index of Refraction	Sometimes you can see the orbital structure better if the orbital is partially clear.	
Animations	Create AVI files or sequences of TIF, PPM, or BMP files.	
Stereo	Red-blue (anaglyph), stereogram (SIRDS), stereoscope, LCD shutter glasses, Chromadepth, and overlay.	
Cutaway	See the interior of the orbital.	
Lighting	Light the orbital from any location. Cast shadows.	
File Formats	Save TIFF, PPM, BMP, AVI, and VRML files.	4f0.wrl

Orbital Viewer - News

14 September 2004: Orbital Viewer 1.04 released: the colors used in red-blue (anaglyph) stereo images can now be changed. The help file and manual have also been updated.

10 April 2002: Orbital Viewer 1.03 released: added output option for Digistar files.

8 October 2001: Rearranged the site slightly. I also switched web hosting companies, which means the old ~cprimus address will no longer work.

Grand Orbital Table

All atomic orbitals with n<=10 are presented here. Note that t
in six different ways, n and l versus m, n and m versus l, l and n
the 1s0 orbital, all s0 orbitals are shown as cutaways to show t

n and l versus m

Figure 9: Orbital Shape and size representedin website
http://www.orbitals.com/orb/orbtable.htm

After the summarizing of the data and information about work ready for report as research article publication. Presently every scientific community/ agency check these data or material for authentic and unique information is reported or copied from the other resource therefore they conduct plagiarism authentication with the help of online softwares, some are free and some are payable in nature. Today not only research journals but also Universities also accept plagiarism authentication before submitting thesis and dissertations were research work has been conducted. Some of the popular softwares are Dupli Checker, Copyleaks, PaperRater, Plagiarisma, Plagiarism Checker, Plagium, PlagScan, PlagTracker, Quetext, Viper, etc.

Advances in softwares making studies much easier and exact analysis of the materials and chemistry can be done. They make advances in chemical laboratory not only in syntheses but also of compounds but also simultaneously analysis and results of the products. These softwares are not only helpful for analyses but also educational and understandable the properties of material applications in future production for mankind applications.

1.3 SUMMARY

In this unit student able to understand the mathematical concepts, Logarithmic relations, Curve sketching, linear graphs and calculation of slopes; Differentiation of functions; maxima and minima, Partial Differentiation and reciprocity relations; Integration of some useful functions; Permutations, combinations and Factorials; Probability and Recreations. Not only the mathematics but also application of Computer with its basics as well as utilization and application in learning and understanding subject Chemistry.

Self Assessment questions:

Q1: Which type of softwares are used for chemical structure representation?

Ans. 1: Chemistry: **ACD/ChemSketch** 10.0-chemical drawing software and Chem-DRAW; AIM2000-A Program to Analyse and Visualize Atoms in Molecules; Alchemie Software Site; ALP-vibro-ALP-vibro is a program for visualization/animation of molecular vibrations computed by Gaussian 98 and Gaussian 03.

1.4 TERMINAL QUESTIONS

Q1. Q1. Explain Logarithms with suitable examples?

Q2. Simplify :(log 75/16-2 log 5/9+log 32/243)

Q3. Find the value of x which satisfies the relationLog$_{10}$ 3+log$_{10}$ (4x+1)=log$_{10}$ (x+1)+1

Q4. Simplify: [1/log$_{xy(}$xyz)+1/log$_{yz}$(xyz)+1/log$_{zx}$(xyz)]

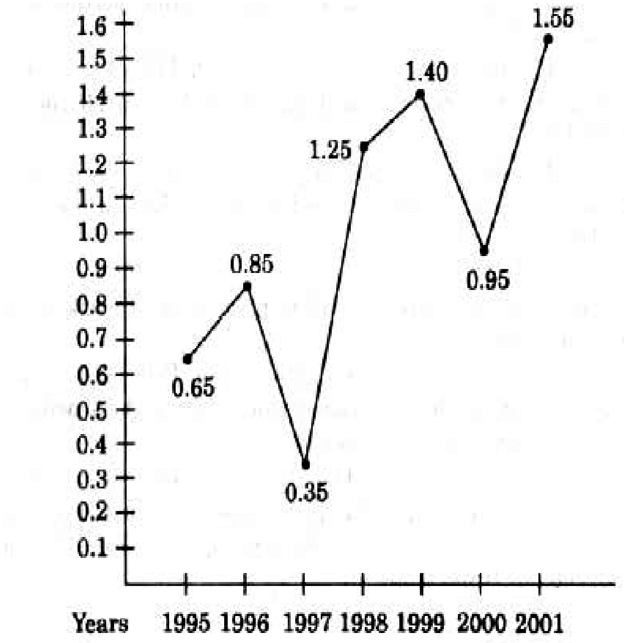
Q5. If log$_{10}$ 2=0.30103,find the value of log$_{10}$ 50.

Q6. If log 2=0.3010 and log 3=0.4771,find the values of:i) log 25 ii)log 4.5

Q7. If log 2=.30103,find the number of digits in 2^{56}.

Q8. The following line- graph the ratio of the amounts of imports by a Company to the amount of exports from that Company over the period from 1995 to 2001. The questions given below are based on this graph.

Ratio of value of Import to Export by a Company over the Years



1. **In how many of the given years were the exports more than the imports?**

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

2. **The imports were minimum proportionate to the exports of the Company in the year:**

a..1995 b.1996 c.1997 d.2001

3. **If the imports of the Company in 1996 was Rs.272 crores, the exports from the Company in 1996 was:**

a. Rs.370 crores b.Rs.320 crores c.Rs.280 crores

d.Rs.275 crores e.Rs.264 crores

4. **What was the percentage increase in imports from 1997 to 1998?**

a. 72 b.56 c.28 d.None of these e.Data inadequate

5. **If the imports in 1998 was Rs.250 crores and the total exports in the years 1998 and 1999 together was Rs.500 crores, then the imports in 1999 was:**

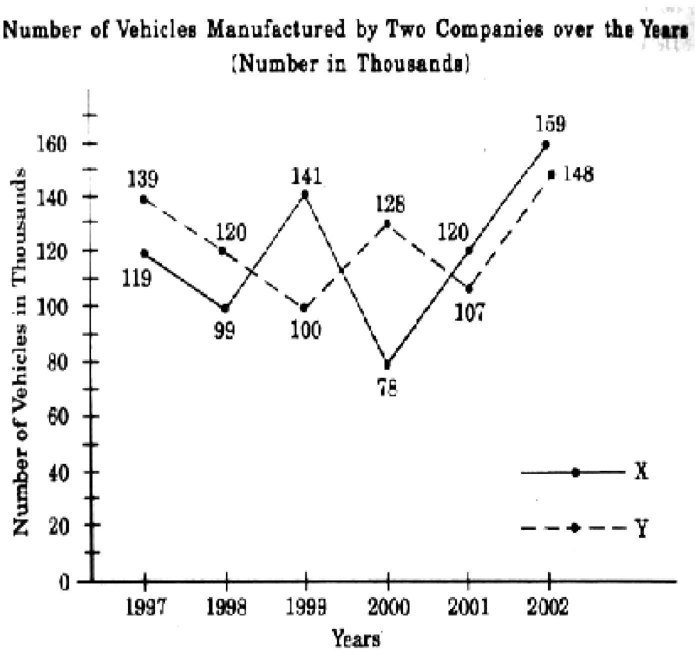
a.Rs.250 crores b.Rs.300 crores c.Rs 357 crores

d.Rs 420 crores e.None of these

Q9. Study the following line-graph and answer the question based on it.

Number of vehicle Manufactured by Two Companies over the Years

(Numbers in thousands)



1. **What is the difference between the total productions of the two Companies in the given years?**

   a. 19000 b. 22000 c.26000 d.28000

   e.29000

2. **What is the difference between the numbers of vehicles manufactured by Company Y in 2000 and 2001?**

   a.50000 b.42000 c.33000 d.21000

   e.13000

3. **What is the average number of vehicles manufactured by Company X over the given period? (rounded off to the nearest integer)**

   a.119333 b.113666 c.112778 d.111223

   e. None of these

4. **In which of the following years, the difference between the productions of Companies X and Y was the maximum among the given years?**

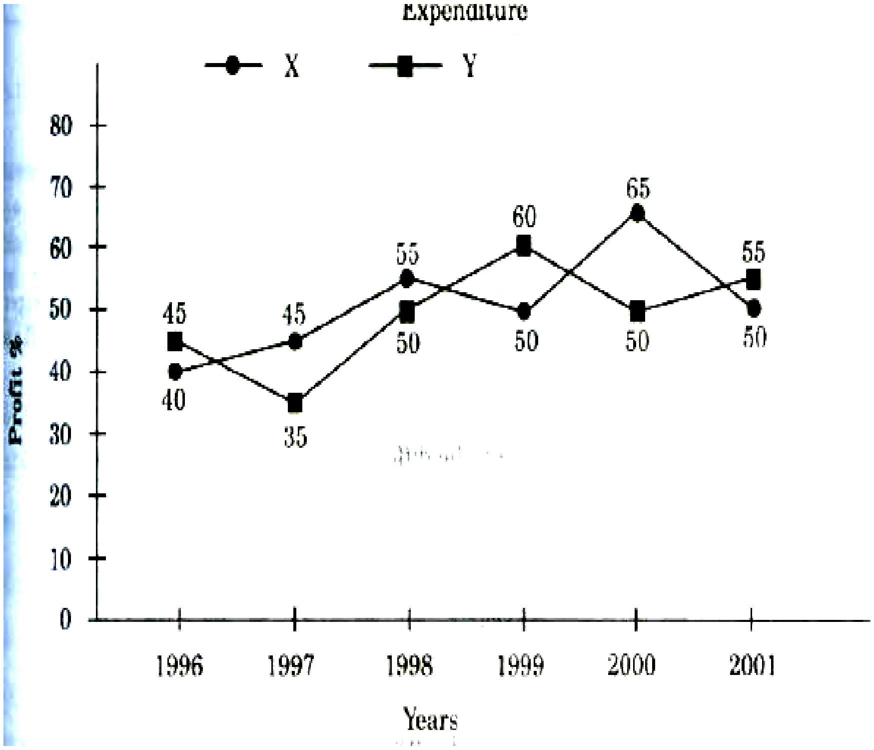
   a.1997 b.1998 c.1999 d.2000 e.2001

5. **The production of Company Y in 2000 was approximately what percent of the production of Company X in the same year?**

   a.173. b.164 c.132 d.97 e.61

Q10. The following line-graph gives the percent profit earned by two Companies X and Y during the period 1996 – 2001. Study the line – graph and answer the questions that are based on on it.

Percentage Profit Earned by Two Companies X and Y over the Given years % profit/ loss = [(Income – Expenditure) / Expenditure] * 100



1. **If the expenditure of Company Y in 1997 was Rs. 220 crores, what was its income in 1997?**

   (a). Rs. 312 crores (b). Rs. 297 crores (c) Rs. 283 crores

   (d) Rs. 275 crores (e)Rs.261 crores

2. **If the incomes of the two companies were equal in 1999,then what was the ratio of expenditure of Company X to that of company Y in 1999 ?**

   (a) 6:5 (b) 5:6 (c) 11:6 (d) 16:15 (e) 15:16

3. **The incomes of the companies X and Y in 2000 were in the ratio of 3:4 respectively.What was the respective ratio of their expenditures in 2000?**

   (a) 7:22 (b) 14:19 (c) 15:22 (d)27:35 (e) 33:40

4. **If the expenditure ofcompanies X and Y in 1996 were equal and the total income of the two companies in 1996 was Rs.342 crores, what was the total profit of the twocompanies together in 1996 ? (Profit = Income – Expenditure)**

   (a) Rs.240crores (b) Rs.171crores (c) Rs.120crores (d) Rs.102crores (e)None of these.

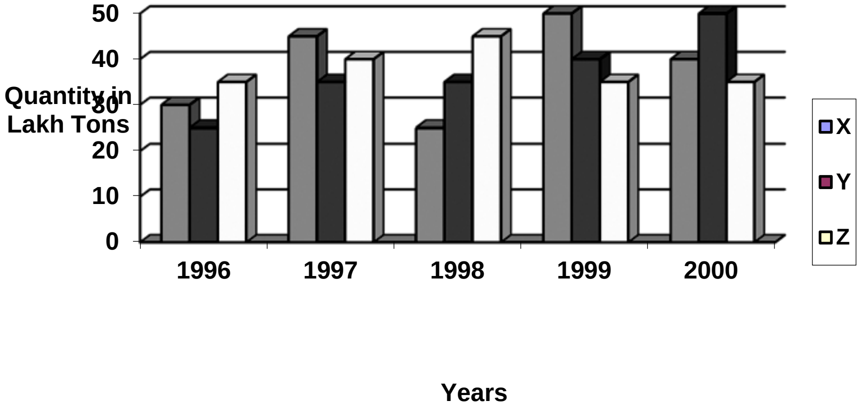
5. **The expenditure ofcompany X in the year 1998 was Rs.200 crores and the income Company X in 1998 was the same as its expenditure in 2001 was:**

   (a) Rs.465crores (b)Rs.385crores (c)Rs.295crores

   (b) (d)Rs.255crores

Q11. The bar graph provided below gives the data of the production of paper (in thousand tonnes) by three different companies x,y and z over the years .study the graph and answer the questions that follow

production of paper(in laks tonnes) by three companys x, y and z over the years



1. **What is the difference between the production of the company Z in 1998 and company y in 1996?**

   a. 2 ,00,000 tons

   b. 20,00,000 tons

   c. 20,000 tons

   d. 2,00,00,000 tons

   e. none of these

2. **What is the ratio of the average production of company x in the period 1998 to 2000 to the average production of company y in the same period?**

   a. 1:1

   b. 15:27

   c. 23:25

   d. 27:29

   e. none of these

3. **What is the percentage increase in the production of company y from1996 to 1999?**

   a. 30%

   b. 45%

   c. 50%

   d. 60%

   e. 75%

4. **The average production of five years was maximum for which company?**

   a. x

   b. y

   c. z

   d. x & y both

   e. x and z both

5. **for which of thw follolwing years the percentage rise / fall in production from previous year is the maximum for company y?**

   a. 1997

   b. 1998

   c. 1999

   d. 2000

   e. 1997 & 2000

6. **in which year was the percentage of production of company z to the production of company y the maximum?**

   a. 1996

   b. 1997

   c. 1998

   d. 1999

   e. 2000

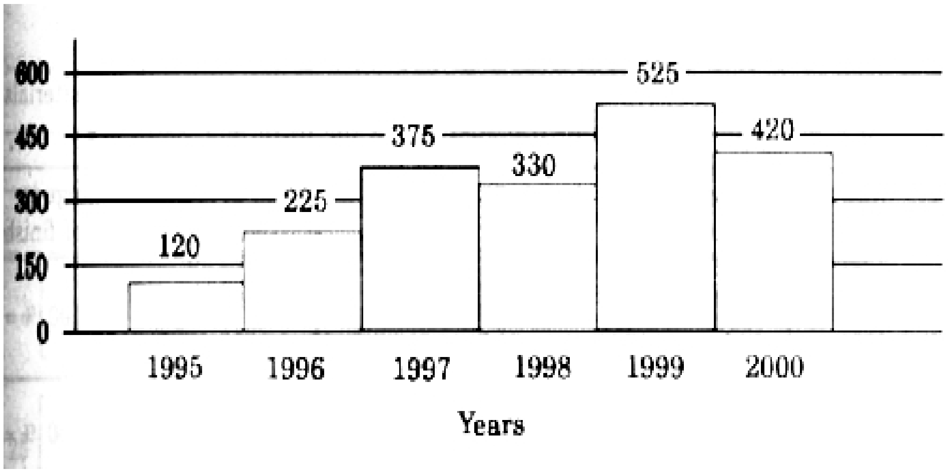
Q12. Outof the two bar graphs provided below, one shows the amounts (in Lakh Rs) invested by a Company in purchasing raw materials over the years and the other shows the values(in Lakh Rs.) of finished goods sold by the Company over the years.

Study the two bar graphs and answer the questions based on them.

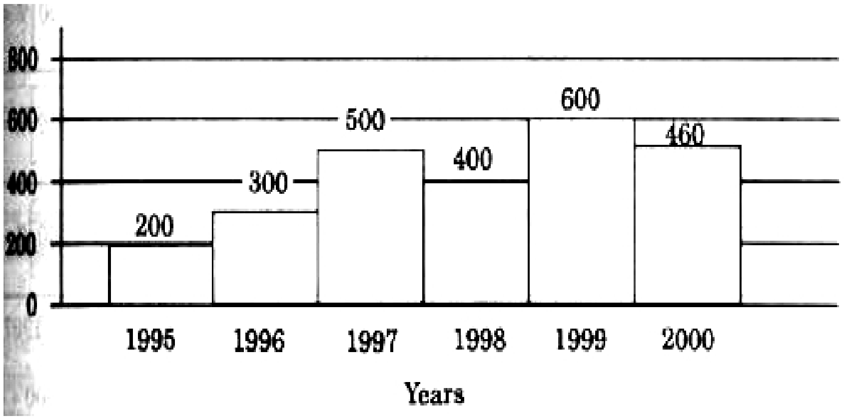
Amount Invested in Raw Materials and the Value of Sales of Finished Goods for

a Company over the Years

Amount Invested in Raw Materials (Rs. in Lakhs)



Value of Sales of Finished Goods (Rs.in Lakhs)



1. **Inwhichyear,there has been a maximum percentage increase in the amount invested inRawMaterials as compared to the previous year?**

   *(a)*1996 (b) 1997 *(c)* 1998 (d) 1999 *(e)* 2000

2. **Inwhichyear, the percentage change (compared to the previous year) in the investment onRaw Materials is the same as that in the value of sales of finished goods?**

   *(a)*1996 *(b)* 1997 *(c)* 1998 (d) 1999 *(e)* 2000

3. **Whatwas the difference between the average amount invested in Raw Materials during the given period and the average value of sales of finished goods during this period**?

*(a)*Rs. 62.5 lakhs *(b)* Rs. 68.5 lakhs *(c)* Rs. 71.5 lakhs

(d)Rs.77.51akhs *(e)* Rs. 83.5 lakhs

4. **The value of sales of finished goods in 1999 was approximately what percent of the average amount invested in Raw Materials in the years 1997,1998 and 1999?**

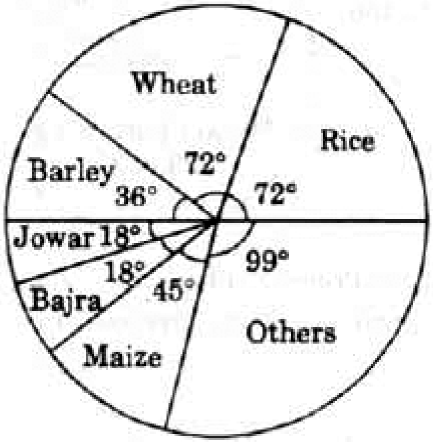
(a) 33% (b) 37% (c) 45% (d) 49%
(e) 53%

5. **The maximum difference between the amount invested in Raw Materials and the value of sales of finished goods was during the year:**

(a) 1995 (b) 1996 (c) 1997 (d) 1998
(e) 1999

Q13. The pie-chart provided below gives the distribution of land (in a village) under various food crops. Study the pie-chart carefully and answer the questions that follow.

DISTRIBUTION OF AREAS (IN ACRES) UNDER VARIOUS FOOD CROPS



1. Which combination of three crops contribute to 50% of the total area under the food crops ?

(a) Wheat, Barley and Jowar

(b)Rice, Wheat and Jowar

(c) Rice, Wheat and Barley

(d)Bajra, Maize and Rice

2. If the total area under jowar was 1.5 million acres, then what was the area (in million acres) under rice?

(a)6 (b)7.5 (c)9 (d)4.5

3. If the production of wheat is 6 times that of barley, then what is the ratio between the yield per acre of wheat and barley ?

(a) 3:2 (b) 3:1 (c) 12:1 (d) 2:3

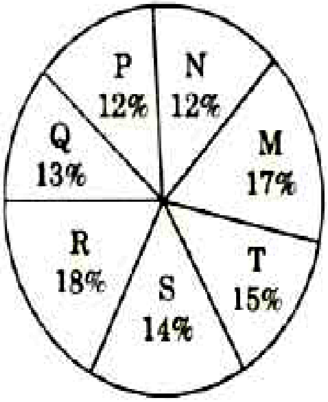
4. If the yield per acre of rice was 50% more than that of barley, then the production of barley is what percent of that of rice ?

(a)30% (b)33 % (c)35%— (d)36%

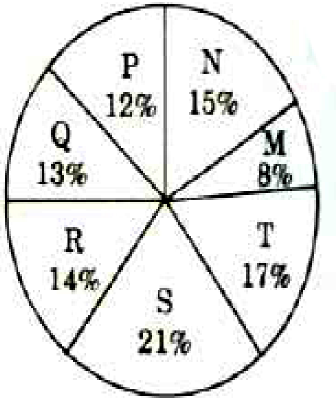
Q14. The following pie-charts show the distribution of students of graduate and post graduate levels in seven different institute-M,N,P,Q,R,S and T in a town.

Distribution of Students at Graduate and Post-Graduate Levels in seven Institutes-M, N, P, Q, R, S and T.

Total Number of students of graduate level



Total Number of students of post graduate level



1. How many students of institutes M and S are studying at graduate level?

(a) 7516 (b) 8463 (c) 9127 (d) 9404

2. Total number of students studying at post -graduate level from institutes N and P is:

(a) 5601 (b) 5944 (c) 6669 (d) 7004

3. What is the total number of graduate and post-graduate level students in institute R?

(a) 8320 (b) 7916 (c) 9116 (d) 8372

4 . What is the ratio between the number of students studying at post graduate and graduate levels respectively from institute S?

(a) 14:19 (b) 19:21 (c) 17:21 (d) 19:14

5. What is the ratio between the number of students studying post graduate level from institute S and the number of students studying at graduate level from institute Q?

(a) 13:19 (b) 21:13 (c) 13:8 (d)19:13

Q15. Define components of a computer, hardware and software?

Q16. Define application of chemical software's in analysis?

Q17.Define application of popular softwares are Dupli Checker, Copyleaks, PaperRater,

Plagiarisma, Plagiarism Checker, Plagium, PlagScan, PlagTracker, Quetext, Viper, etc.

Q18. Convert decimal 15 to binary?

Q19. Convert binary to decimals

i) 10; ii) 101; iii) 11001 ; iv) 111011

1.5 ANSWERS

Ans. 2. Sol: log 75/16-2 log 5/9+log 32/243

= log 75/16-log$(5/9)^2$+log32/243

= log 75/16-log25/81+log 32/243

= log(75/16*32/243*81/25)=log 2

Ans. 3 Sol: $\log_{10} 3+\log_{10} (4x+1)=\log_{10} (x+1)+1$

$\text{Log}_{10} 3+\log_{10} (4x+1)=\log_{10} (x+1)+\log_{10} (x+1)+\log_{10} 10$

$\text{Log}_{10} (3(4x+1))=\log_{10} (10(x+1))$

$=3(4x+1)=10(x+1)=12x+3$

$=10x+10$

$=2x=7=x=7/2$

Ans. 4. Given expression: $\log_{xyz} xy+ \log_{xyz} yz+ \log_{xyz} zx$

$=\log_{xyz} (xy*yz*zx)=\log_{xyz} (xyz)^2$

$2\log_{xyz}(xyz)=2*1=2$

Ans. 5. Soln. $\log_{10} 50=\log_{10} (100/2)$

$=\log_{10} 100-\log_{10} 2$

$=2-0.30103$

$=1.69897.$

Ans. 6. **Soln.**

i) log 25=log(100/4)=log 100-log 4=2-2log 2=(2-2*.3010)=1.398.

ii) log 4.5=log(9/2)=log 9-log 2=2log 3-log 2

=(2*0.4771-.3010)=.6532

Ans. 7. **Soln.** log 2^{56} =56log2=(56*0.30103)=16.85768.

Its characteristics is 16.

Hence,the number of digits in 2^{56} is 17

Ans. 8. 1. d : The exports are more than the imports implies that the ratio of value of imports to exports is less than 1.

Now, this ratio is less than 1 in the years 1995,1996,1997 and 2000.

Thus, there are four such years.

2. c: The imports are minimum proportionate to the exports implies that the ratio of the value of imports to exports has the minimum value.

Now, this ratio has a minimum value of 0.35 in 1997, i.e., the imports are minimum proportionate to the exports in 1997.

3. b: Ratio of imports to exports in the years 1996=0.85.

Let the exports in 1996=Rs.320 crores.

Then,272/x =0.85 implies x=272/.85 = 320.

Exports in 1996 = Rs.320 crores.

4. e: The graph gives only the ratio of imports to exports for different years. To find the percentage increase in imports from 1997 to 1998, we require more details such as the value of imports or exports during these years. Hence, the data is inadequate to answer this question.

5. d: The ratio of imports to exports for the years 1998 and 1999 are 1.25 and 1.40 respectively.

Let the exports in the year 1998 = Rs. x crores

Then, the exports in the year 1999=Rs(500-x) crores.

1.25=250/x implies x=250/1.25=200

Thus the exports in the year 1999=Rs. (500-200)crores=Rs.300 crores

Let the imports in the year 1999=Rs. y crores

Then, 1.4=y/300 implies y=(300*1.4)=420.

Imports in the year 1999=Rs.420 crores.

Ans. 9. From the line-graph it is clear that the productions of Company X in the years 1997,1998,1999,2000,2001 and 2002 are 119000,99000,141000,78000,120000and 159000 respectively and those of Company Y are 139000,120000,100000,128000,107000 and 148000 respectively.

1. (c) : Total production of Company X from 1997 to 2002

= 119000+99000+141000+78000+120000+159000 = 716000

and total production of Company Y from 1997 to 2002

=139000+120000+100000+128000+107000+148000=742000

Difference=742000-716000=26000.

1. (d) : Require difference = 128000-107000 = 21000.
2. (a) : Average number of vehicles manufactured by Company X

   = (91/6)* (119000 + 99000 + 141000 + 78000 + 120000 + 159000) = 119333.

3. (d) : The difference between the production of Companies X and Y in various years are.

   For 1997 = (139000 – 119000) = 20000;

   For 1998 = (120000 – 99000) = 21000;

   For 1999 = (141000 – 100000) = 41000;

   For 2000 = (128000 – 78000) = 50000;

   For 2001 = (120000 – 107000) = 13000;

   For 2003 = (159000 – 148000) = 11000;

   Clearly, maximum difference was in 2000.

4. (b) : Required percentage = [(128000/78000)* 100] % = 164 %.

Ans. 10. Sol.1. (b) : Profit percent ofcompany Y in 1997=35.

Let the income of company Y in 1997 be Rs.x crores

$$\text{Then,}35 = \frac{x-220}{220} \text{ X } 100 \Rightarrow x = 297$$

$\therefore$Income of company Yin 1997 = Rs.297crores

2. (d): Let the incomes of the twocompanies X and Yin 1999 be Rs.x and let the Expenditures of companies X and Y in 1999 be E_1 and E_2 respectively

   Then, for Company X we have:

$$50 = \frac{x-E1}{E1} \times 100 \Rightarrow \frac{50}{100} = \frac{x}{E1} - 1 \Rightarrow x = \frac{150}{100} E1$$

Also, for the Company Y we have:

$$60 = \frac{x-E2}{E2} * 100 \Rightarrow \frac{60}{100} = \frac{x}{E2} - 1 \Rightarrow x = \frac{160}{100} E2$$

From (i) and (ii),we get

$$\frac{150}{100} E1 = \frac{160}{100} E2 \Rightarrow \frac{E1}{E2} = \frac{160}{150} = \frac{16}{15} \text{(Required ratio)}$$

3.(c):Let the incomes in 2000 of companies X and Y be 3x and 4x respectively.And let the expenditure in 2000 of companies X and Y be E1 and E2 respectively.

Then, for company X we have:

$$65 = \frac{3x-E1}{E1} * 100 \Rightarrow \frac{65}{100} = \frac{3x}{E1} - 1 \Rightarrow E1 = 3x * \left(\frac{100}{165}\right)$$

For company Y we have:

$$50 = \frac{4x-E2}{E2} * 100 \Rightarrow \frac{50}{100} = \frac{4x}{E2} - 1 \Rightarrow E2 = 4x * \left(\frac{100}{150}\right)$$

From (i)and(ii) we get:

$$\frac{E1}{E2} = \frac{3x*(100/165)}{4x*(100/150)} = \frac{3*150}{4*165} = \frac{15}{22} \text{(Required ratio)}$$

4. (d):Let the expenditures of each of the Companies X and Y in 1996 be Rs.xcrores.And let the income of Company X in 1996 be Rs.zcrores so that the income of Company Y in 1996 =Rs.(342-z)crores.

Then,for company X we have:

$$40 = \frac{z-x}{x} * 100 \Rightarrow \frac{40}{100} = \frac{z}{x} - 1 \Rightarrow x = \frac{100z}{140}$$

Also for company Y we have:

$$45 = \frac{(342-z)-x}{x} * 100 \Rightarrow \frac{45}{100} = \frac{(342-z)}{x} - 1 \Rightarrow x = \frac{(342-z)*100}{145}$$

From(i)and (ii) we get:

100z = (342-z) *100 =>z = 168

140145

Substituting z=168 in (i),we get: x=120

∴ Total expenditure of companies X and Y in 1996=2x=Rs.240crores.

Total income of companies X and Y in 1996=Rs.342 crores.

∴Total profit =Rs.(342-240)crores =Rs.102 crores

5. (a): Let the income of company X in 1998 be Rs.x crores.

Then,55= x-200 *100 => x = 310.

200

∴Expenditure of Company X in 2001= Income of company X in 1998 = Rs.310crores

Let the income of company X in 2001 be Rs.z crores

Then,50 = z-310 *100 =>z = 465.

310

∴Income of company X in 2001 = Rs.465 crores.

Ans. 11. Sol: **1**(b):required difference = [(45-25)*i,00,000]tons=20,00,000 tons

2 (c):average production of company x in the period 1998-2000=[1/3*(25+50+40)]=(115/3) lakh tons

average production of company y in the period 1998-2000

[1/3*(35+40+50)]=(125/3) lakh tons

therefore req ratio=(115/3)/(125/3)=115/125=23/25

3 (d):percentage increase in the production y from 1996-1999=[(40-25)/25*100]%=(15/25*100)%=60%

4 (e):average production (in lakh tons)in five years for the three company's are:

for company x=[1/5*(30+45+25+50+40)]=190/5=38

for company y=[1/5*(25+35+35+40+50)]=185/5=37

for company z=[1/5*(35+40+45+35+35)]=190/5=38

therefore the average production of maximum for both the company's x and z

5 (a) : Percentage change (rise/fall)in the production of Company Y in comparison to the previous year, for different years are:

For 1997 = [((32-25)/25)*100]% = 40%

For 1998 = [((35-35)/25)*100]% = 0%

For 1999 = [((40-35)/35)*100]% = 14.29%

For 2000 = [((50-40)/40)*100]% = 25%

Hence, the maximum percentage rise/fall in the production of company Y is for 1997.

6 (a) : The percentages of production of company z to the production of company z for various years are:

For 1996 = ((35/25)*100)%=140%; For 1997 = ((40/35)*100)% = 114.29%

For 1998 = ((45/35)*100)%=128.57%; For 1999 = ((35/40)*100)%=87.5%

For 2000 = ((35/50)*100)%=70%

Clearly, this percentage is highest for 1996.

Ans. 12. Sol. 1. (a) : The percentage increase in the amount invested in raw-materials as compared to the previous year, for different years are:

For 1996 = [((225-120)/120)*100]% = 87.5%

For 1997 = [((375-225)/225)*100]% = 66.67%

For 1998 = [((525-330)/330)*100]% = 59.09%

For 2000 there is a decrease.

2. (b)The percentage change in the amount invested in raw-materials and in the value of sales of finished goods for different years are:

year	Percentage change in amount invested in raw-materials	Percentage change in value of sales of finished goods
1996	[((225-120)/120)*100]% = 87.5%	[((300-200)/200)*100]% = 50%
1997	[((375-225)/225)*100]% = 66.7%	[((500-300)/300)*100]% = 66.67%
1998	[((525-330)/330)*100]% = -12%	[((400-500)/500)*100]% = -20%
1999	[((525-330)/330)*100]% = 59.09%	[((600-400)/400)*100]% = 50%
2000	[((420-525)/525)*100]% = -20%	[((460-600)/600)*100]% = -23.33%

Thus the percentage difference is same during the year 1997.

3. (d) : Required difference = Rs. [(1/6)*(200+300+500+400+600+460)

- (1/6)*(120+225+375+330+525+420)] lakhs

= Rs. [(2460/6)-(1995/6)] lakhs = Rs.(410-332.5)lakhs = 77.5 lakhs.

4. (d) : Required percentage = [(600/(375+300+525))*100]% = 48.78% □ 49%

5. (c) : The difference between the amount invested in raw-material and the value of sales of finished goods for various years are :

For 1995 = Rs.(200-120)lakhs = Rs. 80 lakhs

For 1996 = Rs.(200-225)lakhs = Rs. 75 lakhs

For 1997 = Rs. (500-375)lakhs = Rs. 125 lakhs

For 1998 = Rs. (400-330)lakhs = Rs. 70 lakhs.

For 1999 = Rs. (600-525)lakhs = Rs. 75 lakhs

For 2000 = Rs. (460-420)lakhs = Rs. 40 lakhs.

Clearly, maximum difference was during 1997

Ans. 13. solutions

1.(c):The total of the central angles corresponding to the three crops which cover 50% of the total area ,should be 180°.Now, the total of the central angles for the given combinations are:

(i) Wheat,Barley and jowar = (72°+36°+18°)=126°

(ii) Rice,Wheat and Jowar = (72°+72°+18°)=162°

(iii) Rice,Wheat and Barley = (72°+72°+36°)=180°

(iv) Bajra,Maize and Rice = (18°+45°+72°) = 135°

Clearly:(iii) is the required combination.

2. (a): The area under any of the food crops is proportional to the angle corresponding to that crop.
Let the area under the rice production be x million acres.
Then, 18:72 = 1.5:x ⇒ x=(72*15/18)=6
Thus, the area under rice production be = 6 million acres.

3. (b): Let the total production of barley be T tones and let Z acres of land be put under barley production.
Then, the total production of wheat =(6T) tones.
Also,area under wheat production = (2Z) acres.

$$\therefore \frac{\text{Area Under Wheat Production}}{\text{Area Under Barley Production}} = \frac{72^\circ}{36^\circ} = 2$$

And therefore,Area under wheat = 2*Area under Barley = (2Z)acres

Now, yield per acre for wheat = (6T/2Z) tones/acre = (3T/Z) tones/acre

And yield per acre for barley = (T/Z) tones/acre.

$$\therefore \text{Required ratio} = \frac{3T/Z}{T/Z} = 3:1.$$

4. (b):Let Z acres of land be put under barley production.

$$\text{Then, } \frac{\text{Area Under Rice Production}}{\text{Area Under Barley Production}} = \frac{72^\circ}{36^\circ} = 2.$$

∴ Area under rice production = 2 * area under barley production = (2Z) acres.

Now,if p tones be the yield per acre of barley then ,yield per acre of rice

=(p+50% of p) tones =(3/2 p) tones.

∴ Total production of rice = (yield per acre) * (area under production)

= (3/2 p)*2Z=(3pZ) tones.

And,Total production of barley = (pz) tones.

∴ Percentage production of barley to that rice = (pZ/3pZ *100)%= 33 1/3% .

Ans. 14.

1. (b):Students of institute M at graduate level = 17% of 27300 = 4641.

Students of institute S at graduate level = 14% of 27300 = 3822

∴ Total number students at graduate level in institutes M and S = 4641+3822=8463

2. (c):Required number = (15% of 24700) + (12% of 24700) = 3705 + 2964 = 6669.

3. (d):Required number = (18% of 27300) + (14% of 24700) = 4914 + 3458 = 8372.

4. (d):Required ratio = $\frac{(21\% \text{ of } 24700)}{(14\% \text{ of } 27300)} = \frac{21 * 24700}{14 * 27300} = \frac{19}{14}$

5. (d):Required ratio = $\frac{(21\% \text{ of } 24700)}{(13\% \text{ of } 27300)} = \frac{21 * 24700}{13 * 27300} = \frac{19}{13}$

Ans. 15 Study Section 1.2.5 use and application of different software in the chemistry

Ans. 16 Study Section 1.2.5 use and application of different software in the chemistry

Ans.17 Study Section 1.2.5 use and application of different software in the chemistry

Ans. 18 To convert decimal to binary

Divide the decimal number by 2

- If there IS a remainder the rightmost column will be a 1
- If there is NO remainder, the rightmost column will be a 0.

Then repeat the process, moving one column to the left each time until you have divided down to
15/2 = 7 remainder 1 (Binary number = ???1)
7/2 = 3 remainder 1 (Binary number = ??11)
3/2 = 1 remainder 1 (Binary number = ?111)
The final result will always be 1 in the leftmost column (Binary number = 1111)

Ans.19 To convert binary to decimal, each digit is multiplied by the value of its position, and the results are added.

$10 = (1*2^1) + (0*2^0) = 1*2 + 0*1 = 2 + 0 = 2 \rightarrow$ 10 (binary) =2 (decimal)

$101 = (1*2^2) + (0*2^1) + (1*2^0) = 1*4 + 0*2 + 1*1 = 4 + 0 + 1 = 5 \rightarrow$ 101 (binary) =5 (decimal)

$11001 = (1*2^4) + (1*2^3) + (0*2^2) + (0*2^1) + (1*2^0) = 1*16 + 1*8 + 0*4 + 0*2 + 1*1 = 16 + 8 + 0 + 0 + 1 = 25 \rightarrow$ 11001 (binary) =25 (decimal)

$111011 = (1*2^5) + (1*2^4) + (1*2^3) + (0*2^2) + (1*2^1) + (1*2^0) = 1*32 + 1*16 + 1*8 + 0*4 + 1*2 + 1*1 = 32 + 16 + 8 + 0 + 2 + 1 = 59 \rightarrow$ 111011 (binary) =59 (decimal)

SUGGESTED READINGS:

Unit-2 : GASEOUS AND LIQUID STATES

Structure

Content

2.1 INTRODUCTION OF STATES OF MATTER

Matter exists in solid, liquid or gaseous state depending on temperature and pressure. A familiar example is the compound H_2O, which can exist as ice; water or steam. The study of the gaseous state is the easiest as gas laws take a simple form at low pressure and high

temperature. However, these laws are not valid at all temperatures and ptessures. Also.the

range of validity depends on the nature of the substance. itself. In a gas, the molecules on the average are separated by large intermolecular distances and at such distances, interactions between these molecules are very weak. This is not so in solids and liquids. Hence, the molecules in a gas have greater freedom of motion. As a reult of this, they move about randomly and tend to occupy the paximum space available to them. Hence, gases have no particular shape or volume. Another consequence of their random motion is that each gas molecule collides with other molecules and also with the walls of the container. The constant bombardment against the walls of the container manifests itself as the pressure exerted by the gas.

The gas laws based on certain assumptions regarding molecules and their interaction with each other. Some of these assumptions are not valid under all conditions: the gases obey ideal gas laws only: room temperature, low pressures and high temperatures. To start with the deviation of the real gases from ideal gas behavior will be discussed in this unit. The features of the isotherms at different temperatures will he explained. Afterwards, van der Waals equation will be deduced. This will be followed by a discussion on critical phenomena and critical constants. The relationships between critical constants and van der Walls constants will be derived. The principle of corresponding states will be explained. After this, the methods of liquefaction of gases will be outlined. Finally the nature of intermolecular forces and their effect on gases will be discussed.

Objectives

After studying this unit, you should be able to :

- State the difference in behaviour between real and ideal gases,
- Deduce van der Waals equation,
- Define the terms critical temperature. critical pressure and critical volume.
- Derive the relationships between the critical constants and van der Waals constants.
- State and discuss the principle of corresponding states,
- State the principles of liquefaction methods,

- Explain the nature of intermolecular forces, and discuss the effect of intermolecular forces on the condensation of gases into liquid and solids.

(A) THE GASEOUS STATE

All matter exists in three states gas, liquid and solid. The behavior of gases is very important to a chemist. On account of their compressibility and thermal expansion, gases are affected by changes in pressure and temperature. The quantitative effect of change of pressure and temperature is described by Gas Laws.

2.1.1 POSTULATES OF KINETIC THEORIES OF GASES

The kinetic model is based on three assumptions:

1. The gas consists of molecules of mass m in continual random motion.
2. The size of the molecules is negligible, in the sense that their diameters are much smaller than the average distance travelled between collisions.
3. The molecules interact only through brief, irregular and elastic collisions. An elastic collision is a collision in which the total translational kinetic energy of the molecules is conserved.

There are no attractive forces operating between molecules or between molecules and the walls of the vessel in which the gas has been contained. The molecule moves independently of one direction to another. The pressure of the gas is the hits recorded by the molecules on the walls of the container in which the gas is contained. The average kinetic energy of gas molecules is directly proportional to absolute temperature. This means that the average kinetic energy of molecules is the same at a given temperature. This must be clear to you that all the above postulates are applicable to ideal gases only i.e. the gas which obey Boyle’s and Charle’s law under all conditions of temperature and pressure. These are only approximately valid for real gases.

DERIVATION OF KINETIC GAS EQUATION

Suppose a volume of gas enclosed in a cubical vessel at a fixed temperature.

Let us consider one single molecule of a gas can be evaluated by calculating the momentum during collisions.

Suppose:

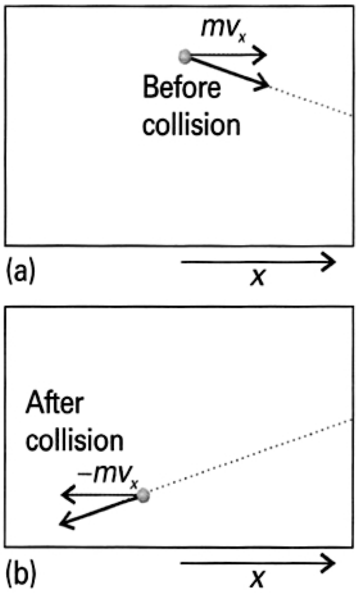
the length of each side of cube = l cm

the number of gas molecules = n

the mass of one molecule = m

the velocity of a molecule = ν

According to kinetic model the molecules of the gas are moving in straight lines in all possible directions. They collide with one another frequently as also with the walls of the container. Since their mutual collisions are perfectly elastic and do not involve the loss of energy, these may be neglected. Here we will, therefore, assume that gas molecules moves in all directions but rebound whenever they strike the wall of the container. Now you proceed to derive kinetic gas equation in the following steps



According to the kinetic theory, a molecule of a gas can move with velocity in any direction velocity is a vector quantity can be resolved into components ν_x, ν_y, ν_z along the X, Y and Z axes. These components are related to velocity by the following expression.

$$\nu^2 = \nu_x^2 + \nu_y^2 + \nu_z^2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots..(1)$$

Let us consider a molecule moving in ox direction between opposite faces A and B. It will strike the face A with velocity ν_x and rebound with velocity $-\nu_x$. To hit the same face again the molecule must travel l cm to Collide with opposite face B and then again l cm to return to face A. Therefore time taken between two collisions can be calculated as follows

The molecule travels ν_x cm in 1 sec

hence 1 cm in $1/\nu_x$ sec

And 2l cm in $2l/\nu_x$ sec ....(2)

In $2l/\nu_x$ sec molecule suffers 1 collision

In 1 sec no of collisions = $\nu_x/2l$ ....(3)

Each impact of the molecule on the face A causes a change of momentum which is mass x velocity.

Momentum of the molecule before impact = m ν_x

Momentum of the molecule after impact = - m ν_x

Hence change of momentum = m ν_x – (-m ν_x) = 2m ν_x

But the number of collision per second on face A= $\nu_x/2l$

Therefore total change of momentum per second on face

A caused by one Molecule = 2mν_x x $\nu_x/2l$

= m ν_x^2/l ....(4)

As there are two faces along x- direction,

The total change of momentum per second considering both the faces along x-direction will be

2m ν_x^2/l ....(5)

Pressure

It is the force exerted by the impacts of the molecules of a gas per unit surface area. It is measured in **torr** or **mm** Hg or **atmosphere.** The SI unit of pressure is **Pascal (Pa).**

1atm = 760 mm Hg = 760 torr = 1.013 × 105 Pa

Temperature

It is the degree of hotness or coldness of a gas. It determines the average kinetic energy of the gas molecules and is measured in **degrees Celsius.** The absolute temperature is measured in **degrees Kelvin.**

K = °C + 273

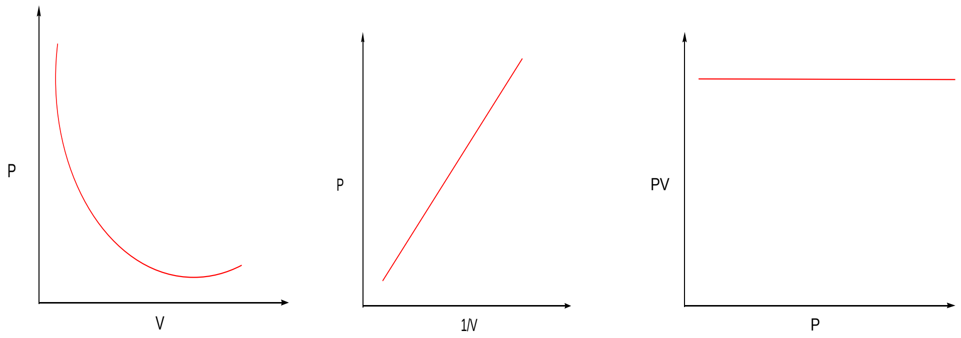
BOYLE'S LAW

The volume of a given sample of a gas varies **inversely** as its pressure at constant temperature.

Mathematically, we can write

$$V \infty \frac{1}{P} \text{ or } V \infty \frac{k}{P} \text{ or } PV = k \text{ (At constant Temperature)}$$

Graphically Boyle's law can be expressed in the following ways:



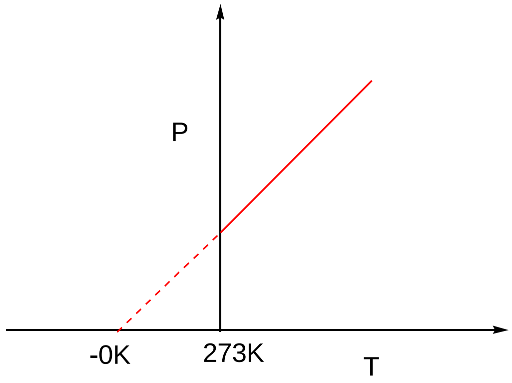
Graphical representation of Boyle's Law

CHARLE'S LAW

The volume of a given sample of a gas is **directly** proportional to its Kelvin or absolute temperature at constant pressure. Mathematically,

$$V \infty T \ \text{ or } \ V = kT \ \text{ or } \ \frac{V}{T} = k \text{ (At constant Pressure)}$$

we can write Graphically, Charle's law can be represented as



ABSOLUTE ZERO

The volume of the gas theoratically becomes zero at –273°C or 0 K and this temperature is called absolute zero of temperature. In actual practice, the gas changes to liquid or solid before this temperature is attained.

STANDARD CONDITIONS OF TEMPERATURE AND PRESSURE (STP)

The volume of gases present in two different samples can be compared only if these are at same

temperature and pressure. For this purpose it is useful to adopt a set of standard conditions of temperature and pressure. By universal agreement, the standard temperature is chosen as 273K (0°C) and the standard pressure as exactly as one atm (760 torr). These conditions of temperature and pressure are referred to as **Standard conditions** or **Standard temperature and pressure (STP).**

AVOGADRO'S LAW

Equal volumes of all gases at same temperature and pressure contain equal number of molecules or moles. Mathematically,

$$V \propto n \text{ or } V = A \times n$$

where A is a constant of proportionality.

For two gases we have (T and P constant)

$$n_1 = n_2 \quad \text{if } V_1 = V_2 \quad (T \text{ and } P \text{ constant})$$

COMBINED GAS LAWS OR IDEAL GAS EQUATION

The simultaneous effect of change of pressure and temperature of a gas can be studied by combining Boyle's law and Charles' law. The derived new equation is called combined gas law or ideal gas equation.

$$\text{Boyle's law } V \infty \frac{1}{P} \text{ constant)}$$

$$\text{Charles' law } V \propto T \text{ (}P\text{ constant)}$$

$$\therefore \qquad V \infty \frac{T}{P} \text{ or}$$

$$V = \frac{kT}{P} \quad \text{or} \quad k = \frac{PV}{T}$$

Or

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

This expression is a mathematical statement of combined gas law. If $T_1 = T_2$, the equation reduces to $P_1V_1 = P_2V_2$ (Boyle's law). Alternatively, if $P_1 = P_2$ the expression becomes

$$V_1/ T_1 = V_2 / T_2 \text{ (Charles' law)}$$

2.1.2 IDEAL BEHAVIOUR

An ideal gas is one which obeys the gas laws for the equation PV = RT, at all pressures and temperatures. However, no gas is ideal. They approach perfection as the temperature gets farther from their boiling points.

Thus the gases H_2, N_2 and CO_2 which fail to obey the ideal-gas equation and termed as non ideal or real gases. The extent to which a real gas departs from ideal behaviour may be depicted in terms of a function called compressibility factor (Z).

$$Z = \frac{PV}{RT}$$

For an ideal gas Z =1. For real gases the deviation from ideal behaviour will be determined by the value of Z being greater or less than unity.

Effect of pressure

The compressibility factor Z, plotted against pressure for H_2, N_2 and CO_2 at constant temperature.

At very low pressure for all these gases Z is approximately one. This indicates that all real gases exhibit ideal behaviour (upto 10 atm). For H_2 curve lies above ideal gas curve at all pressure. For N_2 and carbon CO_2, Z first decreases. It passes to a minimum then increases continuously with increase of pressure. For gas like CO_2 the dip in the curve is greatest as it is most easily liquified.

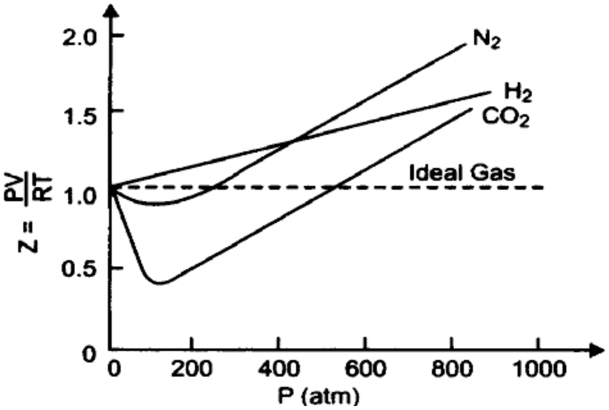


Figure: For compressibility factor Z, plotted against pressure for H_2, N_2 and CO_2

at constant temperature

Effect of temperature

The compressibility factor Z against P at different temperature for N_2. It is clear from the plot that at low temperature deviation are more and at high temperature the gas tends to become more ideal.

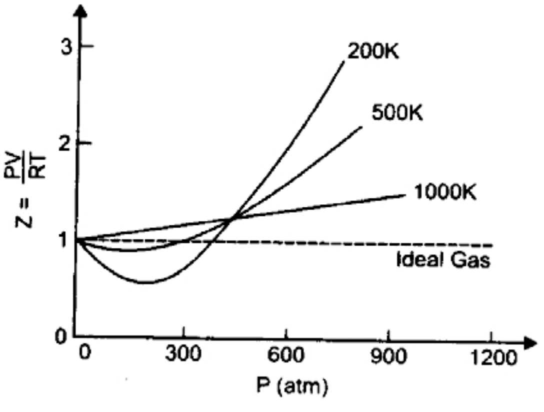


Figure: For compressibility factor Z against P at different temperature for N_2

2.1.3 VAN DER WAALS EQUATION OF STATE

1873, Von der Waal’s studied the postulates of kinetic theory in detail and found that there are two imperfect postulates.

(i) The molecules in a gas are point masses and possess no volume.

(ii) There are no intermolecular attractions in a gas.

Von der Waal's was the first to introduce systematically the correction terms due to the above two invalid assumptions in the ideal gas equation PV = nRT. His corrections are given below.

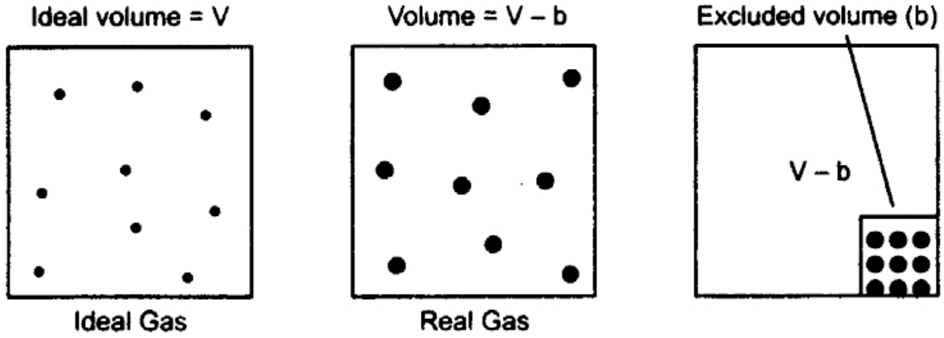
Volume correction

Volume of the gas in the available space for the movement of gas molecules. Volume V of an ideal gas is the same as the volume of the container. The dot molecule of ideal gas has zero-volume and the entire space in the container is available for their movement. But von der Waals assume that molecules of real gas are rigid spherical particles which posses a definite volume. The volume of real gas is therefore, ideal volume minus the volume occupied by gas molecules. If b is the effective volume of molecules per mole of the gas,

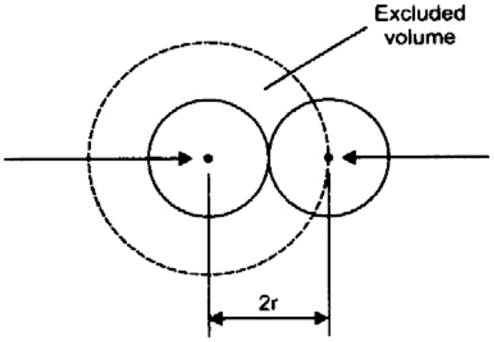
Then corrected volume should be $V - b = V_{ideal}$,

For n moles $V_{ideal} = V - nb$,

b is also known as excluded volume.



Now let us consider two molecules of radius r colliding with each other, Therefore, the space indicated by the dotted sphere having radius 2r will not be available to all other molecules of the gas.



In other words the dotted space is excluded volume per pair of molecules. Thus,

$$\text{Excluded volume for two molecules} = \frac{4}{3}\pi(2r)^3$$

$$= 8\frac{4}{3}\pi r^3$$

Excluded volume per molecules $= \frac{1}{2} 8 \frac{4}{3} \pi r^3$

$$= 4\frac{4}{3}\pi r^3 = b$$

Thus, for n molecules $= n4\frac{4}{3}\pi r^3 = nb$

Pressure correction

A molecule in a gas is attracted by other molecules on all sides, but these attractive forces cancel out. However, a molecule about to strike the wall of the vessel is attracted by molecules on one side only. Hence, it experiences an inward pull due to unbalanced forces.

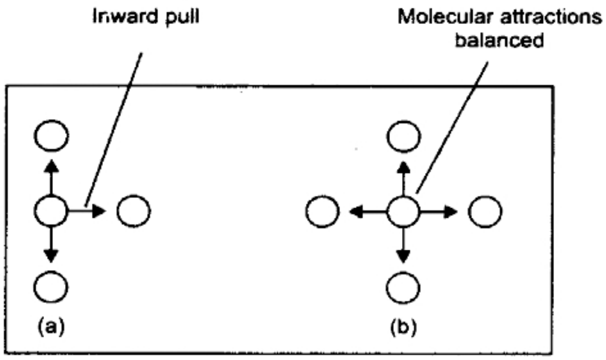


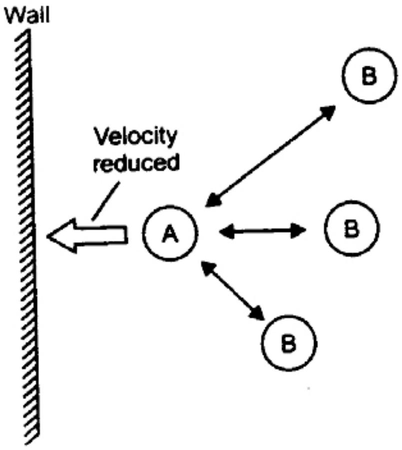
Figure: A molecule in a gas is attracted by other molecules and vessel side

Therefore, it strikes the wall with reduced velocity and the actual pressure of the gas P, will be less than ideal pressure if the pressure P, is less than P_{ideal} by a quantity p,

Thus we have $P = P_{ideal} - p$

Or $P_{ideal} = P + p$

Value of p is determined by the force of attraction between molecules, A striking the wall of the container and molecules, B pulling them inward shown in figure below.



Therefore the net force of attraction is proportional to the concentration of A type molecules and also of B type of molecules.

Thus $p \; \alpha \; C_a C_b$

Or $\alpha \; a \frac{n}{v} \times \frac{n}{v}$

$$\alpha \; a \frac{n^2}{v^2}$$

Where, n= total number of gas molecules in gas volume V.

Hence, at ideal pressure $Pi = P + a \frac{n^2}{V^2}$

On substituting the value of corrected volume and pressure in the ideal gas equation

$$PV = nRT$$

We have

$$P + a \frac{n^2}{V^2} + (V - nb) = nRT$$

This is equation for n moles for one mole

$$(P + \frac{a}{V^2}) + Vb = nRT$$

Von der Waal's equation can justify the deviations from ideal gas behavior as given below

The equation can be written as

$$PV - Pb + \frac{a}{V} + \frac{ab}{V^2} = RT = P_i V_i$$

$\frac{ab}{V^2}$ is very small quantity, as it can be neglected

Thus we get $PV - Pb + \frac{a}{V} = = P_i V_i$

(i) **At low pressure,** Pb is small as compared to a/v

Thus $PV + \frac{a}{V} = = P_i V_i$

Or $PV = P_i V_i - + \frac{a}{V}$

This means PV is less than P_iV_i, if gas is ideal.

(ii) **At high pressure**, Pb over weighs to a/v

Thus $PV - Pb = P_i V_i$

Or $PV = P_i V_i + Pb$

This means PV is greater than P_iV_i.

(iii) **At high temperature,** as V is large, Pb and a/V will be negligibly small.

Thus $PV = P_iV_i$

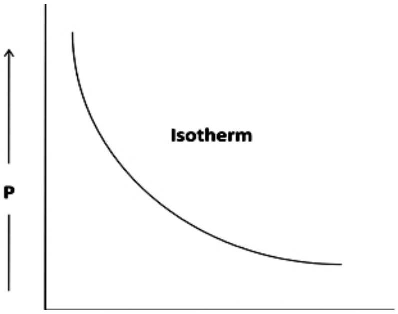
(iv) **Exceptional behavior of light gas like H_2:** This is due to the very small mass of the hydrogen molecule due to which the forces of attraction between molecules are almost negligible. Therefore neglecting the term a/V.

Thus $PV = P_iV_i + P_b$

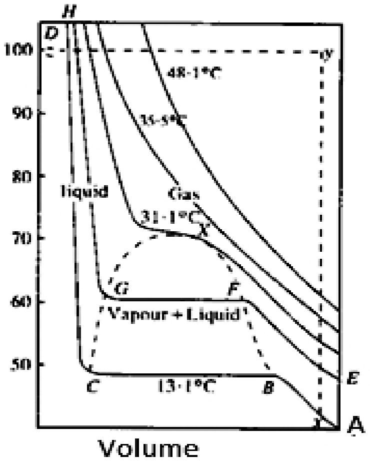
Therefore behavior of light gases like hydrogen, at low pressure PV is greater than P_iV_i.

2.2 CRITICAL PHENOMENA: PV isotherms of real gases

For ideal gas the product of PV is constant and hence the isotherm would be rectangular hyperbola. For most of the gases at normal temperature the shape of P, V curve is the same as it is for CO_2 gas. Isotherm means pressure-volume curve at constant temperature.



Andrews in 1869 determined the isotherm of carbon dioxide at different temperatures. The isotherms of carbon dioxide determined by him at different temperature are shown in figure Consider the first Isotherm at 13.1^o C.



PV isotherm of CO_2 gas

The point A represents CO_2 in the gaseous state, occupying a certain volume under a certain pressure. On increasing the pressure its volume diminishes as is indicated by the curve AB. At B liquification of gas commences and there after a rapid decrease in volume takes place at the same pressure as more and more of gas is converted into the liquid state. At C, the gas has been completely liquified. Now, as the liquid is only slightly compressible further increase of pressure produces only a very small decrease in volume. This is shown by a steep line CD which is almost vertical. Thus along AB, carbon dioxide exists as gas; along BC, it exists partly as gas and partly as liquid while along CD, it exists entirely as liquid. The curve EFGH at 21.5^{o} C shows a similar behaviour except that now the liquification commences at higher pressure and the horizontal portion FG, representing decrease in volume, becomes smaller. At still higher temperature, the horizontal portion of the curve becomes shorter and shorter until at 31.1^{o} C it reduces just to a point represented by X.

The curve passing through this point X marks the boundary between gaseous carbon dioxide and on the right and liquid carbon dioxide on the left. Andrews noted that above 31.1^{o}C there was no possibility of liquefaction of CO_2, how great the pressure is applied. At this temperature the gas is in critical state. The point X is then called the **critical point**. The isotherm passing through this point is called the **critical isotherm** and the temperature corresponding to this isotherm is called critical temperature and the volume occupied by one mole of the gas under these conditions is called critical volume.

2.2.2 VAN DER WAALS CONSTANTS

In 1871, Thomas studied the isotherms of carbon dioxide drawn by Andrews. He suggested that there should be no sharp points in the isotherms below the critical temperature. These isotherms should really exhibit a complete continuity of state from gas to liquid. This he showed by a theoretical wavy curve of CO_2 given below.

In the curve MLB represents a gas compressed in a way that would remain stable. The curve MNC represents a superheated liquid. This type of discontinuity of state is predicted by von der Waals cubic equation.

According to values of P and T there should be three values of v. These values are indicated by B, M and C of the curve. The three values of v become closer as the horizontal part of the isotherm. At the critical point, these values become identical. This enables the calculation of critical temperature, critical pressure and critical volume in terms of von der Waals constants.

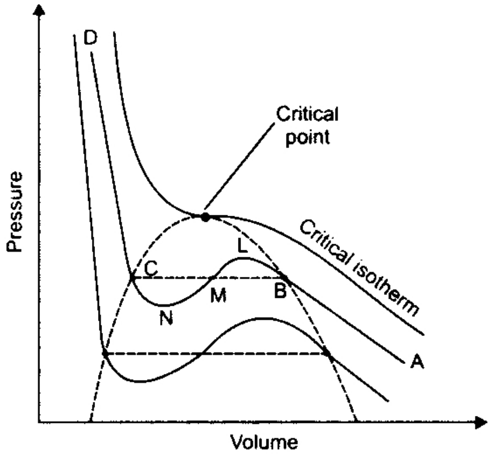


Figure: P-V isotherm of carbon dioxide

Von der Waals equations can be written as $PV - Pb + \frac{a}{V} + \frac{ab}{V^2} = RT$

Or $PV^3 - (RT + Pb)V^2 + aV - ab = 0$

at critical volume V_c $V = V_c$

$$(V - V_c)^3 = 0$$

$$V^3 - 3V^2V_c + 3VV_c^2 - V_c^3 = 0 \text{ ---------------------------(i)}$$

Thus at critical point

$$V^3 - \left(\frac{RT_c}{P+b}\right)V^2 + \left(\frac{a}{P_c}\right)V - \frac{ab}{P_c} = 0\text{-----------------------(ii)}$$

$$3V_c = \frac{RT_c}{P_c} + b\text{----------------------(iii)}$$

$$3V_{c^2} = \frac{a}{P_c}\text{-------------------------(iv)}$$

Or $\boldsymbol{a = 3V_{c^2} + P_c}$

$$V_c^3 = \frac{ab}{P_c}\text{------------------------(v)}$$

From equation (iv) and (v)

$$V_c = 3b\text{-----------------------(iv)}$$

Or $\boldsymbol{b = \frac{V_c}{3}}$

Substituting value of V_c in equation (iv)

$$P_c = \frac{a}{27b^2}\text{------------------(vii)}$$

Thus substituting the values of V_c and P_c in equation (iii)

$$T_c = \frac{8a}{27Rb} \quad \text{----------------------(viii)}$$

By substituting the value values of **a** and **b,** critical constants can be calculated.

Table: Van der Waals coefficients

Gas	a (atm dm^6 mol^{-2})	b (10^{-2} dm^3 mol^{-1})
Ar	1.337	3.20
CO_2	3.610	4.29
He	0.0341	2.38
Xe	4.137	5.16

The actual determination of critical constants is often a task of considerable difficulty of these critical pressure and critical temperature can be measured relatively easily with the help of Cagniard de la Tour's apparatus.

2.2.3 REDUCED EQUATION OF STATE

An equation which expresses the relation between pressure volume and temperature of a gas is called the equation of state or the characteristic equation. When we express the actual pressure, volume and temperature as fractions of the critical pressure, volume and temperature respectively, we get the reduced equation of state.

If the values of pressure, volume and temperature be expressed in fractions of the corresponding critical values, then we get

$$\boldsymbol{\frac{P}{P_c} = \pi \;;\; \frac{V}{V_c} = \Phi \;;\; \frac{T}{T_c} = \theta}$$

Where, $\pi, \Phi\ and\ \theta$ is termed as reduced pressure, reduced volume and reduced pressure respectively.

Or $$\boldsymbol{P = \pi P_c \;;\; V = \Phi\, V_c \;;\; T = \theta\, T_c}$$

Substituting P, V, and T by πP_c ; $\Phi\, V_c$; $\theta\, T_c$ respectively in

Von dar Waal equation $$(P + \frac{a}{V^2}) + Vb = nRT$$

$$\{(\boldsymbol{\pi P_c} + \frac{a}{(\boldsymbol{\Phi\, V_c})^2}\} + (\boldsymbol{\Phi\, V_c} b) = nR\boldsymbol{\theta\, T_c}$$

By substituting the value of V_c and P_c from equation (vi), (vii) and (viii), $V_c = 3b$, $P_c = \frac{a}{27b^2}$ and $T_c = \frac{8a}{27Rb}$.

Thus $$\left\{\pi \frac{a}{27b} + \frac{a}{9\Phi^2 b^2}\right\} 3(\Phi b - b) = R\theta \frac{8a}{27Rb}$$

After, dividing **a/27b,** both of side in above equation.

We get $$\left\{\pi \frac{3}{\Phi^2}\right\} \{3\Phi - 1\} = 8\theta$$

The law of corresponding states:

Van der Waals reduced equation of state

$$\left\{\pi \frac{3}{\Phi^2}\right\}\{3\Phi - 1\} = 8\theta$$

In this equation the quantities a, b P_c, V_c and T which are characteristic of a given gas have cancelled out, thus making it applicable to all substances in the liquid or gaseous state, irrespective of their specific nature. It is clear that when two substances have the same reduced temperature and pressure they will have the same reduced volume. This is known as the law of corresponding states. When two or more substances are at the same reduced temperature and pressure, they are said to be in corresponding state.

2.3 MOLECULAR VELOCITIES

2.3.1 Root mean square

Velocity (*v)* which if possessed by each of the molecules of the gas leads to correct calculation of total kinetic energy of the gas is known as root mean square velocity.

$$Total\ kinetic\ energy = n\frac{1}{2}mv^2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..2$$

We will proceed to test the validity of the above equation-2 mathematically. Out of the total number of molecules n contained in the given sample of gas, let n_1 , molecules have velocity $v1$, n_2 molecules have velocity v_2 and so on then,

$\boldsymbol{n = n_1 + n_2 + n_3}$

Then the total kinetic energy KE of the n molecules is the sum of the kinetic energies of the individual molecules.

Thus

$$KE = \boldsymbol{n_1}\frac{1}{2}\boldsymbol{m_1 v_1}^2 + \boldsymbol{n_2}\frac{1}{2}\boldsymbol{m_2 v_2}^2 + \cdots \ldots\ldots\ldots\ldots\ldots$$

$$\frac{1}{2}nv^2 = \boldsymbol{n_1}\frac{1}{2}\boldsymbol{m_1 v_1}^2 + \boldsymbol{n_2}\frac{1}{2}\boldsymbol{m_2 v_2}^2 + \cdots$$

$$nv^2 = \boldsymbol{n_1 v_1}^2 + \boldsymbol{n_2 v_2}^2 + \cdots$$

$$v^2 = \frac{\boldsymbol{n_1 v_1}^2 + \boldsymbol{n_2 v_2}^2 + \cdots}{n}$$

thus v^2 is the mean of squares of the velocities of all the n molecules in the gas and is termed as mean square velocity.

So

$$v = \sqrt{\frac{\boldsymbol{n_1 v_1}^2 + \boldsymbol{n_2 v_2}^2 + \cdots}{n}}$$

Here *v* is root of the mean of squares of velocities and is called root mean square velocity and is often written simply as rms velocity. Its value can be calculated as

$$V_{rms} = \sqrt{\frac{3\mathrm{RT}}{M}}$$

2.3.2 Average velocity

The average velocity is given by the arithmetic mean of different velocities possessed by the molecules of the gas at a given temperature.

Suppose one molecule is moving with velocity v_1 one molecule with v_2 and third molecule with velocity v_3, so on. Then total velocity will be ..

$v_1 + v_2 + v_3 +..$

If there are n numbers molecules

Then $v = \frac{\boldsymbol{v_1+v_2+v_3+..}}{\boldsymbol{n}}$

Thus average velocity v_a can be calculated

$$v_a = \sqrt{\frac{2\mathrm{RT}}{M}}$$

2.3.3 Most probable velocities

Velocity possessed by most number of molecules is known as most probable velocity.

Most probable velocity

$$v_{mp} = \sqrt{\frac{8\mathrm{RT}}{\Pi M}}$$

It is found that

$$v_{rms} > v_a > v_{mp}$$

$$v_{rms} : v_a : v_{mp} = 1.0 : 0.92 : 0.82$$

2.3.1 QUALITATIVE DISCUSSION OF THE MAXWELL'S DISTRIBUTION OF MOLECULAR VELOCITIES

Molecules of the gas moves with very high velocity and the velocity changes because of collisions with in very short time. but with the help of Maxwell’s distribution law and molecular kinetic energy molecular velocity can be calculated. It will be clear to you, when you study numerical problems.

a. Effect of temperature on velocity distribution

It is clear from figure given below, that the velocity distribution of molecules in gas is influenced by a rise in temperature. At a higher temperature about 600K the curve maintains the same general trend of distribution. However, it becomes more flattened with the peak shifting to a higher velocity region. In other words, there is more even distribution of velocities about ‘most probable velocity’ and the number of molecules having velocities near this value becomes more. Thus higher the temperature, higher is the most probable velocity.

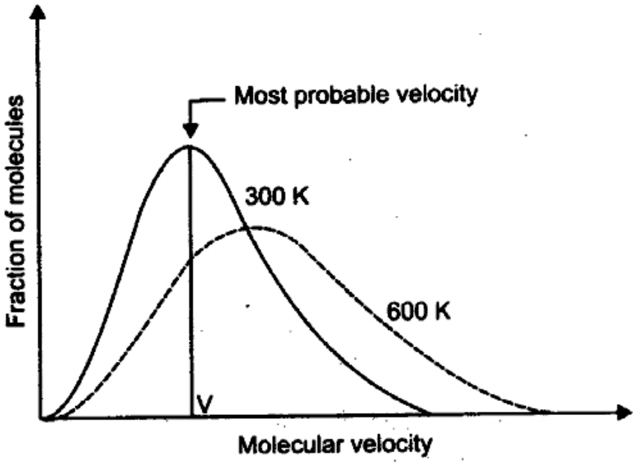


Figure: Distribution of molecular velocities at two temperatures

2.3.1.1 COLLISION NUMBER, MEAN FREE PATH AND COLLISION DIAMETER

2.3.1.1 Collision number/frequency:

The number of collisions taking place per second per unit volume (c.c. = cubic centimeter) of the gas. Let a gas contain N molecules per cc. From kinetic considerations it has been established that the number of molecules n, with which a simple molecule will collide per second, is given by the relation given below

$$n = \sqrt{2\Pi v_a \sigma^2 N}$$

Where $\boldsymbol{v_a}$ =collision velocity $\boldsymbol{\sigma^2}$ = collision diameter

If the total number of collisions taking place per second is denoted by Z, we have

$$Z = \sqrt{2\Pi v_a \sigma^2 N} \, . N$$

$$Z = \sqrt{2\Pi v_a \sigma^2 N^2}$$

Since each collision involves two molecules, the number of collision per second per cc, of the gas will be z/2.

Thus Collision frequency $= \frac{\sqrt{2\Pi v_a \sigma^2 N^2}}{2}$

$$= \frac{\Pi v_a \sigma^2 N^2}{\sqrt{2}}$$

Obviously, the **collision frequency of a gas increases with increase in temperature,** molecular size and the number of molecules per c.c.

Effect of pressure on collision frequency

$$Z \; \alpha \; N^2$$

Where; N = number of molecules per c.c.

Because $P \; \alpha \; N$

Hence; $Z \; \alpha \; P^2$

Finally we can say, collision frequency is directly proportional to the square of pressure of the gas.

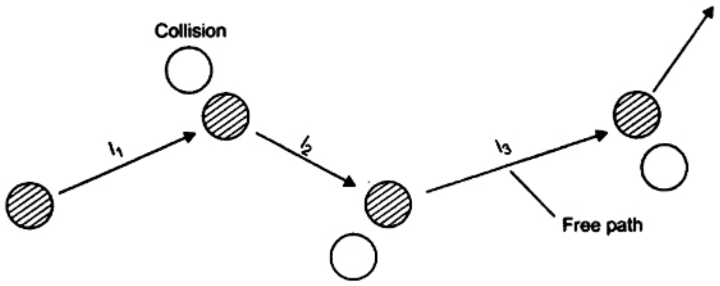
2.3.1.2 Mean free path

A very important quantity in kinetic theory of gases is the mean free path. At a given temperature, a molecule travels in straight line before collision with another molecule.

The distance travelled by the molecule before collision is termed free path. The mean distance travelled by a gas molecule between two successive collisions is called the mean free path. It is denoted by λ. If l_1, l_2, l_3 are the free paths for a molecule of a gas, its free path

$$\lambda = \frac{l_1 + l_2 + l_3 + ..}{n}$$

Where; n = number of molecules with which the molecule collides.



Mean free path denoted by l_1, l_2 and l_3

Thus, molecular collisions will be less at a lower pressure or lower density and longer will be the mean free path. Mean free path is also related with viscosity of the gas.

Thus $$\lambda = \acute{\eta}\sqrt{\frac{3}{P_d}}$$

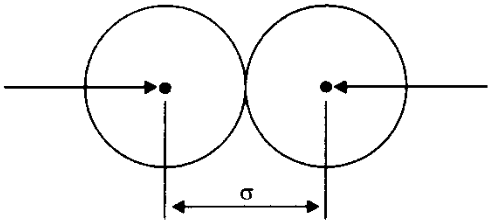
Where; P= pressure of the gas

$\acute{\eta}$ = coefficient of viscosity of the gas

d = density of the gas

Effect of temperature on mean free path

2.3.1.3 Collision Diameter: The kinetic theory of gases treats molecule as point masses. When two such molecules approach each other, a point is reached at which they cannot come closer beyond a certain distance. The closest distance between the centres of the two molecules taking part in collision is called the collision diameter. It is denoted by σ.



Whenever the distance between the centres of two molecules is σ, a collision occurs. The collision diameter can be determined from viscosity measurements. The collision diameter of hydrogen is 2.74Å and that of oxygen is 3.61Å.

2.3.2 LIQUEFACTION OF GASES

The general behavior of gases with the decrease of temperature with increase of pressure is shown by the Andrew isotherm of carbon dioxide.

It is clear from Andrews isotherm, it is necessary to cool a gas below its critical temperature before it can be liquified. In the case of gases like ammonia, Chlorine, sulphur dioxide or carbon dioxide, which has a fairly high critical temperature, by the application of pressure gas can be liquified.

Gases such as hydrogen, oxygen, helium and nitrogen have low critical temperature. So these gases cannot be liquified by this simple technique.

These gases can be liquified if they first cooled below these respective critical temperature. Some of the gases and their critical temperature are shown below in the table

Table: Critical temperatures of various gases

Gas	Critical Temperature (K)
H_2	5.2
Ne	44.2
H_2	33.0
N_2	126.2
O_2	154.8
CO_2	304.2
NH_3	405.0

Two principles are usually applied in cooling gases below these critical temperature.

a. **Joule-Thomson effect:** Joule and Thomson observed that when a gas under high pressure is made to expand into a region of low pressure it suffers a fall in temperature. This phenomenon is known as Joule-Thomson effect.

Experiments have shown that gases become cooler during the Joule-Thomson expansion only when they are below a certain temperature known as inversion temperature T_i. The inversion temperature is characteristic of each gas. The inversion temperature is related to von der Waals constants a and b of the gas concerned by the expression.

$$T_i = \frac{2a}{Rb}$$

(B) LIQUID STATE

2.4.1 INTERMOLECULAR FORCES, STRUCTURE OF LIQUIDS (A QUALITATIVE DESCRIPTION)

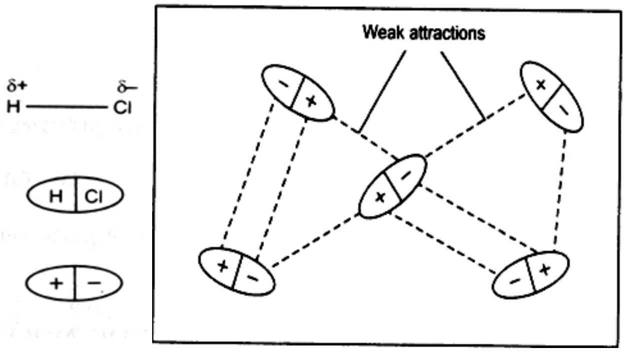
The molecules in a liquid are not far apart from each other, the intermolecular forces are fairly strong. Intermolecular forces in liquids are collectively called Von-der Waal’s forces. The characteristic properties of liquid arise from the nature and the magnitude of these intermolecular forces. These forces are essentially electrical in nature and result from the attraction of charges of

opposite sign. The intermolecular forces are three kinds:

- **(i)** Dipole-dipole interaction
- **(ii)** London forces
- **(iii)** Hydrogen bonding

(i) Dipole-dipole interaction

HCl is an example of a polar molecule. Such molecule has a partial positive charge at one end and a partial negative charge at the other. They are called dipoles. The positive end of one dipole attracts the negative end of the other shown in given figure. These forces are referred to as dipole-dipole attractions.

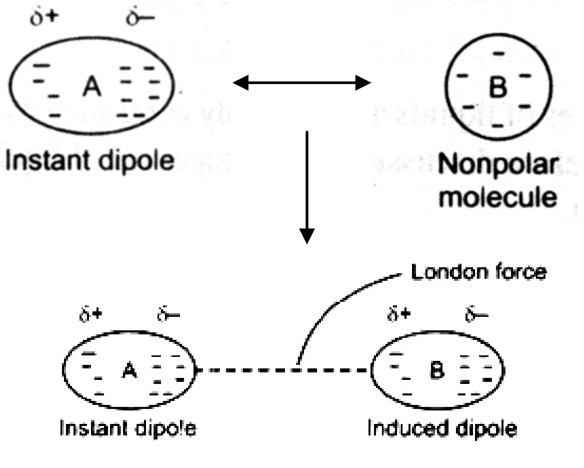


Weak attraction between polar HCl molecules

The thermal energy of molecules tends to disturb these attractions but still there exists a net attraction between the polar molecules. Such attractions are about 1% as strong as covalent bond. Important is the attractions between the opposite poles are greater than repulsive forces between like poles. Thus these molecules have net attraction to each other.

(ii) London forces

Fritz London in 1930 first presented a simple explanation of weak forces between nonpolar molecules or atoms. In a molecule or atom, electrons are constantly moving. Most of the time electrons in the molecules could not be visualized as distributed symmetrically. However according to the principle of probability, for an instant the electrons may concentrate on one side of the molecule than the other. This causes the molecule to become temporarily polar and we call it instant dipole (A). The negative side of the instantaneous dipole repels the electrons of an adjacent molecule (B). As a result the second molecule B also becomes a dipole by induced polarity. This is called induced dipole.



Explanation of London forces

The instantaneous dipole of A and the induced dipole of B will now attract each other. Because the electrons keep moving an instant dipole may vanish the next moment and new are produced. This continual process produces a weak overall attraction between molecules of liquid.

The temporary attraction between the molecules of liquid caused by instantaneous-dipole and induced- dipole attractions are called London forces. These London forces are present in polar molecules also in addition to other von der Waal's forces.

(iii) Hydrogen bonding

In compounds of hydrogen with strongly electronegative elements, such as fluorine, oxygen and nitrogen, the electron pair shared between the two atoms lies far away from the hydrogen atom as a result of which the hydrogen atom becomes highly electropositive with respect to other atom which become electronegative.

This phenomenon of charge separation in water is represented as electronegativity difference in H and O is so large that the electron pair in the covalent bond, H-O is shifted toward O. It leaves a partial positive charge on the H atom. This leads to a strong electrostatic attraction between positively charged H atom and an unshared electron pair on the O atom of another molecule. Thus you can understand that two or more molecules may associate together to form large cluster of molecule.

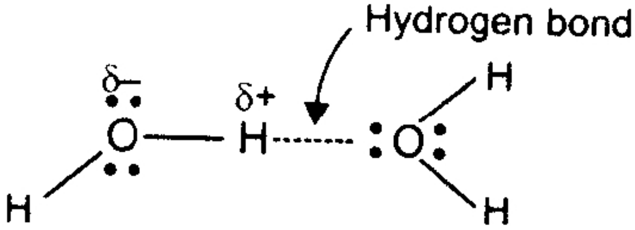


Figure: Showing Hydrogen bonding

In case HF, while the length of covalent bond between H and F atoms is found to be 1.00Å, the length of the hydrogen bond between H and F atoms of neighbouring molecules has been found to be 1.55Å.

The hydrogen bonding is the strongest of all intermolecular forces including the dipole-dipole attractions and London forces.

Characteristic properties of Liquids:

The important properties of liquids are

a. Vapour pressure

b. Surface tension

c. Viscosity

d. Refraction

a. Vapour pressure

When a liquid is an open vessel, it evaporates. You have studied in the gases, that the gas molecules have a particular velocity. This is so in case of liquids also. Only a few liquid molecules have lower or higher velocity, i.e. lower or higher kinetic energies.

When a liquid is placed in an open vessel it evaporates. The molecules in the liquid are moving with different kinetic energies. The molecules that possess above average kinetic energies can overcome the intermolecular forces that hold them in the liquid. These energies molecules escape from the surface as vapour. This process by which molecules of a liquid goes into gaseous state is called vaporisation or evaporation. The reverse process whereby gas molecules become liquid is called condensation.

A stage comes when the number of molecules escaping from the liquid is equal to the number of molecules returning to the liquid. Thus a dynamic equilibrium is established between the liquid and the vapour at a given temperature.

$$\text{Vapour} \rightleftharpoons \text{Liquid}$$

Temperature is the vapour pressure of the liquid. As the temperature rises, the number of molecules escaping from the liquid surface increases as there in increase in the number of vapour molecules in the space above the liquid when equilibrium is attained. Hence vapour pressure of the liquid increases with increase of temperature.

Determination of vapour pressure

Static method:

A simple apparatus used in this method, a sufficient amount of the liquid whose vapour pressure is to be determined in placed in the bulb connected to a mercury manometer and a vacuum pump.

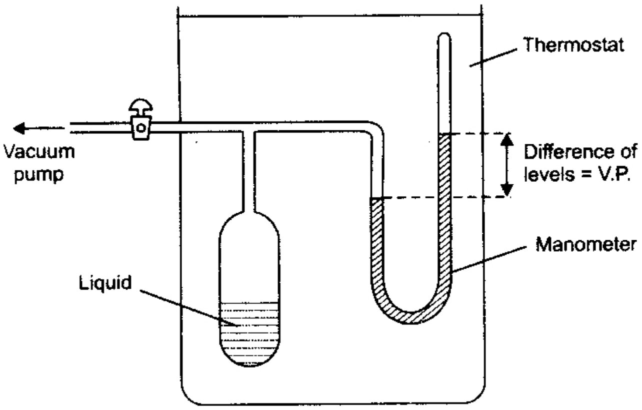


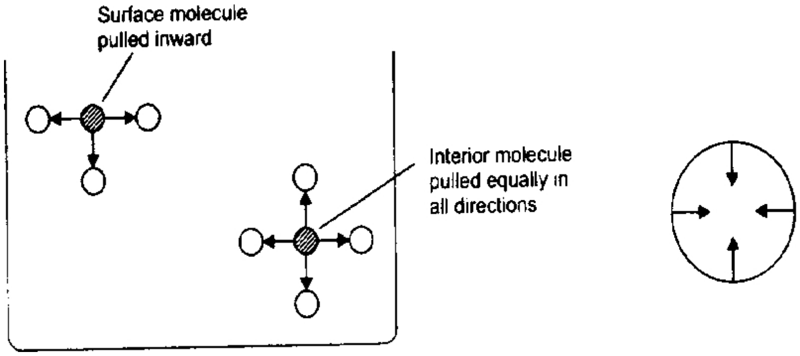
Figure: Setup of Determination of vapour pressure by static method

All the air from the bulb is removed by working the vacuum pump and the stopcock closed. A part of liquid evaporates. The system is then maintained at a fixed temperature for enough time so that equilibrium is attained. The difference in the levels of mercury in the manometer is equal to vapour pressure of the liquid. This method is used for liquids having vapour pressure up to one atmosphere.

(b) Surface tension

The intermolecular forces of attraction in liquids gives rise to a property known as surface tension. A molecule in the interior of a liquid is attracted equally in all directions by the molecules around it. A molecule in the surface of a liquid is attracted only sideways and towards the interior. The forces on the sides being counterbalanced, the surface is pulled only inward the liquid. These unbalanced attractive forces acting downward tend to draw the surface molecules into the body of the liquid and, therefore, tend to reduce the surface to minimum. The liquid then behaves as if it were under a strain or tension. It is this force which is called surface tension. It may be defined as “the force in dynes acting on the surface of the liquid at right angles to one centimetre length of the surface”. It is represented by a symbol γ (gama).

In CGS system, the unit of surface tension is dynes per centimetre (dyne cm^{-1}) and in SI system, the unit is Newton per metre (Nm^{-1}).



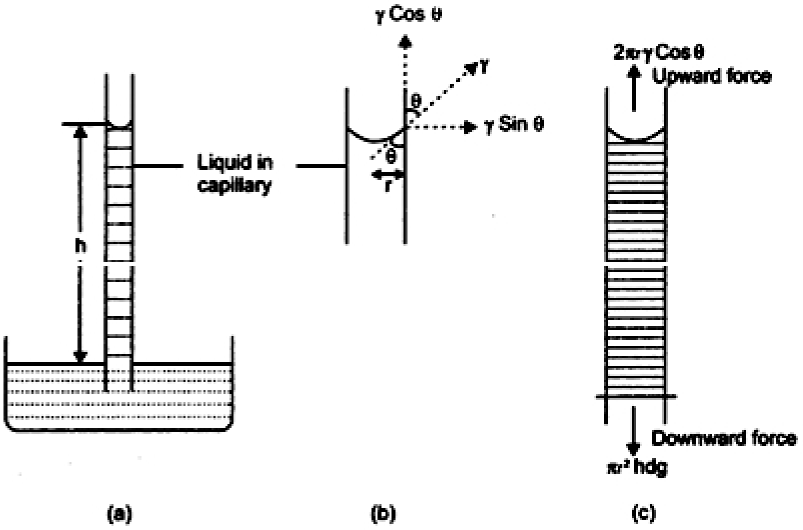
$$\textbf{Surface energy} = \frac{\textbf{force} \times \textbf{work}}{\textbf{area}}$$

When temperature increases, there is increase in kinetic energy of liquid molecules (KEαT) thereby decreasing intermolecular forces. It results in decrease in inward pull functioning on the surface of the liquid. That means you can say surface tension decreases with increase in temperature. As surface tension arises of the attractional forces operating between the molecules, Ramsay and Shields gave the following relationship between the surface tension of a liquid and its temperature.

Determination of surface tension

Capillary rise method:

In this method a capillary tube of radius r is vertically inserted into the liquid. The liquid rises to a height h and form a concave shape at apex.



The surface tension γ acting in the inner circumference of the tube exactly supports the weight of the liquid column. surface tension is force per 1 cm acting at a tangent to the surface. If the angle between the tangent and the tube wall is θ, the vertical component of surface tension is γ cosθ. The total surface tension along the circular contact line of meniscus is 2πr times.

Thus $$Upward\ force = 2\pi r\gamma Cos\theta$$

Where, r = radius of capillary and θ= 0 thus, Cosθ =0, reduced to

$$Upword\ force = 2\pi r\gamma$$

Viscosity

The flow is a characteristic property of liquids. Let us consider flow of a liquid. A liquid may be considered to be consisting of molecular layers arranged one over the other. Some of the liquids flow more rapidly than others. In other words, liquid molecules pose resistance to the flow of one layer over the other. This property of liquids which determines their flow is termed as viscosity. The property of the liquid which determines its flow is called viscosity of the liquid.

The resistance to flow of one layer of liquid molecules over another depends on the following factors.

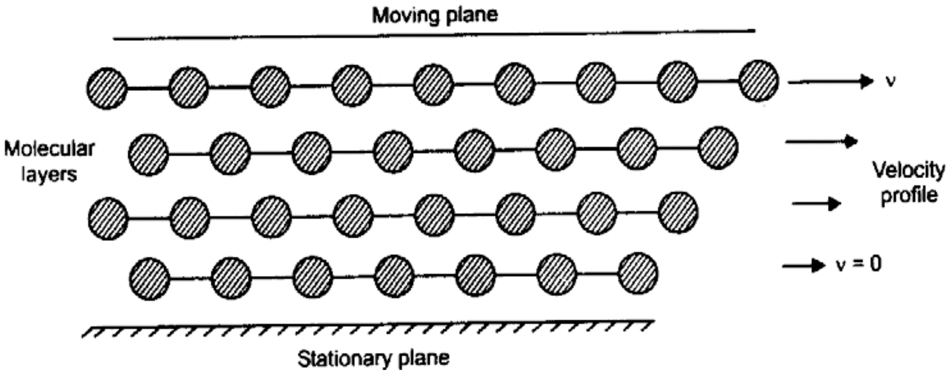
1. The molecular weight of the molecules of a liquid also determines flow of the liquid. Thus heavier the molecule of a given liquid the greater will be its viscosity.

2. The intermolecular attractive forces do not permit a free flow of molecules in a liquid. The strength of intermolecular forces gives viscosity of the liquids.

3. Shape of the molecules of a liquid place an important role in influencing its viscosity. Liquids with the large irregularly shaped molecules are generally known to be more viscous than those with small and symmetrical molecule.

4. An increase in temperature decreases the viscosity of the liquid, the molecular motion increases causing resistance to flow.

5. The increase of pressure goes to strengthen the cohesive forces between molecules. Hence with increase of pressure the viscosity of a given liquid increases somewhat.



Viscosity of a liquid is a measure of its frictional resistance. However the force of friction between the layers offers resistance to this flow. Let us examine a liquid flowing on a glass surface. The molecular layer in contact with the stationary surface has zero velocity. The successive layers above it move with increasingly higher velocities in the direction of the flow. Now consider two adjacent moving layers of a liquid.

The force of friction (F) resisting the relative motion of the two layers is directly proportional to the area A and velocity difference d*v*, while it is inversely proportional to the distance between the layer dx.

Hence, $F \propto A \frac{d_v}{d_x}$

$$F = ή\, A \frac{d_v}{d_x}$$

Or

$$ή = \frac{F}{A} \times \frac{d_x}{d_v}$$

Where, $ή\ (eta) = coefficent\ of\ viscosity$ or viscosity of liquid

= force/area x distance/velocity

= mass x length x time^{-2}/length^{2} X length/length/time

= mass x length^{-1} x time^{-1}

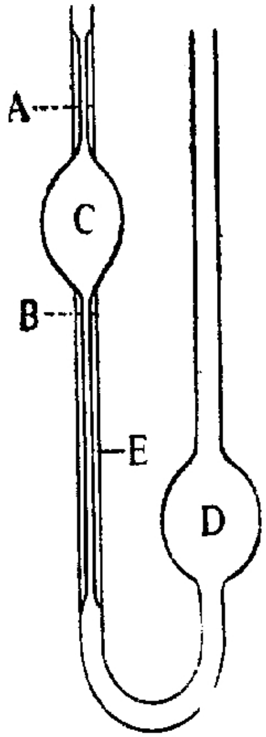
The reciprocal of viscosity is known as fluidity.

Effect of temperature on viscosity

As the temperature increases, the molecular motion increases at the expense of cohesive forces causing resistance to flow. Therefore, the viscosity of liquids is found to decrease by 1 to 2 per cent for each degree rise of temperature.

Determination of viscosity

The apparatus used for determination of viscosity in the laboratory is knwon as Ostwald's viscometer. A left- hand limb is essentially a pipette with two calibration marks A and B. A length of capillary tube joins the pipette to the bulb D in the right-hand limb. A definite volume of liquid about 25 ml is poured into the bulb D with a pipette. The liquid is sucked up near to the top of the left-hand limb with the help of rubber tubing attached to it. The liquid is then released to flow back into the bulb D.



Ostwald viscometer

Time t_1 to flow from A to B is noted with a stopwatch. The time of flow of water t1 from A to B is recorded.

The time of flow of water t_1 from A to B is recorded.

$$\frac{\eta}{\eta_w} = \frac{dt_1}{d_w t_2}$$

where is η is coefficient of viscosity of the experimental liquid and η_w is the coefficient of viscosity of water. Knowing the value of coefficient of viscosity of water at the temperature of experiment, the absolute viscosity coefficient η of the given liquid can be found.

Viscosity and chemical constitution

Viscosity is also dependent on the shape, size and mass of the liquid molecules. As you know viscosity is largely due to intermolecular attractions which resist the flow of liquid. Therefore some sort of relationship between viscosity and molecular structure should be there. The following general rules have been discovered.

(i) Dunstan Rule:

Dunstan in 1909, showed that coefficient of viscosity η and molecular volume as d/M were related as

$=d/M \times \eta x 10^6$

= 40 to 60

For example the value for benzene is 73;

For water it is 559;

For ethanol it is 189.

(ii) Molar Viscosity:

The product of molar surface and viscosity is termed as molar viscosity. That is

molar viscosity = molar surface x viscosity

$=(M/d)^{2/3} \times \acute{\eta}$

(iii) Rheochor:

Newton Friend in1943, showed that if molecular volume (M/d) be multiplied by the eighth root of the coefficient of viscosity it gives a constant value R, it is termed as Rheochor

$R= M/d \times \eta^{1/8}$

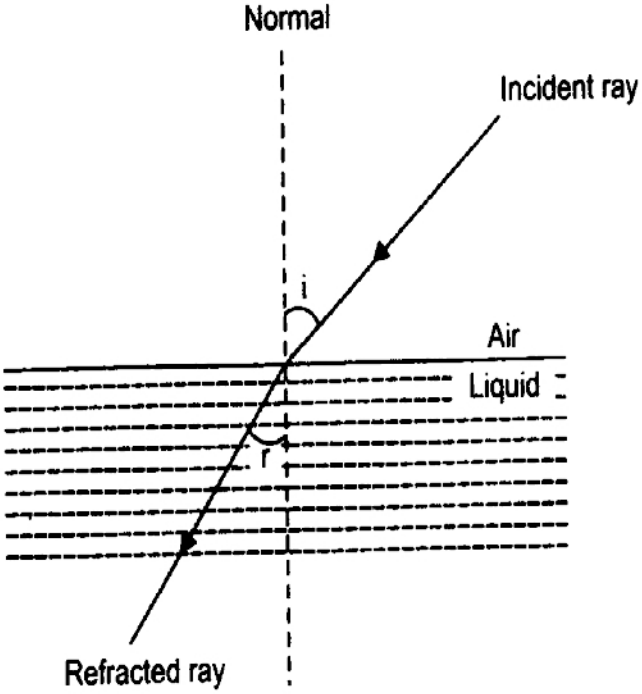
Like parachor, rheochor is both additive and constitutive property.

Refractive Index

When a ray of light passes from air into denser medium say a liquid, it is bent or refracted towards the normal. The ratio of the sine of angle of incidence and the sine of angle of refraction is constant and characteristic of that liquid. This is known as Snell's law. The constant ratio n is called refractive index of the liquid and may be written as

$$n = \frac{Sin\, i}{Sin\, r}$$

$$\text{Or } n = \frac{velocity\ in\ air}{velocity\ in\ liquid}$$



$$\text{Or} \qquad \frac{Sin\ i}{Sin\ r} = \frac{n_2}{n_1}$$

Where, n_1 = refractive index of rarer medium and n_2= refractive index of denser medium

Refractive index and chemical constitution

Lozentz in 1880, purely from theoretical considerations derived the following relation for refracting power of substance

Specific reflection $$R = \frac{n^2 - 1}{n^2 + 2} \times \frac{1}{d} \ldots\ldots\ldots\ldots\ldots\ldots .. (1)$$

Where, d= density; n= refractive index and the value of R constant all temperature.

Molar refraction:

It is defined as the product of specific refraction and molecular mass. Thus molar refraction is obtained by multiplying equation by molecular mass (M).

$$R_M = \frac{n^2 - 1}{n^2 + 2} \times \frac{M}{d} \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

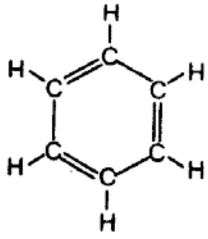
Molar refraction R is an additive and constitutive property. The molar refraction of a molecule is thus a sum of the contributions of the atoms and bonds. From the observed value of R_M of appropriate compound.

Table: Some atomic and bond refractions

Atom	Refraction	Bond	Refraction
C	2.418	3- membered ring	0.71
H	1.100	4- membered ring	0.48
Cl	5.967	6- membered ring	0.15
Br	8.861	O in OH gp.	1.525
I	13.9	O in CO gp.	2.21
Double bond	1.73	O in ether	1.64
Triple Bond	2.39		

Example: Benzene

The molar refraction of benzene (C_6H_6) on the basis of Kekule formula may be calculated as:



Kekule formula

6C = 6x2.591 = 15.546

6H = 6x1.028 = 6.168

3C =C = 3x1.575 =4.725

One 6 C ring ` = -0.150

Total R_M = 26.289$cm^3 mole^{-1}$

The observed value of R_M for benzene is 25.93. This is in good agreement with the calculated value. Hence, the Kekule formula for benzene is supported.

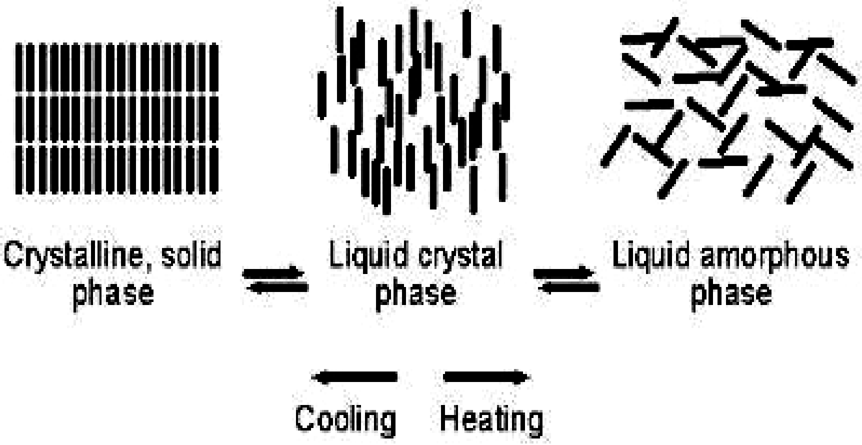
2.5 LIQUID CRYSTALS

Liquid crystals: Difference between liquid crystal, solid and liquid.

Solids are crystalline state: 3D long range order (∞ position- and orientation order). Glasses are just short range order, positions of molecules statistically distributed, kinetically frozen molecular motion. Liquids are fluid states: no long range order, just short range order, positions of molecules statistically distributed.

Mesophases (mesomorphic phases) (meso (*gr.)*: middle; morphe: shape): long range (but not perfect) order in respect to the position and/or orientation of molecules; anisotropic (like crystals) but fluid properties (like liquids).

The concept of a state of matter which is liquid like and crystalline at the same time seems absurd. It is however, fully justified: liquid crystalline mesophases possess some typical properties of a liquid, such as fluidity and the inability to support shear, formation and coa-lescence of droplets. These mesophases also have certain crystalline properties, such as anisotropy of optical, electrical and magnetic properties, as well as a periodic arrangement of molecules in one or more spatial directions.



Terminology of Liquid Crystals (LC): Formation of the mesophase:

Thermotropic LC: temperature induced formation of the LC phases

*Lyotropic LC***:** formation of LC phase upon solvation

Structure of the mesophase:

Friedelian classes: Nematic, smectic, cholesteric LC´s

2.5.1 STRUCTURE OF LIQUID CRYSTALS

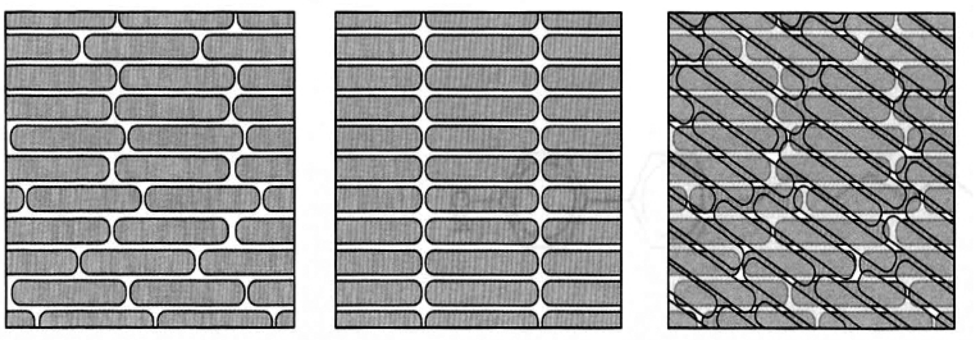
Structure of the mesophase:

Friedelian classes: Nematic, smectic, cholesteric LC´s

In a liquid the molecules have random arrangement and they are able to move fast each other. In a solid crystal the molecules have an ordered arrangement and are in fixed positions. In a liquid crystal, however, molecules are arranged parallel to each other and can flow like a liquid. Thus liquid crystals have the fluidity of liquid and optical properties of solid crystals. Accordingly to their molecular arrangement, the liquid crystals are classified into three types

(i) Nematic liquid crystals: in nematic liquid crystals molecules are parallel to each other like soda straws but they are free to slide or roll individually.

(ii) Smetic liquid crystals: The molecules in this type of liquid crystals are also parallel but these are arranged in layers. These layers can slide past each other (Fig 4.18).



(a) **(b)** **(c)**

(i) Cholesteric liquid crystals: As in nematic crystals in this type liquid crystals the molecules are parallel but arranged in layers. The molecules in successive layers are slightly rotated with respect to the layers above and below so as to form spiral structure.

Figure: The arrangement of molecules in (a) the nematic phase, (b) the smectic phase, and (c) the cholesteric phase of liquid crystals. In the cholesteric phase, the stacking of layers continues to give a helical arrangement of molecules.

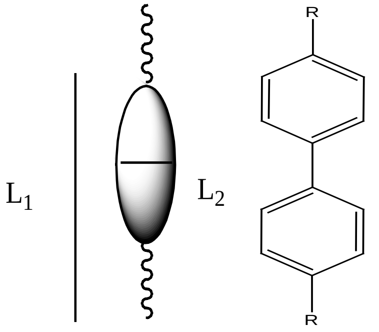
Structure of the mesogens:

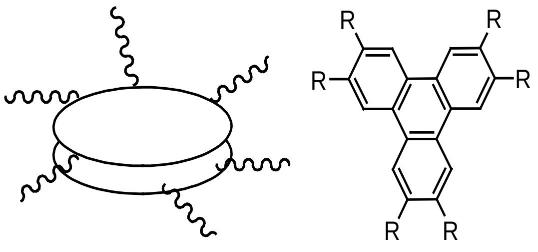
Calamitic, discotic, banana shape LC´s, LC-polymers

Requirement: Geometrical anisotropic units (mesogens) Requirement: Geometrical anisotropic units (mesogens).

Mesogens (Definition): Rigid molecule or molecule segment with anisometric (geometrical anisotropic) architecture.

$L_{krit} = L_1/L_2$





Calmatic **discotic**

History of Liquid Crystal:

1888 Friedrich Reinitzer: Derivates of cholesterole melt at 145.5°C to milky fluid. Further heating up to 178.5°C makes the liquid clear and transparent. (two melting points)

1890 Otto Lehmann identifies a “new and distinct state of matter“, the “liquid crystal phase” **1904** First commercially available Liquid-crystals (Merck-AG)

1922 Friedel establishes the names of the three liquid crystalline phases (nematic, smectic and cholesteric).

Next 30 yrs. The scientific community gradually losses interest in LC materials. LC materials were widely considered as an interesting, but essentially useless, laboratory curiosity.

End of 1960s Suggestion of cholesteric LC´s as temperature indicators, analytical metrology, cancer diagnostics and non-destructive testing of materials 1968 George Heilmeier first prototype of LCD‘s

1970-71 Fergason, Schadt, Helfrich: Invention of the twisted nematic (TN) cell - extensive R&D efforts in LC materials and LCD´s all over the world 1980s-1990s LCDs replace conventional display devices in many applications portable PC´s, mobile telephones, electronic toys.

Today: Broad applications in display technology, high modulus fibres and opto-electronic devices

2.5.2 APPLICATIONS OF LIQUID CRYSTAL

Cholesteric (Chiral nematic) phases as optical materials: The Exocuticles of Beetles contain Layers of Chitin, a naturally occurring polysaccaride that possesses a cholesteric liquid crystal Structure. A supra-molecular helical structure defined by twitting sense (right or left) and pitch length leads to selective reflection. LC´s as opto-electronic materials. Cholesteric Liquid crystals are 1D (chiral) photonic crystals- circular polarized light from dyes incorporated into CLCs.

2.6 SUMMARY

After study of this unit, behavior of gases on account of their compressibility and thermal expansion, gases are affected by changes in pressure and temperature by means of different laws. Molecular velocity of gases and the velocity and collisions with the help of Maxwell’s distribution law and molecular kinetic energy molecular velocity can be calculated. The characteristic properties of liquid arise from the nature and the magnitude of these intermolecular forces. Liquid crystals behavior of fluidity as liquid and solid as crystals properties. Classification accordingly to their molecular arrangement and type in the liquid crystals.

2.7 TERMINAL QUESTIONS

Q1. The molecules which have partial positive charge at one end and partial negative charge at the other are called:
(a) ion pairs (b) charged molecules
(c) dipole (d) electric molecule

Q2. With the rise of temperature the surface tension of a liquid

(a) Increases

(b) decreases

(c) remains the same

(d) none of the above

Q3. Small droplets are spherical in shape. It is due to:

(a) High viscosity

(b) Their tendency to acquire minimum surface area

(c) Less viscosity

(d) Their tendency to acquire maximum surface area

Q4. Write a note on liquid crystals.

Q5. Explain the term viscosity of a liquid.

Q6. Why do you use the same viscometer for the liquid and water during the

experimental determination of the viscosity of the liquid by Ostwald viscometer? Describe the experiment.

Q7. Define the terms surface tension and surface energy.

2.8 ANSWERS

Ans.1: `(c) Dipole

Ans.2: `(b) Decreases

Ans.3: `(b) Their tendency to acquire minimum surface area

Ans.4: `Section 2.5, a note on liquid crystals is given.

Ans.5: `Section 2.4.1 term viscosity of a liquid explained.

Ans.6: `Section 2.4.1 sub section viscosity, experimental determination of the viscosity of the liquid explained.

Ans.7: `Section 2.4.1 terms surface tension and surface energy explained.

2.9 Suggested Readings

1. Physical Chemistry, By Atkins
2. Elements of Physical Chemistry, By B.R. Puri, L.R. Sharma & M.S. Pathania.

UNIT-3 : SOLID STATE

Structure

0.3. INTRODUCTION

The matter has three common states amongst them gaseous state is simplest one. The laws of gaseous behaviour are more uniform and are better understood. The well known laws of gaseous behaviour are Boyle's law, Charle's law, Graham's law, Dalton's law and Avogadro's law. However, Kronig, Clausius, Maxwell and Boltzmann developed a theory known as kinetic molecular theory of gases, which provided sound theoretical basis for the various gas laws.

As you have studied in the unit 2.1 that there are two opposite molecular forces, the forces of attraction and the disruptive forces operating between molecules. If the thermal energy is much greater than the forces of attraction, then we have matter in its gaseous state.

In contrast with solids and liquids gases occupy the same volume as that of the closed vessel, they are characterized by low density and high compressibility.In the liquid state the forces of attraction are greater than the thermal energy. You have also studied that molecules in liquid state too have kinetic energy, they cannot move very far away because of the larger forces of attraction amongst them. Because of this property, liquids have definite volume but they do not have definite shape. Liquids also resemble gases in their ability to flow. Gaseous and liquid states are therefore, both classified as fluids. Out of the three states of matter, solids are characterized by incompressibility, rigidity and mechanical strength. The molecules, atoms or ions in solids are closely packed.

It is clear to you now that intermolecular attraction is minimum in the gaseous state and this disappears completely when the gas in ideal. The interaction is stronger in liquids and is strongest in solids. Thermal motion of the molecules increases or decreases by raising or lowering of temperature. The attractive interaction between the molecules keep them together tries and the thermal motion is opposed to that. Hence, it is possible to change a substance from one state to another by changing its temperature.

A true solid possesses the following characteristics

(a) A sharp melting point

(b) A characteristic heat of fusion

(c) General incompressibility

(d) A definite three-dimensional arrangement of constituent units.

Hence solids are characterized by high density and low compressibility compared to those of the gas phase. In solids, atoms, ions and molecules are held together by relatively strong chemical forces- ionic bond, covalent bond or by intermolecular van der Waal’s forces. They do not translate although they vibrate to some extent on their fixed positions. This explains why solids are rigid and have definite shape.

Objective

After studying this unit, you should be able to know

- Space lattice and unit cell
- Laws of crystallography
- X-ray diffraction
- Derivation of Bragg’s equation
- Defects in crystals
- Semiconductors
- Superconductors
- Nanomaterials

3.1 DEFINITION OF SPACE LATTICE AND UNIT CELL

Solids can generally be classified into two broad categories:

(i) Crystalline solids

(ii) Amorphous solids

A crystalline solid exists as small crystals, each crystal having a characteristic geometrical shape. In a crystal, the atoms, molecules or ions are arranged in a regular, repeating three-dimensionl pattern called the crystal lattice. examples are sugar, salt etc. An amorphous solid has atoms, molecules or ions arranged at random and lacks the ordered crystalline arrangement. Examples of amorphous solids are rubber, plastics and glass. In their disordered structure, amorphous solids are regarded as supercooled liquids with high viscosity. The liquid nature of glass is sometimes apparent in very old window panes that have become slightly thicker at the bottom due to gradual downward flow.

Anisotropy and isotropy:

Amorphous substances differ from crystalline solids and resemble liquids in another important aspect. Their properties such as electrical conductivity, thermal conductivity mechanical strength and refractive index are same in all directions. Amorphous substances are said to isotropic. Liquids and gases are also isotropic.

Crystalline solids on the other hand are anisotropic, because their physical properties are different in different directions. For example the velocity of light through a crystal varies with the direction in which it is measured. Thus, a ray of light enter such a crystal may split up into two components each following different velocity.

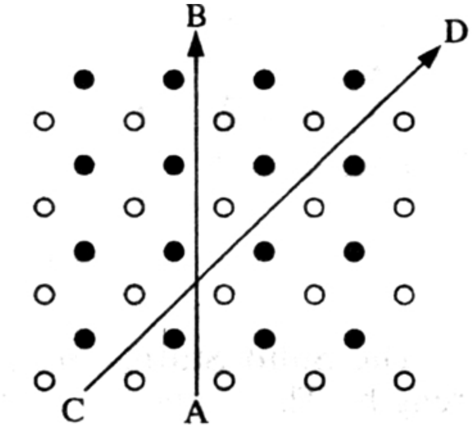
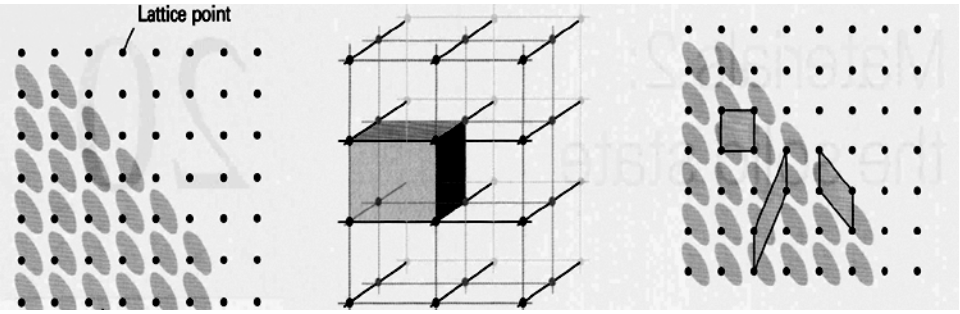


Fig. 3.1 Anisotropy in crystals is due to different arrangement of particles in different directions

This phenomenon is known as double refraction. This can be shown in figure 3.1 in which simple two-dimensional arrangement of only two different kinds of atoms is depicted if the properties are measured along the direction indicated by the slanting line CD, they will be different from those measured in the direction indicated by the vertical line AB. The reason is that while in the first case, each row is made up of alternate types of atoms, in the second case; each row is made up of one type of atoms only. In amorphous solids, atoms or molecules exist randomly and in a disorderly manner and, therefore all directions are identical and all properties are alike in all directions.

In a crystal, you have this imaginary array of points in 3D space, called the lattice. The unit cell is a repeating part of the crystal structure. Thus crystal lattice as being made of multiple unit cells stacked together.



3.2 LAWS OF CRYSTALLOGRAPHY

The geometric crystallography is based on the three fundamental laws:

3.2.1 The laws of constancy of interfacial angles

The crystals of a substance can have different shapes depending upon the number and size of the faces but the angle at which the two adjacent faces intersect remains always constant.

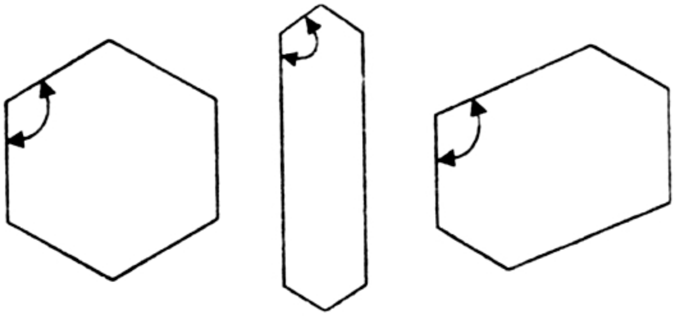


Fig. 3.2 Constancy of interfacial angle

3.2.2 Rationality of indices: Hauy's law of rationality of indices: The intercepts of any face of plane of a crystal on suitable crystallographic aces can be expressed by small multiples of three unit distances a,b,c. Thus each crystal plane lies parallel to the crystal face as also to the unit cell face. These planes cut the three axes along the three crystallographic axes (OX, OY, OZ), Hauy proposed that a given crystal plane could be described in terms of intercepts along the axes. The reciprocals of these intercepts are small whole numbers, these numbers h,k and l are called Miller indices after the name of British Scientist W.H. Miller. Thus Miller indices of a plane may be defined as the reciprocals of the intercepts which the plane makes with the axes.

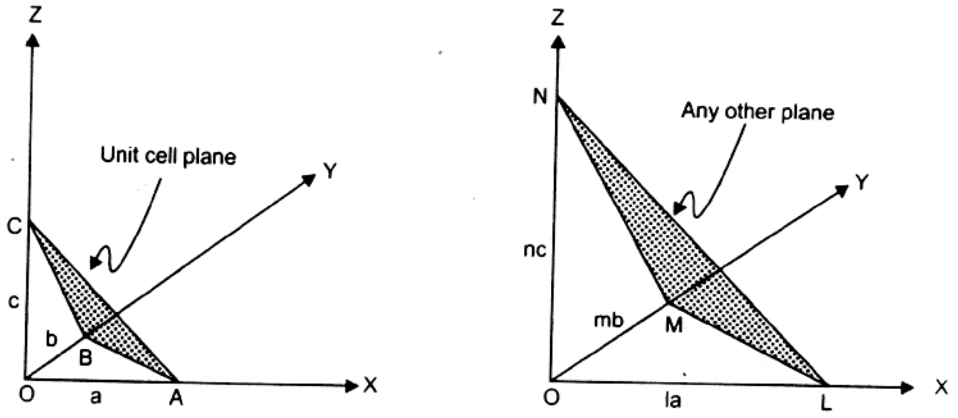


Fig.3.3 A unit cell plane intercepts the axes to give interests a, b

Any other plane intercepts the axes and c to give intercepts equal to la, mb and nc

For example let us consider a crystal system with the axes OX, OY and OZ. In fig 3.3 ABC represents a unit cell surface while LMN in fig 3.3 depicts another crystal plane under study

The intercepts of the unit plane are OA, OB and OC which have the length a,b and c respectively. The intercepts of the plane under study are OL, OM and ON. These can be expressed as multiples of the intercepts a, b, c i.e. la, mb and nc. Here l m and n are either integral whole numbers or fraction of whole numbers. The reciprocal of these numbers are written together in brackets (h,k,l) to give the Miller indices of the plane under study.

To find the Miller indices proceed as follows.

- **(i)** Write the intercepts as multiples of a,b,c say la, mb, nc
- **(ii)** Take the reciprocals of l, m and n
- **(iii)** Clear fraction to get whole numbers h,k,l.
- **(iv)** Miller indices to the plane are (h,k,l).

Self Assessment Question

Q1: Calculate the Miller indices of crystal planes which cut through the crystal axes at 2a, 3b, c.

Ans:--

Sol.

a	b	c	
2	3	1	intercepts
½	1/3	1	reciprocals
3	2	6	clear fraction

Hence, Miller indices is (326)

3.2.3 LAW OF SYMMETRY - SYMMETRY ELEMENTS IN CRYSTALS

According to this law, all crystals of the same substance possess the same elements of symmetry.

Besides the interfacial angles, another important property of crystals is their symmetry. Symmetry in a crystal may be with respect to a plane, a line or a point, accordingly there are three types of symmetry associated with a crystal.

1. Plane of symmetry: When an imaginary plane can divided a crystal into two parts such that one is the exact mirror image of the other, the crystal is said to have a plane of symmetry.

2. Axis of symmetry: An axis of symmetry is a line about which the crystal is rotated such that it presents the similar appearance more than once during complete rotation i.e. rotation through an angle of 360°. Depending upon its nature, a crystal may have 2-fold, 3-fold, 4-fold or 6-fold axes of rotation.

Symmetry elements of a crystal- Any molecule of the crystal will have some combinations of symmetry elements. These combinations of symmetry elements are known as point groups. These points groups are called classes or systems.

The seven crystal systems

System	**Relationships between lattice parameters**	**Unit cell defined by**	**Essential symmetries**
Triclinic	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90°$	$a\ b\ c\ \alpha\ \beta\ \gamma$	None
Monoclinic	$a \neq b \neq c$ $\alpha \neq \gamma \neq 90°$ $\beta = 90°$	$a\ b\ c\ \alpha\ \gamma$	One two-fold rotation axis and/or a mirror plane
Orthorhombic	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90°$	$a\ b\ c$	Three perpendicular two-fold

Rhombohedral	$a \neq b \neq c$ $\alpha = \beta = \gamma \neq 90°$	α	One three-fold rotation axis
Tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90°$	*ac*	One four-fold rotation axis
Hexagonal	$a = b \neq c$ $\alpha = \beta = 90° \gamma = 120°$	*ac*	One six-fold rotation axis
Cubic	$a = b = c$ $\alpha = \beta = \gamma = 90°$	*a*	Four three-fold rotation axes tetrahedrally arranged

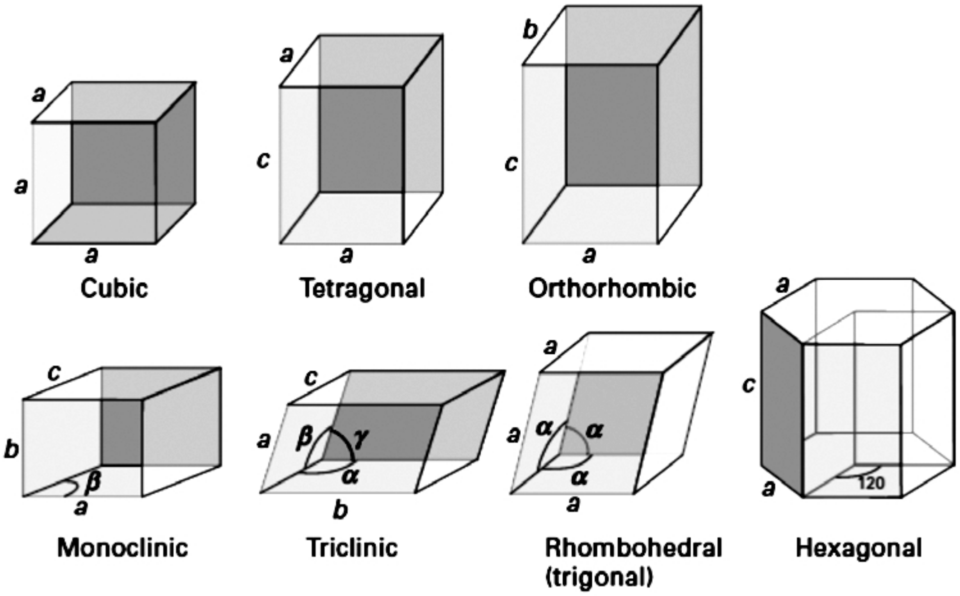


Figure: The seven crystal systems

3.4 X-RAY DIFFRACTION

It is a well known fact that, if light is allowed to strike on a surface consisting either of a series of edges or lines spaced closely enough to be of the same order of magnitudes as that of the wavelength of light, the beam of light is diffracted. The various radiations are dispersed into a series of spectra known as, first, second, third etc. order of spectra. Further, there is definite relation between the angle of diffraction, the wavelength of radiation and the spacing of the lines on the ruled grating.

Since x-rays are of the same nature as light, it should be theoretically possible to determine the wavelength of this radiation in the same way. However, it is impossible by any mechanical means to rule a grating as fine as that required, namely one with 10^8 lines per centimeter. Laue (1912) suggested that crystal can act as grating to x-rays as wavelength of x-rays is comparable to the interatomic distance.

When x-rays is allowed to fall on a crystal, a large number of images of different intensities are formed. If the diffracted waves are in the same phase, they reinforce each other and a series of bright spots are produced on a photographic plate placed in their path. On the other hand, if the diffracted waves are out of phase, dark spots are caused on the photographic plate. Diffraction pattern produced by a crystal, can get there at the detailed information regarding the position of particles in the crystal.

3.4.1 Derivation of Bragg's equation

Bragg's pointed that the scattering of x-rays by crystal could be taken to be equivalent to reflection from successive planes of atoms in the crystal. However the reflection of x-rays can take place only at certain angles which are dependent on wavelength of the x-rays and the distance between the planes of the crystal.

The fundamental equation which gives a simple relation between the wave length of x-rays, the interplaner distance in the crystal and the angle of reflection is known as Bragg's equation. This equation can be derived as follows.

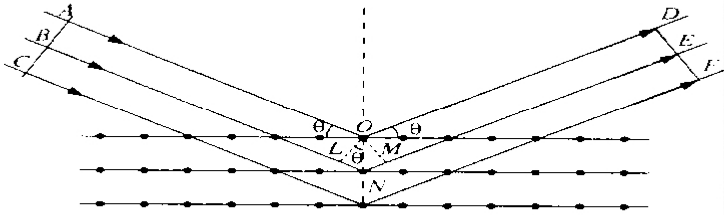


Figure: x-ray diffraction by crystals

Let the planes ABC and DEF drawn perpendicular to the incident and reflected beams, respectively. The waves reflected from different planes will be in phase will one another only if the difference in the path length of the wave reflected from the successive planes is equal to an integral number of wavelengths. Drawing perpendicular OL and OM to the incident and reflected beams, it will be seen that the path difference in the wavelength, say δ of the wave reflected from the first two planes is given by

$$\delta = LN + NM \text{ .... } (1)$$

This should be equal to a whole number multiple of wavelength λ,i.e.

$$n\,\lambda = LN+NM\text{.................}(2)$$

Since the two triangle ONL and ONM are congruent LN=NM

$$n\,\lambda = 2LN = 2d\mathrm{Sin}\theta\text{.................}(3)$$

Equation (3) is known as **Bragg's equation.**

For a given set of lattice planes, d has a fixed value. Therefore possibility of getting maximum diffraction (i.e., the possibility of getting reflected waves in phase with one another) depends upon θ. If θ is increased gradually, a number of positions will be found at which the reflection will be maximum.

At these positions, n will have values 1,2,3,4...etc. generally, in experiments on x-ray diffractions, any set as equal to 1. If λ in known, it is possible to determine d, the distance between atomic planes in the crystal by determining θ experimentally. Thus if d is known λ can be calculated.

Powder method

Powder method is the simplest technique for obtaining x-ray diffraction. It was first used by P.J.W. Debye and P. Scherer. Instead of taking a single crystal having a definite orientation to the impinging x-rays, we can take a mass of finely divided crystal with random orientation This method is better adopted due to its simplicity and versatility.

In this method, the crystal sample in need not to be taken in large quantity but as little as one milligram of the material is sufficient for study. The power, in fact consists of many small crystals which are oriented in all possible directions. As a result of this x-rays are scattered from all set of planes (e.g., 100,110, etc.). The scattered rays are detected by using an x-ray sensitive film. A narrow beam of x-rays is allowed to fall on the powder. The diffracted x-rays strike a strip of photographic film arranged in the form of circular arc, as shown in the given below Figure.

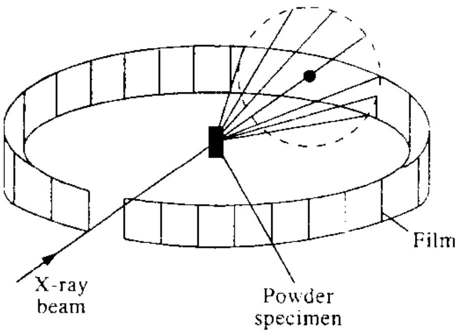
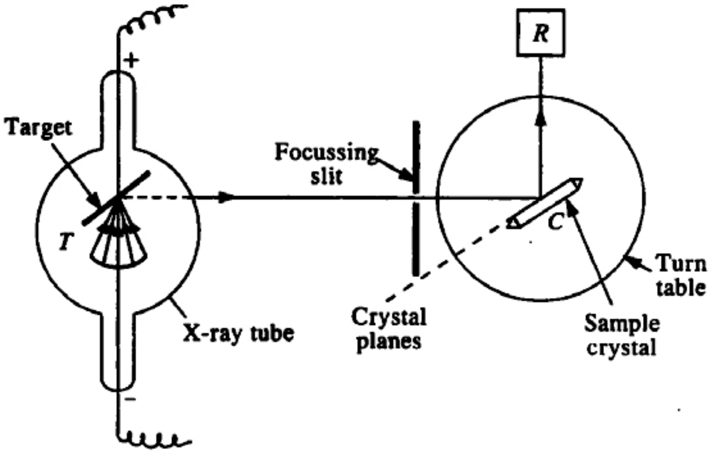


Figure: Experiment set-up of Powder method

Rotating crystal method

X-ray generated in the tube-T are passed through a slit so as to obtain a narrow beam which is then allowed to strike a single crystal C, mounted on the rotating table. The crystal is rotated gradually by means of the rotating table as to increase the glancing angle at which X-rays are incident at the exposed phase of the crystal. The intensities of the refracted rays are measured on a recording device. The recording device may be either a photographic plate or an ionisation chamber- R. The angle for which reflections are maximum give the value of θ. The process is carried out for each plane of the crystal. The lowest angle at which maximum reflection occurs corresponds to n=1. This is called first order reflection. The next higher angle at which maximum reflection occurs again, corresponds to n = 2, This is second order reflection and so on.



Setup of X-ray rotating crystal method

Self Assessment Question:

Q1. What is Bragg's equation?

Ans.………………………………………………………………………
…………………………………………………………………………
…………………………………………………………………………
…………………………………………………………………………

Q2. What is wavelength of x-ray?

Ans..……………………………………………………………………
…………………………………………………………………………
…………………………………………………………………………
…………………………………………………………………………

3.4.2 DETERMINATION OF CRYSTAL STRUCTURE OF NaCl, CsCl and KCl

Structure of NaCl crystal

The ionic crystal of NaCl, each sodium ion is surrounded by six chloride ions and each chloride ions is surrounded by six sodium ions. The maximum intensity of reflection occurs at the glancing angle of 5.9°, 8.4° and 5.2° for 100, 110 and 111 planes, respectively for first order reflection.

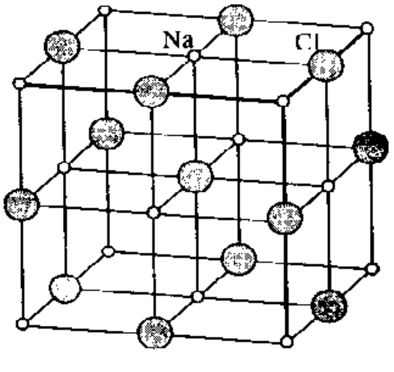


Figure: Structure of NaCl crystals

We know that

$$n\lambda = 2d\sin\theta$$

$$\frac{1}{d} = 2\frac{Sin\theta}{n\lambda}$$

Therefore for a particular order of reflection

$$d \, \alpha \frac{1}{\mathrm{Sin}\theta}$$

If only first order reflection are considered than,

$$d_{100}: d_{110} : d_{111} = \frac{1}{Sin5.9^o} : \frac{1}{Sin8.4^o} : \frac{1}{Sin5.2^o}$$

$$= \frac{1}{0.103} : \frac{1}{0.146} : \frac{1}{0.091}$$

$$= 1: 0.704 : 1.155$$

For face-centred cubic (fcc) system the planes can be passed through the atom having Miller indices 100, 110 and 111 at the relative spacing $\frac{a}{2}:\frac{a}{2\sqrt{2}}:\frac{a}{\sqrt{3}}$

$$\text{Thus } d_{100}: d_{110} : d_{111} = \frac{a}{2}:\frac{a}{2\sqrt{2}}:\frac{a}{\sqrt{3}}$$

$$= 1: 0.707 : 1.154$$

Above ratio is almost identical with the ratio we have calculated from experimental observations. Hence, **NaCl crystal is face-centred cubic system**.

Structure of KCl crystal

The KCl crystal, the maximum reflection of x-rays, corresponding to first order reflections are observed to occur at the glancing angles of 5.38°, 7.61° and 9.38° for (100),(110) and (111) faces, respectively, Therefore,

$$d_{100}: d_{110} : d_{111} = \frac{1}{Sin5.38^o} : \frac{1}{Sin7.61^o} : \frac{1}{Sin9.38^o}$$

$$= 1: 0.704 : 1.575$$

For the simple cubic system the planes can be passed through the atoms having Miller indices (100),(110) and (111) and the relative spacing for the unit cell is $a:\frac{a}{\sqrt{2}}:\frac{a}{\sqrt{3}}$

$$\text{Thus } d_{100}: d_{110} : d_{111} = \frac{a}{2}:\frac{a}{2\sqrt{2}}:\frac{a}{\sqrt{3}}$$

$$= 1: 0.707 : 0.577$$

Therefore, **KCl crystal has a simple cubic lattice.**

Potassium Chloride is isomorphous with sodium chloride. The explanation for this apparent anomaly is very simple and can be explained on the basis that the x-rays scattering power for an atom or ion is governed by the number of extra-planetary electrons. viz. atomic number.

The atomic numbers of potassium (K=19) and chlorine (Cl=17) are not very different and the x-rays are unable to detect any difference between the two kinds of atoms. If we imagine all the atoms to be identical, it is evident that face-centred arrangement has become a simple cubic arrangement. This is the reason for the KCl spectrum corresponding apparently to the simple cubic lattice. With KCl, the structure is face-centred, but the face-centred characteristics are marked by the fact that the two types of atoms composing the substance have nearly the same atomic numbers and atomic weights (K=39, Cl=35.5).

But in the case of sodium chloride the atomic numbers differ considerably (Na=11, Cl=17), and so their scattering powers are different and hence the true structure as two interpenetrating face-centred lattices become apparent. It is only the (111) face spectra which allows us to distinguish between the simple cubic lattice and the face-centred cubic lattice.

Structure of CsCl crystal

Cesium chloride, CsCl, has a body centred cubic structure. In its crystal lattice, each Cs^+ ion is surrounded by 8 Cl^- ions and its coordination number is 8. The value of distance between Cs^+ ion and Cl^- ion as determined by Bragg's spectrometer is 3.510 Å.

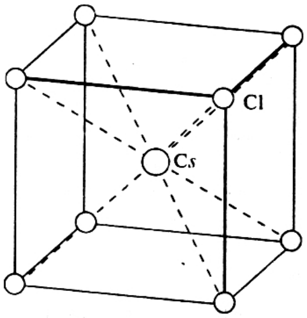


Figure: Cesium chloride crystal lattice

Self Assessment Question

Q1: NaCl crystal is fcc, bcc and sc?

Ans: Face-centred cubic (fcc) system.

Q2: KCl crystal is fcc, bcc and sc?

Ans: Simple cubic (sc) lattice.

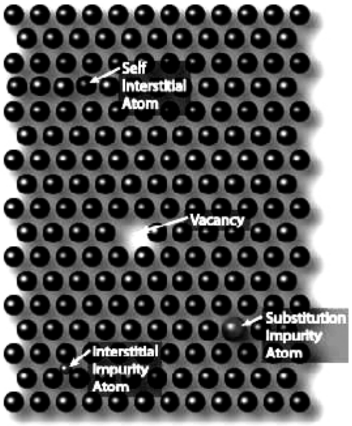
Q3: CsCl crystal is fcc, bcc and sc?

Ans: Body centered cubic (bcc) lattice.

Q4: What is an ionic crystal?

Ans: Crystal/solid form by combination of positive and negative non metallic ions is called ionic crystals.

3.5 A BRIEF INTRODUCTION TO POINT DEFECTS IN CRYSTALS



No crystal is perfect, no crystal’s with every atom of the same type in the correct position. All crystals have some defects. Defects contribute to the mechanical properties of metals. In fact, using the term “defect” is sort of a misnomer since these features are commonly intentionally used to manipulate the mechanical properties of a material. Adding alloying elements to a metal is one way of introducing a crystal defect. Nevertheless, the term “defect” will be used, just keep in mind that crystalline defects are not always bad. There are basic classes of crystal defects:

- Point defects, which are places where an atom is missing or irregularly placed in the lattice structure. Point defects include lattice vacancies, self-interstitial atoms, substitution impurity atoms, and interstitial impurity atoms.
- Linear defects, which are groups of atoms in irregular positions. Linear defects are commonly called dislocations.
- Planar defects, which are interfaces between homogeneous regions of the material. Planar defects include grain boundaries, stacking faults and external surfaces.

Point Defects

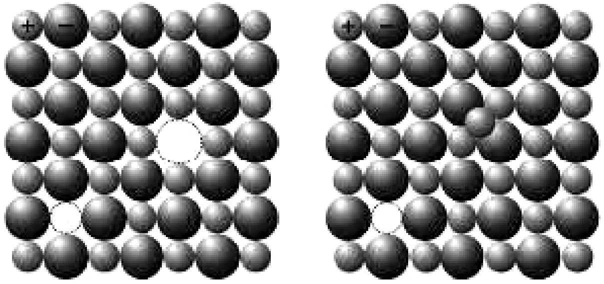
Point defects are where an atom is missing or is in an irregular place in the lattice structure. Point defects include self interstitial atoms, interstitial impurity atoms, substitutional atoms and vacancies. A self interstitial atom is an extra atom that has crowded its way into an interstitial void in the crystal structure. Self interstitial atoms occur only in low concentrations in metals because they distort and highly stress the tightly packed lattice structure.

Schottky Defect

This defect occurs in non ionic lattice. In this defect same no. of cations and anions leave their lattice site.

Frenkel Defect

It is a type of defect in crystalline solids wherein an atom is displaced from its lattice position to an interstitial site, creating a vacancy at the original site and an interstitial defect at the new location within the same element without any changes in chemical properties.

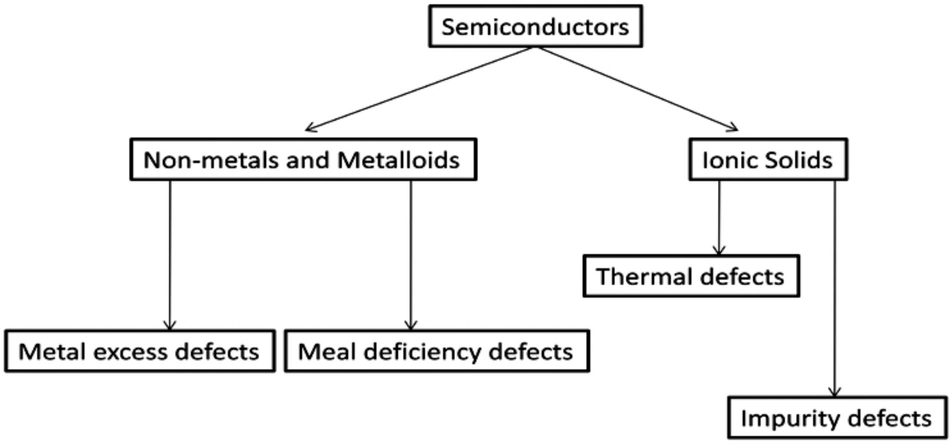


(a) Schottky defect (b) Frenkel defect

3.5.1 Semiconductors

The crystals of the compounds with metal deficiency defects can also act as semiconductors due to the movement of electrons from one ion of normal oxidation state to that of higher oxidation state to create another higher oxidation at its position. This type of movement of electrons between the ions appears as an apparent movement of positive holes thereby making the crystal a semiconductor.

This is obvious from the fact that there are some materials which may be insulators at low temperature, (i.e. absolute zero) but become conductors at elevated temperatures (thermal defects) or on adding certain impurities (impurity defects). These are called semiconductors, e.g. crystals of silicon (Si) and germanium (Ge).



The conductivity of the semiconductors arises in two ways:

(i) Intrinsic semiconductors (thermal defects)

A semiconductor which is obtained by heating an insulator is called intrinsic semiconductor, i.e. the defect in the crystal is produced by thermal energy. Pure silicon, pure germanium are some examples of materials which act as semiconductors.

Actually at elevated temperatures, sufficient amount of energy is available to break the covalent bonds in the crystal to make some electrons free. These electrons can migrate through the crystal leaving behind positive holes at the site of missing bonds. We can thus conclude that the heat energy promotes some electrons from the filled band into the next higher energy conduction band across the small energy gap and the material becomes conductor. With the rise in temperature the conductivity of semiconductors increases.

i) Extrinsic semiconductors (impurity defects):

n-type and p-type semiconductors: Certain defects in crystals arise from the presence of chemical impurities called impurity defects. Thus the materials obtained by adding impurity atoms to the insulators and making them conductors are called extrinsic semiconductors which are said to have impurity defects.

For example: Addition of phosphorus, arsenic, boron or gallium atoms to silicon or germanium crystals makes them semiconductors. These are of two types:

(a) n- type semiconductors (n = normal)

If a very small amount of arsenic, the element of group 15th, is added as impurity to the pure crystal of silicon, the element of group 14, by a suitable means, the process is called doping and we get the so called arsenic doped silicon. During the process of doping, a minute proposition of Si atoms is randomly replaced by arsenic atoms with one extra electron in their outer shell because only four outer electrons of As are required to form bonds with neighbouring Si atoms in the lattice (Si: ns^2, p^2 & As: ns^2, p^3, i.e. Si has 4 and As has 5 valence electrons.), these free electrons migrate through the crystal lattice to conduct the electricity in the normal way as happens in the metallic conductors. Hence this is called n-type semiconduction and the material so obtained in known as n-type extrinsic semiconductor. In these materials, the impurity atoms act as charge carriers.

(b) p-type semiconductors (p-positive hole)

Here the pure crystal of Si is doped with a minute quantity of gallium, an element of group 13

(Ga: ns^2,p^1, i.e. 3 electrons in the valence shell) in which some of the Si atoms are substituted by Ga atoms. Each Ga atom forms three electron pair bonds with neighbouring Si atoms. Fourth neighbouring Si atom forms a weak one electron bond with Ga atom which behaves as free electron at Si atom. This creates electron deficiency or positive hole in the lattice site from where the electron is missing.

There are as many positive holes as the number of Ga atoms. At normal temperature, these free electrons move through the crystal from one vacancy site to another thereby leaving new vacancies or positive holes behind. Thus, it appears that the positive holes are moving though actually it is the flow of electrons that takes place to conduct electric current through the crystal on applying the electric field. The flow of electrons and the movement of positive holes occurs in opposite directions.

This process is, therefore, called p-type semi conduction and the material so produced in known as p-type extrinsic semiconductor.

For detail study, kindly go through again the UGCHE-01 of section 2.8 for conductor, semiconductor and insulator with band gaps description as you studied earlier.

3.5.2 SUPERCONDUCTORS

Superconductivity is a phenomenon of exactly zero electrical resistance and expulsion of magnetic flux fields occurring in certain materials, called superconductors, when cooled below a characteristic critical temperature. It was discovered by Dutch physicist H. K. Onnes on April 8, 1911. Like ferromagnetism and atomic spectral lines, superconductivity is a quantum mechanical phenomenon.

The electrical resistance of a metallic conductor decreases gradually as temperature is lowered. In ordinary conductors, such as copper or silver, this decrease is limited by impurities and other defects. Even near absolute zero, a real sample of a normal conductor shows some resistance. In a superconductor, the resistance drops abruptly to zero when the material is cooled below its critical temperature.

Superconducting magnets are some of the most powerful electromagnets known. They are used in MRI/NMR machines, mass spectrometers, the beam-steering magnets used in particle accelerators and plasma confining magnets in some tokamaks. They can also be used for magnetic separation, where weakly magnetic particles are extracted from a background of less or non-magnetic particles, as in the pigment industries.

3.5.3 Nanomaterials (only qualitative idea)

Nanotechnology is the science and engineering of making materials on the order of a nanometer scale in one dimension. In scientific terms, “Nano” means 10^{-9} m, where 1 nanometer (nm) is equivalent to one thousandth of a micrometer (µm), one millionth of a millimeter, and one billionth of a meter. In Greek, "nanotechnology" derives from the nanos which means dwarf and technologia means systematic treatment of an art or craft.

Nanoscale is a magical point on the dimensional scale: Structures in nanoscale (called nanostructures) are considered at the borderline of the smallest of human-made devices and the largest molecules of living systems. Nanotechnology has become a very active and vital area of research which is rapidly developing in industrial sectors and spreading to almost every field of science and engineering.

Nanostructures are loosely defined particles, grains, functional structures and devices with dimensions in the 1–100 nanometer (nm) range. Nanostructures include quantum dots, quantum wires, grains, particles, nanotubes, nanorods, nanofibers, nanofoams, nanocrystals, nanoprecision self-assemblies and thin films, metals, inter-metallics, semiconductors, minerals, ferroelectrics, dielectrics, composites, alloys, blends, organics, organominerals, biomaterials, biomolecules, oligomers, polymers, functional structures and devices.

The reasons why nanoscale has become so important:

1. Nanoscale components have very high surface to volume ratio, making them ideal for use in composite materials, reacting systems, drug delivery, and chemical energy storage (such as hydrogen and natural gas).
2. A key feature of biological entities is the systematic organization of matter on the nanoscale. Developments in nanoscience and nanotechnology would allow us to place man-made nanoscale things inside living cells. It would also make it possible to make new materials using the self-assembly features of nature. This certainly will be a powerful combination of biology with materials science.
3. The quantum mechanical properties of electrons inside matter are influenced by variations on the nanoscale. By nanoscale design of materials it is possible to vary their micro and macroscopic properties, such as charge capacity, magnetization and melting temperature without changing their chemical composition.
4. Macroscopic systems made up of nanostructures can have much higher density than those made up of microstructures. They can also be better conductors of electricity. This can result in new electronic device concepts, smaller and faster circuits, more sophisticated functions and greatly reduced power consumption

simultaneously by controlling nanostructure interactions and complexity.

An abundance of scientific data is now available to make useful comparisons between nanosize materials and their counterpart microscale or bulk materials. For example, the hardness of nanocrystalline copper increases with decreasing grain size and 6 nm copper grains show five times hardness than the conventional copper.

One Feynman (φ) ≡1 Nanometer (nm) = 10 Angstroms(Å)= 10^{-3}Micron(μ) = 10^{-9}Meter(m)

Nanomaterials:

Materials	**Example**	**Size (approx.) diam. in nm**
Metals, semiconductors, magnetic materials	Nano-crystals and clusters (quantum dots)	1–10
Ceramic oxides	Other Nanoparticles	1–100
Metals, semiconductors, oxides, sulfides, nitrides	Nano-wires	1–100
Carbon, layered metal chalcogenides	Nano-tubes	1–100
Zeolites, phosphates etc.	Nanoporous solids	Pore diam. 0.5–10
Metals, semiconductors, magnetic materials	2-Dimensional arrays (of nano particles)	Several nm^2–μm^2
A variety of materials	Surfaces and thin films	thickness 1–1000
Metals, semiconductors, magnetic materials	3-Dimensional structures (super lattices)	Several nm in the 3D

3.6 SUMMARY

In this unit you learn the gaseous behavior by laws of gases are Boyle’s law, Charle’s law, Graham’s law, Dalton’s law and Avogadro’s law, etc. which provided sound theoretical basis for the various gas laws. Types of solids compositions/arrangement of atoms, molecules or ions arranged at random and crystalline. Whereas, in crystalline solids on the other hand are anisotropic, because their physical properties are different in different directions. Symmetry in a crystal may be with respect to a plane, a line or a point, accordingly there are three types of symmetry associated with a crystal.

The fundamental laws of crystallography by fundamental equation which gives a simple relation between the wave length of x-rays, the interplaner distance in the crystal and the angle of reflection is known is known as Bragg's equation. Crystal defect, and their types along with applications. Some basics of semiconductors and superconductors and a brief introduction about nanomaterials importance and their applications.

3.7 TERMINAL QUESTIONS

Q1. Which is incorrect for hexagonal crystal system?

(i) a=b=c (ii) $a \neq b = c$

(iii) $\alpha=\beta=90^0$, $\gamma=120^0$ (iv) None of these

Q2. Explain the terms anisotropy and isotropy?

Q3. Why is rotation of crystal is not necessary in power method for the determination of crystal structure?

Q4. (i) Derive the equation $2d \sin \theta = n\lambda$.

(ii) Draw structure of NaCl crystal.

Q.5 X-rays of wavelength $1.542\text{x}10^{-10}$m, be reflected by plains separated by $3.5\text{x}10^{-10}$ m, what should be a angle θ.

Q.6 Metallic gold Au=197 is face centred cubic(fcc) lattice. Calculate (a) how many atoms occupy the gold unit cell and (b) what is the mass numbr of a gold unit cell.

Q.7 Diffraction angle $2\theta=16.8^0$, for a crystal having interplaner distance in the crystal is 0.400nm when second order reflaction was observed. Calculate the wavelength of the x-rays used.

3.8 ANSWERS

Ans. 1. (i)

Ans. 2. Go through Section 3.1 of this unit.

Ans. 3. In Section 3.4 of x-ray diffraction method explained.

Ans. 4. (i) In Section 3.4.1 Derivation of Bragg's equation

(ii) In Section 3.4.2 Structure of NaCl crystal

Ans. 5. From Bragg's equation

$2d\sin\theta = n\lambda$

$\sin\theta = n\lambda/2d$

$\theta = \sin^{-1} n\lambda/2d$

Substituting the values of n, λ and d in equation

$\theta = \sin^{-1} 1\times1.542\text{x}10^{-10}/2\times3.5\text{x}10^{-10}$

$\theta = 12.73^{0}$

Ans.- Angle $\theta = 12.73^{0}$.

Ans.6. For fcc lattice,

Corner atom is shared by 8 unit cells, hence share of one unit cell is 1/8, for 8 corners 1/8x8=1 atom

There are six faces, each contain 1 atom and share of one unit cell is ½ x 6 =3 atoms for six faces

Thus, atoms occupy the gold unit cells = 1+3 = 4

So, Mass of unit cell = $\frac{molar\ mass}{Avagadro\ Number} = \frac{197}{6.023 \times 10^{23}} \times 4 = 130.83\times 10^{-23}$ g

Ans.- Mass of unit cell $=130 \times 10^{-23}$ g

Ans. 7. Given that n = 2,

$d=0.400\text{nm} = 0.4\text{x}10^{-9}$ m,

$2\theta=16.8^{0}$, so $\theta = 8.4^{0}$

$n\lambda = 2d\sin\theta$

$\lambda = \frac{2 \times 0.4\text{x}10^{-9} \times \sin 8.40}{2}$

$= 0.4\text{x}10^{-9}\times 0.146$ m

$= 0.584\times 10^{-10\ \text{m}}$

= 0.584 Å

Ans.- wavelength of the x-rays used = 0.584 Å

Suggested readings

1. Essentials of Physical Chemistry By B.S. Bahl, Arun Bahl, G.D. Tuli
2. Principles of Physical Chemistry by Puri and Sharma
3. Physical Chemisty By Walter J. Moore
4. Physical Chemisty by Atkins.
5. Fundamentals of Nanoteccnology, by C. N. R. Rao

Uttar Pradesh Rajarshi Tandon
Open University

UGCHE-103
Physical Chemistry-I
(Basic Physical Chemistry)

BLOCK

2

PHYSICAL CHEMISTRY-I

NMDC-183

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Note: Symbols [α] = Block-1 (Unit-01,02 and 03) and [β] = Block-2 (Unit-04,05 and 06)

ISBN :

Printed By - *K.C.Printing & Allied Works, Panchwati, Mathura -281003.*

NMDC-183

Unit-4 : THERMODYNAMICS-I

Structure

4.1 Introduction

The word “thermodynamics” arises from the Greek terms representing heat (therme) and power (dynamis). The original objective was to gain the maximum power (energy per unit time) from a given amount of energy stored in some fuel (which was typically turned into heat). Thus thermodynamics can be defined as the science of energy. Energy can be viewed as the ability to cause changes. Thermodynamics is concerned with the mathematical modeling of the real world. In order that the mathematical deductions are consistent, we need some precise definitions of the basic concepts.

This unit introduces to important terms, concept and calculation related to thermodynamics. In this unit we study the first law of thermodynamics which is simply an expression of the conservation of energy principle, and it asserts that energy is a thermodynamic property. Further the unit discusses the several aspect of thermochemistry as subfield of thermodynamics. This includes the study of Hess’s law of constant heat summation, heat of reaction, bond dissociation energy and its calculation from thermo-chemical data.

Objective

After studying this unit you would be able to :

- Differentiate between system and surrounding
- List intensive and extensive property
- Explain state and path function and their differential
- Make distinction between reversible and irreversible processes
- Understand concept of heat ,work, internal energy, enthalpy, heat capacities and their relationship
- calculate w, q, dU & dH for the expansion of ideal gases.
- define standard state, standard enthalpy of formation- Hess's Law of constant heat summation and heat of reaction.
- Work out calculation of bond energies from thermochemical data and Kirchhoff's equation

4.2 System and Surroundings

All space in the universe outside the thermodynamic system is known as the *surroundings*, the *environment*, or a *reservoir*. A system is separated from its surroundings by a *boundary*, which may be notional or real but, by convention, delimits a finite volume. Transfers of work, heat, or matter and energy between the system and the surroundings may take place across this boundary. A thermodynamic system is classified by the nature of the transfers that are allowed to occur across its boundary, or parts of its boundary

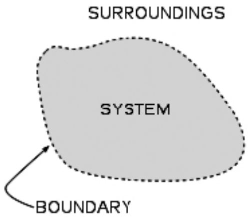


Fig4.1 System

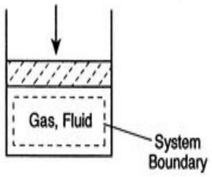


Fig.4.2 Piston (boundary) and gas (system)

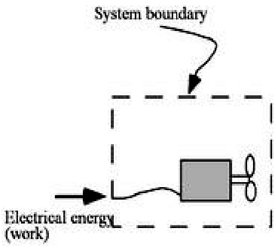


Fig. 4.3 Boundary motor around electric motor (system)

Energy transfer is studied in three types of systems:

4.2.1 Open System

Open systems can exchange both matter and energy with an outside system. They are portions of larger systems and in intimate contact with the larger system. Your body is an open system.

Example: Hot water in a beaker placed on table is an open system.

4.2.2 Closed systems

Closed systems exchange energy but not matter with an outside system. Though they are typically portions of larger systems, they are not in complete contact. The Earth is essentially a closed system; it obtains lots of energy from the Sun but the exchange of matter with the outside is almost zero.

Examples:

i) A specific quantity of hot water in a sealed vessel constitutes a closed system

ii) A cylinder fitted with gas and fitted with piston also constitutes a closed system.

4.2.3 Isolated systems

Isolated systems can exchange neither energy nor matter with an outside system. While they may be portions of larger systems, they do not communicate with the outside in any way. The physical universe is an isolated system; a closed thermos bottle is essentially an isolated system (though its insulation is not perfect).

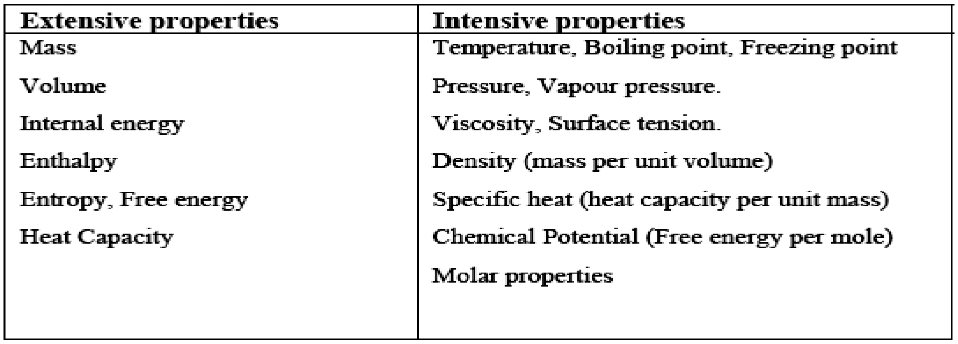
Example: Water in contact with its vapour in a closed and insulated vessel

Heat can be transferred between open systems and between closed systems, but not between isolated systems.

4.3 Intensive and Extensive Property

Thermodynamic properties can be divided into two general classes, intensive and extensive properties. An *intensive property* is independent of the amount of mass. The value of an extensive *property* varies directly with the mass. Thus, if a quantity of matter in a given state is divided into two equal parts, each part will have the same value of intensive property as the original and half the value of the extensive property. Temperature, pressure, specific volume, and density are examples of intensive properties. Mass and total volume are examples of extensive properties.

Table- 4.1 : Properties of a System



Extensive properties	Intensive properties
Mass	Temperature, Boiling point, Freezing point
Volume	Pressure, Vapour pressure.
Internal energy	Viscosity, Surface tension.
Enthalpy	Density (mass per unit volume)
Entropy, Free energy	Specific heat (heat capacity per unit mass)
Heat Capacity	Chemical Potential (Free energy per mole)
	Molar properties

4.4 State Function

In thermodynamics, a state function, function of state, state quantity, or state variable is a property of the system that depends only on the current state of the system, not on the way in which the system acquired that state (independent of path). A state function describes the equilibrium state of a system. For example, density is a state function because a substance's density is not affected by how the substance is obtained. Lets say we have a certain amount H_2O, it does not matter whether that H_2O is obtained from one's tap, from a well, or from a bottle, because as long as all three have the same states, they will have the same density. When deciding whether a certain property is a state function or not, keep this rule in mind: is this property or value affected by the path or way taken to establish it? If the answer is no, then there is a state function, but if the answer is yes, then there is no state function.

4.4.1 Enthalpy and Internal Energy as state function

Both enthalpy and the internal energy are often described as state functions. This means that they depend only on the *state* of the system, i.e., on its pressure, temperature, composition, and amount of substance, but not on its previous history. Thus any solution of NaCl at 25°C and 1 bar (100 kPa) which contains a mixture of 1 mol NaCl and 50 mol H_2O has the same internal energy and the same enthalpy as any other solution with the same specifications. It does not matter whether the solution was prepared by simply dissolving NaCl(*s*) in H_2O, by reacting NaOH(*aq*) with HCl(*aq*), or by some more exotic method.

The fact that the internal energy and the enthalpy are both state functions has an important corollary. It means that when a system undergoes any change whatever, then the alteration in its enthalpy (or its internal energy) depends only on the initial state of the system and its final state. The initial value of the enthalpy will be H_1, and the final value will be H_2. No matter what pathway we employ to get to state 2, we will always end up with the value H_2 for the enthalpy. The enthalpy change $\Delta H = H_2 - H_1$ will thus be independent of the path used to travel from state 1 to state 2. This corollary is of course the basis of Hess' law. The change in enthalpy for a given chemical process is the same whether we produce that change in one or in several steps.

The opposite of a state function is a path function.

4.5 Path Functions

Properties or quantities whose values depend on the transition of a system from the initial state to the final state.

For path functions, the path from an initial state to the final state is crucial. Each part, or segment of the path to the final state is necessary to take into account. For example, a person may decide to hike up a 500 ft mountain. Regardless of what path the person takes, the starting place and the final place on top of the mountain will remain constant. The person may decide to go straight up to the mountain or decide to spiral around to the top of the mountain. There are many different ways to get to the final state, but the final state will remain the same.

Two important examples of a path function are heat and work. These two functions are dependent on how the thermodynamic system changes from the initial state to final state.

These two functions are introduced by the equation ΔU which represents the change in the internal energy of a system.

$$\Delta U=q+w$$

Note: U is a state function (it does not depend on how the system got from the initial to the final state).

Several conditions that could apply

- **Constant Volume:** if $\Delta V = 0$, the work is also zero since $w= -P(\Delta V)$ and substituting zero for the volume would ultimately make the entire term become zero. ***So: at constant volume:*** $\Delta U = q$
- **Constant Pressure:** When a reaction takes place at constant pressure, the volume is able to expand or contract to ensure that the pressure is constant. Thus, the volume will change ***so work will be done.*** So, the equation for ΔU in this reaction is: $\Delta U = q + w$
- **Constant Volume vs. Constant Pressure**: note that whether a reaction is carried out under constant volume or constant pressure, ΔU will ultimately be the same (because it is a state function). However, in the constant pressure situation, ***q(heat)*** can be slightly lower or higher (depending on the situation) (than ***q*** or the constant volume situation) because the amount of ***w(work)*** done will make up for it (the paths by which the reaction achieves ΔU can differ).
- **Reversible Process:**It is a process carried out by making really, really small changes to a component of the system without a loss of energy. Because the changes are so small, the system remains at rest throughout the entire process. A real world example of a reversible process is the measurement in efficiency of a heat engine (a device used to convert thermal energy to mechanical work). It is called a reversible process when no heat is lost or wasted and so the machine runs as efficiently as possible.

4.5.1 State Functions vs. Path Functions

The main way we define state functions is by comparing it to path functions. As stated before, a state function is a property whose value does not depend on the path taken to reach that specific function or value. In essence, what we are saying is that if something is not a path function, it is probably a state function. In order to have a better understanding of state functions, lets first define path functions and then compare path and state functions:

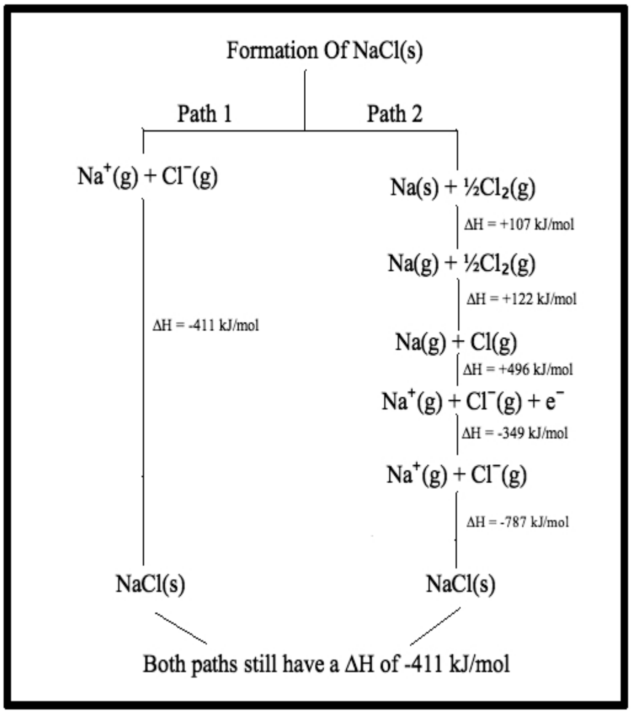


Fig. 4.4 State functions in the form of enthalpy

In this figure, two different steps are shown to form NaCl(s). The first path takes only one step: $Na^+(g) + Cl^-(g) = NaCl(s)$, which has an enthalpy of formation of -411 kJ/mol. The second path takes 5 steps to form NaCl(s) and when we add the enthalpy of formation of all these steps, the enthalpy of formation of NaCl(s) still ends up as -411 kJ/mol. This is the epitome of state functions as we have just stated that no matter what path we take to form NaCl(s), we still end up with the same enthalpy of formation of -411 kJ/mol.

Table 4.2 Differences between a state and path function

State Function	Path Function
Independent of path taken to establish property or value.	Dependent on path taken to establish property or value.
Can integrate using final and initial values.	Need multiple integrals and limits of integration in order to integrate.
Multiple steps result in same value.	Multiple steps result in different value.
Based on established state of system (temperature, pressure, amount, and identity of system).	Based on how state of system was established.

4.5.2 Differential of Path and State Function

A path function (work or heat increment) when integrated between an initial state and a final state, depends on the path chosen. For example, the work done during an isothermal expansion between (PA, VA, TA) and (PB VB, TB= TA) depends on the path chosen. If the path is a reversible one, then the work is - nRTln (VB/VA). If the work is done irreversibly under an external pressure equal to PB, then the work is - PB(VB- VA). These works are different. If a function is a path function, then its differential is inexact.For example, δq can be written for an ideal gas undergoing some reversible expansion or compression as:

$$\delta q = dU - \delta q = 3/2\ R\ dT + P\ dV$$

You can show for yourself that, indeed, δq is an inexact differential.

4.6 Reversible and irreversible processes

A thermodynamic reverse process is one which takes place in infinite number of infinitesimally small steps and takes infinite time to occur and its direction at any point can be reversed by an infinitesimal change in the state of the system.

In a reversible process, the system is every time in internal equilibrium i.e. all the intermediate states can be defined by thermodynamic variables like temperature and pressure. At every step, the system is also in virtual equilibrium with the surroundings, because by effecting an infinitesimal amount, and finite process takes infinite time to go to completion.

Thermodynamic reversibility can be illustrated with several processes like expansion or compression of a gas.

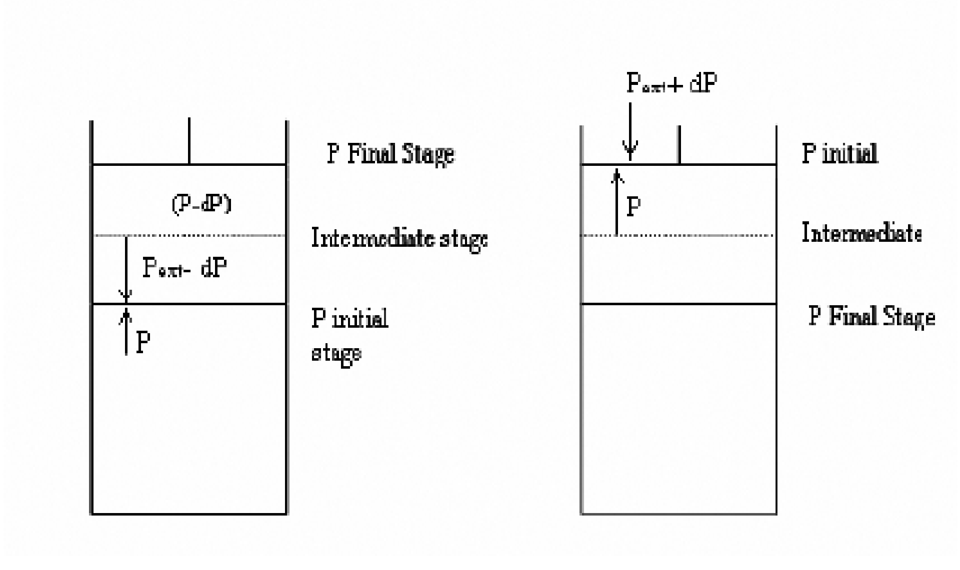


Fig. 4.5 Reversible expansion of a gas and Reversible compression through intermediate steps which involves infinitesimal changes in pressure

The process which is carried out in a single step in finite time and cannot be reversed is called irreversible process. It is in equilibrium state only at the initial and final stages of the operation. e.g. Expansion and compression of gas rapidly in a single step.

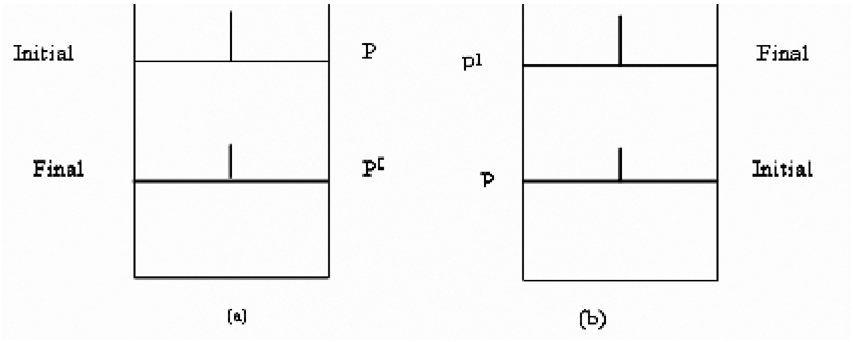


Fig. 4.6 Irreversible compression (a) and expansion (b) of a gas in a single step.

4.7 Concept of heat and Work

4.7.1 Heat

Energy is transferred between a system and its surroundings as a result of a temperature difference. Energy that passes from a warmer body (with a higher temperature) to a colder body (with a lower temperature) is transferred as heat. At the molecular level, molecules of the warmer body, through collisions, lose kinetic energy to those of the colder body. Thermal energy is transferred—"heat flows"—until the average molecular kinetic energies of the two bodies become the same, until the temperatures become equal. Heat, like work, describes energy in transit between a system and its surroundings.

Not only can heat transfer cause a change in temperature but, in some instances, it can also change a state of matter. For example, when a solid is heated,the molecules, atoms, or ions of the solid move with greater vigor and eventually break free from their neighbors by overcoming the attractive forces between them. Energy is required to overcome these attractive forces. During the process of melting, the temperature remains constant as a thermal energy transfer (heat) is used to overcome the forces holding the solid together. A process occurring at a constant temperature is said to be *isothermal*. Once a solid has melted completely, any further heat flow will raise the temperature of the resulting liquid

Heat is simply a form in which a quantity of energy may be *transferred* across a boundary between a system and its surroundings. It is reasonable to expect that the quantity of heat, *q*, required to change the temperature of a substance depends on

- how much the temperature is to be changed
- the quantity of substance
- the nature of the substance (type of atoms or molecules)

Historically, the quantity of heat required to change the temperature of one gram of water by one degree Celsius has been called the calorie (cal). The calorie is a small unit of energy, and the unit *kilocalorie* (kcal) has also been widely used. The SI unit for heat is simply the basic SI energy unit, the joule (J).Heat and thermal energy must be carefully distinguished. Equally important, we need to distinguish between energy changes produced by the action of forces through distances—*work*—and those involving the transfer of thermal energy—*heat*.

4.7.2 Work

"A process that does work is one that can be used to bring about a change in the height of a weight somewhere in the surroundings

"

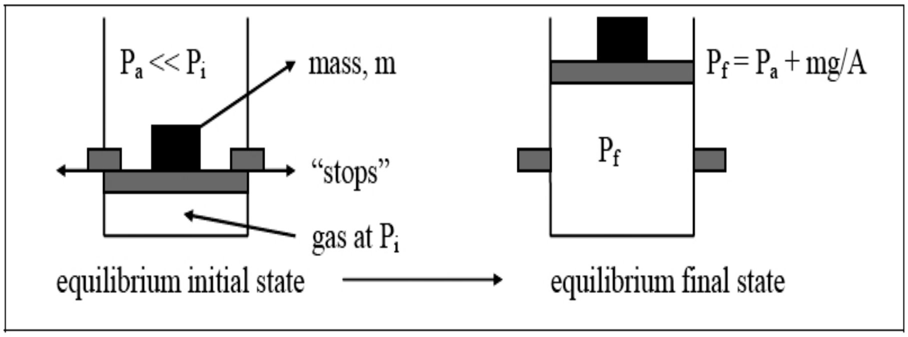


Fig 4.7 work done 'by'and on the system by surrounding

When work is done "by" the system on the surroundings, it is negative. When work is done "on" the system by the surroundings, it is positive. Work is always defined as the product of "an opposing external force" and "a displacement".

4.7.3 Heat Vs. Work

Distinction should be made between the energy terms heat and work. Both represent energy in transition. Work is the transfer of energy resulting from a force acting through a distance. Heat is energy transferred as the result of a temperature difference. Neither heat nor work are thermodynamic properties of a system. Heat can be transferred into or out of a system and work can be done on or by a system, but a system cannot contain or store either heat or work. Heat into a system and work out of a system are considered positive quantities.

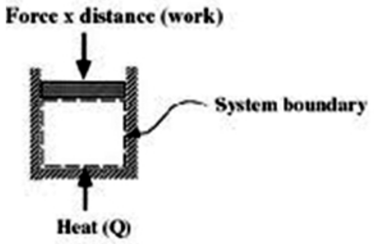


Fig.4.8 Heat and work relationship

4.8 The First Law of Thermodynamics

The absorption or evolution of heat and the performance of work require changes in the energy of a system and its surroundings. When considering the energy of a system, we use the concept of internal energy and how heat and work are related to it.

4.8.1 Internal energy, U

It is the total energy (both kinetic and potential) in a system, including *translational kinetic energy* of molecules, the energy associated with molecular rotations and vibrations, the energy stored in chemical bonds and intermolecular attractions, and the energy associated with electrons in atoms. Every thermodynamic system is associated with characteristic properties like temperature, pressure and composition etc. One of its important characteristic properties is internal energy. It is the energy ssociated with a system by virtue of its molecular constitution and the motion of its molecules.

The internal energy encompasses:

- The kinetic energy associated with the motions of the atoms
- The potential energy stored in the chemical bonds of the molecules
- The gravitational energy of the system

In thermodynamics, the total energy of a system is called its internal energy and is denoted U (in this class). Thermodynamics allows us to find expressions for how the internal energy of a system changes during a process. However, thermodynamics does not allow us to calculate U for a given state. The change in internal energy during a process is defined by ΔU and is equal to the difference between the energy of the system in the final state and the energy of the system in the initial state. $\boldsymbol{\Delta U = Uf - Ui}$

Internal energy is a state function because it depends only on the state of the system and not on the process used to reach that state i.e the value of internal energy of a system depends on the quantity of matter contained in a system; it is also classified as an extensive property.

Symbol and Sign conventions: Symbol of internal energy is **U** or **E**

It is impossible to find out the absolute value of internal energy of a system. In thermodynamics we consider only the change in internal energy of system **(ΔE)** when a system undergoes a change from one state to another.

If, E_1 = internal energy of initial state

E_2 = internal energy of final state.

Then $\Delta E = E_2 - E_1$

If $E_2 > E_1$, then **ΔE** will be **+ve** (Endothermic reaction)

When $E_2 < E_1$, then **ΔE** will be **–ve** (Exothermic reaction)

A system may transfer energy as heat or work or both

The SI unit for internal energy of a system is Joule (J)

Although we cannot calculate the absolute value of U, thermodynamics tells us that the value of U depends only on the characteristics of the state of that system.

Clausius stated "The Energy of the Universe is constant" Energy can be transferred from the system to its surroundings, or vice versa, but it can't be created or destroyed.

$$\Delta E_{\text{univ}} = \Delta E_{\text{sys}} + \Delta E_{\text{surr}} = 0$$

A system contains *only* internal energy. A system does not contain energy in the form of heat or work. Heat and work are the means by which a system exchanges energy with its surroundings. *Heat and work exist only during a change in the system*. The relationship between heat work and changes in internal energy is dictated by the law of conservation of energy, expressed in the form known as the **first law of thermodynamics**.

$$\Delta E_{\text{sys}} = q + w$$

The internal energy and temperature of a system decrease ($\Delta E < 0$) when the system either loses heat or does work on its surroundings. Conversely, the internal energy and temperature increase ($\Delta E > 0$) when the system gains heat from its surroundings or when the surroundings do work on the system.

4.8.2 Enthalpy

There are two different situations of interest in thermodynamics. First is the process taking place at constant volume and second is the processes taking place at constant pressure. For the processes carried at constant volume no **PV** work is done and total heat content is same as internal energy **E**. But in the processes at constant pressure the system also expends energy in doing **PV** work. Therefore the total heat content of a system at constant pressure is equivalent to the sum of internal energy **E** and the **PV** energy. This is called enthalpy of the system and represented by the symbol **H**. Thus enthalpy can be defined as total heat content of system at constant pressure.

$$H = E + PV \text{ -------------(i)}$$

As **E**, **P** and **V** all are the state functions and value of **H**, depends on the value of state function, **H** must also be a state function of a system and its value is independent of path by which this change has been accomplished.

Change in enthalpy, $\Delta H = H_2 - H_1$ ------------------------------(ii)

$\mathbf{H_1}$ and $\mathbf{H_2}$ are enthalpies of initial and final states respectively.

$H_1 = E_1 + PV_1$

$H_2 = E_2 + PV_2$

Substituting the value of $\mathbf{H_1}$ and $\mathbf{H_2}$ in equation (ii)

$\Delta H = (E_2 + PV_2) - (E_1 + PV_1)$

$= E_2 + PV_2 - E_1 - PV_1$

$= (E_2 - E_1) - +(PV_2 - PV_1)$

$= (E_2 - E_1) - +P(V_2 - V_1)$

$$\Delta H = \Delta E + P\Delta V \text{ ---------------- ----------(iii)}$$

$$\text{also, } \Delta H = \Delta E + w \text{ --------------- ----------------(iv)}$$

From the first law; $\Delta E = q - w$ --(v)

From equation (iv) and (v)

$\Delta H = q$ (heat transferred when change in state occurs at constant pressure).

This can be written as

$\Delta H = H_2 - H_1$

If $\mathbf{H_2 < H_1}$, $\mathbf{\Delta H}$ is negative and the process will be exothermic.

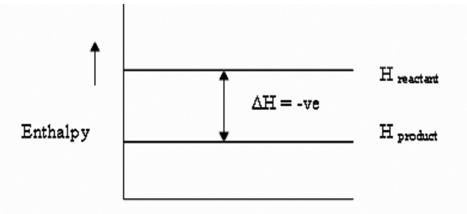


Fig 4.9 Enthalpy change for an exothermic reaction

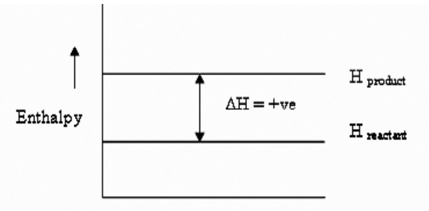


Fig 4.10 Enthalpy change for an endothermic reaction

For a chemical reaction at constant pressure,

$\Delta H = H_{products} - H_{reactants.}$

The units of **ΔH** are kilo calorie (K.Cal) or Kilo Joules (KJ).

4.8.3 Relationship between ΔH and ΔE [qp and qv]

From the first law , $\Delta q = \Delta E + P\Delta V$ ----------------(i)

At constant volume, $\Delta V = 0$

$$\Delta q = q_v = \Delta E \text{ -------------------(ii)}$$

At constant pressure

$$q_p = \Delta E + P\Delta V \text{ ---------------- (iii)}$$

q_p and q_v are the heat change at constant pressure and constant volume respectively. Enthalpy change ΔH is given by the following expression

$$\Delta H = \Delta E + P\Delta V \text{ -----------------(iv)}$$

From equation (iii) & (iv)

$$\Delta H = q_p \text{ -----------------------------(v)}$$

Also, $\Delta H = \Delta E + P\Delta V$

$$q_p = q_v + P\Delta V \text{ ---------------------(vi)}$$

If gases are involved in a reaction and we have n_1 moles of gases before reaction and n_2 moles of gases after reactions. Assuming ideal gas behaviors, we have

$PV = nRT$ (ideal gas equation)

$PV_2 = n_2RT$

$PV_1 = n_1RT$

$P(V_2-V_1) = (n_2-n_1)RT$

$P\Delta V = \Delta nRT$

By putting the value in equation (iv), we get

$\Delta H = \Delta E + \Delta nRT$

$q_p = q_v + \Delta nRT$

Also $q_p - q_v = \Delta nRT$

4.9 Heat Capacity

Enthalpy and internal energy function are used to determine heat changes accompanying a process at constant pressure and constant volume respectively. Heat capacity is a new function which relates the heat changes to the temperature changes at constant volume. Heat capacity means the capacity to absorb energy and store it. As the system absorb heat energy its kinetic energy increase which in turn rises the temperature of the system. Thus heat capacity can be defined as,

"Heat absorbed in raising temperature by one degree at a particular temperature."

Heat capacity is given by the following expression.

$$c = \frac{q}{m(T_2 - T_1)}$$

q = heat absorbed

m = mass

T_1 & T_2 = Temperature before and after absorbing heat.

If m = 1g then it is called specific heat capacity.

If we consider mass as 1mole then the heat capacity is known as molar heat capacity, denoted by **C**.

$$c = \frac{q}{(T_2 - T_1)(m = 1mole)}$$

Molar heat capacity of a system is defined as the quantity of thermal energy that must be absorbed by 1mole of the system to produce a change of temperature of one degree. Since the heat capacity **(C)** varies with temperature, its value will be given as:

$C = \frac{dq}{dT}$ (Ratio of amount of heat absorbed to the rise in temperature)

The units of molar heat capacity are calories per degree per mole (Cal K^{-1} mol^{-1}) or Joules per degree per mole (J K^{-1} mol^{-1})

Heat capacity is not a state function; we must specify the process by which temperature is raised by one degree. There are two types of molar heat capacities viz at constant volume and at constant pressure.

4.9.1 Molar heat capacity at constant volume Cv

$dq = dE + PdV$ -------------(i) (From the first law)

Dividing the equation by **dT**

$$\frac{dq}{dT} = \frac{dE + PdV}{dT}$$

$$\frac{dq}{dT} = \frac{dE}{dT} + \frac{PdV}{dT} \text{ ---------------------(ii)}$$

At constant volume, $dV = 0$

Equation (ii) reduces to

$$C_V = \left[\frac{dE}{dT}\right]_V \text{ ------------- (iii)}$$

Thus the heat capacity of constant volume, **Cv** is defined as the rate of change of internal energy with temperature at constant volume.

4.9.2 Molar Heat capacity at constant pressure C_P

Consider equation (ii)

$$\frac{dq}{dT} = \frac{dE}{dT} + \frac{PdV}{dT} \text{ ....(ii)}$$

We know that; $H = E + PV$

Differentiating this equation w.r.t temperature at constant pressure, we get

$$\left[\frac{dH}{dT}\right]_P = \left[\frac{dE}{dT}\right]_P + P\left[\frac{dV}{dT}\right]_P \text{ ---------------------------(iv)}$$

Comparing equation (ii) & (iv)

$$C_P = \left[\frac{dH}{dT}\right]_P \text{ -----------------(v)}$$

Thus the heat capacity at constant pressure **(C_P)** is defined as the rate of change of enthalpy with temperature at constant pressure.

4.9.3 Relationship between Cp and Cv

We know,

$$C_P = \frac{dH}{dT} \text{ --------------------(i)}$$

$$C_V = \frac{dE}{dT} \text{------------------(ii)}$$

$$H = E + PV \text{ -------------------(iii)}$$

For one mole of ideal gas $PV = RT$

H = E+RT ---------------------(iv)

Differentiating w.r.t to temperature, **T**

$$\frac{dH}{dT} = \frac{dE}{dT} + R$$

Or Cp = Cv +R (From equation (i) and (ii))

Cp – Cv =R

Thus **Cp** is greater than **Cv** by a gas constant value 1.987 Cal K^{-1} mol^{-1} or 8.314 JK^{-1} mol^{-}

4.10 Expansion of an ideal gas and changes in Thermodynamic Properties.

We can calculate the change in thermodynamic properties like q, w, ΔU, ΔH with the help of first law of thermodynamics. The expansion can be isothermal which can be reversible or irreversible or it can be adiabatic which can also be reversible or irreversible. This is explained below:

Isothermal Expansion

*Calculation **of** **ΔU:***

During the expansion in isothermal process, temperature remains constant throughout the process. As internal energy U for an ideal gas depends only on the temperature and in isothermal process the temperature remains constant. This means internal energy U of the gas remains constant.

That is ΔU = 0

Calculation of ΔH:

As we know that H = U + PV

Therefore ΔH = Δ (U + PV) = ΔU + ΔPV

= ΔU + ΔnRT

Since, for an isothermal process, temperature is constant as well as internal energy U remains constant of the gas. That is ΔT as well as ΔU are equal to zero,

Hence,

ΔH = 0

Calculation of q and w:

From first law of thermodynamics, ΔU = q + w

As for isothermal process, ΔU = 0

Hence, w= -q

This means in an isothermal expansion, the work is done at the expense of the heat absorbed.

The magnitude of w and q depends on the way in which the expansion process is carried out, i.e., whether it is carried reversibly or irreversibly.

4.11 Standard States and Standard Enthalpy Changes

When most chemical reactions occur, heat is either taken in from the surroundings, causing the temperature of the reaction mixture to rise, or is given out to the surroundings. Many common chemical reactions are carried out at constant pressure (e.g. in an open beaker or flask) and under these conditions, the heat transfer, q, is equal to the enthalpy change, ΔH. The terms heat and enthalpy are often used interchangeably although, strictly, this is only true under conditions of constant pressure.

The measured enthalpy change for a reaction has a unique value *only* if the initial state (reactants) and final state (products) are precisely described. If we define a particular state as *standard* for the reactants and products, we can then say that the standard enthalpy change is the enthalpy change in a reaction in which the reactants and products are in their standard states. This so-called standard enthalpy of reaction is denoted with a degree symbol, $\Delta \boldsymbol{H}°$**.** The standard state of a solid or liquid substance is the pure element or compound at a pressure of *1 bar* and at the temperature of interest. For a gas, the standard state is the pure gas behaving as an (hypothetical) ideal gas at a pressure of 1 bar and the temperature of interest.

Although temperature is not part of the definition of a standard state, it still must be specified in tabulated values of $\Delta \boldsymbol{H}°$ **,** because $\Delta \boldsymbol{H}°$ depends on temperature.

The standard state of a substance is its most thermodynamically stable state under a pressure of 1 bar (1.00 x 10^5 Pa) and at a specified temperature, T. Most commonly, T=298.15 K, and the notation for the standard enthalpy change of a reaction at 298.15K is then $\Delta_r H^o$(298.15 K). It is usually sufficient to write $\Delta_r H^o$ (298 K).

4.11.1 Standard enthalpy of formation

The standard enthalpy of formation of a compound, $\Delta_f H^o$ (298 K), is the enthalpy change at 298K that accompanies the formation of a compound in its standard state from its constituent elements in their standard states.The standard state of an element at 298K is the thermodynamically most stable form of the element at 298K and 1.00 x 10^5 Pa. Some examples of the standard states of elements under these conditions are:

. hydrogen: $H_2(g)$

. oxygen: $O_2(g)$

. nitrogen: $N_2(g)$

. bromine: $Br_2(l)$

. iron: Fe(s)

. copper: Cu(s)

. mercury: Hg(l)

. carbon: C(graphite)

. sulfur: S8(s)

The one exception to the definition of standard state of an element given above is phosphorus. The standard state of phosphorus is defined as being white phosphorus, P_4(white), rather than the thermodynamically more stable red and black allotropes. By definition, the standard enthalpy of formation of an element in its standard state is 0 kJ mol.

Heat of Formation, $\square^{o}_{f}H$ is the heat evolved from the synthesis reaction of one mole of the substance from the Standard State of its' constituent elements. The $\square^{o}_{f}H$(Diamond) is not zero because it is not the Standard State of the element Carbon.

4.12 Hess’s law of constant heat summation

This is the direct consequence of the first law of thermodynamics. According to Hess’s law the total thermal effect in a chemical reaction depends on the initial sate of reactants and the final state of products and not upon the intermediate stages involved in the conversion of reactants into products.

This law can also be stated as “The net heat change in a reaction is the same, whether the reaction takes place in one step or several steps.”

Let us consider a general reaction of conversion of **A** to **Z** in one step and in several steps.(Fig.4.11)

i) $A \longrightarrow Z \quad \Delta H=+q$

q heat evolved in direct change

ii) $A \longrightarrow B \quad \Delta H=+q_1$

iii) $B \longrightarrow C \quad \Delta H=+q_2$

iv) $C \longrightarrow Z \quad \Delta H=+q_3$

According to Hess’s law

$$q = q_1 + q_2 + q_3$$

Hess’s law has been tested experimentally and shown to be true.

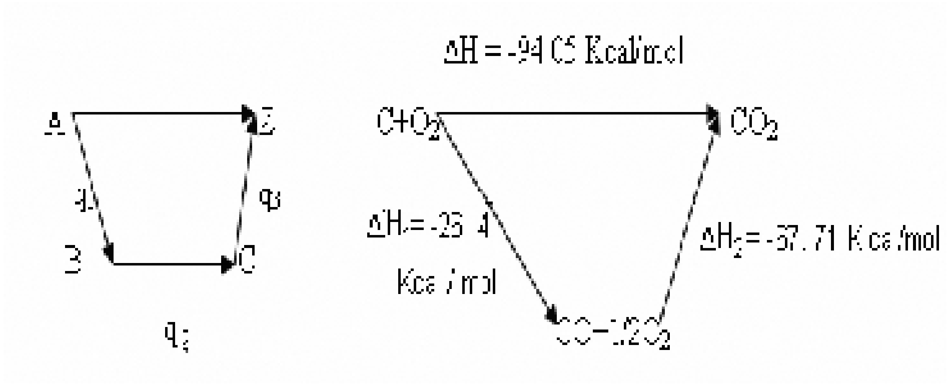


Fig.4.11 Thermal effect depend on initial and final state

Thus standard enthalpy of an overall reaction is the sum of the standard enthalpies of the individual reactions into which the overall reaction may be divided - Individual steps may not be “real” reactions, but must balanced

Since we are interested in calculating a difference, the absolute enthalpy of the elements in their standard states is unimportant , and we adopt the convention that the enthalpy of formation of an element in its standard state is zero.

The standard enthalpy of formation of a compound is the standard enthalpy change of a reaction in which the compound is formed from the reference forms of its elements in their standard states. Standard enthalpies of formation (usually listed at 25.00 °C) can be used to calculate standard enthalpies of reaction through the following equation (where the symbols (v_r) and (v_p) are stoichiometric coefficients):

$$\Delta H^\circ = \sum \nu_p \times \Delta H_f^\circ(\text{products}) - \sum \nu_r \times \Delta H_f^\circ(\text{reactants})$$

4.13 Heat of Reaction

It is the amount of heat that must be added or removed during a chemical reaction in order to keep all of the substances present at the same temperature. If the pressure in the vessel containing the reacting system is kept at a constant value, the measured heat of reaction also represents the change in the thermodynamic quantity called enthalpy, or heat content, accompanying the process—***i.e.,*** the difference between the enthalpy of the substances present at the end of the reaction and the enthalpy of the substances present at the start of the reaction. Thus, the heat of reaction determined at constant pressure is also designated the enthalpy of reaction, represented by the symbol Δ***H***. If the heat of reaction is positive, the reaction is said to be endothermic; if negative, exothermic.

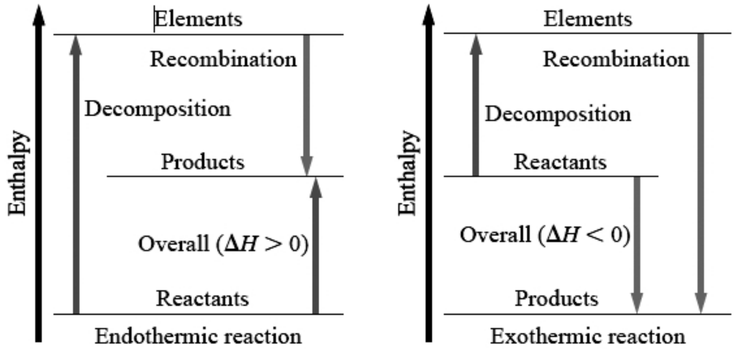


Fig.4.12 Heat of reaction for endothermic and exothermic reaction

4.14 Bond Energy

In chemical reactions the formation of a chemical bond is accompanied by the release of energy. Conversely energy has to be supplied for the breaking of a bond.

Bond strengths are commonly described by their bond dissociation energy which is the energy required to break one mole of a bond of a particular type. This is a definite quantity and is expressed in kJ mol^{-1}. For diatomic molecules the bond dissociation energy is the same as bond energy, whereas in polyatomic molecules the bond energy is taken as the mean average of the various bond dissociation energies of the bonds of a given type.

In general the bond dissociation energy ΔU is greater than the true bond dissociation energy, ΔU by an amount corresponding to the zero point energy even at 0 K. Bond energy is defined as the amount of energy required to break the covalent bond between the atoms and to separate them to an infinite distance in the gaseous state under standard conditions

The thermochemical data is useful in determining the bond energies of different bonds.

Bond energy is average energy required to dissociate a particular type of bond in one mole into the gaseous atoms, separated by a distance over which there is no attraction between the atoms.

Thus the bond energy of **H-H** bond is the energy required to break all the bonds in one mole of hydrogen gas. Bond energy is the measure of strength of bond. It depends upon sizes of the atoms, their electro negativity and bond length.

Knowledge of bond energy is useful for calculating heats of reaction for gaseous reactions for which no thermal data is available. The bond energy is one fourth of the total energy required to break all the four **C-H** bonds in 1 mole of methane.

$$CH_{4(g)} \longrightarrow C_{(g)} + 4H_{(g)} ;\ \Delta H = ?$$

The energy required to dissociate completely a molecule into the constituent atoms is calculated from (i) enthalpy of formation of compound (ii) enthalpy of sublimation of solid element (Cs) from which compound is formed(iii) enthalpy of dissociation of gaseous molecule **(** $\mathbf{H_{2(g)}}$ **)** into the atoms.

$$C_{graphite} + 2H_{2(g)} \longrightarrow CH_4 ;\ \Delta H_1 = -75.0\ KJ$$

$$C_{graphite} \longrightarrow C(g);\ \Delta H_2 = 720.0\ KJ$$

$$H_{2\,(g)} \longrightarrow 2H_{(g)} ;\ \Delta H_3 = 435.0\ KJ$$

Through the suitable rearrangement of the above thermo chemical equations and using Hess's law we can readily obtain the heat of desired reaction.

$$\Delta H = (2 \mathbf{x} \Delta H_3) + \Delta H_2 - \Delta H_1$$

$$CH_{4(g)} \longrightarrow C_{(g)} + 4H_{(g)} ;\ \Delta H = 1665\ KJ$$

Hence the C-H bond energy = ¼ **x** 1665 = 416.2 kJ.

4.14.1 Thermochemical equations

There are number of factors other than constant volume or pressure conditions, on which heat of reaction or enthalpy of reaction depends. These are

i) Physical state of reactants and products.

ii) Amount of the reactants and products

iii) Temperature

A thermo chemical equation is an equation which indicates the amount of heat change in the reaction or process. A thermo chemical equation necessarily be:

a) balanced

b) mention the physical states of reactants and products.

c) give the value of **ΔE** or **ΔH** in accordance with the quantities of substances given by the equation.

Thermo chemical equations may be multiplied, added or subtracted, like ordinary algebraic equations. With the help of Hess's law we can calculate the enthalpies of certain reactions in terms of enthalpies of other related reactions. Suppose the heat of formation of methane is to be calculated. The relevant equation is

$C(s) + 2\,H_2(g) \longrightarrow CH_4\,(g)$; $\Delta H_F(CH_4) = \mathbf{x}$ K cal / mole---------(i)

The following data are available.

$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$; $\Delta H_f\,(CO_2) = -96.0$ K cal ------------(ii)

$H_{2\,(g)} + \frac{1}{2}/O_{2(g)} \longrightarrow H_2O_{(l)}$; $\Delta H_f(H_2O) = -68.0$ K cal ------------(iii)

$CH_{4\,(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2\,H_2O_{(l)}$; $\Delta H_C(CH_4) = -212.8$ K cal----.(iv)

We should aim at finding the value of heat of formation of methane. We have to manipulate these equations so as to get the required equation (equation (i))

Multiplying equation (iii) by **2** and adding to equation (i) we get,

$C_{(s)} + O_{2(g)} + 2\,H_2 + O_{2(g)} \longrightarrow CO_{2(g)} + 2\,H_2O_{(l)}$;

$$\Delta H = [2 \text{ X } \Delta H_F\,(H_2O)] + \Delta H_F(CO_2)$$

$$= [2 \text{ X } -68.0 \text{ K cal}] + (-96.0) \text{ K.cal.}$$

$$= -232.0 \text{ K. cal.}$$

On subtracting (iii) from (v) we get

$C_{(s)} + 2\,H_{2(g)} \longrightarrow CH_{4(g)}$; $\Delta H_f(CH_4) = -232.0$ K. cal –(-212.8 K. cal)

$$= -19.2 \text{ K. cal.}$$

Or

$\Delta H_f\,(CH_4) = [2 \text{ X } \Delta H_f\ (H_2O)] + \Delta H_f\,(CO_2) - \Delta H_{C\,(CH_4)}$

Similarly second application of Hess's law is calculation of heats of formation of compounds through the use of bond energy data.

4.15 Temperature Dependence of Heat or Enthalpy-Kirchoff's equation

The heat or enthalpy of reaction varies with temperature of gas due to variation in its specific heat. The expressions representing the variation of heat change of reaction with temperature are known as Kirchoff's equations.

Heat change of a reaction at constant volume is given by

$\Delta E = E_2 - E_1$ Type equation here.

(E_1 & E_2 are internal energies of reactants and products.)

Differentiating this equation w.r.t temperature at constant volume, we have

$$\frac{d(\Delta E)}{dTv} = \frac{dE2}{dTv} - \frac{dE1}{dTv} \text{…………………………….(i)}$$

We have defined heat capacity of a substance at constant volume as

$$C_v = \left[\frac{dE}{dT}\right]_V$$

Therefore;

Or $[\frac{d(\Delta E)}{dT}] = (Cv2 - (Cv)1 = \Delta Cv$ ………………………………………….(ii)

$(C_v)_1$ and **$(C_v)_2$** are the heat capacities for the reactants and products respectively. Thus change in heat of reaction with temperature at constant volume is equal to the difference in heat capacities of products and reactants, at constant volume.

$\frac{d(\Delta E)}{dT} = C_v dT$

Or $d(\Delta E) = \Delta C_v\, dT$

Integrating this equation between temperature **T_1** and **T_2**, we get

Assuming ΔCv remain constant in the temperature range from T_1 to T_2, then ΔCv can be taken our of integration sign.

$\Delta E_2 - \Delta E_1 = \Delta C_v [T_2 - T_1]$------------- ----------(iii)

Similarly at constant pressure Heat of reaction is given as

$\Delta H = H_2 - H_1$

Where H_2 & H_1 are the enthalpies of products and reactants respectively

Differentiating this equation with respect tot temperature, we get

$$\frac{d(\Delta H)}{dT} = \frac{dE2}{dTv} - \frac{dE1}{dTv} \quad \text{…. …………………….. (iv)}$$

We have defined heat c apacities at constant pressure as

$Cp = [dH/dT]_P$

Therefore

$$\frac{d(\Delta H)}{dT} = (Cp)_2 - (Cp)_1 = \Delta Cp \text{…………………………..(V)}$$

$(Cp)_2$ and **$(Cp)_1$** are the heat capacities at constant pressure for products and reactants respectively. Thus change in heat of reactant at constant pressure (enthalpy change) with temperature is equal to the difference in heat capacities of products and reactants at constant pressure.

$$[\frac{\partial(\Delta H)}{\partial T}] = \Delta Cp \text{ or } d(\Delta H) = \Delta CpdT$$

Integrating this equation between temperature T_1 & T_2 we get

$$\int_{T1}^{T2} d(\Delta H) = \int_{T1}^{T2} \Delta CpdT = \int_{T1}^{T2} dT$$

ΔH_2 and ΔH_1 are the enthalpy change at temperature T_2 & T_1 respectively. Assuming ΔCp remaining constant, in the temperature range T_1 and T_2, then ΔCp can be taken our of integration sign.

$$\Delta H_2 - \Delta H_1 = \Delta C_P (T_2 - T_1) \text{ ----------(vi)}$$

The relations **(ii), (iii), (v)** and **(vi)** are called Kirchoff's equations. These equations can be used to calculate the heat of reaction at given temperature if heat of reaction at some other temperature and ΔCp is known.

4.16 Summary

The subject of a thermo chemical study is considered into the system of interest and the portions of the universe with which the system may interact, the surroundings. An open system can exchange both energy and matter with its surroundings. A closed system can exchange only energy and not matter. An isolated system can exchange neither energy nor matter with its surroundings.

Energy is the capacity to do work, and work is performed when a force acts through a distance.

Heat is energy transferred between a system and its surroundings as a result of a temperature difference between the two.

Quantity of heat is the product of the heat capacity of the system and the temperature change. In turn, heat capacity is the product of mass and specific heat, the amount of heat required to change the temperature of one gram of substance by one degree Celsius

In a chemical reaction, a change in the chemical energy associated with the reactants and products may appear as heat. The heat of reaction is the quantity of heat exchanged between a system and its surroundings when the reaction occurs at a constant temperature. In an exothermic reaction, heat is given off by the system while an endothermic reaction the system absorbs heat

Internal energy (U) is the total energy (both kinetic and potential) in a system. The first law of thermodynamics relates changes in the internal energy of a system to the quantities of heat and work exchanged between the system and its surroundings. The relationship requires that a set of sign conventions be consistently followed. A function of state (state function) has a value that depends only on the exact condition or state in which a system is found and not on how that state was reached. Internal energy is a state function. A path-dependent function, such as heat or work, depends on how a change in a system is achieved. A change that is accomplished through an infinite number of infinitesimal steps is a reversible process, whereas a change accomplished in one step or a series of finite steps is irreversible.

For reactions at constant pressure a more useful function is enthalpy *(H)* defined as the internal energy (U) of a system plus the pressure–volume product (P-V). The enthalpy change ΔH in a reaction proves to be the heat of reaction at constant pressure. Most heats of reaction are reported as values ΔH. In most of the cases heat of reaction are reported as the values of ΔH. A substance under a pressure of 1 bar and at the temperature of interest is said to be in its standard state. If the reactants and products of a reaction are in their standard states, the enthalpy change in a reaction is called the standard enthalpy of reaction and designated as Enthalpy changes $\Delta H^{O.}$ Often an unknown value can be established indirectly through Hess's law, which states that an overall enthalpy change is the sum of the enthalpy changes of the individual steps leading to the overall process. By arbitrarily assigning an enthalpy of zero to the reference forms of the elements in their standard states, the enthalpy change in the formation of a compound from its elements becomes a standard enthalpy of formation (ΔH_f^O)

4.17 Terminal Question

1. Differentiate between

(i) Extensive and Intensive properties.

(ii) State and Path functions.

2. Derive an equation relating Cp and Cv.

3. Discuss thermo chemical equations used for obtaining the heat of desired reaction.

4. Explain how heat of reaction is related to exothermic and endothermic reactions.

5. How much heat is required to raise the temperature of 7.35 g of water from 21.0 to 98.0 ^{0}C (assume the specific heat of water as 4.18 J g^{-1} °C^{-1} throughout this temperature range.)

6. Given that $\Delta H°$ [$BaSO_4(s)$] = -1473 kJ/mol what is the standard enthalpy change for the precipitation of barium sulfate?

7. Using heat combustion data determine ΔH^0_f of the reaction.

$$3\,C(\text{graphite}) + 4\,H_2(g) \longrightarrow C_3H_8(g) \qquad \Delta H^\circ = ?$$

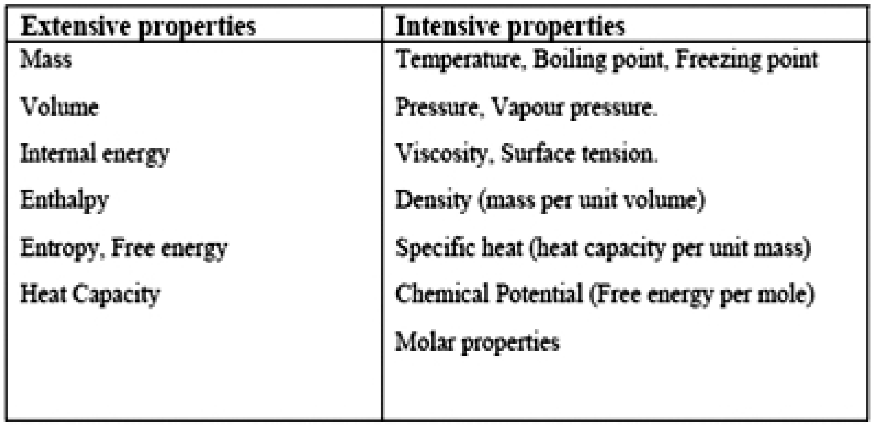
Given

$$
\begin{aligned}
\Delta H^{\circ}_{\text{comb}} \quad C_3H_8(g) &= -2219.9\ \text{kJ/mol}\ C_3H_8(g) \\
C(\text{graphite}) &= -393.5\ \text{kJ/mol}\ C(\text{graphite}) \\
H_2(g) &= -285.8\ \text{kJ/mol}\ H_2(g)
\end{aligned}
$$

Answers

1.

(i) Difference between extensive and intensive properties.



Extensive properties	**Intensive properties**
Mass	Temperature, Boiling point, Freezing point
Volume	Pressure, Vapour pressure.
Internal energy	Viscosity, Surface tension.
Enthalpy	Density (mass per unit volume)
Entropy, Free energy	Specific heat (heat capacity per unit mass)
Heat Capacity	Chemical Potential (Free energy per mole)
	Molar properties

(ii) Difference between state and path function

State Function	**Path Function**
Independent of path taken to establish property or value.	Dependent on path taken to establish property or value.
Can integrate using final and initial values.	Need multiple integrals and limits of integration in order to integrate.
Multiple steps result in same value.	Multiple steps result in different value.
Based on established state of system (temperature, pressure, amount, and identity of system).	Based on how state of system was established.

2. We know,

$$C_P = \frac{dH}{dT} \text{ ---------------------(i)}$$

$$C_V = \frac{dE}{dT} \text{--------------------(ii)}$$

$$H = E + PV \text{ --------------------(iii)}$$

For one mole of ideal gas PV = RT

H = E+RT ---------------------(iv)

Differentiating w.r.t to temperature, **T**

$$\frac{dH}{dT} = \frac{dE}{dT} + R$$

Or Cp = Cv +R (From equation (i) and (ii))

Cp – Cv =R

Thus **Cp** is greater than **Cv** by a gas constant value 1.987 Cal K^{-1} mol^{-1} or 8.314 JK^{-1} mol^{-}

3.

A thermo chemical equation is an equation which indicates the amount of heat change in the reaction or process. A thermo chemical equation necessarily be:

a) balanced .

b) mention the physical states of reactants and products.

c) give the value of **ΔE** or **ΔH** in accordance with the quantities of substances given by the equation.

Thermo chemical equations may be multiplied, added or subtracted, like ordinary algebraic equations. With the help of Hess's law we can calculate the enthalpies of certain reactions in terms of enthalpies of other related reactions. Suppose the heat of formation of methane is to be calculated. The relevant equation is

$C(s) + 2\,H_2(g) \longrightarrow CH_4\,(g)$; $\Delta H_F(CH_4) = \mathbf{x}$ K cal / mole---------(i)

The following data are available.

$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$; $\Delta H_f\,(CO_2) = -96.0$ K cal ------------(ii)

$H_{2\,(g)} + \frac{1}{2}/O_{2(g)} \longrightarrow H_2O_{(l)}$; $\Delta H_f(H_2O) = -68.0$ K cal ------------(iii)

$CH_{4\,(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2\,H_2O_{(l)}$; $\Delta H_C(CH_4) = -212.8$ K cal----….(iv)

We should aim at finding the value of heat of formation of methane. We have to manipulate these equations so as to get the required equation (equation (i))

Multiplying equation (iii) by **2** and adding to equation (i) we get,

$C_{(s)} + O_{2(g)} + 2\,H_2 + O_{2(g)} \longrightarrow O_{2(g)} + 2\,H_2O_{(l)}$;

$\Delta H = [2 \text{ X } \Delta H_F(H_2O)] + \Delta H_F(CO_2)$

= [2 X -68.0 K. cal] +(-96.0) K.cal.

= -232.0 K. cal.

On subtracting (iii) from (v) we get

$$C_{(s)} + 2\,H_{2(g)} \longrightarrow CH_{4(g)}\ ;\ \Delta H_f(CH_4) = -232.0 \text{ K. cal} - (-212.8 \text{ K. cal})$$

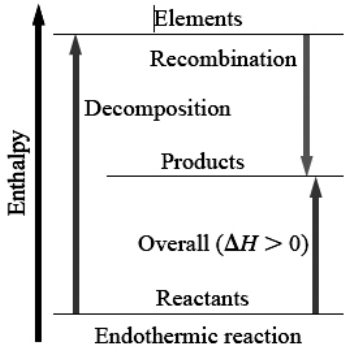
$$= -19.2 \text{ K. cal.}$$

Or

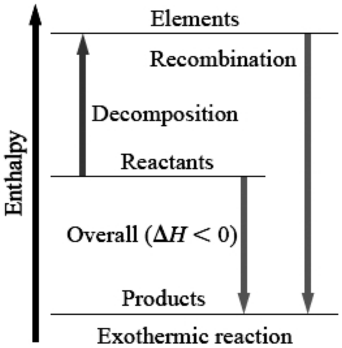
$$\Delta H_f(CH_4) = [2 \text{ X } \Delta H_f\ (H_2O)] + \Delta H_f(CO_2) - \Delta H_{C\,(CH_4)}$$

Similarly second application of Hess's law is calculation of heats of formation of compounds through the use of bond energy data.

4. The amount of heat that must be added or removed during a chemical reaction in order to keep all of the substances present at the same temperature. If the pressure in the vessel containing the reacting system is kept at a constant value, the measured heat of reaction also represents the change in the thermodynamic quantity called enthalpy, or heat content, accompanying the process—***i.e.,*** the difference between the enthalpy of the substances present at the end of the reaction and the enthalpy of the substances present at the start of the reaction. Thus, the heat of reaction determined at constant pressure is also designated the enthalpy of reaction, represented by the symbol Δ***H***. If the heat of reaction is positive, the reaction is said to be endothermic; if negative, exothermic.

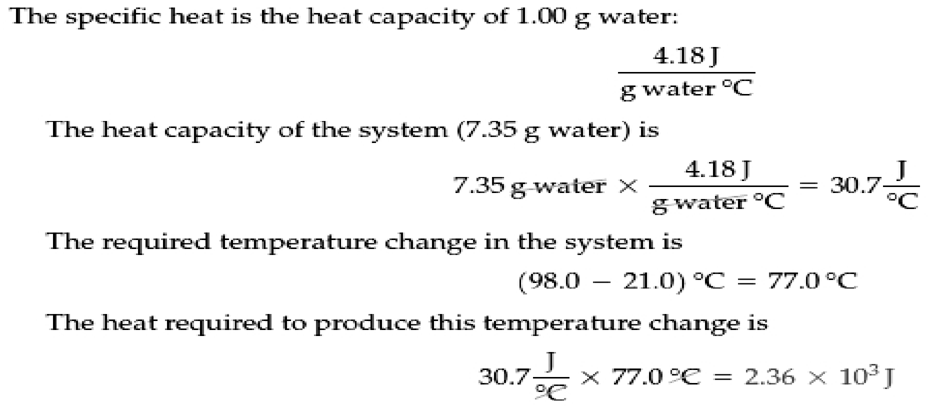


Endothermic reaction



Exothermic reaction

5. To answer this question, we begin by multiplying the specific heat capacity by the mass of water to obtain the heat capacity of the system. To find the amount of heat required to produce the desired temperature change we multiply the heat capacity by temperature difference



The specific heat is the heat capacity of 1.00 g water:

$$\frac{4.18\text{ J}}{\text{g water }°\text{C}}$$

The heat capacity of the system (7.35 g water) is

$$7.35\ \cancel{\text{g water}} \times \frac{4.18\text{ J}}{\cancel{\text{g water}}\ °\text{C}} = 30.7\frac{\text{J}}{°\text{C}}$$

The required temperature change in the system is

$$(98.0 - 21.0)\ °\text{C} = 77.0\ °\text{C}$$

The heat required to produce this temperature change is

$$30.7\frac{\text{J}}{\cancel{°\text{C}}} \times 77.0\ \cancel{°\text{C}} = 2.36 \times 10^3\text{ J}$$

6. First, write the net ionic equation for the reaction and introduce the relevant data. Then make use of equation .

$$\Delta H^\circ = \sum v_p \Delta H_f^\circ(\text{products}) - \sum v_r \Delta H_f^\circ(\text{reactants})$$

$$\begin{array}{lllll} Ba^{2+}(aq) & + \; SO_4^{2-}(aq) & \longrightarrow & BaSO_4(s) & \Delta H^\circ = ? \\ -537.6 & -909.3 & & -1473 & \end{array}$$

ΔH_f°, kJ/mol

Then substitute data in the above equation

$\Delta H^0 = 1$ mol $BaSO_4$ x $\Delta H_f^0[BaSO_4(s)]$-1mol Ba^{2+} x $\Delta H_f^0[Ba^{2+}(aq)]$-1mol SO_4^{2-} x $\Delta H_f^0[SO_4^{2-}(aq)]$

$$\begin{aligned} &= 1\,\text{mol}\,BaSO_4 \times (-1473\,\text{kJ/mol}\,BaSO_4) - 1\,\text{mol}\,Ba^{2+} \times (-537.6\,\text{kJ/mol}\,Ba^{2+}) \\ &\quad - 1\,\text{mol}\,SO_4^{2-} \times (-909.3\,\text{kJ/mol}\,SO_4^{2-}) \\ &= -1473\,\text{kJ} + 537.6\,\text{kJ} + 909.3\,\text{kJ} = -26\,\text{kJ} \end{aligned}$$

7. To determine an enthalpy change with Hess's law, we need to combine the appropriate chemical equations. A good starting point is to write chemical equations for the given combustion reactions based on *one mole* of the indicated reactant.

Begin by writing the following reactions

$$\begin{array}{lll} \textbf{(a)} & C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l) & \Delta H^\circ = -2219.9\,\text{kJ} \\ \textbf{(b)} & C(\text{graphite}) + O_2(g) \longrightarrow CO_2(g) & \Delta H^\circ = -393.5\,\text{kJ} \\ \textbf{(c)} & H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) & \Delta H^\circ = -285.8\,\text{kJ} \end{array}$$

Because our objective in reaction is to *produce* $C_3H_8(g)$, the next step is to find a reaction in which $C_3H_8(g)$ is formed—the *reverse* of reaction **(a)**.

$$-(a)\text{: } 3CO_2(g) + 4H_2O(l) \longrightarrow C_3H_8(g) + 5O_2(g) \qquad \Delta H^\circ = -(-2219.9)\,\text{kJ} = +2219.9\,\text{kJ}$$

Now, we turn our attention to the reactants, C(graphite) and $H_2(g)$. To get the proper number of moles of each, we must multiply equation (b) by three and equation (c) by four.

$$\begin{array}{lll} 3 \times (b)\text{:} & 3C(\text{graphite}) + 3O_2(g) \longrightarrow 3CO_2(g) & \Delta H^\circ = 3(-393.5\,\text{kJ}) = -1181\,\text{kJ} \\ 4 \times (c)\text{:} & 4H_2(g) + 2O_2(g) \longrightarrow 4H_2O(l) & \Delta H^\circ = 4(-285.8\,\text{kJ}) = -1143\,\text{kJ} \end{array}$$

Here is the overall change we have described: 3 mol C(graphite) and 4 mol $H_2(g)$ have been consumed, and 1 mol $C_3H_8(g)$ has been produced. This is exactly what is required in equation . We can now combine the three modified equations.

$$\begin{array}{lll} -(a)\text{:} & \cancel{3CO_2(g)} + \cancel{4H_2O(l)} \longrightarrow C_3H_8(g) + \cancel{5O_2(g)} & \Delta H^\circ = +2219.9\,\text{kJ} \\ 3 \times (b)\text{:} & 3C(\text{graphite}) + \cancel{3O_2(g)} \longrightarrow \cancel{3CO_2(g)} & \Delta H^\circ = -1181\,\text{kJ} \\ 4 \times (c)\text{:} & 4H_2(g) + \cancel{2O_2(g)} \longrightarrow \cancel{4H_2O(l)} & \Delta H^\circ = -1143\,\text{kJ} \\ \hline \end{array}$$

$$3C(\text{graphite}) + 4H_2(g) \longrightarrow C_3H_8(g) \quad \Delta Hf^0 = +104\%$$

Reference Books

1. Physical Chemistry by G.W.Castellan, 3rd edition.
2. Physical Chemistry by Gordon M. Barrow, 5th edition.
3. Physical Chemistry by Robert J. Silbey and Robert A. Alberty, 6th edition.
4. Physical Chemistry by Peter Atkins & Julio De Paula; Oxford University Press.

Unit-5 : ELECTROCHEMISTRY–I AND SOLUTIONS

Structure

5.1 Introduction

In this unit we shall be concerned with electrical conduction through aqueous solutions. Although water is itself a very poor conductor of electricity, the presence of ionic species in solution increases the conductance considerably. The conductance of such electrolytic solutions depends on the concentration of the ions and also on the nature of the ions present (through their charges and mobilities). Conductance behavior as a function of concentration is different for strong and weak electrolytes. We will study both strong and weak electrolytes, at a number of dilute concentrations and laws and theories related to it. The acid dissociation constant (also called acidity constant or acid-ionization constant) for a weak electrolyte will be calculated from the data obtained.

Properties of solutions that depend on the number of molecules present and not on the kind of molecules are called colligative properties. In this unit using colligative properties will discuss how to measure the molecular weight and experimental method of its determination.

Objective

After studying this Unit, you will be able to

- Explain conductance in metals and in electrolytes
- Distinguish between specific and equivalent conductances.
- State and explain Kohlraush law and conductivity due to migration of ions.
- Understand Arrhenius theory of electrolyte dissociation and its limitation.
- Differentiate between weak and strong electrolytes.
- Known uses and limitations of Ostwald's dilution law
- Elementary idea about Debye-Huckel-Onsager's equation for strong electrolytes.
- Define and determine transport number
- Derive relation between molecular weight and elevation in boiling point and depression in freezing point
- Know experimental method for determination of various colligative properties.
- Explain abnormal molar masses exhibited by some solutes in solution.
- Understand discrepancies between observed and calculated values of colligative properties due to association and dissociation of solute molecules

5.2 Conduction in Metals and in Electrolyte Solutions

Conductors can be divided broadly into two categories:

(i) Metallic or electronic conductors

(ii) Electrolytic conductors

5.2.1 Metallic Conductors

Metals are the best conductor and it remains unchanged with the passage of current. A metallic conductor behaves as if it contains electrons which are relatively free to move. So electrons are considered as charge carriers in metals. Therefore, these conductors are also called *electronic conductors.* Metallic conduction or electronic conduction is the property possessed by pure metals, most of the alloys, carbon and certain solid salts and oxides.

5.2.2 Electrolytic Conductors

Generally electrolytic solutions are prepared by dissolving a salt, acid or base in water or other solvents. There is a special class of conductors, which conduct partly electronically and partly electrolytically, are known as *mixed conductors.* For example, solution of the alkali and alkaline earth metals in liquid ammonia are mixed conductors. Fused cuprous sulphide conducts electronically, but a mixture with sodium or ferrous sulphide also shows electrolytic conduction.

5.2.3 Conduction in Electrolyte Solutions

The passage of current through solutions of salts of metals such as zinc, iron, nickel, cadmium, lead, copper, silver and mercury results in the liberation of these metals at the cathode and from solutions of salts of the metals. If the anode consists of an attackable metal, the flow of the current is accompanied by the passage of the metal into solution. When the anode is made of an inert metal, e.g., platinum, an element is generally set free at this electrode; from solutions of nitrates, sulphates,phosphates, etc., oxygen gas is liberated, whereas from halide solutions, other than fluorides, the free halogen is produced. The decomposition of solutions by the electric current, resulting in the liberation of gases or metals, is known as *electrolysis.*

5.3 Conductance

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Consider a uniform bar of conductor of length '*l*' cm and cross-sectional area '*a*' sq. cm and the cross section is rectangular and that the whole body is placed into cubes of one cm. side, as shown in

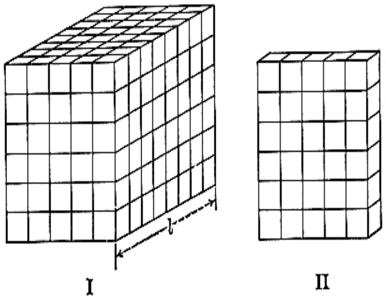


Fig. 5.1

Ohm's law states that 'The magnitude of current (I) passing through a conductor is directly proportional to the potential difference (E) applied across it and inversely proportional to the resistance (R) of the conductor'.

$$i = E/R$$

Thus, metallic conductor and electrolytes obey Ohm's law. Conductance is the reciprocal of resistance and is expressed in Siemen (S).

$$\text{Conductance} = 1/R$$

5.4 Specific Conductance or Conductivity

The resistance of the bar (Fig.5.1) to the passage of electricity through it is proportional to its length 'l' (cm) and inversely proportional to the area of cross section 'a', therefore, the resistance 'R' is given by the relationship.

$$R \propto l/a$$

$$\text{or } R = \rho\, l/a \text{ ohms}$$

Where, 'ρ ' is a constant known as specific resistance or resistivity.

$$\text{If, } l = 1\text{cm., } a = 1 \text{ cm}^2$$

$$\text{Then, } \rho = R \text{ ohm cm}$$

Specific conductance of any conducting material is defined as the reciprocal of its specific resistance. It is given the symbol 'κ' and is stated in reciprocal ohm cm^{-1}, nowadays called Scm^{-1}.

Conductance 'C' is then defined as

$$C = \kappa a / l \text{ S}$$

$$C = 1/R$$

The conductance (C) is the reciprocal of resistance, i.e. $C = 1/R$

5.5 Equivalent Conductance

It is the conductance of one gram equivalent of the electrolyte dissolved in V cc of the solution. Equivalent conductance is represented by Λ

Mathematically, $\Lambda = k \times V$

$$A = \frac{K \, x 1000}{\text{Normality}}$$

Where, κ = Specific conductivity

V = Volume of solution in cc. containing one gram equivalent of the electrolyte.

The specific conductance is measured and the equivalent conductance (Λ) is calculated using the following formula:

$$A = \frac{1000\,k}{c}$$

where c = the equivalents of electrolytes per liter (same as molarity for +1 ions).

For substance such as acetic acid that do not ionize completely the equivalent conductance will be lower than if it were completely ionized (i.e., at infinite dilution). The fraction of ionization (α_c) may be approximated by:

$$\alpha e = \frac{\wedge c}{\wedge o}$$

where Λ_c is the equivalent conductance at concentration c and Λ^0 is the equivalent conductance in dilute solution.

The equivalent conductance of a strong electrolyte in dilute solution can be estimated by using the equation:

$$\Lambda_c = \Lambda^0 - b\sqrt{c}$$

Therefore for a plot of Λ versus the square root of the electrolyte concentration, for strong electrolytes, yields a straight line. The y-intercept (where c=0, i.e. infinite dilution) = Λ^0.

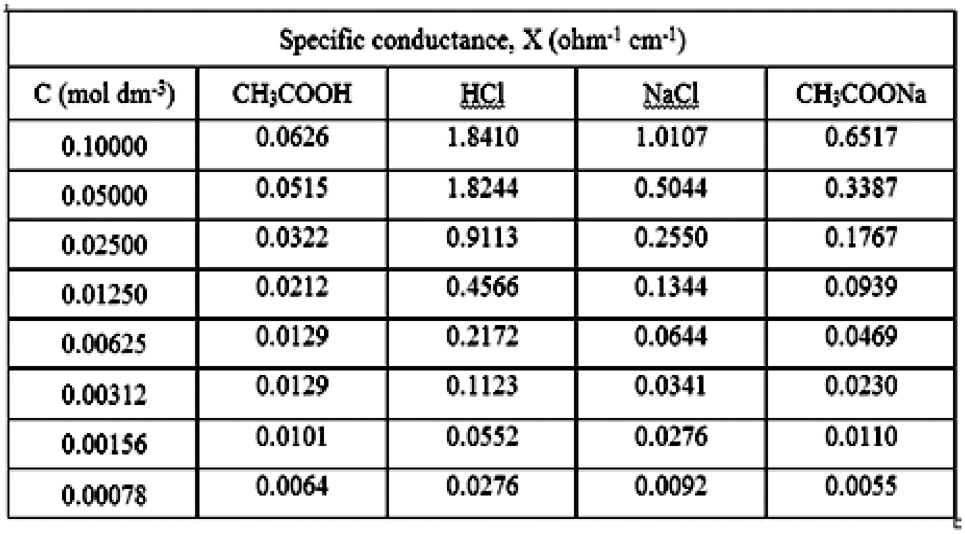
The equivalent conductance for a weak electrolyte can be estimated by using Kohlrausch's Law. For an acetic acid solution this would be:

$$\Lambda^0{}_{\text{Acetic acid}} = \Lambda^0{}_{\text{HCl}} + \Lambda^0{}_{\text{CH3COONa}} - \Lambda^0{}_{\text{NaCl}}$$

5.6 Effect of Dilution on Specific and Equivalent Conductance

5.6.1 Effect of dilution on specific conductance

The specific conductance depends on the number of ions present per unit volume of the solution. Since on dilution the degree of dissociation increases but the number of ions per unit volume decreases, therefore it is expected that the specific conductance of a solution decrease on dilution



Specific conductance, X (ohm^{-1} cm^{-1})				
C (mol dm^{-3})	CH_3COOH	HCl	NaCl	CH_3COONa
0.10000	0.0626	1.8410	1.0107	0.6517
0.05000	0.0515	1.8244	0.5044	0.3387
0.02500	0.0322	0.9113	0.2550	0.1767
0.01250	0.0212	0.4566	0.1344	0.0939
0.00625	0.0129	0.2172	0.0644	0.0469
0.00312	0.0129	0.1123	0.0341	0.0230
0.00156	0.0101	0.0552	0.0276	0.0110
0.00078	0.0064	0.0276	0.0092	0.0055

Table 5. 1: Specific Conductance :effect of dilution

5.6.2 Effect of dilution on equivalent conductance

The value of equivalent conductance increases with dilution. This is due to the fact that degree of ionization increases with dilution thereby increasing the total number of ions in solution. Solution which contains large number of ions compared to another solution of the same concentration at the same temperature has more conductance and is said to be stronger electrolyte. The one which has relatively small number of ions s called a weak electrolyte. The number of ions from an electrolyte depends on the degree of dissociation.

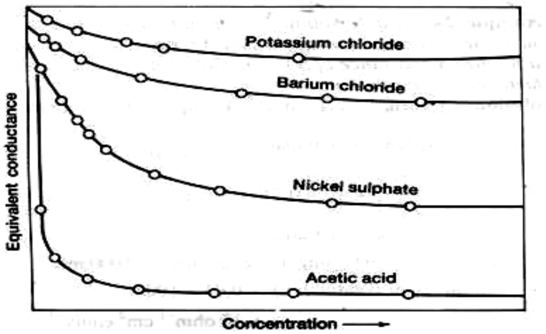


Fig.5.2 Conductance curve

The curve (Fig.5.2) shows the variation of the equivalent conductance of some electrolytes with dilution.

(i) Electrolytes like KCl have high value of conductance even at low concentration and there is no rapid increase in their equivalent conductance on dilution. Such electrolytes are termed strong electrolytes. In the case of strong electrolytes, there is a tendency for equivalent conductance to approach a limiting value when the concentration approaches zero. When the whole of the electrolyte has ionized, further addition of the water does not bring any change in the value of equivalent conductance. This stage is called infinite dilution. The equivalent conductance has a limiting value at infinite dilution and is represented by Λ_∞ .

(ii) Electrolytes like acetic acid have a low value at high concentration and there is a rapid increase in the value of equivalent conductance with dilution. Such electrolytes are termed weak electrolytes. There is no indication that a limiting value of equivalent conductance can be attained even when the concentration approaches zero. Thus, graphically, Λ_∞ of weak electrolytes cannot be obtained.

5.7 Migration of Ions

As in a solution of an electrolyte the electricity is conducted by migration of ions and the ions move in solution independently towards the oppositely charged electrodes. This fact can be illustrated by following simple experiments:

(i) Lodge's moving boundary evidence

A glass tube of the shape as shown in the Figure 5.3 is taken and its middle portion between two arms is filled with a jelly of agar-agar. A trace of sodium hydroxide (or any alkali) and phenolphthalein are added during the preparation of the jelly. It becomes red due to phenolphthalein in alkaline medium. The jelly is allowed to set. After that dilute sulphuric acid is added to the left arm containing the anode and sodium sulphate solution to the right arm in which the cathode is placed. On passing the current, hydrogen ions migrate along the solution towards the cathode and their movement can be monitored by observing the gradual fading of red colour in the jelly due to the neutralization of the alkali by the hydrogen ions and the movement of the original boundary. Experiment clearly shows that positively charged hydrogen ions (H^+) are moving towards negatively charged cathode.

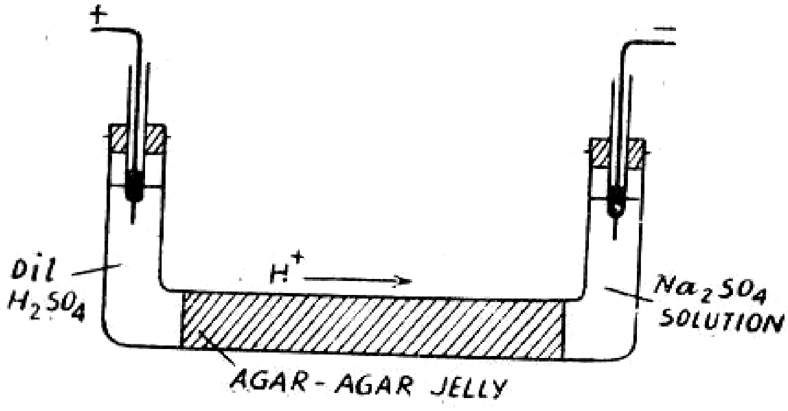
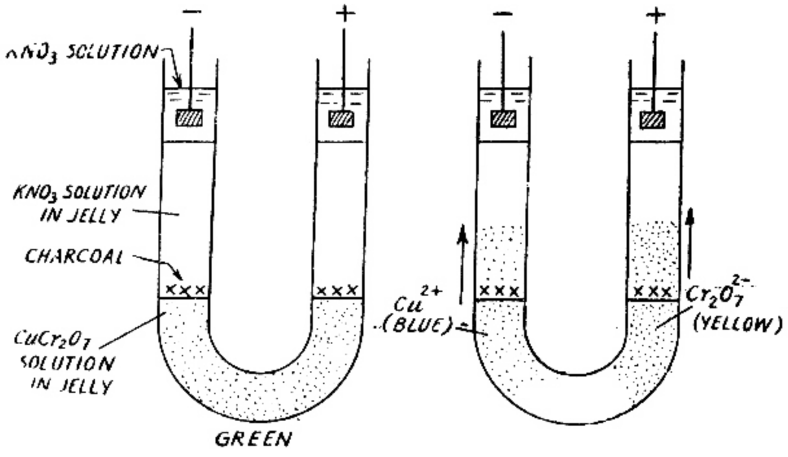


Fig.5.3: Lodge’s moving boundary experiment

(ii) Movement of coloured ions

A U shaped glass tube is taken and its middle portion is filled with an aqueous solution of 5% agar-agar and a mixture of copper sulphate and potassium dichromate in distilled water. This dark green-coloured solution after cooling forms a jelly and sets. The position of the surface of green solution in both the arms of the U-tube is marked by placing small amount of charcoal on it as shown in the Figure 5.4(A)



(A) (B)

Fig.5.4 : Migration of ions

In both the arms then a solution of potassium nitrate and agar-agar is filled. This on cooling also set as jelly. Over this jelly, solution of potassium nitrate in distilled water is added and the electrodes are immersed in it. With the application of potential difference across the electrode the blue colour of copper ions rises in to the jelly towards the cathode. The reddish yellow dichromate ions move up in the other arm of the tube towards the anode. In this experiment two types of ions can be clearly seen moving with well-defined boundaries {Figure 5.4(B)}.

5.7.1 Speeds of migration of ions during electrolysis

During electrolysis ions are liberated according to Faraday’s law at cathode and anode but their relative rate of movement towards the electrodes may be different.

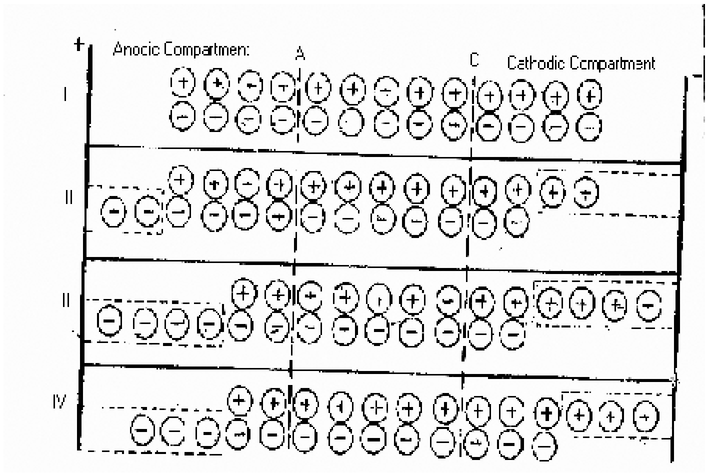


Fig. 5.5: Anodic and Cathodic compartments showing speeds of migration of ions during electrolysis

In the Figure. 5.5 ‘A’ and ‘C’ are two porous diaphragms, which prevent convention currents but allow the passage of ions. The cell is divided into an anodic and cathodic compartment. Suppose initially 13 molecules were present. The number of molecules in each anode and cathode compartment is equal i.e.in the middle compartment AC,five molecules are present. {Fig.5.5(I)}.Consider the following possibilities in reference to the above experiment.

(i) {Fig.5.5 (II)} shows the movement of two anions alone, here only anions are capable of movement.

(ii) Both anions and cations move at the same rate towards the opposite charged electrodes, the condition as shown in {Fig.5.5 (III)}.

(iii) In another situation cations move at twice the rate of the anions (Fig.5.5 (IV)}.

In all the above conditions ions are always liberated in equivalent amounts; the effect of difference in their rate only cause a change of concentration around electrodes. Further, from the above experiment the following expression can be deduced.

$$\frac{\text{Concentration fall in anodic compartment}}{\text{Concentration fall in cathodic compartment}} = \frac{\text{Speed of cation}}{\text{Speed of anion}}$$

Kohlrausch’s law states that *limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte.*

5. 8 Kohlrausch's Law of Independent Migration of Ions

It has been observed that the conductivity of solution increases with dilution until it reaches its limiting value at infinite dilution is represented as $\wedge\infty m$ Kohlrausch made a systematic study of $\wedge^{\infty}m$ for different electrolytes and concluded that each ion contributes a characteristic value of its own to molar conductivity at infinite dilution irrespective of the nature of the other ion present. Consider the values in Table 5.2 to appreciate the law

Table 5.2. Values of Λo for different electrolytes

	Electrolyte	Λ_o at 25° (Scm^2)	Difference (Scm^2)
I.	KCl	130.16	21.17
	NaCl	108.99	
II.	KNO_3	126.50	21.17
	$NaNO_3$	105.33	
III.	KCl	130.16	3.66
	KNO_3	126.50	
IV.	NaCl	108.99	3.66
	$NaNO_3$	105.33	

Electrolytes in set I and II have a common anion so that the difference can only be due to the difference in contribution to Λ by K^+ and Na^+ ions. In the same way in sets III and IV the constant difference may be attributed to the difference in contribution to $\wedge\infty m$ made by the Cl^- and NO_3^- ions. These observations can be explained by Kohlrausch's law of independent migration of ions which states that:

"At infinite dilution, where the electrolytes are fully dissociated and free from interionic effects,each ion migrates independently of its co-ion. As such each ion contributes its definite share to the total equivalent conductivity of the electrolyte, which depends only on the nature of the contributing ions and not at all on the ion with which it is associated as a part of the electrolyte". In other words, the molar conductivity at infinite dilution of an electrolyte is equal to the sum of the ionic conductances of the ions composing it, provided the solvent and temperature are the same.

$$\wedge^{\infty}m = \nu+\wedge c + \nu -\wedge a$$

Where, Λa and Λc are the ionic conductances of the anion and cation respectively at infinite dilution and ν+ and ν −is the number of cations and anions. For anion and cation this value is constant at a fixed temperature and in a given solution.

5.9 Arrhenius Theory of Electrolytic Dissociation

Arrhenius (1887) put forward the theory of electrolytic dissociation, as a more explicit form of one he had proposed in 1883, which forms the basis of the modern treatment of electrolytes. The assumption made was that when an acid, base or salt is dissolved in water, a considerable portion becomes spontaneously dissociated into positive and negative ions. Considering an electrolyte $\nu+ \ A \ \nu- \ B$, which might undergo complete dissociation to form + ν positive ions and − ν negative ions

according to the equation.

$$A_{\nu+} B_{\nu-} = \nu_+ A^{z+} + \nu_- B^{z-} \qquad (1)$$

We must calculate the net number of particles that result from a degree of dissociation α. If m is the molality of the electrolyte, α is the degree of dissociation, the concentration of undissociated electrolyte will be m -α m = m (1 - α). In addition, the concentration of $Az+$ and $Bz-$ will be $_+\nu\alpha m$ and $_-\nu\alpha m$, respectively. Here the concentration of particles is m (1 - α) + ($_+$ ν)α m + ($_-$ ν)α m and let ν be the total number of ions yielded by complete dissociation of the electrolyte, i.e, ν = + ν + − ν . With this notation the molality of particles for the partially dissociated electrolyte is m(1-α) + α ν m rather than the value of 'm' expected for no dissociation.

The van't Hoff factor 'I' can be written as

$$= \frac{m(1-\alpha)+\alpha\nu m}{m} = 1-\alpha+\alpha\nu \qquad (2.)$$

From this interpretation of *i* , one obtains

$$\alpha = \frac{i-1}{\nu-1} \qquad (3)$$

This relation can also be used inspite of the relation $\underline{\alpha =} \Lambda\infty$ for calculating the degree of dissociation of an electrolyte Λm

5.10 Strong and Weak Electrolytes

Solutes giving conducting solution in a suitable solvent are called electrolytes. On the basis of degree of ionization, these electrolytes have been divided into two categories.

(i) Strong electrolytes

(ii) Weak electrolytes

5.10.1 Strong Electrolytes

Substances, which are highly dissociated and give solutions with high conductance in water, are called *strong electrolytes*. Due to the high degree of dissociation of strong electrolytes these substances are good conductor of electricity i.e., aqueous solutions of these substances have high value of molar conductance and on dilution the increase in their molar conductance is very small. This is due to the fact that such electrolytes are completely ionized at all dilutions therefore on further dilution the number of current carrying particles does not increase in the solution. Thus, solutions of electrolytes that have high molar conductance, which increases very slowly on dilution. These electrolytes have a high degree of dissociation and are called *strong electrolytes.*

During the passage of an electric current through solutions, flow of electricity is associated with the movement of particles, which are called *ions.* The ions carrying positive charges and moving in the direction of the current, i.e., towards the cathode, are referred to as *cations* and those carrying a negative charge and moving in the opposite direction, i.e., towards the anode, are called *anions*

5.10.2 Weak Electrolytes

Weak acids and weak bases, e.g., amines, phenols, most carboxylic acids and some inorganic acids and bases, such as hydrocyanic acid and ammonia, and a few salts, e.g., mercuric chloride and cyanide, are dissociated only to a small extent at reasonable concentration; this group of compounds in general are called as *weak electrolytes.*The molar conductance of the solutions of these electrolytes increases rapidly on dilution.The reason of this is that more molecules ionize on dilution inspite of this they are never completely ionized. For these electrolytes, the nature of the solvent is also important; a particular compound may be strong electrolyte, being dissociated to large extent, in one solvent, but may behave as weak electrolyte in other solvent due to low degree of dissociation.

5.11 Ostwald's Dilution Law

The weak electrolyte ionizes to a very small extent and their molar conductivity doesn't attain a limiting value at high dilution. In such solutions there is equilibrium between free ions and undissociated molecules. The equilibrium can be written in the form:

$$MA \rightleftharpoons M^+ + A^- \qquad (1)$$

Initial Conc.	c	0	0
Conc. at equilibrium	c(1-α)	α	α

Where $M^+ = A^-$ = free ions

MA = undissociated portion of the electrolyte including both nonionized molecules and ion pairs.If c represent the initial concentration of electrolyte molecules in moles per litre and α the degree of dissociation, then equilibrium concentration of ions is equal to c_{α} and that of undissociated electrolyte is c (1-α)

By law of equilibrium,

$$K = \frac{a_{M^+} \text{ x } a_{A^-}}{a_{MA}} \qquad (2)$$

Where, a’s = activities of indicated species

K = the equilibrium constant called dissociation constant of the electrolyte

Equation (1) can be written as the product of concentration C, in g ions or moles per litre, and the activity coefficient *f*, above equation becomes;

$$K = \frac{c_{M^+} \;\; x \;\; c_{A^-}}{c_{MA}} - \frac{f_{M^+} \;\; x \;\; f_{A^-}}{f_{MA}} \qquad (3)$$

Both C_{M+} and C_{A-} are equal to α_C while C_{MA} is equal to c (1- α) then eq. (3) can be written as,

$$K = \frac{\alpha^2 c}{(1-\alpha)} - \frac{f_{M^+} \;\; x \;\; f_{A^-}}{f_{MA}} \qquad (4)$$

In sufficiently dilute solution the activity coefficient is approximately unity, then eq. (4) takes the form:

$$K = \frac{\alpha^2 c}{(1-\alpha)} \qquad (5)$$

This is the expression of the dilution law, first derived by W. Ostwald in 1988. For weak electrolytes like acetic acid (CH_3COOH) or ammonium hydroxide (NH_4OH) the value of degree of dissociation is very small, i.e., (1 – α) ≈1

eq. (5) can be written as;

$$K = \alpha^2 c \qquad (6)$$

$$\alpha^2 = \frac{K}{c} \qquad (7)$$

$$\alpha = \sqrt{\frac{K}{c}} \qquad (8)$$

5.11.1 Applications of Ostwald's Dilution Law

Applications of ostwald's dilution law are many. Some of them are discussed below: -

(i) Dissociation constant of monobasic acid

Dissociation constant of weak electrolytes such as weak acids, weak bases can be determined with the help of Ostwald's dilution law. Consider the solution of a weak acid HA with concentration'c'. If α is the degree of dissociation at equilibrium, then

$$HA \rightleftharpoons H^+ + A^- \qquad (1)$$

$$\qquad\quad 0 \qquad 0 \quad \text{(initial conc.)}$$

$$c(1-\alpha) \qquad c\alpha \qquad c\alpha \quad \text{(equilibrium conc.)}$$

By applying the law of mass action,

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad (2)$$

where Ka is the dissociation or ionization constant of the acid.

Substituting $[H^+]$, $[A^-]$ and [HA] in eq. (2), we get

$$K_a = \frac{\alpha^2 c}{(1-\alpha)} \qquad (3)$$

(ii) Dissociation constant of a weak base

Let us consider a weak base BOH dissolved in water. With concentration 'c'. Let 'α' be the degree of dissociation at equilibrium, the following ionic equilibrium exist in solution,

$$BOH \rightleftharpoons B^+ + OH^- \qquad (4)$$

$$c(1-\alpha) \qquad c\alpha \qquad c\alpha$$

The dissociation or ionization constant is given by

$$K_b = \frac{[B^+][OH^-]}{[BOH]} = \frac{\alpha^2 c}{(1-\alpha)} \qquad (5)$$

(iii) Experimental determination of dissociation constant

We have already shown that the dissociation constant of weak acids and weak base can be represented by

$$K_a = \frac{\alpha^2 c}{(1-\alpha)} \qquad (6)$$

Here ‘α’ can be determined from the expression,

$$\alpha = \frac{\wedge_m^c}{\wedge_m^\infty}$$

$$K_a = \frac{c\left(\frac{\wedge_m^c}{\wedge_m^\infty}\right)^2}{\left(1 - \frac{\wedge_m^c}{\wedge_m^\infty}\right)} \qquad (7)$$

$$= \frac{c \ \wedge_m^{c^2}}{\wedge_m^\infty \ (\wedge_m^\infty - \wedge_m^c)} \qquad (8)$$

The value of $\wedge^c{}_m$ of the solution is determined from its specific conductivity.

$\wedge^\infty{}_m$ of this solution is calculated from ‘Kohlrausch law’ i.e.

$$\wedge_m^\infty = \wedge_a^\infty + \wedge_c^\infty \qquad (9)$$

Where, $\wedge^\infty{}_a$ and $\wedge^\infty{}_c$ are ionic conductance of anion and cation of weak acids or bases.

By knowing the value of$\wedge^\infty{}_a$ and $\wedge^\infty{}_c$ *c* values of α can be calculated. The dissociation constant can also be calculated using equation (6).

5.12. Debye-Huckel-Onsagar Equation

In order to explain the abnormal behaviour of strong electrolytes number of scientists worked in this field viz. Noyes (1904), Sutherland (1906), Bjerrum (1909) and Milner (1912), Debye and Huckel in 1923, and Onsagar in 1926 put forward the modern theory of strong electrolytes known as Debye-Huckel-Onsagar theory of strong electrolyte.

Debye-Huckel treatment deals with the distribution of ions around a given ion and the net effects of these neighbouring ions have on the central ion. Debye and Huckel derived an equation based on the quantitative treatment of inter ionic attraction. This equation was later on modified by Onsagar and is known as Debye-Huckel-Onsagar (DHO) equation for strong electrolyte. It shows how the potential energy of an ion in solution depends on the ionic strength of the solution.

In the case of strong electrolytes the value of molar conductance at infinite dilution is much less than unity due to following effects:

(i) Relaxation effect

Interionic forces are present and each ion has a tendency to be surrounded on the time average by ions of opposite charge called the ionic atmosphere. A negative ion is surrounded by the ions of opposite charge called the ionic atmosphere. When an EMF is applied, the negative ions migrate towards the anode where the ionic atmosphere of positive ions is left behind to disperse, at this time a new ionic atmosphere is under formation. The rate of formation of new ionic atmosphere is not the same at which the previous ionic atmosphere disperses and the later takes more time. This time is called the ‘relaxation time’. In the case of the moving ion there will always be an excess of ions of opposite charge. The ions will always be dragged back. This effect will decrease the mobility of the ions and is known as ‘relaxation effect or asymmetric factor’.

(ii) Electrophoretic effect

The solvent molecules attach themselves to ionic atmosphere and the ions move in the direction opposite to that of central ion. It produces friction due to which the mobility of the central ion is retarded. This effect is called the electrophoretic effect. The electrophoretic effect reduces the molbility of the ions and hence also reduces their conductivities. The quantitative formulation of these effects is far from simple, but the Debye-Huckel-Onsager theory is an attempt to obtain quantitative expression at about the same level of sophistication as the Debye-Huckel-theory itself. The theory leads to a Kohlrausch like expression in which

$$\kappa = A + B \wedge_m^{\infty} \qquad (1)$$

with $$A = \frac{z^2 e F^2}{3\pi\eta}\left(\frac{2}{\varepsilon RT}\right)^{1/2} \qquad B = \frac{q z^3 e F}{24\pi\varepsilon RT}\left(\frac{2}{\varepsilon RT}\right)^{1/2} \qquad (2)$$

Where, η = flux of momentum

ε = electric permittivity of the solvent and

q = 0.586 for a 1,1-electrolyte

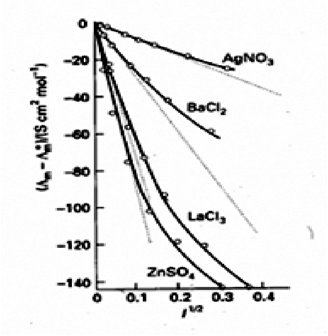


Fig. 5.6 The dependence of molar conductivities on the square root of the ionic strength, and comparison (shown by dotted lines) with the dependence predicted by the Debye-Huckel-Onsager theory.

Figure 5.6 shows the dependence of molar conductivities on the square root of the ionic strength and comparison with the dependence predicted by the Debye – Huckel – theory. The agreement is quite good at very low molar concentrations (less than about 10^{-3} M, depending on the charge type).

Green – Kubo relationship can be applied on electric conduction, which expresses a transport properly in terms of the fluctuations in microscopic properties of a system. The electrical conductivity is related to the fluctuations in the sample that arises from variations in the velocities of the ions.

$$\kappa = \frac{1}{KTV}\int_0^\infty \langle j(0)j(t)dt \qquad (3)$$

$$j = \sum_i^N z_i e \nu_i \qquad (4)$$

where ν is the velocity of the ion *i* at a given instant and the angular brackets denote an average over the sample. If the ions are very mobile, there will be large fluctuations in the instantaneous currents in the same, and the conductivity of the medium will be high. If the ions are locked into position, as in an ionic solid, there will be no instantaneous currents, and the ionic conductivity will be zero. The velocities of the ions are calculated explicitly in a molecular dynamics simulation, so the correlation function, the quantity $\langle j(0)\, j(t)$, can be evaluated reasonably simply.

5.13 Activity and Activity Coefficient

Activity is the result of the effects of interactions between ion or molecule and its surroundings. Since it is hard to define, it is usually measured with reference to an ideal state.

An activity coefficient is a factor used in thermodynamics to account for deviations from ideal behaviour in a mixture of chemical substances. In an ideal mixture, the interactions between each pair of chemical species are the same (or more formally, the enthalpy change of solution is zero) and, as a result, properties of the mixtures can be expressed directly in terms of simple concentrations or partial pressures of the substances present e.g. Raoult's law. Deviations from ideality are accommodated by modifying the concentration by an *activity coefficient*. Analogously, expressions involving gases can be adjusted for non-ideality by scaling partial pressures by a fugacity coefficient.

the activity of a species *i*, denoted a_i, is defined

$$a_i = \exp\left(\frac{\mu_i - \mu_i^{\ominus}}{RT}\right)$$

where μ_i is the chemical potential of the species under the conditions of interest, $\mu^{\ominus}_i$ is the chemical potential of that species in the chosen standard state, R is the gas constant and T is the thermodynamic temperature. This definition can also be written in terms of the chemical potential:

$$\mu_i = \mu_i^{\ominus} + RT \ln a_i$$

Hence the activity will depend on *any factor* that alters the chemical potential. These include temperature, pressure, chemical environment etc. In specialised cases, other factors may have to be considered, such as the presence of an electric or magnetic field or the position in a gravitational field. However, the most common use of activity is to describe the variation in chemical potential with the composition of a mixture.

The activity also depends on the choice of standard state, as it describes the difference between an actual chemical potential and a standard chemical potential. In principle, the choice of standard state is arbitrary, although there are certain conventional standard states which are usually used in different situations.

The activity coefficient γ, which is also a dimensionless quantity, relates the activity to a measured amount fraction x_i (or y_i in the gas phase), molality b_i, amount concentration c_i or mass concentration ρ_i:

$$a_i = \gamma_{x,i} x_i \ = \gamma_{b,i} \frac{b_i}{b^{\ominus}} \ = \gamma_{w,i} w_i \ = \gamma_{c,i} \frac{c_i}{c^{\ominus}} \ = \gamma_{\rho,i} \frac{\rho_i}{\rho^{\ominus}}$$

The division by the standard molality $b^{\ominus}$ or the standard amount concentration $c^{\ominus}$ is necessary to ensure that both the activity and the activity coefficient are dimensionless, as is conventional.

The activity is the same regardless of the ways to express composition and the standard state chosen so the above expressions are equal.

When the activity coefficient is close to one, the substance shows almost ideal behaviour according to Henry's law. In these cases, the activity can be substituted with the appropriate dimensionless measure of composition x_i, $b_i/b^{\ominus}$ or $c_i/c^{\ominus}$. It is also possible to define an activity coefficient in terms of Raoult's law: the International Union of Pure and Applied Chemistry (IUPAC) recommends the symbol f for this activity coefficient, although this should not be confused with fugacity.

$$a_i = f_i x_i.$$

5.14 Transport Numbers

The transport number (t) is defined as the fraction of total current carried by the particular ionic species in the solution. In a simple case of a single electrolyte yielding the ions designated by the suffixes (+)and (-), the corresponding transference numbers are given as follows:

$$t_+ = \frac{q_+}{Q} \tag{1}$$

Where + q is the quantity of electricity carried by the cation and Q is the total quantity of electricity carried by all the ions through the solution. Similarly, the anion transport number t_- is defined as:

$$t_- = \frac{q_-}{Q} \tag{2}$$

Where q_- is the quantity of electricity carried by the anion, equations (2) and (3) can be expressed as:

$$t_+ = \frac{c_+u_+}{c_+u_+ \ + \ c_-u_-} \tag{3}$$

The quantities c_+ and c_- which represent the concentrations of the ions, are equal and therefore for this type of the electrolyte.

$$t_+ = \frac{c_+u_+}{c_+u_+ \ + \ c_-u_-} \tag{4}$$

$$t_- = \frac{c_-u_-}{c_+u_+ \ + \ c_-u_-} \tag{5}$$

$$\text{and } t_+ + \ t_- = 1$$

u_+ and u_- are the mobilities of the ions in the same solution and we know that the speed of an ion in a solution at any concentration is proportional to the conductance of the ion at that concentration and therefore the transference number may be represented in the form;

$$t_+ = \frac{\wedge_+}{\wedge_m} \text{ and } t_- = \frac{\wedge_-}{\wedge_m} \tag{6}$$

Where the values of $\wedge_+$ and $\wedge_-$ (ion conductance) and Λ_m (molar conductance) of the solution, are at that particular concentration at which the transference numbers are applicable.

5.14.1 Determination of Transport Number

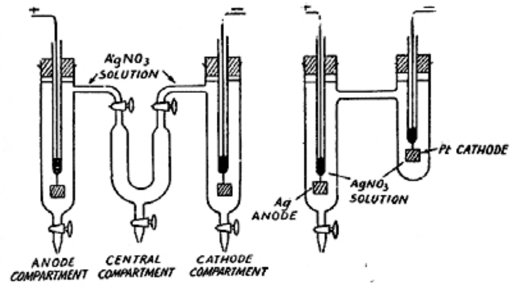
Three method have been generally employed for the experimental determination of transference numbers: the first, based on the procedure originally proposed by Hittorf, involves measurement of changes of concentration in the vicinity of the electrodes; in the second, known as the " moving boundary" method, the rate of motion of the boundary between two solutions under the influence of current is studied; the third method, is based on electromotive force measurements of suitable cells.

(i) Hittorf's Method

This method of determining transport numbers was described as long ago as 1901.

Apparatus

To understand the principle involved consider the overall description of the method given below. The apparatus consists of two separated compartments joined by a substantial middle compartment and may be of any of the shape as shown in figure 5.7 (A) and (B). Let us take silver nitrate solution in a cell having silver electrodes. Before the experiment begins, the concentration of $AgNO_3$ is the same throughout the cell. The experiment involves passage of a direct electric current from a power source through the cell.



(a) (b)

Fig. 5.7 Hirtoff cell

At the left-hand electrode, Ag dissolves and increases the $AgNO_3$ concentration in its compartment. In the right-hand compartment, Ag+ ions deposits so the $AgNO_3$ concentration decreases in the solution. Measurement of the changes in concentration in each compartment after a 2-3 h passage of current yields the transport number of the anion (since $t_+ + t_- = 1$, it also gives that of the cation). The current is passed for a fixed time. Thereafter, the anolyte (Figure 5.8) has an increased concentration $c_1$and the catholyte a decreased concentration c_3. The middle compartment does not change its concentration of silver nitrate, which will be designated c_2.

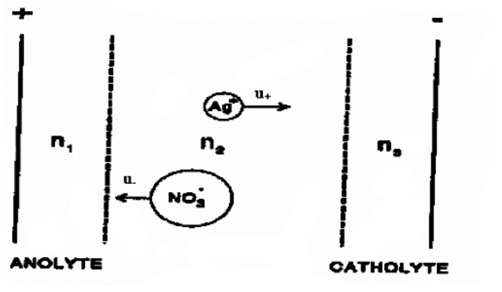


Fig. 5.8: The Principle of Hittorf's experiment

(ii) Moving boundary method

The moving boundary method is based on measuring the rate of migration of one or both of the ionic species of the electrolyte, away from the similarly charged electrodes and by this method we can directly observe the migration of ions under the influence of an applied potential unlike the Hittrof's method in which concentration changes at the electrodes are observed. This method is very accurate and has been used in recent years for precision measurements.

In the practical application of the moving boundary method one boundary only is observed, and so the necessity of finding two indicator solutions is obviated; the method of calculation is as follows.

If one faraday of electricity passes through the system, 't_+' equiv. of the cation must pass at any given point in one direction; if 'c' mole of the unit volume is the concentration of the solution in the vicinity of the boundary formed by the 'M' ions, this boundary must pass through a volume $t+ / c$ while one faraday is passing.

The volume ϕ taken out by the cations for the passage of Q coulombs is thus

$$\Phi = Q\, t+ / F\, c \qquad (1)$$

Where F is one faraday, i.e., 96,500 coulombs. If the cross section of the tube in which the boundary moves is α sq. cm., and the distance through which it moves during the passage of Q coulombs is l cm., then Φ is equal to $l\, \alpha$, and therefore from eq. (1)

$$t_+ = l\, \alpha F\, c / Q \qquad (2)$$

Since the number of coulombs passing can be determined, the transference number of the ion may be calculated from the rate of movement of one boundary.

The apparatus used for the determination of the transport number by this method, consist a long vertical tube of uniform bore fitted with two electrodes at the two ends as shown in figure 5.9

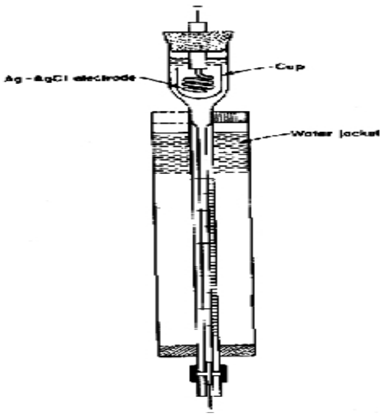


Fig.5.9: Cell for the determination of transport number by moving boundary method

5.15 Elevation of Boiling Point

The vapour pressure of a liquid increases with increase of temperature. It boils at the temperature at which its vapour pressure is equal to the atmospheric pressure. For example, water boils at 373.15 K (100° C) because at this temperature the vapour pressure of water is 1.013 bar (1atmosphere). Vapour pressure of the solvent decreases in the presence of non-volatile solute.Fig. 5.10 depicts the variation of vapour pressure of the pure solvent band solution as a function of temperature. For example, the vapour pressure of an aqueous solution of sucrose is less than 1.013 bar at 373.15 K. In order to make this solution boil, its vapour pressure must be increased to 1.013 bar by raising the temperature above the boiling temperature of the pure solvent (water). Thus, the boiling point of a solution is always higher than that of the boiling point of the pure solvent in which thesolution is prepared as shown in Fig. 5.10. Similar to lowering of vapour pressure, the elevation of boiling point also depends on the number of solute molecules rather than their nature. A solution of 1 mol of sucrose in 1000 g of waterboils at 373.52 K at one atmospheric pressure.

Let T_b^obe the boiling point of pure solvent and Tb be the boiling point of solution. The increase in the boiling point ΔTb =Tb- Tb^{o}is known as **elevation of boiling point**.

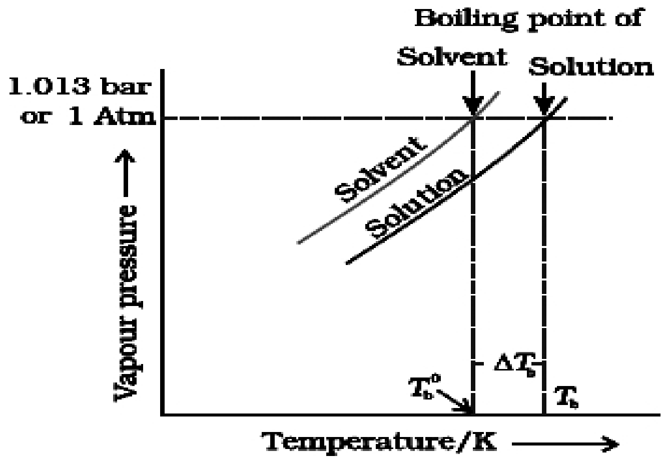


Fig 5.10 The vapour pressure curve for solution lies below the curve for pure water. The diagram shows that ΔTb denotes the elevation of boiling point of a solvent in solution.

Experiments have shown that for **dilute solutions** the elevation of boiling point ΔT_b is directly proportional to the molal concentration of the solute in a solution.

Thus

$$\Delta T_b \propto m \quad (1)$$

or $$\Delta T_b = K_b\ m \quad (2)$$

Here *m* (molality) is the number of moles of solute dissolved in 1 kg of solvent and the constant of proportionality, K_b is called **Boiling Point. Elevation Constant or Molal Elevation Constant (EbullioscopicConstant)**. The unit of Kb is K kg mol^{-1}. If w_2 gram of solute of molar mass $M_2$is dissolved in w_1 gram of solvent, then molality, m of the solution is

given by the expression:

$$\mathrm{m} = \frac{w_2/\mathrm{M}_2}{w_1/1000} = \frac{1000 \times w_2}{M_2 \times w_1} \qquad (3)$$

Substituting the value of molality in equation (2) we get

$$\Delta T_b = \frac{K_b \times 1000 \times w_2}{M_2 \times w_1}$$

$$M_2 = \frac{1000 \times w_2 \times K_b}{\Delta T_b \times w_1} \qquad (4)$$

Thus, in order to determine M_2, molar mass of the solute, known mass of solute in a known mass of the solvent is taken and ΔT_b is determined experimentally for a known solvent whose K_b value is known.

5.16 Depression of Freezing Point

The lowering of vapour pressure of a solution causes a lowering of the freezing point compared to that of the pure solvent (Fig. 5.11). We know that at the freezing point of a substance, the solid phase is in dynamic equilibrium with the liquid phase. Thus, the freezing point of a substance may be defined as the temperature at which the vapour pressure of the substance in its liquid phase is equal to its vapour pressure in the solid phase. A solution will freeze when its vapour pressure equals the vapour pressure of the pure solid solvent as is clear from Fig. 5.11. According to Raoult’s law,when a non-volatile solid is added to the solvent its vapour pressure decreases and now it would become equal to that of solid solvent at lower temperature. Thus, the freezing point of the solvent decreases.

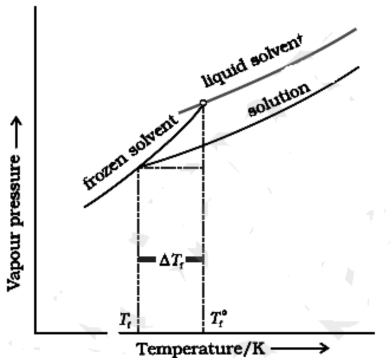


Fig. 5.11 Diagram showing ΔTf depression of freezing point of a solvent in a solution

Let T_f^o be the freezing point of pure solvent and T_f be its freezing point when non-volatile solute is dissolved in it. The decrease in freezing point.

$\Delta T_f = T_f^{\,o} - T_f$ is known as depression in freezing point.Similar to elevation of boiling point, depression of freezing point (ΔT_f) for dilute solution (ideal solution) is directly proportional to molality,m of the solution. Thus,

$$\Delta T_f \propto m \qquad (5)$$

$$\text{or} \quad \Delta T_f = K_f\, m$$

The proportionality constant, K_f, which depends on the nature of the solvent is known as Freezing Point Depression Constant or Molal Depression constant or Cryoscopic Constant. The unit of K_f is K kg mol-1. If w_2 gram of the solute having molar mass as M_2, present in $w_1$gram of solvent, produces the depression in freezing point ΔT_f of the solvent then molality of the solute is given by the equation

$$m = \frac{w_2 / M_2}{w_1/1000} \qquad (6)$$

Substituting this value of molality in equation (6) we get

$$\Delta T_f = \frac{K_f \times w_2 / M_2}{w_1 / 1000}$$

$$\Delta T_f = \frac{K_f \times w_2 \times 1000}{M_2 \times w_1} \qquad (7)$$

$$M_2 = \frac{K_f \times w_2 \times 1000}{\Delta T_f \times w_1} \qquad (8)$$

Thus for determining the molar mass of the solute we should know the quantities w_1, w_2, ΔT_f, along with the molal freezing point depression constant. The values of K_f and K_b, which depend upon the nature of the solvent, can be ascertained from the following relations

$$K_f = \frac{R \times M_1 \times T_f^2}{1000 \times \Delta_{fus} H} \qquad (9)$$

$$K_b = \frac{R \times M_1 \times T_b^2}{1000 \times \Delta_{vap} H} \qquad (10)$$

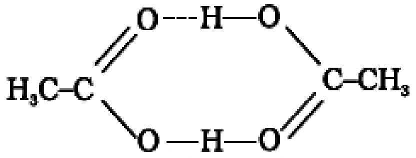
Here the symbols R and M_1 stand for the gas constant and molar mass of the solvent, respectively and T_f and T_b denote the freezing point and the boiling point of the pure solvent respectively in kelvin. Further, $H\Delta_{fus}$ and $H\Delta_{vap}$ represent the enthalpies for the fusion and vapourisation of the solvent, respectively.

5.17 Molar Masses

Ionic compounds when dissolved in water dissociate into cations and anions. For example, if we dissolve one mole of KCl (74.5 g) in water, we expect one mole each of K^+ and Cl^- ions to be released in the solution.

If this happens, there would be two moles of particles in the solution. If we ignore interionic attractions, one mole of KCl in one kg of water would be expected to increase the boiling point by 20.52 K = 1.04 K. Now if we did not know about the degree of dissociation, we could be led to conclude that the mass of 2 mol particles is 74.5 g and the mass of one mole of KCl would be 37.25 g. This brings into light the rule that, when there is dissociation of solute into ions, the experimentally determined molar mass is always lower than the true value.

$$2\,CH_3COOH \rightleftharpoons (CH_3COOH)_2$$



Molecules of ethanoic acid (acetic acid) dimerise in benzene due to hydrogen bonding. This normally happens in solvents of low dielectric constant. In this case the number of particles is reduced due to dimerisation. Association of molecules is depicted as follows:

It can be undoubtedly stated here that if all the molecules of ethanoic acid associate in benzene, then ΔT_b or ΔT_f for ethanoic acid will be half of the normal value. The molar mass calculated on the basis of this ΔT_b or ΔT_f will, therefore, be twice the expected value. Such a molar mass that is either lower or higher than the expected or normal value is called as abnormal molar mass.

In 1880 van't Hoff introduced a factor *i*, known as the van't Hoff factor, to account for the extent of dissociation or association. This factor *i* is defined as:

$$\text{Normal molar mass } i = \frac{\text{Normal molar mass}}{\text{Abnormal molar mass}}$$

$$= \frac{\text{Observed Colligative Property}}{\text{Calculated Colligative Property}}$$

$$i = \frac{\text{Total numbers of moles of particles after}}{\text{Number of moles of particles before}}$$

Here abnormal molar mass is the experimentally determined molar mass and calculated colligative properties are obtained by assuming that the non-volatile solute is neither associated nor dissociated. In case of association, value of *i* is less than unity while for dissociation it is greater than unity. For example, the value of *i* for aqueous KCl solution is close to 2, while the value for ethanoic acid in benzene is nearly 0.5.

Inclusion of van't Hoff factor modifies the equations for colligative properties as follows:

Relative lowering of vapour pressure of solvent,

$$\frac{p_1^\circ - p_1}{p_1^\circ} = i.\frac{n_2}{n_1}$$

Elevation of Boiling point, $\Delta T_b = i\, K_b$ m
Depression of Freezing point, $\Delta T_f = i\, K_f$ m
Osmotic pressure of solution, $\Pi = i\, n_2\, R\, T\, /\, V$

Molecular masses can be calculated by measuring any of the colligative properties. The relation between colligative properties and molecular mass of the solute is based on following assumptions.

(1) The solution is dilute, so that Raoult's law is obeyed.

(2) The solute neither undergoes dissociation nor association in solution.

5.18 Association/Dissociation

In case of solutions where above assumptions are not valid we find discrepencies between observed and calculated values of colligative properties. These anomalies are primarily due to

(i) Association of solute molecules.

(ii) Dissociation of solute molecules.

(i) Association of solute molecules : Certain solutes in solution are found to associate. This eventually leads to a decrease in the number of molecular particles in the solutions. Thus, it results in a decrease in the values of colligative properties.

Colligative property ∝ 1/ molecular mass of solute

therefore, higher values are obtained for molecular masses than normal values for unassociated molecules.

(ii) Dissociation of solute molecules : A number of electrolytes dissociate in solution to give two or more particles (ions). Therefore, the number of solute particles, in solutions of such substances, is more than the expected value. Accordingly, such solutions exhibit higher values of colligative properties. Since colligative properties are inversely proportional to molecular masses, therefore, molecular masses of such substances as calculated from colligative properties will be less than their normal values.

5.19 Van't Hoff's factor (i)

In 1886, Van't Hoff introduced a factor 'i' called Van't Hoff's factor, to express the extent of association or dissociation of solutes in solution. It is ratio of the normal and observed molecular masses of the solute, i.e., i = Normal molecular mass / Observed molecular mass

In case of association, observed molecular mass being more than the normal, the factor i has a value less than 1. But in case of dissociation, the Van't Hoff's factor is more than 1 because the observed molecular mass has a lesser value than the normal

molecular mass. In case there is no dissociation the value of 'i' becomes equal to one.

Since colligative properties are inversely proportional to molecular masses, the Van't Hoff's factor may also be written as,

$$i = \frac{\text{Observed value of colligative property}}{\text{Calculated value of colligative propert}}$$

Calculated value of colligative property

$$i = \frac{\text{No.of particles after association or dissociation}}{\text{No.of particles before association or dissociation}}$$

No. of particles before association or dissociation

Introduction of the Van't Hoff factor modifies the equations for the colligative properties as follows,

Relative lowering of vapour pressure = $P^o{}_A - P_A/P^o{}_A = iX_B$

Elevation of boiling point, $\Delta T_b = ik_bm$

Depression in freezing point, $\Delta T_f = ik_fm$

Osmotic pressure, $\pi = inRT/V$; $\pi = iCRT$

From the value of 'i', it is possible to calculate degree of dissociation or degree of association of substance.

5.19.1 Degree of dissociation (α)

It is defined as the fraction of total molecules which dissociate into simpler molecules or ions.

$\alpha = (i-1) / (m - 1)$; m= number of particles in solution

5.19.2 Degree of association (α)

It is defined as the fraction of the total number of molecules which associate or combine together resulting in the formation of a bigger molecules.

$\alpha = (i-1) / (1/ m - 1)$; m = number of particles in solution.

5.20 Summary

Electrochemistry is the study of the exchange between electrical and chemical energy, has important applications in everyday life stretching from the battery that powers your portable radio to the electrorefining that produces the copper pipes carrying your drinking water.

Solutes giving conducting solution in a suitable solvent are called electrolytes. On the basis of degree of ionization, these electrolytes have been divided into two categories.

(i) Strong electrolytes **(ii)** Weak electrolytes

Metallic conductor and electrolytes obey Ohm's law. Conductance is the reciprocal of resistance and is expressed in Siemen (S). Conductance =1/R

As in a solution of an electrolyte the electricity is conducted by migration of ions and the ions move in solution independently towards the oppositely charged electrodes. This fact can be illustrated by following simple experiments viz.Lodge's moving boundary evidence

It has been observed that the conductivity of solution increases with dilution until it reaches its limiting value at infinite dilution is represented as $\wedge\infty m$ Kohlrausch made a systematic study of $\wedge\infty m$ for different electrolytes and concluded that each ion contributes a characteristic value of its own to molar conductivity at infinite dilution irrespective of the nature of the other ion present.

Arrhenius (1887) put forward the theory of electrolytic dissociation, as a more explicit forms which for the basis of modern treatment.

Debye-Huckel treatment deals with the distribution of ions around a given ion and the net effects of these neighbouring ions have on the central ion.

The transport number (t) is defined as the fraction of total current carried by the particular ionic species in the solution.

The properties of solutions which depend on the number of solute particles and are independent of their chemical identity are called colligative properties. These are lowering of vapour pressure, elevation of boiling point, depression of freezing point and osmotic pressure. Colligative properties have been used to determine the molar mass of solutes. Solutes which dissociate in solution exhibit molar mass lower than the actual molar mass and those which associate show higher molar mass than their actual values. Quantitatively, the extent to which a solute is dissociated or associated can be expressed by van't Hoff factor i. This factor has been defined as ratio of normal molar mass to experimentally determined molar mass or as the ratio of observed colligative property to the calculated colligative property.

5.21 Terminal Questions

1. Explain Arrhenius Theory of Electrolytic Dissociation

2. Explain why the boiling point increases, on a molecular level, when a solute is added to a pure solvent. Derive a relation between molecular weight and elevation in boiling point .

3. A solution containing 0.00739g of $AgNO_3$ per gram of water was electrolyzed between silver electrodes. During the experiment 0.0078g of silver was deposited in a silver coulometer placed in series. At the end of experiment, the anodic solution contains 23.14g of water and 0.236g of $AgNO_3$.What are the transport number of Ag+ and NO_3^- ions?

4. The boiling point of benzene is 353.23 K. When 1.80 g of a non-volatile solute was dissolved in 90 g of benzene, the boiling point is raised to 354.11 K. Calculate the molar mass of the solute. *K*b for benzene is 2.53 K kg mol^{-1}

5. Discuss Conduction in Metals and in Electrolyte Solutions.

5.22 Answers

1. The assumption made was that when an acid, base or salt is dissolved in water, a considerable portion becomes spontaneously dissociated into positive and negative ions. Considering an electrolyte *v*+ *A v*− *B* , which might undergo complete dissociation to form ν + positive ions and ν − negative ions

according to the equation.

$$A_{\nu+} B_{\nu-} = \nu_+ A^{z+} + \nu_- B^{z-} \qquad (1)$$

We must calculate the net number of particles that result from a degree of dissociation α . If m is the molality of the electrolyte, α is the degree of dissociation, the concentration of undissociated electrolyte will be m -α m = m(1 - α). In addition, the concentration of *Az*+ and *Bz*− will be+ ν α m and − ν α m, respectively. Here the concentration of particles is m(1 - α) + (+ ν)α m + (− ν)α m and let ν be the total number of ions yielded by complete dissociation of the electrolyte, i.e, ν = ν+ + ν− . With this notation the molality of particles for the partially dissociated electrolyte is m(1-α) + α ν m rather than the value of ‘m’ expected for no dissociation.

The van’t Hoff ‘I’ factor can be written as

$$= \frac{m(1-\alpha)+\alpha\nu m}{m} = 1-\alpha+\alpha\nu \qquad (2.)$$

From this interpretation of *i* , one obtains

$$\alpha = \frac{i-1}{\nu-1} \qquad (3)$$

This relation can also be used inspite of the relation $\alpha = \Lambda_\infty$ for calculating the degree of dissociation of an electrolyte Λ_m

2. The elevation of boiling point depends on the number of solute molecules rather than their nature. A solution of 1 mol of sucrose in 1000 g of water boils at 373.52 K at one atmospheric pressure Fig.5.10 depicts the variation of vapour pressure of the pure solvent band solution as a function of temperature. For example, the vapour pressure of an aqueous solution of sucrose is less than 1.013 bar at 373.15 K. In order to make this solution boil, its vapour pressure must be increased to 1.013 bar by raising the temperature above the boiling temperature of the pure solvent (water). Thus, the boiling point of a solution is always higher than that of the boiling point of the pure solvent in which the solution is prepared as shown in Fig. 5.10. Similar to lowering of vapour pressure, the elevation of boiling point also depends on the number of solute molecules rather than their nature. A solution of 1 mol of sucrose in 1000 g of water boils at 373.52 K at one atmospheric pressure.

Let T_b^obe the boiling point of pure solvent and Tb be the boiling point of solution. The increase in the boiling point ΔT_b $T_b^o$is known as **elevation of boiling point**.

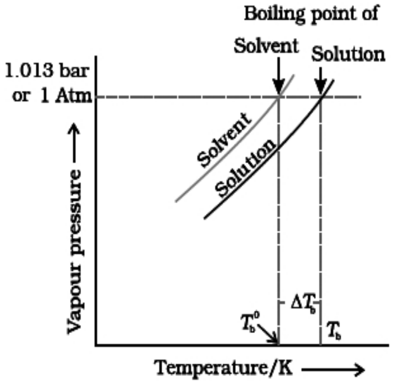


Fig 5.10 The vapour pressure curve for solution lies below the curve for pure water. The diagram shows that ΔT_b denotes the elevation of boiling point of a solvent in solution.

Experiments have shown that for **dilute solutions** the elevation of boiling point ΔT_b is directly proportional to the molal concentration of the solute in a solution.

Thus

$$\Delta T_b \propto m \qquad (1)$$

$$\text{or} \quad \Delta T_b = K_b\, m \qquad (2)$$

Here m (molality) is the number of moles of solute dissolved in 1 kg of solvent and the constant of proportionality, K_b is called **Boiling Point Elevation Constant or Molal Elevation Constant (EbullioscopicConstant)**. The unit of K_b is K kg mol-1. If w_2 gram of solute of molar mass M_2 is dissolved in w_1 gram of solvent, then molality, m of the solution is

given by the expression:

$$m = \frac{w_2/M_2}{w_1/1000} = \frac{1000 \times w_2}{M_2 \times w_1} \qquad (3)$$

Substituting the value of molality in equation (2) we get

$$\Delta T_b = \frac{K_b \times 1000 \times w_2}{M_2 \times w_1}$$

$$M_2 = \frac{1000 \times w_2 \times K_b}{\Delta T_b \times w_1} \qquad (4)$$

Thus, in order to determine M_2, molar mass of the solute, known mass of solute in a known mass of the solvent is taken and ΔT_b is determined experimentally for a known solvent whose K_b value is known.

3.

- **Before electrolysis:** Mass of water = 1g
  Mass of $AgNO_3$ = 0.00739g
  Number of gram equivalent of Ag = $\frac{0.00739}{170}$
  $= 4.347 \times 10^{-5}$
- **After electrolysis:** Mass of water = 23.14 g
  Mass of $AgNO_3$ = 0.236g
  Number of gram equivalent of Ag in 1g of water
  $= \frac{0.236}{23.14} \times \frac{1}{170}$
  $= 5.992 \times 10^{-5}$

Increase in concentration of Ag^+ in the anodic compartment where no silver ions migrate = $\frac{0.0078}{170} = 4.588 \times 10^{-5}$

Increase in concentration of Ag^+ in the anodic compartment when Ag^+ ions migrate.
= Concentration of Ag after electrolysis – Concentration of Ag before electrolysis
$= 5.992 \times 10^{-5} - 4.347 \times 10^{-5}$
$= 1.645 \times 10^{-5}$
Fall in concentration of Ag^+ in anodic compartment
$= 4.588 \times 10^{-5} - 1.645 \times 10^{-5}$
$= 2.943 \times 10^{-5}$

$$\text{Transport number of } Ag^+ \text{ ions} = \frac{\textit{Fall in conc. around anode}}{\textit{Silver deposited on Ag electrode}}$$

$$= \frac{2.943 \times 10^{-5}}{4.588 \times 110^{-5}} = 0.641$$

Also transport number of NO_3^- ions can be calculated as
$= 1 - t_{Ag^+}$
$= 1 - 0.641$
$= 0.359$

4. The elevation in the boiling point = 354.11 K – 353. 23 K = 0.88 K

Substituting these values in expression

$$M_2 = \frac{1000 \times w_2 \times K_b}{\Delta T_b \times w_1}$$

we get $M2 = \frac{1000 \text{ g kg–1 X } 1.8 \text{ g x } 2.53 \text{ K kg mol}-1}{0.88 \text{ K} \times 90 \text{ g}}$

= 58 g mol–1

Therefore, molar mass of the solute, $M2$ = 58 g m

5. Conductors can be divided broadly into two categories:

(i) Metallic Conductors

Metals are the best conductor and it remains unchanged with the passage of current. A metallic conductor behaves as if it contains electrons which are relatively free to move. So electrons are considered as charge carrier in metals. Therefore, these conductors are also called *electronic conductors*. Metallic conduction or electronic conduction is the property possessed by pure metals, most alloys, carbon and certain solid salts and oxides.

(ii) Electrolytic Conductors

Generally electrolytic solutions are prepared by dissolving a salt, acid or base in water or other solvents. There is a special class of conductors, which conduct partly electronically and partly electrolytically, are known as *mixed conductors*. For example, solution of the alkali and alkaline earth metals in liquid ammonia are mixed conductors. Fused cuprous sulphide conducts electronically, but a mixture with sodium or ferrous sulphide also shows electrolytic conduction.

Conduction in Electrolyte Solutions

The passage of current through solutions of salts of metals such as zinc, iron, nickel, cadmium, lead, copper, silver and mercury results in the liberation of these metals at the cathode and from solutions of salts of the metals. If the anode consists of an attackable metal, the flow of the current is accompanied by the passage of the metal into solution. When the anode is made of an inert metal, e.g.,platinum, an element is generally set free at this electrode; from solutions of nitrates, sulphates ,phosphates, etc., oxygen gas is liberated, whereas from halide solutions, other than fluorides, the free halogen is produced. The decomposition of solutions by the electric current, resulting in the liberation of gases or metals, is known as *electrolysis*

Reference Books

1. Electrochemical Methods : Fundamental ana Application by Allen J. Bard, Lary R. Faulkner

2. Electrochemistry:Principles Method by Christopher BrettMA

3. Physical Chemistry by Peter Atkins & Julio De Paula;Oxford University Press

4. Solution Chemistry and Minerals by P. Somasundraram, Diazuowang, 1st edition

Unit-6 : CHEMICAL KINETICS AND CATALYSIS

Structure

6.1 Introduction

Chemical kinetics is conventionally regarded as a topic in physical chemistry. In this guise this covers the measurement of rates of reaction, and the analysis of the experimental data to give a systematic collection of information which summarizes all the quantitative kinetic information about any given reaction. This, in turn, enables comparisons of reactions to be made and can afford a kinetic classification of reactions.

Very important aspect of modern reaction kinetics is to develop theories as to why and how reactions occur. Arrhenius, in the 1880s, laid the foundations of the subject by postulating that not all molecules can react: only those which have a certain critical minimum energy, called the activation energy, can react. Early theoretical work using the Maxwell Boltzmann distribution led to collision theory. This gave an expression for the rate of reaction in terms of the rate of collision of the reacting molecules.

This unit further incorporates the catalysis, its types, application of catalyst in industrial process and kinetics of enzymatic process.

Objective

After studying this unit, you will be able to

- define rate of a reaction
- express the rate of a reaction in terms of change in concentration of either of the reactants
- or products with time;
- discuss the dependence of rate of reactions on concentration, temperature and catalyst
- determine the rate constants for zeroth, first and second order reactions;
- determine the rate law from experimental data
- determine the basic decay equation and mean life time.
- know the experimental techniques to monitor reactions.
- explain temperature dependence of rate.
- describe collision and transition state theory

6.2 Rate of reaction

Some reactions such as ionic reactions are very fast, e.g. precipitation of silver chloride by mixing of aqueous solutions of silver nitrate and sodium chloride occurs instantaneously. On the other hand, some reactions are very slow, for example, rusting of iron in the presence of air and moisture. Also there are reactions like inversion of cane sugar and hydrolysis of starch, which proceed with a moderate speed. Can you think of more examples from each category? You must be knowing that speed of an automobile is expressed in terms of change in the position or distance covered by it in a certain period of time. Similarly, the speed of a reaction or the rate of a reaction can be defined as the change in concentration of a reactant or product in unit time. To be more specific, it can be expressed in terms of:

(i) the rate of decrease in concentration of any one of the reactants,

(ii) the rate of increase in concentration of any one of the products.

(iii) Consider a hypothetical reaction, assuming that the volume of the system remains constant.

$$R \rightarrow P$$

One mole of the reactant R produces one mole of the product P. If $[R]_1$ and $[P]_1$ are the concentrations of R and P respectively at time t_1 and $[R]_2$ and $[P]_2$ are their concentrations at time t_2 then,

$$\Delta t = t_2 - t_1$$

$$\Delta[R] = [R]_2 - [R]_1$$

$$\Delta [P] = [P]_2 - [P]_1$$

The square brackets in the above expressions are used to express molar concentration.

$$\text{Rate of disappearance of R} = \frac{\text{Decrease in concentration of R}}{\text{Time taken}} = \frac{\Delta[R]}{\Delta t} \qquad (1)$$

$$\text{Rate of appearance of P} = \frac{\text{Increase in concentration of P}}{\text{Time taken}} = +\frac{\Delta[P]}{\Delta t} \qquad (2)$$

Since, $\Delta[R]$ is a negative quantity (as concentration of reactants is decreasing), it is multiplied with –1 to make the rate of the reaction a positive quantity.

Equations (1) and (2) given above represent the average rate of a reaction, r_{av}.

Calculation of average rate is not very useful because the rate of a reaction changes continuously. Thus it is better to estimate the rate of reaction instantly at a particular time. For this purpose time interval and the difference in concentration is made as small as possible. If the difference in concentration and the difference in time, both are made infinitesimally small T (i.e Δt as well as Δ concentration both approach zero) then the rate is referred to as instantaneous rate T (r_{inst}).This is obtained by drawing a tangent at a particular point on the graph, the slope of tangent gives the instantaneous rate (r_{inst}).This is written in calculus as:

$$= \frac{\text{Infinitesimally small decrease in concentration of R}}{(r_{inst}) \text{ Infinitesimally small increase in time}}$$

$$= -\frac{d[R]}{dt} \qquad (1a)$$

or

$$= \frac{\text{Infinitesimally small increase in concentration of P}}{(r_{inst}) \text{ Infinitesimally small increase in time}}$$

$$= \frac{d[P]}{dt} \qquad (2a)$$

Both rates are shown graphically in Fig 6.1(a and b)

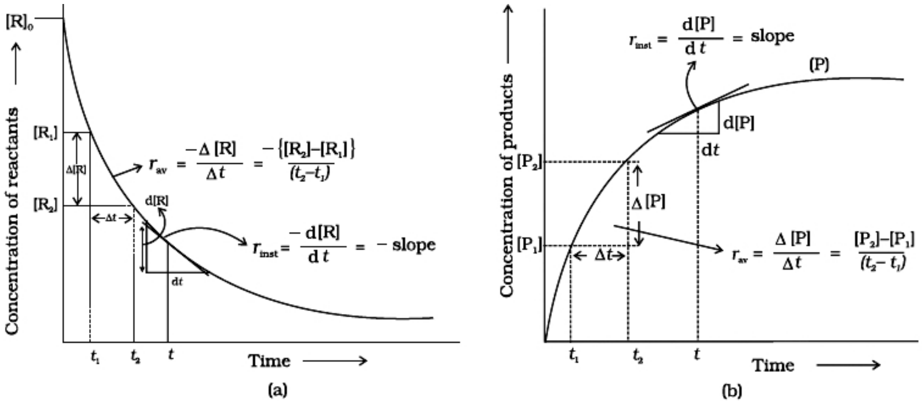


Fig 6.1 Instantaneous and average rates of a reaction

6.2.1 Units of rate of a reaction

From equations (1) and (2), it is clear that units of rate are concentration time^{-1}. For example, if concentration is in mol L^{-1} and time is in seconds then the units will be mol L^{-1}s^{-1}. However, in gaseous reactions, when the concentration of gases is expressed in terms of their partial pressures, then the units of the rate equation will be atm s^{-1}.

6.3 Factors Effecting Rate of Reaction

Chemical reactions proceed at different rates. The factors that affect reaction rates are:

- surface area of a solid reactant
- concentration or pressure of a reactant
- temperature
- nature of the reactants
- presence/absence of a catalyst.

A change in one or more of these factors may alter the rate of a reaction. In this lesson, you will define these factors, and describe and predict their effects on reaction rates.

6.3.1 Surface Area

Surface area is the exposed surface of a solid substance.

The rate of reaction of a solid substance is related to its surface area. In a reaction between a solid and an aqueous/liquid/gas species, increasing the surface area of the solid-phase reactant increases the number of collisions per second and therefore increases the reaction rate.

In a reaction between magnesium metal and hydrochloric acid, magnesium atoms must collide with the hydrogen ions. However, the number of collisions per second between magnesium and hydrogen is higher, and the rate of reaction is faster, when the magnesium atoms form one big lump.

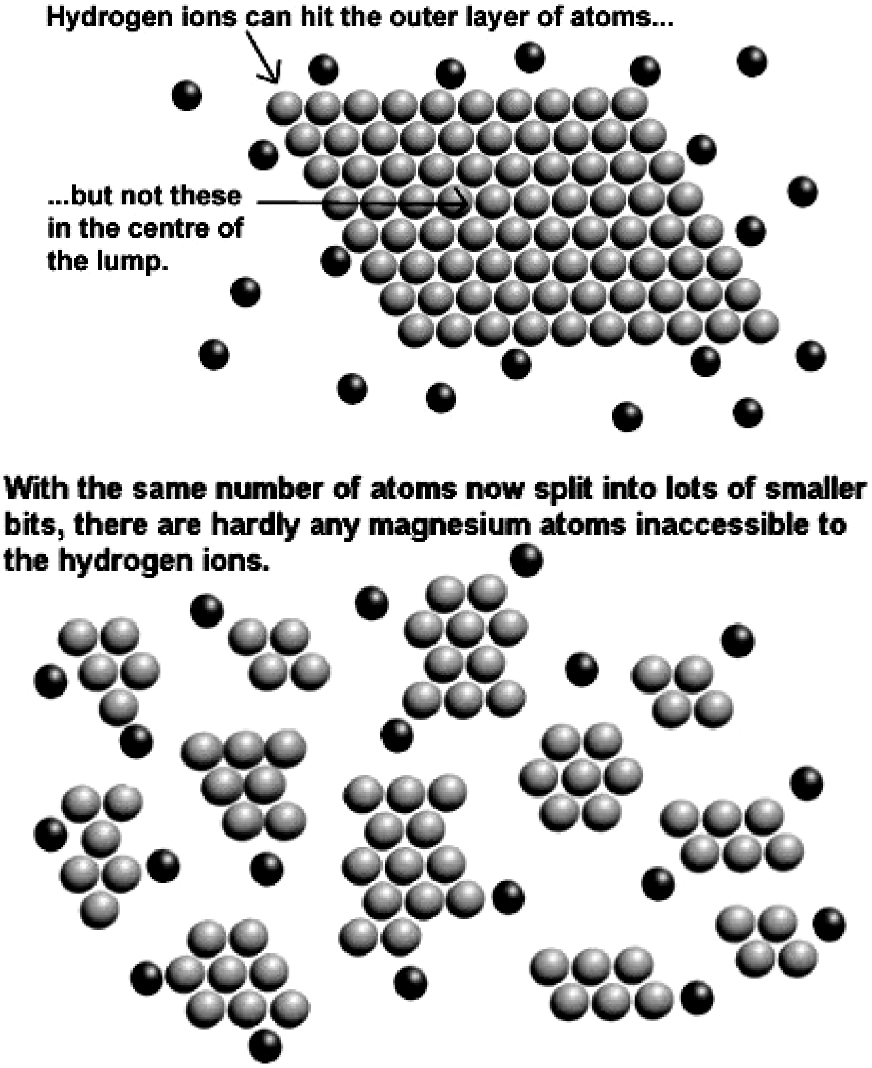


Fig.6.2 Increasing the surface area of a solid reactant increases the reaction rate

By increasing surface area, there are more collisions per unit time. That's why many solids are powdered using a mortar and pestle before being used in a reaction.

Examples of other reactions where surface area is important are:

- active metals with acids, e.g. HCl with zinc
- coal dust with oxygen gas
- grain dust with oxygen gas

6.3.2 (a) Concentration

The concentration of a substance can be expressed in a variety of ways depending on the nature of a substance. Aqueous solutions typically have their concentrations expressed in mol/L. For example, a solution made by dissolving sodium hydroxide in water has its concentration expressed as moles of NaOH per litre of solution. Gases can also have their concentrations expressed in mol/L.

In terms of the collision theory, increasing the concentration of a reactant increases the number of collisions between the reacting species per second which increases the reaction rate.

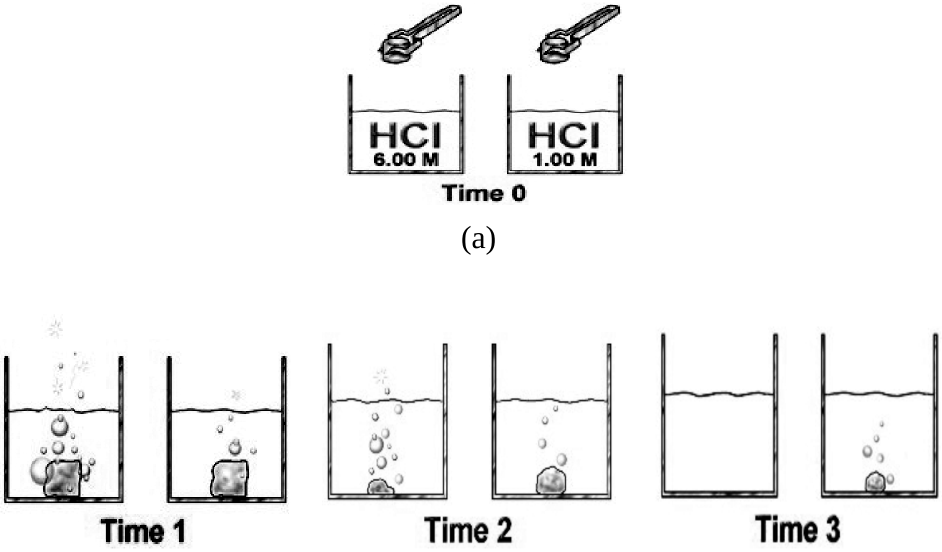
Consider the reaction between hydrochloric acid and zinc metal.

$$Zn_{(s)} + 2HCl_{(aq)} \rightarrow H_{2\,(g)} + ZnCl_{2\,(aq)}$$

In one beaker, 6.00 mol/L HCl is reacted with 2.00 g of Zn.In another, 1.00 mol/L HCl is reacted with 2.00 g of Zn.

Which reaction should occur at the faster rate?

In terms of the collision theory, collisions between zinc atoms and hydrochloric acid are more frequent in the beaker containing 6.0 M HCl because there is more acid per unit of volume available.



(a)

(b)

Fig 6.3(a), (b) Experimental verification of effect of rate on concentration

You can change the concentration of an aqueous species by simply adding more solute (to make it more concentrated) or adding more solvent (to make it more dilute).

You can change the concentration of a gas by adding more gas keeping volume of container constant or by decreasing the volume of the container. On the other hand concentration of a gas can be decreased by decreasing amount of gas in the container (evacuating) or by increasing the volume of container keeping amount of gas constant..

6.3.2 (b) Pressure

The concentration of a gas is a function of the pressure on the gas. Increasing the pressure of a gas is exactly the same as increasing its concentration. If you have a certain number of gas molecules, you can increase the pressure by forcing them into a smaller volume.

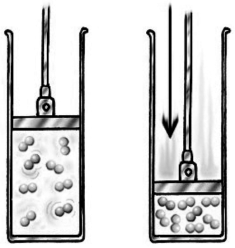


Fig. 6.4 Collision increases on increasing pressure

Under higher pressure or at a higher concentration, gas molecules collide more frequently and react at a faster rate. Conversely, increasing the volume of a gas decreases pressure which in turn decreases the collision frequency and thus reduces the reaction rate.

It is important to note however that there are reactions involving gases in which a pressure change does not affect the reaction rate. For this reason, the rates of reactions involving gases have to be determined by experiment.

Also note that solids and liquids are not affected by pressure changes.

6.3.3. Temperature

With the exception of some, about all chemical reactions take place at a faster rate at higher temperatures.

Temperature (in Kelvin degrees) is proportional to the kinetic energy of the particles in a substance. For example, if the Kelvin temperature of a substance is doubled, then the average kinetic energy of the particles in that substance is doubled.

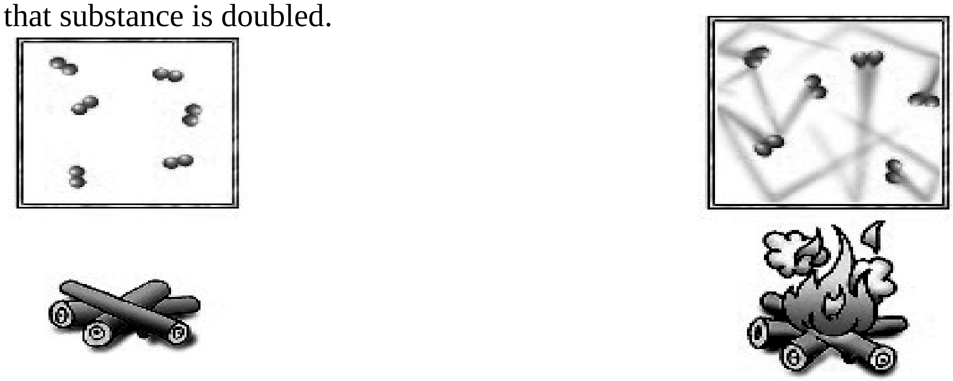


Fig 6.5 At higher temperatures, particles collide more frequently and with greater intensity.

Now, let's look at the effect graphically. Individual particles have different kinetic energies. Some are moving fast some are moving slowly, and most are moving at some intermediate speed.

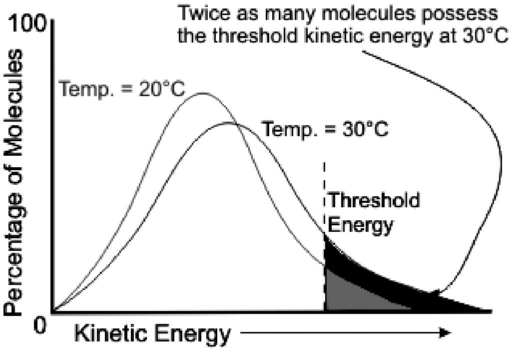


Fig.6.6 No. of molecules Vs. Kinetic Energy

Increase in the temperature from 20 ^{0} C to 30^0 C increases the number of molecules having higher kinetic energy as shown in shaded part of fig.6.6.This results in more molecules having energy equal to or greater tha the threshold energy.Thus more molecules may form the activated complex on collision with other molecules resulting in increase in the reaction rate.

Now consider the relationship between threshold kinetic energy and the activation.energy.

Activation energy is the difference between the threshold energy and the energy actually possessed by the molecules.On the other hand threshhold energy is the minimum amount of energy required for colliding particles to react.

Thus,

Thresh hold energy = Activation energy + Energy actually possesed by the molecules.

As you see in the Fig. 6.6 that an incresase in 10^{0}C in temperature nearly doubles the area of the shaded portion in the figure.This means that a 10^{0}C rise in temperature may double the reaction rate.

Thus there are two effects of increasing temperature: greater collision intensity and more frequent collisions.

Generally a10^{0}C increase in temperature may double the reaction rate. It turns out that the increase in the reaction rate is mainly a function of the more intense collisions. Increased collision frequency is not as significant a factor.

6.3.4 Nature of Reactants

Individual properties of substances also affect reaction rates. The scope of these properties is broad and there are few generalizations that you can apply consistently. Some of the properties in this category are state of matter, molecular size, bond type, bond strength and number of bonds.

6.3.4 (a) State of Matter

Gases tend to react faster than solids or liquids: It takes energy to separate particles from each other. In order to burn candle wax, the solid wax has to be melted and then vaporized before it reacts with oxygen. Methane gas is already in the gas state so it burns faster than wax.

$$CH_{4\,(g)} + 2\,O_{2\,(g)} \rightarrow CO_{2\,(g)} + 2\,H_2O_{(g)} \qquad \text{fast}$$

$$C_{25}H_{52\,(s)} + 38\,O_{2\,(g)} \rightarrow 25\,CO_{2\,(g)} + 26\,H_2O_{(g)} \qquad \text{slow}$$

Aqueous ions tend to react faster than species in other states of matter: Solid lead(II) nitrate will react with solid potassium iodide, but the reaction is really very slow. That's because the ionic bonding in each reactant is strong and the ions in each compound are hard to separate from each other. When aqueous solutions of these compounds are mixed, the formation of lead(II) iodide is rapid. In aqueous solutions, the ions of each compound are already dissociated. When the two solutions are mixed together, all that is required for a reaction to occur is contact between the lead(II) ions and the iodide ions.

$$Pb(NO_3)_{2\,(s)} + 2\,KI_{(s)} \rightarrow PbI_{2\,(s)} + 2\,KNO_{3\,(s)} \qquad \textit{slow}$$

$$Pb(NO_3)_{2\,(aq)} + 2\,KI_{(aq)} \rightarrow PbI_{2\,(s)} + 2\,KNO_{3\,(aq)} \qquad \textit{fast}$$

6.3.4 (b) Bond Type

Reactions involving ionic species tend to proceed faster than reactions involving molecular compounds.

$$2\,CO_{(g)} + O_{2\,(g)} \rightarrow 2\,CO_{2\,(g)} \qquad \textit{slow (at 25°C)}$$

$$5\,Fe^{2+}_{(aq)} + MnO^{-}_{4(aq)} + 8\,H^{+}_{(aq)} \rightarrow 5\,Fe^{3+}_{(aq)} + Mn^{2+}_{(aq)} + 4\,H_2O_{(l)} \qquad \textit{fast}$$

6.3.4 (c) Bond Strength

Reactions involving the breaking of weaker bonds proceed faster than reactions involving the breaking of stronger bonds. For example, double carbon to carbon bonds are stronger than single C-C bonds.

$$2\,C_2H_{6\,(g)} + 7\,O_{2\,(g)} \rightarrow 4\,CO_{2\,(g)} + 6\,H_2O_{(g)} \qquad \textit{very, very fast}$$

$$C_2H_{4\,(g)} + 3\,O_{2\,(g)} \rightarrow 2\,CO_{2\,(g)} + 2\,H_2O_{(g)} \qquad \textit{very fast}$$

6.3.4 (d) Number of Bonds/Molecular Size

Reactions involving the breaking of fewer bonds per reactant proceed faster than those involving the breaking of a larger number of bonds per reactant.

$$5\,Fe^{2+}_{(aq)} + MnO^{-}_{4\,(aq)} + 8\,H^{+}_{(aq)} \rightarrow 5\,Fe^{3+}_{(aq)} + Mn^{2+}_{(aq)} + 4\,H_2O_{\,(l)} \quad \textit{fast}$$

$$5\,OOCCOO^{2-}_{(aq)} + 2MnO^{-}_{4\,(aq)} + 16\,H^{+}_{(aq)} \rightarrow 2Mn^{2+}_{(aq)} + 4\,H_2O_{\,(l)} + 10\,CO_{2\,(l)} \quad \textit{slow}$$

The simple ion Fe^{2+} reacts faster than oxalate ($OOCCOO^{2-}$).

Kerosene burns more slowly than methane because there are more bonds to be broken per molecule of kerosene than are per molecule of methane. Kerosene is a bigger molecule.

$$CH_{4\,(g)} + 2\,O_{2\,(g)} \rightarrow CO_{2\,(g)} + 2\,H_2O_{(g)} \quad \text{fast}$$

$$C_{13}H_{28\,(s)} + 20\,O_{2\,(g)} \rightarrow 13\,CO_{2\,(g)} + 14\,H_2O_{(g)} \quad \text{slow}$$

6.3.5 Catalyst

A **catalyst** is a species that speeds up a chemical reaction without itself being chemically changed upon completion of the reaction. In other words, the mass of a catalyst is the same before and after a reaction occurs.

Common examples of catalysts include:

- MnO_2 in the decomposition of H_2O_2
- Fe in the manufacture of NH_3
- Pt in the conversion of NO and CO to N_2 and CO_2

Recall that collisions only result in reactions if the particles collide with enough energy to get the reactions started (i.e. to overcome the activation energy barrier).

Also recall that activation energy is related with threshold energy.

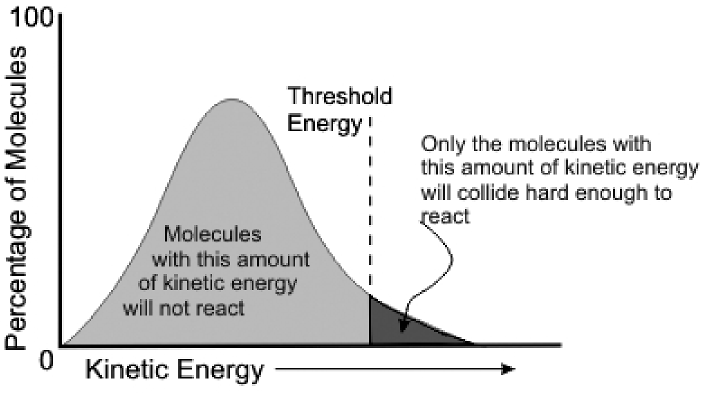


Fig 6.7 Activation energy corresponds to threshold energy

Only collisions involving particles with sufficient kinetic energy result in the formation of an activated complex. Particles possessing less than the threshold energy simply bounce apart upon collision.

The number of successful collisions per unit of time be increased by lowering the threshold energy (or in terms of potential energy, lowering the activation energy).

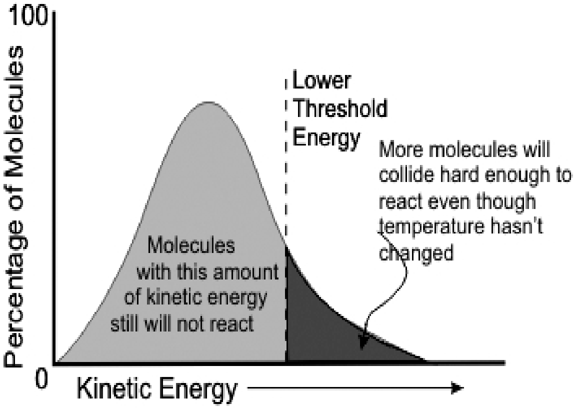


Fig 6.8 collisions per unit of time be increased by lowering the threshold energy

Adding the appropriate catalyst to a chemical system has exactly this effect on threshold/activation energy.

A catalyst provides an alternative pathway for the reaction - a pathway that has a lower activation energy.

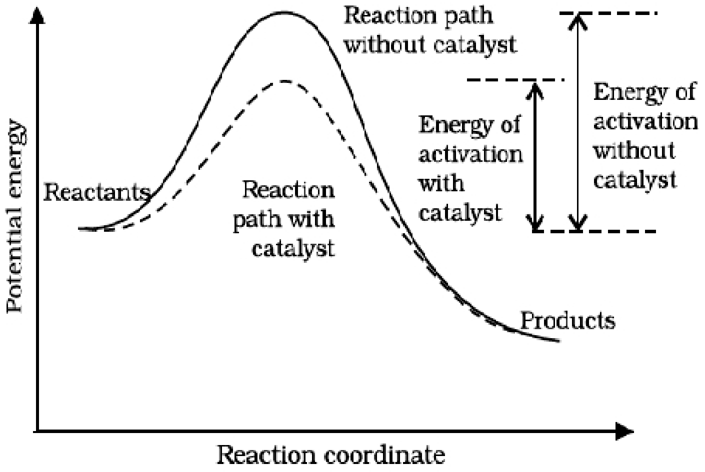


Fig.6.9 Alternative path provided by catalyst

The catalyzed pathway (shown as a dotted green line above) has *lower* activation energy. Relating this back to the kinetic energy diagram, you see that more particles will have sufficient kinetic energy to react. In other words, the addition of the catalyst increases the reaction rate.

6.4 Mathematical characteristics of simple chemical reactions Concentration dependence of rates

6.4.1 Zero Order Reaction

Zero order reaction means that the rate of the reaction is proportional to zero power of the concentration of reactants. Consider the reaction,

$$R \rightarrow P$$

$$\text{Rate} = -\frac{d[R]}{dt} = k[R]^0$$

As any quantity raised to power zero is unity

$$\text{Rate} = -\frac{d[R]}{dt} = k \times 1$$

$$d[R] = -k\,dt$$

Integrating both sides

$$[R] = -kt + I \qquad (1)$$

At $t = 0$, the concentration of the reactant R = $[R]_0$, where $[R]_0$ is initial concentration of the reactant.

Substituting in equation (1)

$$[R]_0 = -k \times 0 + I$$

$$[R]_0 = I$$

Substituting the value of I in the equation (1)

$$[R] = -kt + [R]_0 \qquad (2)$$

Comparing (2) with equation of a straight line, y = mx + c, if we plot [R] against t, we get a straight line (Fig.) with slope = $-k$ and intercept equal to [R]0.

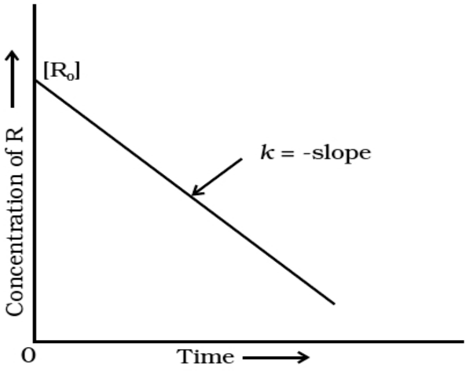


Fig.6.10Variation in the concentration vs time plot for a zero order reaction

Further simplifying equation (2) we get the rate constant, *k* as

$$k = \frac{[R]_0 - [R]}{t} \qquad (3)$$

Zero order reactions are relatively uncommon but they do occur under special conditions

Examples

1. Some enzyme catalysed reactions and reactions which occur on metal surfaces.
2. The decomposition of gaseous ammonia on a hot platinum surface at high pressure.

$$2NH_3(g) \xrightarrow[\text{Pt catalyst}]{1130K} N_2(g) + 3H_2(g)$$

$$\text{Rate} = k\,[NH_3]^0 = k$$

6.4.2 First Order Recation

In this class of reactions, the rate of the reaction is proportional to the first power of the concentration of the reactant R.

$$R \rightarrow P$$

$$\text{Rate} = -\frac{d[R]}{dt} = k[R]$$

$$\text{or} \quad \frac{d[R]}{[R]} = -k\,dt$$

Integrating this equation, we get

$$\ln [R] = -kt + I \qquad (4)$$

Again, I is the constant of integration and its value can be determined easily.

When $t = 0$, $R = [R]_0$, where $[R]_0$ is the initial concentration of the reactant.

Therefore, equation (4) can be written as

$$\ln [R]_0 = -k \times 0 + I$$
$$\ln [R]_0 = I$$

Substituting the value of I in equation (4)

$$\ln[R] = -kt + \ln[R]_0 \qquad (5)$$

Rearranging this equation

$$\ln\frac{[R]}{[R]_0} = -kt$$

$$\text{or } k = \frac{1}{t}\ln\frac{[R]_0}{[R]} \quad (6)$$

In a first order if initial concentration of the reactant is $[R]_0$ when $t=0$ and it is $[R]_1$ and $[R]_2$ at times t_1 and t_2,respectively,then

At time t_1 from equation (4)

$$\ln[R]_1 = -kt_1 + \ln[R]_0 \quad (7)$$

At time t_2

$$\ln[R]_2 = -kt_2 + \ln[R]_0 \quad (8)$$

Subtracting equation (8) from(7)

$$\ln[R]_1 - \ln[R]_2 = -kt_1 - (-kt_2)$$

$$\ln\frac{[R]_1}{[R]_2} = k(t_2 - t_1)$$

$$k = \frac{1}{(t_2 - t_1)}\ln\frac{[R]_1}{[R]_2} \quad (9)$$

Equation (5) can also be written as

$$\ln\frac{[R]}{[R]_0} = -kt$$

Taking antilog of both sides

$$[R] = [R]_0\, e^{-kt} \quad (10)$$

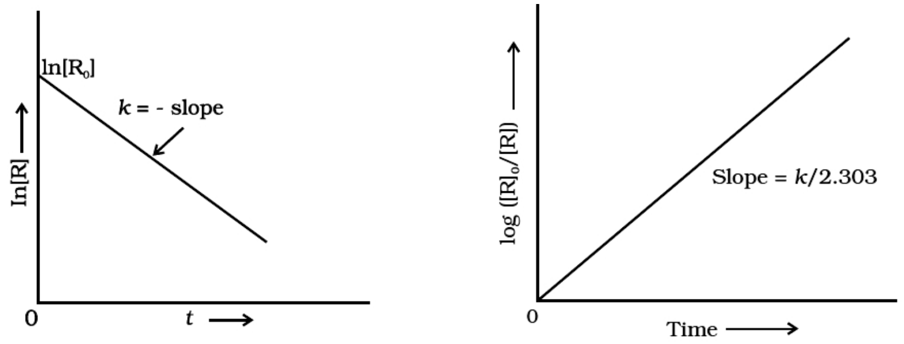
Comparing equation (5) with y = mx + c, if we plot ln [R] against t (Fig. 6.11 a) we get a straight line with slope = $-k$ and intercept equal to ln $[R]_0$

The first order rate equation (6) can also be written in the form

$$k = \frac{2.303}{t}\log\frac{[R]_0}{[R]} \quad (11)$$

$$\log\frac{[R]_0}{[R]} = \frac{kt}{2.303}$$

If we plot a graph between log $[R_{]0}/[R]$ vs t, (Fig. 6.11 b),the slope = $k/2.303$



(a) **(b)**

Fig. 6.11 (a and b) First order Kinetics

Example

1. Hydrogenation of ethene is an example of first order reaction

$$C_2H_4(g) + H_2\ (g) \rightarrow C_2H_6(g)$$
$$\text{Rate} = k\,[C_2H_4]$$

2. All natural and artificial radioactive decay of unstable nuclei take place by first order kinetics.

$$^{226}_{88}\text{Ra} \rightarrow {}^{4}_{2}\text{He} + {}^{222}_{86}\text{Rn}$$
$$\text{Rate} = k\,[\text{Ra}]$$

6.4.2.1 Pseudo First Order Reaction

The order of a reaction is sometimes altered by conditions. Considera chemical reaction between two substances when one reactant is present in large excess. During the hydrolysis of 0.01 mol of ethyl acetate with 10 mol of water, amounts of the various constituents at the beginning (t = 0) and completion (t) of the reaction are given as under.

	$CH_3COOC_2H_5$	$+ H_2O$	$\xrightarrow{H^+}$	CH_3COOH	+	C_2H_5OH
$t = 0$	0.01 mol	10 mol		0 mol		0 mol
t	0 mol	9.09 mol		0.01 mol		0.01 mol

The concentration of water does not get altered much during the course of the reaction. So, in the rate equation

$$\text{Rate} = k'\,[CH_3COOC_2H_5]\,[H_2O]$$

the term $[H_2O]$ can be taken as constant. The equation, thus, becomes

$$\text{Rate} = k\,[CH_3COOC_2H_5]$$
$$\text{where } k = k'\,[H_2O]$$

and the reaction behaves as first order reaction. Such reactions are called pseudo first order reactions.

Inversion of cane sugar is another pseudo first order reaction.

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$\text{Rate} = k\ [C_{12}H_{22}O_{11}]$$

6.4.3 Second Order Reaction

(i) Case 1: When two molecules of same reactant give rise to product

A + A → P or→2A P

The rate at which A decreases can be expressed using the **differential rate equation**.

$$-\frac{d[A]}{dt} = k[A]^2$$

The equation can then be rearranged:

$$\frac{d[A]}{[A]^2} = -kdt$$

Since we are interested in the change in concentration of A over a period of time, we integrate between t = 0 and t, the time of interest.

$$\int_{[A]_o}^{[A]_t} \frac{d[A]}{[A]^2} = -k\int_0^t dt$$

To solve this, we use the following rule of integration:

$$\int \frac{dx}{x^2} = -\frac{1}{x} + constant$$

We then obtain the **integrated rate equation**.

$$\frac{1}{[A]_t} - \frac{1}{[A]_o} = kt \quad (12)$$

Upon rearrangement of the integrated rate equation, we obtain an equation of the line:

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_o}$$

The crucial part of this process is not understanding precisely how to derive the integrated rate law equation, rather it is important to understand how the equation directly relates to the graph which provides a linear relationship. In this case, and for all second order reactions, the linear plot of $1/[A]t$ versus time will yield the graph below.

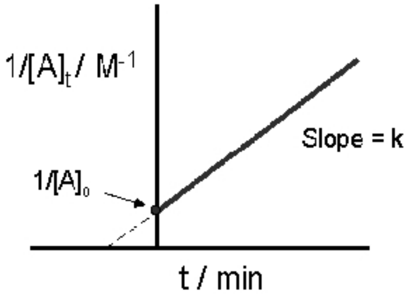


Fig.6.12 Second order kinetics (Same reactant)

This graph is useful in a variety of ways. If we only know the concentrations at specific times for a reaction, we can attempt to create a graph similar to the one above. If the graph yields a straight line, then the reaction in question must be second order. In addition, with this graph we can find the slope of the line and this slope is k, the reaction constant. The slope can be found by finding the "rise" and then dividing it by the "run" of the line. For an example of how to find the slope, please see the example section below. There are alternative graphs that could be drawn.

The plot of $[A]t$ versus time would result in a straight line if the reaction was zeroth order. It does, however, yield less information for a second order graph. This is because both the graphs of a first or second order reaction would look like exponential decays. The only obvious difference, as seen in the graph below, is that the concentration of reactants approaches zero more slowly in a second-order, compared to that in a first order reaction.

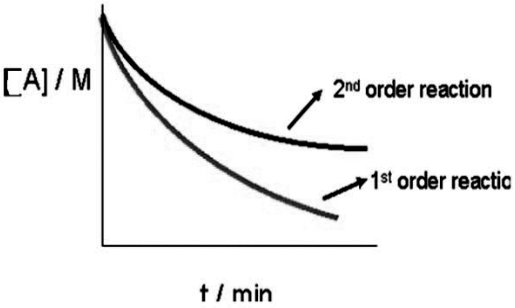


Fig. 6.13 Exponential decrease

(ii) Case 2: When two different reactants give rise to product

$$A + B \rightarrow P$$

As before, the rate at which A decreases can be expressed using the differential rate equation.

$$\frac{d[A]}{dt} = k[A][B]$$

Since,

$$-\frac{d[A]}{dt} = \frac{dx}{dt}$$

- *Situation a*: $[A]_0 \neq [B]_0$ (when $[B]_0 > [A]_0$)

Let x = concentration of each species reacted at time t.

Let $[A]_0 = a$; $[B]_0 = b$ then $[A] = a - x$; $[B] = b - x$

New expression of rate law becomes:

$$\frac{dx}{dt} = k([A]_o - x)([B]_o - x)$$

The equation can them be rearranged to:

$$\frac{dx}{([A]_o - x)([B]_o - x)} = kdt$$

We integrate between t = 0 (when x = 0) and t, the time of interest.

$$\int_0^x \frac{dx}{([A]_o - x)([B]_o - x)} = k\int_0^t dt$$

To solve this integral, we use the method of partial fractions.

$$\int \frac{1}{(a-x)(b-x)}\,dx = \frac{1}{b-a}\left(ln\,\frac{1}{a-x} - ln\,\frac{1}{b-x}\right) + constant$$

Evaluating the integral gives us:

$$\int \frac{dx}{([A]_o - x)([B]_o - x)} = \frac{1}{[B]_o - [A]_o}\left(ln\,\frac{[A]_o}{[A]_o - x} - ln\,\frac{[B]_o}{[B]_o - x}\right)$$

Applying the rule of logarithm, the equation simplifies to:

$$\int \frac{dx}{([A]_o - x)([B]_o - x)} = \frac{1}{[B]_o - [A]_o}\,ln\,\frac{[B][A]_o}{[A][B]_o}$$

We then obtain the integrated rate equation (under the condition that [A] and [B] are not equal).

$$\frac{1}{[B]_o - [A]_o}\,ln\,\frac{[B][A]_o}{[A][B]_o} = kt \qquad (13)$$

Upon rearrangement of the integrated rate equation, we obtain:

$$ln\frac{[B][A]_o}{[A][B]_o} = k([B]_o - [A]_o)t$$

Hence, from the last equation, we can see that a linear plot of $ln[A]o[B]/[A][B]o$ versus time is also characteristic of second-order reactions.

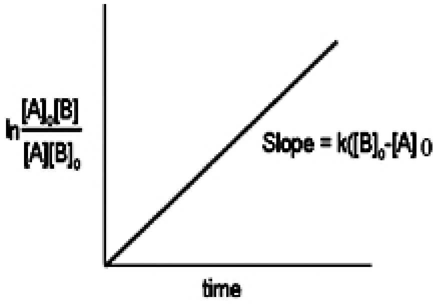


Fig.6.14 Second order kinetics(reactants are not same)

- *Situation b*: $[A]_0 = [B]_0$

Because A + B → P

A and B react 1 to 1, $[A]= [A]_0 -x$ and $[B] = [B]_0 -x$

at any time t, [A] = [B] and the rate law will be, rate = k[A][B] = k[A][A] = $k[A]^2$. Thus, it is assumed as given in case1.

6.5 Half Life of Reaction

The half-life of a reaction is the time in which the concentration of a reactant is reduced to one half of its initial concentration. It is represented as $t_{1/2}$. For a zero order reaction, rate constant is given by equation (3) i.e

$$k = \frac{[R]_0 - [R]}{t}$$

$$\text{At } t = t_{1/2}, \quad [R] = \frac{1}{2}[R]_0$$

The rate constant at $t_{1/2}$ becomes

$$k = \frac{[R]_0 - 1/2[R]_0}{t_{1/2}}$$

$$t_{1/2} = \frac{[R]_0}{2k} \qquad (14)$$

It is clear that $t_{1/2}$ for a zero order reaction is directly proportional to the initial concentration of the reactants and inversely proportional to the rate constant.

For the first order reaction,(11)

$$k = \frac{2.303}{t}\log\frac{[\mathrm{R}]_0}{[\mathrm{R}]}$$

$$\text{at } t_{1/2} \quad [\mathrm{R}] = \frac{[\mathrm{R}]_0}{2}$$

So, the above equation becomes

$$k = \frac{2.303}{t_{1/2}}\log\frac{[\mathrm{R}]_0}{[\mathrm{R}]/2}$$

$$\text{or} \quad t_{1/2} = \frac{2.303}{k}\log 2$$

$$t_{1/2} = \frac{2.303}{k} \times 0.301$$

$$t_{1/2} = \frac{0.693}{k} \qquad (15)$$

It can be seen that for a first order reaction, half-life period is constant, i.e., it is independent of initial concentration of the reacting species. The half-life of a first order equation is readily calculated from the rate constant and vice versa.

For a second-order reaction, the half-life is inversely related to the initial concentration of the reactant (A). For a second-order reaction each half-life is twice as long as the life span of the one before.

(i) Consider the reaction 2A --> P:

We can find an expression for the half-life of a second order reaction by using the previously derived integrated rate equation.

$$\frac{1}{[A]_t} - \frac{1}{[A]_o} = kt$$

Since

$$[A]_{t_{1/2}} = \frac{1}{2}[A]_o$$

When

$$t = t_{1/2}$$

Our integrated rate equation becomes:

$$\frac{1}{\frac{1}{2}[A]_o} - \frac{1}{[A]_o} = kt_{1/2}$$

After a series of algebraic steps,

$$\frac{2}{[A]_o} - \frac{1}{[A]_o} = kt_{1/2}$$

$$\frac{1}{[A]_o} = kt_{1/2}$$

We obtain the equation for the half-life of a second order reaction:

$$t_{1/2} = \frac{1}{k[A]_o}$$

This inverse relationship suggests that as the initial concentration of reactant is increased, there is a higher probability of the two reactant molecules interacting to form product. Consequently, the reactant will be consumed in a shorter amount of time, i.e. the reaction will have a shorter half-life. This equation also implies that since the half-life is longer when the concentrations are low, species decaying according to second-order kinetics may exist for a longer amount of time if their initial concentrations are small.

Note that for the second scenario in which A + B → P, the half-life of the reaction cannot be determined. As stated earlier, $[A]_o$ cannot be equal to $[B]_o$. Hence, the time it takes to consume one-half of A is not the same as the time it takes to consume one-half of B. Because of this, we cannot define a general equation for the half-life of this type of second-order reaction.

6.6 Determination of the order of reaction

A kinetics experiment consists of measuring the concentration of one of the reactant or product at various time intervals during the course of reaction. In the present section, we will look at the methods that allow us to use the experimental data to determine the reaction orders with respect to each reactant, and therefore the rate law.

(i) Isolation method

The isolation method is a technique for simplifying the rate in order to determine its dependence on the concentration of a single reactant. Once the rate has been simplified, the differential or integral methods discussed in the following subsections may be used to determine the reaction order

The dependence of the reaction rate on the chosen reactant concentration is done by having all other reactants present in a large excess, so that their concentration remains essentially constant throughout the course of the reaction. By doing this the rate and hence the rate constant, calculated by any method, corresponds to the reactant which has been isolated (or whose concentration is kept small compared to the concentrations of all other reactants) in the reaction. As an example, consider a reaction A + B → P, in which B is present at a concentration 1000 times greater than A. When all of species A has been used up, the concentration of B will only have changed by 1/1000, or 0.1%, and so 99.9% of the original B will still be present. It is therefore a good approximation to treat its concentration as constant throughout the reaction. This greatly simplifies the rate law since the (constant) concentrations of all reactants present in large excess may be combined with the rate constant to yield a single *effective rate constant*. For example, the rate law for the reaction considered above will become:

$$\nu = k\,[A]^a[B]^b \approx k\,[A]^a[B]_0^{\,b} = k_{eff}[A]^a \quad \text{with} \quad k_{eff} = k[B]_0^{\,b}$$

When the rate law contains contributions from a number of reactants, a series of experiments may be carried out in which each reactant is isolated in turn.

(ii) Differential methods

When we have a rate law that depends only on the concentration of one species, either because there is only a single species reacting, or because we have used the isolation method to manipulate the rate law, then the rate law may be written

$$\nu = k[\mathrm{A}]^a$$

$$\log \nu = \log k + a \log[\mathrm{A}]$$

A plot of log ν against log [A] will then be a straight line with a slope equal to the reaction order, *a*, and an intercept equal to log *k*. There are two methods by which the data may be used to plot graph.

1. We can measure the concentration of the reactant [A] as various time to calculate the rate, $\nu = -d[\mathrm{A}]/dt$, .Then slope of the straight line thus obtained gives order of the reaction. The order calculated by this method is known as order with respect to time.

2. We can perform a series of reactions by changing the initial concentration of the reactant and the rate is calculated by plotting concentration Vs. time graph .In this method a constant initial time is selected. Now again the double logarithmic graph between log v Vs. log[A] is plotted. The slope of the straight line thus obtained by this method is known as order with respect to concentration or the true order.

This is to be noted that the second method is more accurate and is commonly used. The technique is known as the initial rate method.

(iii) Integral methods

If we have measured concentrations as a function of time, we may compare their time dependence with the appropriate integrated rate laws. Again, this is most straightforward method if we have simplified the rate law so that it depends on only one reactant concentration. The differential rate law will give rise to different integrated rate laws depending on the value of a.The most commonly encountered ones are:

Zeroth order integrated rate law: $[\mathrm{A}] = [\mathrm{A}]_0 - kt$
A plot of [A] vs *t* will be linear, with a slope of -*k*.

First order integrated rate law: $\ln[\mathrm{A}] = \ln[\mathrm{A}]_0 - kt$
A plot of ln[A] vs *t* will be linear with a slope of -*k*.

Second order integrated rate law: $\dfrac{1}{[\mathrm{A}]} = \dfrac{1}{[\mathrm{A}]_0} + 2kt$
A plot of $\dfrac{1}{[\mathrm{A}]}$ vs *t* will be linear with a slope of 2*k*.

If none of these plots result in a straight line, then more complicated integrated rate laws must be tried.

(iv) Half lives

Another way of determining the reaction order is to investigate the behaviour of the half life as the reaction proceeds. Specifically, we can measure a series of successive half lives. $t = 0$ is used as the start time from which to measure the first half life, $t_{1/2(1)}$. Then $t_{1/2(1)}$ is used as the start time from which to measure the second half life, $t_{1/2(2)}$, and so on.

$$\text{Zeroth order} \qquad t_{1/2} = \frac{[A]_0}{2k}$$

Since at $t_{1/2(1)}$, the new starting concentration is ½$[A]_0$, successive half lives will decrease by a factor of two for a zeroth order reaction

$$\text{First order} \qquad t_{1/2} = \frac{\ln 2}{k}$$

There is no dependence of the half life on concentration, so $t1/2$ is constant for a first order reaction.

For second order reaction half life is given as:

$$\text{Second order} \qquad t_{1/2} = \frac{1}{k[A]_0}$$

The inverse dependence on concentration means that successive half lives will double for a second order reaction.

6.7 Radioactive decay as a first order phenomenon.

The number of nuclei in a radioactive sample that disintegrate during a given time interval decreases exponentially with time. Because the nucleus is insulated by the surrounding cloud of electrons, this rate is essentially independent of pressure, temperature, the mass action law, or any other rate limiting factors that commonly effect chemical and physical changes.

As a result, this decay rate serves as a very useful means of identifying a given nuclide. Since radioactive e decay represents the transformation of an unstable radioactive nuclide into a more stable nuclide, which may also be radioactive, it is an irreversible event for each nuclide

The unstable nuclei in a radioactive sample do not all decay simultaneously. Instead the decay of a given nucleus is an entirely random event. Consequently, studies of radioactive decay events require the use of statistical methods. With these methods, one may observe a large number of radioactive nuclei and predict with fair assurance that, after a given length of time, a definite fraction of them will have disintegrated but not which ones or when.

6.7.1 Basic Decay Equation

Radioactive decay is what chemists refer to as a first order reaction; that is, the rate of radioactive decay is proportional to the number of each type of radioactive nuclei present in a given sample. So if we double the number of a given type of radioactive nuclei in a sample, we double the number of particles emitted by the sample per unit time.This relation may be expressed as :

$$\begin{matrix}\text{The rate of}\\ \text{particle emission}\end{matrix} = \begin{pmatrix}\text{the rate of}\\ \text{disintegration of}\\ \text{radioactive nuclei}\end{pmatrix} \propto \begin{pmatrix}\text{number of}\\ \text{radioactive nuclei}\\ \text{present}\end{pmatrix}$$

Note that the foregoing statement is only a proportion. By introducing the decay constant, it is possible to convert this expression into an equation,

$$\begin{pmatrix}\text{The rate of}\\ \text{disintegration of}\\ \text{radioactive nuclei}\end{pmatrix} = \begin{pmatrix}\text{decay}\\ \text{constant}\end{pmatrix} \times \begin{pmatrix}\text{number of}\\ \text{radioactive}\\ \text{nuclei present}\end{pmatrix} \qquad (1)$$

The decay constant, λ, represents the average probability per nucleus of decay occurring per unit time. Therefore we are taking the probability of decay per nucleus, λ, and multiplying it by the number of nuclei present so as to get the rate of particle emission. The units of rate are (disintegration of nuclei/time) making the units of the decay constant (1/time), i.e., probability/time of decay.To convert the preceding word equations to mathematical statements using symbols,let N represent the number of radioactive nuclei present at time t. Then, using differential calculus, the preceding word equations may be written as.

$$-\frac{dN}{dt} \propto N$$

$$-\frac{dN}{dt} = \lambda N \qquad (2)$$

Note that N is constantly reducing in magnitude as a function of time. Rearrangement of Equation (2) to separate the variables given

$$\frac{dN}{N} = -\lambda\, dt \qquad (3)$$

if we say that at time t= 0 we have N_0 radioactive nuclei present, then integration of Equation (3) gives the radioactive decay law

$$N = N_0 e^{-\lambda t} \qquad (4)$$

This equation gives us the number of radioactive nuclei present at time t. However, in many experiments, we want to know the counting rate that we will get in a detector as a function of time. In other words, we want to know the activity of our samples. Still, it is easy to show that the counting rate in one's radiation detector, C, is equal to the rate of disintegration of the radioactive nuclei present in a sample, A, multiplied by a constant related to the efficiency of the radiation measuring system.

$$C = \varepsilon A = \varepsilon\left(-\frac{dN}{dt}\right) = \varepsilon\lambda N \qquad (5)$$

where ε is the efficiency. Substituting into Equation (4), we get

$$C = C_0 e^{-\lambda t} \qquad (6)$$

where C is the counting rate at some time t due to a radioactive sample that gave counting rate C_0 at time t= 0. Equations (4)and (6) are the basic equations governing the number of nuclei present in a radioactive sample and the number of counts observed in one's detector as a function of time.

The half life for a given nuclide can be derived from Equation (6) when the value of the decay constant is known.

In accordance with the definition of the term half life, when A/A_0= ½,then t = $t_{½}$. Substituting these values into Equation (6)

gives.

$$A/A_0 = 1/2 = e^{-\lambda t_{1/2}} \qquad (7)$$

Hence

$$t_{1/2} = \frac{\ln 2}{\lambda} = \frac{0.693}{\lambda} \qquad (8)$$

Note that the value of the expression for t½ has the units of 1/λ or dimensions of (time).The half lives for different nuclides range from less than 10^{-6} sec to 10^{10} year.

6.8 Mean Lifetime

The mean lifetime represents the average lifetime of an atomic nucleus in a radioactive sample. It is the time, calculated statistically, that a radioactive nucleus in a sample can exist without transforming itself into another one.

$$\Theta_{\text{media}} = \frac{1}{\lambda}$$

The mean lifetime is inversely proportional to the radioactive constant and it is an invariable characteristic for a determined decay of each type of radioactive nucleus.

The years that the individual of a group (region, country, etc.) "can live" is the average life-time of this population. If we add up the ages of all the people who have died in a year (or in another period of time) and we divide it by the total number of individuals we have found the arithmetic average of their lives.

If we add up the ages of all the people who die in a determined year and we divide by the number of deaths we have the average life span of this population

Q_{media}= 70 + 75 +82+ 23+12+ 56+ 72+ 74+..... / total nº

If the sample is large, the ages of several individuals coincide, so that, instead of repeating them in the addition, each age is multiplied by the number of persons who live to the said age.

$Q_{media} = n_1 \cdot t_1 + n_2 \cdot t_2 + n_3 \cdot t_3 + ... / N$
Being $N = n_1 + n_2 + n_3 + ...$

Some more exact mathematical calculations lead us to the following expressions:

$$\Theta_{media} = \frac{1}{N} \int t \, dN$$

The integral represents the sum of the infinite terms of the sample with each one multipled by their time of existence before transmuting:

$$\Theta_{media} = \frac{1}{N} \int_0^\infty t \, (-\lambda \, N \, dt)$$

We have substituted dN for its value deriving from the expression::

$$N = N_0 \cdot e^{-\lambda t}$$

The integral of the expression leads to:

$$\Theta_{media} = \frac{1}{N} \int_0^\infty t \, (-\lambda \, N_0 \, e^{-\lambda t} \, dt) = \frac{1}{\lambda}$$

6.9 Experimental techniques

Experimental techniques have been developed to monitor reactions over timescales varying from hours or days all the way down to a few femto seconds (1 fs = 10-15 s). While it is relatively simple to monitor the kinetics of a slow reaction (occurring over minutes to hours or longer), highly specialized techniques are required in order to study fast reactions, some of which will be considered here. Whatever the details of the experimental arrangement, any kinetics experiment essentially consists of mixing the reactants and initiating reaction on a timescale that is negligible relative to that of the reaction, and then monitoring the concentration(s) of one or more reactants and/or products as a function of time. Because rate constants vary with temperature, it is also important to determine and control accurately the temperature at which the reaction occurs. Most of the techniques we will look at are *batch techniques*, in which reaction is initiated at a single chosen time and concentrations are then followed as a function of time after initiation. We will also consider one or two examples of *continuous techniques*, in which reaction is continuously initiated and the time dependence of the reaction mixture composition is inferred from, for example, the concentrations in different regions of the reaction vessel. The continuous flow method outlined in the next section is an example of such a technique.

(i) Techniques for mixing the reactants and initiating reaction

For slow reactions, occurring over minutes to hours, reaction is usually initiated simply by mixing the reactants together by hand or with a magnetic stirrer or other mechanical device. For fast reactions, a wide range of techniques have been developed.

1. Flow techniques

Flow techniques are typically used to study reactions occurring on timescales of seconds to milliseconds. In the simplest flow method, shown schematically on the left below, reactants are mixed at one end of a flow tube, and the composition of the reaction mixture is monitored at one or more positions further along the tube. If the flow velocity along the tube is known, then measurements at different positions provide information on concentrations at different times after initiation of reaction. In a variation on this method, shown on the right side of figure 6.15, the detector may be used to inject one of the reactants into the flow tube at different positions relative to the detector in order to study the time dependence of the reaction mixture composition. Continuous in a fixed position, but a moveable injector may be used to inject one of the reactants into the flow tube at different positions relative to the detector in order to study the time dependence of the reaction mixture composition. Reactions of atomic or radical species may be studied using the discharge flow method, in which the reactive species is generated by a microwave discharge immediately prior to injection into the flow tube.

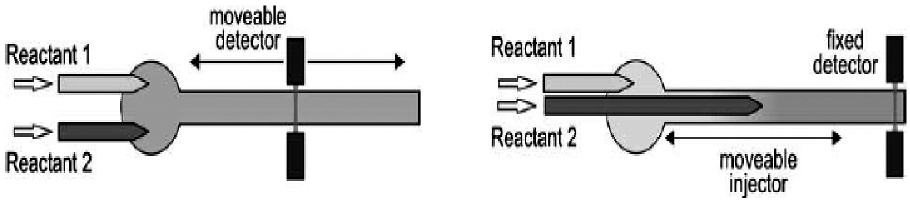


Fig. 6.15 Continuous flow technique

Continuous flow methods have the disadvantages that relatively large quantities of reactants are needed, and very high flow velocities are required in order to study fast reactions. These problems may be avoided by using a *stopped flow technique*. In this method two solutions are forced through jet into a mixing chamber in which mixing is extremely fast and takes place in 10^{-3} sec. From mixing chamber solution passes atonce into the reaction vessel where the flow is stopped suddenly and measurement are taken spectrophotometrically of concentration as a function of time.Readings are continuously by an oscilloscope the trace of which is photographed.(Fig. 6.16)

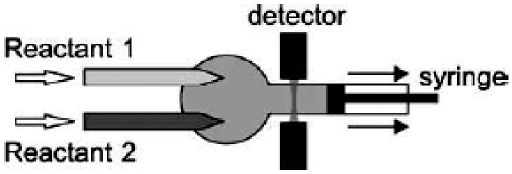


Fig 6.16 stopped flow technique.

Experimental systems may be designed to allow measurements to be made on very small sample volumes, making the stopped flow method popular for the study of biochemical kinetics e.g. enzyme action. Disadvantage of this method is that it is less sensitive than the continuous flow method and only few methods of observation are possible.

All flow techniques share the common problem that contributions from heterogeneous reactions at the walls of the flow tube can complicate the experiments. These can be minimised by coating the inner surface of the flow tube with an unreactive substance such as teflon or halocarbon wax, and the relative contributions from the process under study and reactions involving the walls may be quantified by varying the diameter of the flow tube (and therefore the ratio of volume to surface area).

2. Flash photolysis and laser pump probe techniques

In flash photolysis, reaction is initiated by a pulse of light (the ‘flash’) that dissociates a suitable precursor molecule in the reaction mixture to produce a reactive species, thereby initiating reaction. The concentration of the reactive species is then monitored as a function of time, usually spectroscopically using absorption spectroscopy or fluorescence techniques (see later). The shortest timescale over which reactions may be studied using this technique is determined by the duration of the ‘flash’. Originally, the flash was provided by a discharge lamp, with durations in the region of tens of microseconds to several milliseconds. However, in most modern experiments the flash is provided by a laser pulse, typically with a duration of a few nanoseconds (1 ns = 10-9 s). For studying extremely fast reactions, such as some of the electron transfer processes involved in photosynthesis, laser pulses as short as a few tens of femtoseconds (1 fs = 10^{-15} s) may be used.

Flash photolysis has the advantage that because reactants are produced from well-mixed precursors, there is no mixing time to reduce the time resolution of the technique. Also, because the reactants are generated and monitored in the centre of the reaction cell, there are no wall reactions to worry about as there are in flow methods. Pulse radiolysis is a variation on flash photolysis in which a short pulse of high energy electrons (10^{-9} to 10^{-6} s in duration) is passed through the sample in order to initiate reaction.

For very fast processes, the 'pump-probe' technique is often used, in which pulsed lasers are employed both to initiate reaction (the 'pump') and to detect the products via a pulsed spectroscopic technique (the 'probe'). The time separation between the two pulses can be varied either electronically or with an optical delay line down to a resolution of around 10 femtoseconds (10^{-14} s)

3. Relaxation methods

If we allow a chemical system to come to equilibrium and then perturb the equilibrium in some way,the rate of relaxation to a new equilibrium position provides information about the forward and reverse rate constants for the reaction.

Since a system at chemical equilibrium is already well mixed, relaxation methods overcome the mixing problems associated with many flow methods. As an example the simplest case be given as in the following reaction in equilibrium

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X$$

Where k_1 and k_2 are rate constants for the forward and baclward reactions and the reaction in both directions is of first order.Suppose such a reaction is alowed to come to equilibrium and then the conditions are suddenly changed so that it is no longer in equilibrium.This is done by changing temperatyre by a few degrees (temperature jump technique) or by changing pressure (pressure jump technique) suddenly.In relaxation methods, the perturbation flow equilibrium must take time much smaller than the relaxationtime.Temperature jump and pressure jump tecniques are used for time larger than 10^{-5} sec. For shorter times high electric or magnetic fields or ultasonic vibrations

(10^{8} to 10^{9} Hertz) are used.

If a_0 is the total concentration of A and X, and x is the concentration of x, then the concentration of A would be a_0-x and the equation becomes.

$$\frac{dx}{dt} = k_1[A] - k_{-1}[x] = k_{-1}(a_0 - x) - k_{-1}x$$

At equilibrium rate of forward reaction is equal to that of backward reaction, thus

$$k_1(a_0-x_e)=k_{-1}x_e$$

Where x_e is the equilibrium concentration of X at equilibrium. The deviation equilibrium Δx can be given as $x-x_e$ and its derivative with time is

$\frac{d(\Delta x)}{dt} = \frac{dx}{dt} = k_1(a_0-x)-k_{-1}x=k_1a0-(k_1+k\text{-}_1)x$

Or $\quad \frac{d(\Delta x)}{dt} = k_1a_0-(k_1+k_{-1})(x_e+\Delta x\ ) \quad \{\Delta\ x=x-x_e\ \}$

Or $\quad \frac{d(\Delta x)}{dt} = k_1(a_0-x_e\ ) - k_1\Delta x-\ k_{-\,-1}xe-k_{-1}\ \Delta\ x$

$= -\ (k_1+k_{-1})\ \Delta x$ because $k_1(a_0-x) =k_{-1}\ x_e)$

The quantity Δx varies with time in the same manner as does the concentration of a reactant in a first order reaction. Integration of the equation subject to boundary condition that when t=0 then $\Delta x=(\Delta x)_0$ gives.

$ln\frac{(\Delta x)0}{\Delta x} =(k_1+k\text{-}_1)\ _t$

If we define relaxation time τ as the time corresponding to

$\frac{(\Delta x)0}{\Delta x} = e$ or $ln\frac{(\Delta x)0}{\Delta x} =1$

The relaxation time is thus the time at which the distance from equilibrium is 1/e of the initial distance, and the equation can be written as

$$\tau = \frac{1}{k1+k-1}$$

Therefore if τ is determined experimentally for such a system then $k1/k_{-1}$ can be calculated.

4. Shock tubes

The shock tube method provides a way of producing highly reactive atomic or radical species through rapid dissociation of a molecular precursor, without the use of a discharge or laser pulse.

The method is based on the fact that a very rapid increase in pressure (the shock) causes rapid heating of a gas mixture to a temperature of several thousand Kelvin. Since most dissociation reactions are endothermic, at high temperatures their equilibria are shifted towards products. A rapid increase in temperature therefore leads to rapid production of reactive species (the dissociation products) initiating the reaction of interest. A shock tube (shown schematically below)

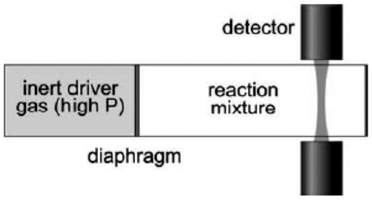


Fig. 6.17 shock tube

essentially consists of two chambers separated by a diaphragm. One chamber contains the appropriate mixture of reactants and precursor, the second an inert gas at high pressure. To initiate reaction, the diaphragm is punctured and a shock wave propagates through the

reaction mixture. The temperature rise can be controlled by varying the pressure and composition of the inert gas. The composition of the reaction mixture after initiation is monitored in real time, usually spectroscopically.

The shock tube approach is often used to study combustion reactions. Suitable precursors for such studies, together with the radical species obtained on dissociation using argon as the shock gas include:

$HCN \rightarrow H + CN$
$SO_2 \rightarrow SO + O$
$CH_3 \rightarrow CH_2 + H$
$H_2S \rightarrow HS + H$
$NO \rightarrow N + O$
$NH_3 \rightarrow NH_2 + H$
$CH_4 \rightarrow CH_3 + H$
$N_2O \rightarrow N_2 + O$
$C_2H_2 \rightarrow C_2H\ \_\ H$
$CF_3Cl \rightarrow CF_3 + Cl$
$C_2H_4 \rightarrow C_2H_3 + H$
$C_2H_4 \rightarrow C_2H_2 + H_2$

The method does have some major drawbacks, not least of which is the fact that the rapid heating is not selective for a particular molecules, and is likely to lead to at least partial dissociation of all of the species in the 'reactants' chamber. This leads to a complicated mixture of reactive species and often a large number of reactions occurring in addition to the reaction under study. Modelling the kinetics of such a system is often challenging, to say the least. Also, because each experiment is essentially a 'one off', no signal averaging is possible, and signal to noise levels are often low.Compare this with laser pump-probe methods, in which hundreds or even thousands of traces may be averaged to obtain good signal to noise.

5. Lifetime methods

In quantum mechanics, you learnt about the Heisenberg uncertainty principle, which relates the uncertainty in position and momentum, $\Delta x \Delta p \geq h/4\pi$. A similar uncertainty principle relates energy and time.

$$\Delta E \Delta t \geq h/4\pi \qquad \text{or, since } E = h\nu, \qquad \Delta\nu \Delta t \geq 1/4\pi$$

The result of this relationship is that an atomic or molecular state has an uncertainty ΔE in its energy that is related to its lifetime Δt. The lifetime of most grounds states is effectively infinite, so that the uncertainty in their energy is negligible. However, excited states are short-lived, and their energy is therefore ‘fuzzy’. Since photons corresponding to any energies within this uncertainty ΔE may be absorbed, this leads to spectral lines having a finite width known as the *natural linewidth*.

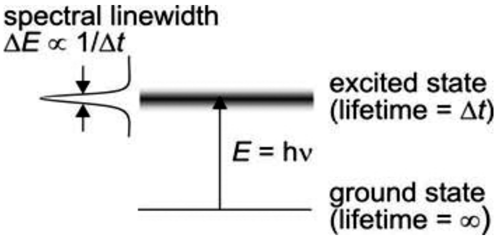


Fig. 6.18 Spectral lines

Kinetic processes involving excited states reduce their lifetime and cause further broadening.

Many such processes have first order kinetics, and in these cases the rate constant is simply equal to the reciprocal of the lifetime, $k = 1/\Delta t$. As a consequence, first order rate constants may be determined from measurements of spectral linewidths, provided that other sources of line broadening are absent. Lifetime techniques cover a broad range of timescales, from around 10-15s in photoelectron spectroscopy to around 1 s in NMR.

(ii) Techniques for monitoring concentrations as a function of time

For slow reactions, the composition of the reaction mixture may be analysed while the reaction is in progress either by withdrawing a small sample or by monitoring the bulk. This is known as a *real time analysis*. Another option is to use the *quenching method*, in which reaction is stopped at a certain time after initiation so that the composition may be analyzed at leisure. Quenching may be achieved in a number of ways. For example:

- sudden cooling
- adding a large amount of solvent
- rapid neutralisation of an acid reagent
- removal of a catalyst
- addition of a quencher

The key requirement is that the reaction must be slow enough (or the quenching method fast enough) for little reaction to occur during the quenching process itself.

Often, the real time and quenching techniques are combined by withdrawing and quenching small samples of the reaction mixture at a series of times during the reaction.

The composition of the reaction mixture may be followed in any one of a variety of different ways by tracking any chemical or physical change that occurs as the reaction proceeds. e.g

- For reactions in which at least one reactant or product is a gas, the reaction's progress may be followed by monitoring the pressure, or possibly the volume.
- For reactions involving ions, conductivity or pH measurements may often be employed.
- If the reaction is slow enough, the reaction mixture may be titrated.
- If one of the components is coloured then colourimetry may be appropriate.
- Absorption or emission spectroscopy are common (more on these later)
- For reactions involving chiral compounds, polarimetry (measurement of optical activity) may be useful.
- Other techniques include mass spectrometry, gas chromatography, NMR/ESR, and many more.

Fast reactions require a fast measurement technique, and as a consequence are usually monitored spectroscopically. A few commonly used techniques are outlined below.

1. Absorption spectroscopy – Beer Lambert Law

Also known as *spectrophotometry*, absorption spectroscopy is widely used to track reactions in which the reactants and products have different absorption spectra. A monochromatic light source, often a laser beam, is passed through the reaction mixture, and the ratio of transmitted to incident light intensity, I/I_0, is measured as a function of time. The quantity $T = I/I_0$ is known as the transmittance, and may be related to the changing concentration of the absorbing species using

$$\mathrm{T} = \frac{I}{I_0} = 10^{-\varepsilon cl} \qquad \text{or} \qquad \mathrm{T} = \frac{I}{I_0} = e^{-\alpha cl}$$

You may come across the Beer Lambert law in either of the forms above, or in log form

$$\log(I/I_0) = -\varepsilon cl \qquad \text{or} \qquad \ln(I/I_0) = -\alpha cl$$

In the above equations, c is the concentration of the absorbing species and l is the path length through the sample. ε and α are known as the molar absorption coefficient and molar exctinction coefficient, and are a measure of the strength of the spectral absorption. The quantity εcl is called the *absorbance*, A. Note that $A = -\log T$. You may also see this quantity referred to as the *optical density*.

2. Resonance fluorescence

Resonance fluorescence is a widely used technique for detecting atomic species such as H, N, O, Br, Cl or F. The light source is a discharge lamp filled with a mixture of helium and a molecular precursor for the atom of interest. A microwave discharge inside the lamp dissociates the precursor and produces a mixture of ground state and excited state atoms. The lamp then emits radiation at characteristic frequencies as the excited state atoms emit photons to relax down to the ground state. This radiation may be used to excite atoms of the same species present in a reaction mixture, and monitoring the intensity of radiation emitted from *these* atoms as they relax back to the ground state provides a measure of their concentration in the reaction mixture. To ensure that the detected light originates from atoms in the reaction mixture and not the lamp, the detector – usually a photomultiplier tube – is placed at right angles to the direction in which radiation exits the lamp.

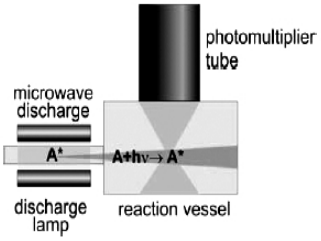


Fig.6.19 Resonance fluorescence

3. Laser-induced fluorescence

In laser-induced fluorescence a laser is used to excite a chosen species in a reaction mixture to an electronically excited state. The excited states then emit photons to return to the ground state, and the intensity of this fluorescent emission is measured. Because the number of excited states produced by the laser pulse is proportional to the number of ground state molecules present in the reaction mixture, the fluorescence intensity provides a measure of the concentration of the chosen species.

(iii) Temperature control and measurement

For any reaction with a non-zero activation energy, the rate constant is dependent on temperature.The temperature dependence is often modelled by the *Arrhenius equation*

$$k = A \exp(-E_a/RT)$$

Where Ea is the activation energy for the reaction, and A is a constant known as the preexponential factor.

This temperature dependence means that in order to measure an accurate value for k, the temperature of the reaction mixture must be maintained at a constant, known value. If activation energies are to be measured as part of the kinetic study, rate constants must be measured at a series of temperatures. The temperature is most commonly monitored using a thermocouple, due to its wide range of operation and potential for automation; however, standard thermometers are also commonly used.

There are numerous ways in which the temperature of a reaction mixture may be controlled. For example, reactions in the liquid phase may be carried out in a temperature-controlled thermostat, while reactions in the gas phase are usually carried out inside a stainless steel vacuum chamber, in which thermal equilibrium at the temperature of the chamber is maintained through collisions of the gas molecules with the chamber walls. High temperatures up to 1300 K may be obtained using conventional heaters. Low temperatures may be achieved by flowing cooled liquid through the walls of the reaction vessel, and very low temperatures may be reached by using cryogenic liquids such as liquid nitrogen (~77 K) or liquid helium (~4 K). Extremely low temperatures (down to a fewKelvin), such as those relevant to reactions in interstellar gas clouds, may be obtained bypreparing the reactant gases in a supersonic expansion .

6.10 Temperature Dependence of the Rate of a Reaction

Most of the chemical reactions are accelerated by increase in temperature. For example, in decomposition of N_2O_5, the time taken for half of the original amount of material to decompose is 12 min at 50^{o}C, 5 h at25^{o}C and 10 days at 0^{o}C. You also know that in a mixture of potassium permanganate ($KMnO_4$) and oxalic acid ($H_2C_2O_4$), potassium permanganate gets decolourised faster at a higher temperature than that at a lower temperature.

It has been found that for a chemical reaction with rise in temperature by 10°, the rate constant is nearly doubled.The temperature dependence of the rate of a chemical reaction can be accurately explained by Arrhenius equation. It was first proposed by Dutch chemist, J.H. van’t Hoff but Swedish chemist, Arrhenius provided its physical justification and interpretation.

$$k = \mathrm{A\ e}\ -E\mathrm{a}\ /RT$$

where *A* is the Arrhenius factor or the frequency factor. It is also called pre-exponential factor. It is a constant specific to a particular reaction. *R* is gas constant and *E*a is activation energy measured in joules/mole

$$k = \mathrm{A\ e}^{-E\mathrm{a}\ /RT}$$

It can be understood clearly using the following simple reaction

$$\mathrm{H_2\,(g) + I_2\,(g) \rightarrow 2HI\,(g)}$$

According to Arrhenius, this reaction can take place only when a molecule of hydrogen and a molecule of iodine collide to form an unstable intermediate (Fig.6.20). It exists for a very short time and then breaks up to form two molecules of hydrogen iodide.

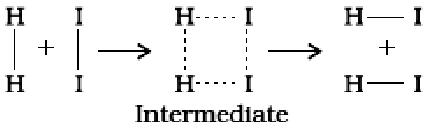


Fig.20 Formation of HI through the intermediate

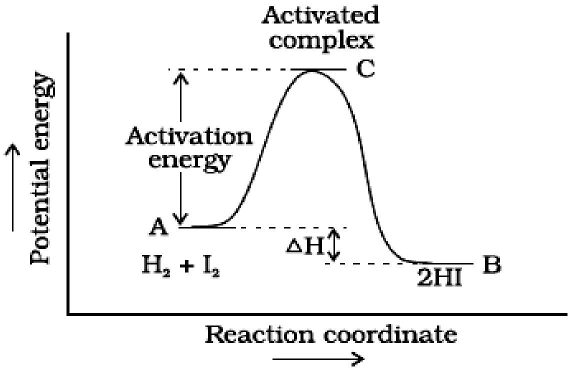


Fig.6.21 Potential energy vs reaction coordinate

The energy required to form this intermediate, called activated complex (C), is known as activation energy (*E*a). Fig 6.21 is obtained by plotting potential energy vs reaction coordinate. Reaction coordinate represents the profile of energy change when reactants change into products. Some energy is released when the complex decomposes to form products. So, the final enthalpy of the reaction depends upon the nature of reactants and products.

All the molecules in the reacting species do not have the same kinetic energy. Since it is difficult to predict the behaviour of any one molecule with precision, Ludwig Boltzmann and James Clark Maxwell used statistics to predict the behaviour of large number of molecules.

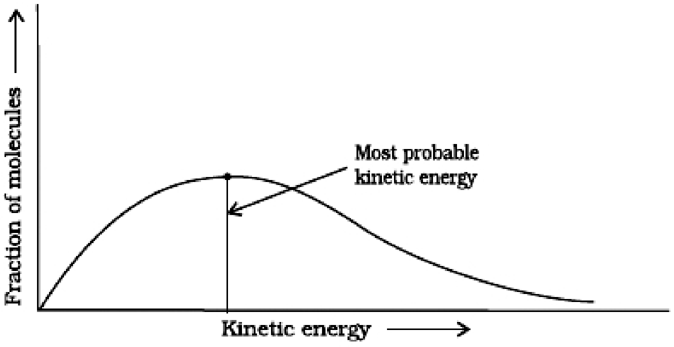


Fig. 6.22 Curve showing energies among gaseous molecules.

According to them, the distribution of kinetic energy may be described by plotting the fraction of molecules (*N*E/*NZ*) with a given kinetic energy (E) vs kinetic energy (Fig.6.22) Here, *N*E is the number of molecules with energy *E* and *N*T is total number of molecules. The peak of the curve corresponds to the most probable kinetic energy,i.e., kinetic energy of maximum fraction of molecules (Fig. 6.22). There are decreasing number of molecules with energies higher or lower than this value. When the temperature is raised, the maximum of the curve moves the higher energyvalue (Fig.6.23) and the curve broadens out, i.e., spreads to the right such that there is a greater proportion of molecules with much higher energies. The area under the curve must be constant since total probability must be one at all times. We can mark the position of *E*a on Maxwell Boltzmann distribution curve (Fig.23).

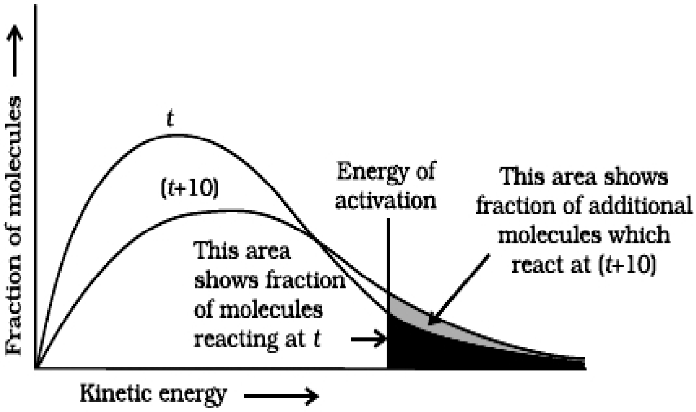


Fig.6.23 Distribution curve showing temperature dependence of rate of a reaction

Increasing the temperature of the substance increases the fraction of molecules, which collide with energies greater than *E*a. It is clear from the diagram that in the curve at (*t* + 10),the area showing the fraction of molecules having energy equal to or greater than energy of activation gets doubled leading to doubling the rate of a reaction

In the Arrhenius equation the factor e $^{-Ea/RT}$ corresponds to the fraction of molecules that have kinetic energy greater than *E*a.

Taking natural logarithm of both sides of equation

$$\ln k = -\frac{E_a}{RT} + \ln A \qquad (1)$$

The plot of ln *k* vs 1/T gives a straight line according to the equation (1) as shown in Fig.6.24. Thus, it has been found from Arrhenius equation that increasing the temperature or decreasing the activation energy will result in an increase in the rate of the reaction and an exponential increase in the rate constant.

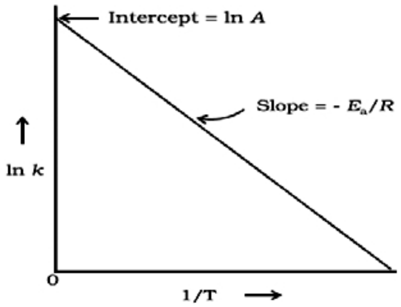


Fig. 6.24 : A plot between ln k and 1/T

In Fig.6.24 , slope = – a *E*/ *R* and intercept = ln *A*. So we can calculate *E*a and *A* using these values.

At temperature T_1, equation (1) is

$$\ln k_1 = -\frac{E_a}{RT_1} + \ln A \qquad (2)$$

At temperature T_2, equation (1) is

$$\ln k_2 = -\frac{E_a}{RT_2} + \ln A \qquad (3)$$

(Since *A* is constant for a given reaction) k_1 and k_2 are the values of rate constants at temperatures T_1 and T_2 respectively.

Subtracting equation (2) from (3), we obtain

$$\ln k_2 - \ln k_1 = \frac{E_a}{RT_1} - \frac{E_a}{RT_2}$$

$$\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \qquad (4)$$

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303\mathrm{R}}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

6.11 The Arrhenius equation and activation energies

It is found experimentally that the rate constants for many chemical reactions follow the Arrhenius equation.

$$k = A \exp(-E_a/RT) \quad \text{or equivalently} \quad \ln k = \ln A - \frac{E_a}{RT} \qquad (1)$$

where *A* is the pre-exponential factor and *E*a is the activation energy. These parameters may be determined from experimental rate data by plotting ln *k* against 1/*T*. This is known as an Arrhenius plot, and has an intercept of ln *A* and a slope of –*E*a/*R*. For most reactions, the Arrhenius equation works fairly well over at least a limited temperature range. However, there are often deviations.

These are generally due to the temperature dependence of the pre-exponential factor A (which you will cover in detail in statistical mechanics next year), but may also be due to more exotic effects, such as the influence of quantum mechanical tunnelling mechanisms on the reaction rate at low temperatures.

For an elementary reaction, both *E*a and *A* have definite physical meanings; in particular, the activation energy may be interpreted as the energy difference between the reactants and the transition state involved in the collision and associated chemical rearrangement (fig.6.25)

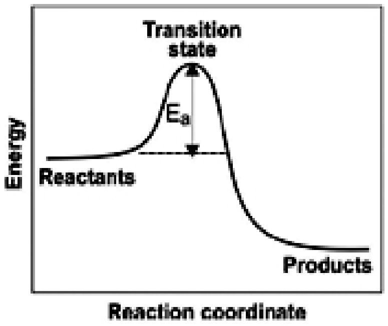


Fig. 6.25 Progress of reaction

When the Arrhenius equation is applied to the overall kinetics of a multi-step reaction, *E*a simply becomes an experimental parameter describing the temperature dependence of the overall reaction rate. *E*a may vary with temperature, and may take positive or negative values.

6.12 CollisionTheory of Chemical Reactions

Though Arrhenius equation is applicable under a wide range of circumstances, collision theory, which was developed by Max Trautz and William Lewis in 1916 -18, provides a greater insight into the energetic and mechanistic aspects of reactions. It is based on kinetic theory of gases. According to this theory, the reactant molecules are assumed to be hard spheres and reaction is postulated to occur when molecules collide with each other. The number of collisions per second per unit volume of the reaction mixture is known as collision frequency (Z). Another factor which affects the rate of chemical reactions is activation energy (as we have already studied). For a bimolecular elementary reaction

$$A + B \rightarrow \text{Products}$$

$$\text{Rate} = Z_{AB}e^{-E_a/RT} \qquad (1)$$

where Z_{AB} represents the collision frequency of reactants, A and B and $e^{-Ea/RT}$ represents the fraction of molecules with energies equal to or greater than E_a. Comparing (1) with Arrhenius equation, we can say that *A* is related to collision frequency.

Equation (1) predicts the value of rate constants fairly accurately for the reactions that involve atomic species or simple molecules but for complex molecules significant deviations are observed. The reason could be that all collisions do not lead to the formation of products. The collisions in which molecules collide with sufficient kinetic energy (called threshold energy) and proper orientation, so as to facilitate breaking of bonds between reacting species and formation of new bonds to form products are called as effective collisions.

For example, formation of methanol from bromoethane depends upon the orientation of reactant molecules as shown in Fig.6.26 . The proper orientation of reactant molecules lead to bond formation whereas improper orientation makes them simply bounce back and no products are formed.

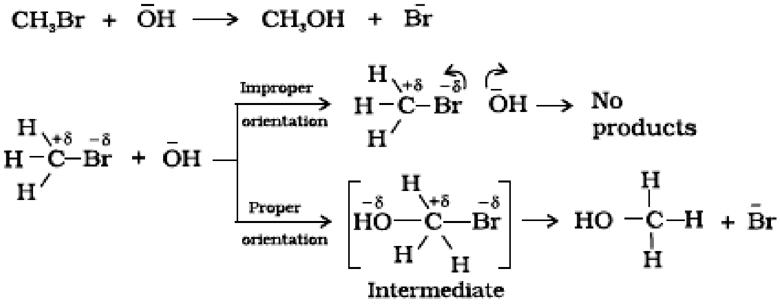


Fig.6.26 Diagram showing molecules having proper and improper orientation

To account for effective collisions, another factor *P*, called the probability or steric factor is introduced. It takes into account the fact that in a collision, molecules must be properly oriented i.e.,

$$\text{Rate} = PZ_{AB}e^{-E_a/RT}$$

Thus, in collision theory activation energy and proper orientation of the molecules together determine the criteria for an effective collision and hence the rate of a chemical reaction. Collision theory also has certain

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drawbacks as it considers atoms/molecules to be hard spheres and ignores their structural aspect.

6.13 Transition State Theory

The theory suggests that as reactant molecules approach each other closely they are momentarily in a less stable state than either the reactants or the products.

It takes a lot of energy to achieve the transition state, so the state is a high-energy state. The potential energy of the system increases at this point because:

- The approaching reactant molecules must overcome the mutual repulsive forces between the outer shell electrons of their constituent atoms
- Atoms must be separated from each other as bonds are broken

This increase in potential energy corresponds to an energy barrier over which the reactant molecules must pass if the reaction is to proceed. The transition state lies at the maximum of this energy barrier. The transition state is an unstable transitory combination of reactant molecules that occurs at a potential energy maximum. The combination can either go on to form products or fall apart to return to the unchanged reactants.

The energy difference between the reactants and the potential energy maximum is referred to as the activation energy.

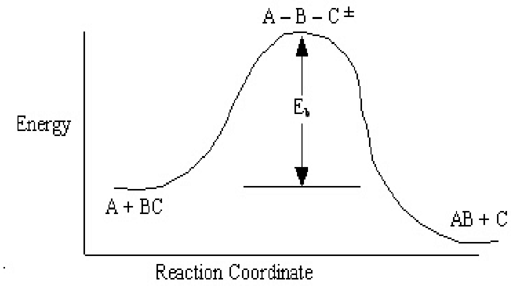


Fig.6.27 Formation of activated complex

In transition state theory an activated molecule is formed during the reaction at the transition state between forming products from reactants.

$$A+BC \longleftrightarrow A\text{-}B\text{-}C^{\#} \longrightarrow AB+C$$

The rate of reaction is equal to the product of the frequency, v_I, of the activated complex crossing the barrier and the concentration of the transition state complex

$$-r_A = v_I C_{ABC^{\#}}$$

The transition state molecule and the reactants are in pseudo equilibrium at the top of the energy barrier.

$$K_C^{\#} = \frac{C_{ABC^{\#}}}{C_A C_{BC}}$$

Combining

$$-r_A = v_I K_C^{\#} C_A C_{BC}$$

The fundamental assumption of this theory is that the transition state is in equilibrium with the reactants and products.

6.14 Expression for the rate constant

The relationship between forward and reverse rate constants for an equilibrium system is shown in an equilibrium constant expression and quantified by an equilibrium constant (***K***). An equilibrium constant expression is written by rearranging the equation relating forward and reverse reaction rates. When the rate of forward and reverse reaction rates is equal, the chemical system is at equilibrium and the ratio of forward and reverse rate constants is equal to the equilibrium constant, ***K***. For the $Fe(SCN)^{2+}$ equilibrium system, for example,

Rate (forward) = Rate (reverse)

$k_{forward}[Fe^{3+}][SCN^-] = k_{reverse}[FeSCN^{2+}]$

Note that because rate constants change with temperature, the equilibrium constant will also vary with temperature.

The magnitude of the equilibrium constant provides information about the relative rate constants of the forward and reverse reactions and the relative amounts of reactants and products at equilibrium.

- $K >> 1$

  A large value of ***K*** ($K >> 1$) means that at equilibrium, the concentration of products is much larger than the concentration of reactants. The rate constant for the forward reaction is much larger than the reverse reaction rate constant ($k_{forward} >> k_{reverse}$), and at equilibrium the system contains mostly products. This is called a product-favored reaction. For example, consider the product-favored reaction between gaseous iodine and chlorine:

  $I_2(g) + Cl_2(g) \rightleftarrows 2\ ICl(g) \qquad K = 2.1 \times 10^5$ at 25 °C

  This is a product-favored reaction, and at equilibrium there will very little I_2 or Cl_2 in the reaction flask.(Fig.6.28 a)

- ***K*** << 1

  A small value of ***K*** (***K*** << 1) means that at equilibrium, the concentration of reactants is much larger than the concentration of products. The rate constant for the reverse reaction is much larger than the forward reaction rate constant ($\boldsymbol{k}_{\text{reverse}} >> \boldsymbol{k}_{\text{forward}}$), and at equilibrium the system contains mostly reactants. This is called a reactant-favored reaction. For example, consider the reaction of acetic acid with water:

  $CH_3CO_2H(aq) + H_2O(\ell) \rightleftarrows CH_3CO_2^-(aq) + H_3O^+(aq)$ $\quad$ $\boldsymbol{K} = 1.8 \times 10^{-5}$ at 25 °C

  This is a reactant-favored reaction, and at equilibrium there will very little $CH_3CO_2^-$ or H_3O^+ in the reaction flask(Fig.6.28 b)

- K ≈ 1

  A value of ***K*** very close to 1 (***K*** ≈ 1) means that at equilibrium, significant amounts of both reactants and product are found in the reaction vessel. The rate constants for the forward and reverse reactions are comparable ($\boldsymbol{k}_{\text{forward}} \approx \boldsymbol{k}_{\text{reverse}}$), and at equilibrium the system contains a mixture of both reactants and products. For example, consider the dimerization of nitrogen dioxide to form dinitrogen tetraoxide:

  $2\ NO_2(g) \rightleftarrows N_2O_4(g)$ $\quad$ $\boldsymbol{K} = 1.4$ at 50 °C

  The equilibrium constant has a value close to 1, so at equilibrium significant amounts of both NO_2 and N_2O_4 will be found in the reaction flask.

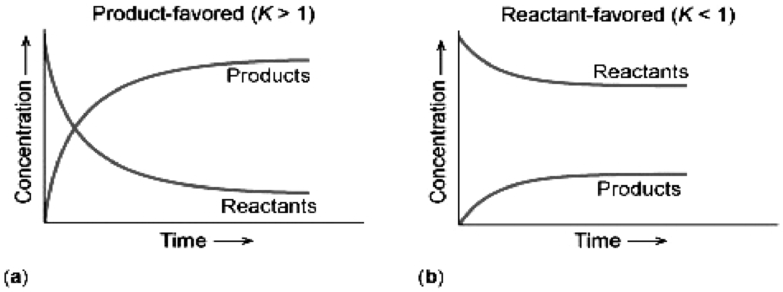


Fig.6.28 Graphical representations of (a) product-favored and (b) reactant-favored chemical reactions.

6.15 Characteristics of Catalytic Reactions

(i) The catalyst remains unchanged in amount and chemical composition at the end of the reaction; it may, however, undergo considerable change in physical form.

(ii) A small quantity of the catalyst is capable of producing the desired effect.

(iii) The action of a catalyst is specific to a large extent. Thus, the decomposition of $KClO_3$ is catalyzed by MnO_2 but not by platinum.

(iv) The catalyst does not initiate a reaction; it merely accelerates the reaction that is already occurring.

(v) A catalyst does not alter the final state of equilibrium in a reversible reaction. It only hastens the approach of equilibrium.

A certain minimum energy must be possessed by the reactants so that they may react and produce the products. This is called the activation energy (Ea) for the reaction. A catalyst is said to lower the activation energy and thus increase the rate of the reaction.(Fig.6.29)

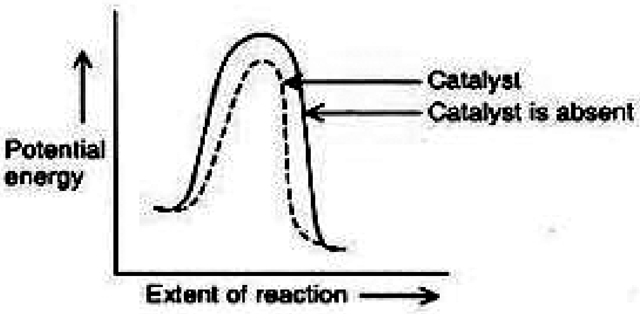


Fig. 6.29 Change in rate with catalyst

6.16 Classification of catalysis

Catalytic agent or a catalyst is a substance which alters the rate of reaction without itself being changed permanently. This process of changing the rate of chemical reaction by the catalyst is commonly known as catalysis, which can be classified as.

(1) Positive catalysis:- A positive catalyst is that which increases the rate of reaction while this process is known as positive catalysis

(2) Negative catalysis:- A negative catalyst is that which retards the rate of chemical reaction and this process is known as negative catalysis

(3) Auto-catalysis:-When one of the products formed acts as a catalyst for that reaction. This is known as Auto-catalysis

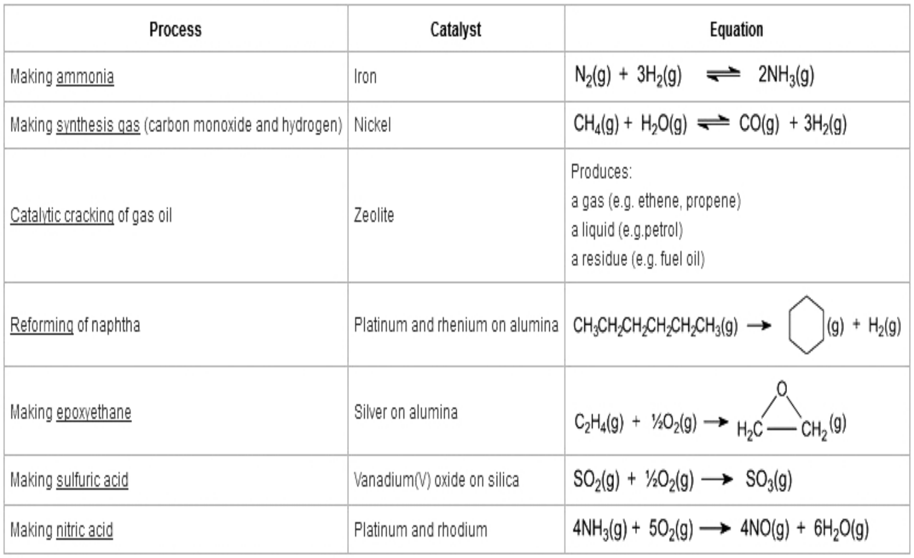
(4) Induced catalysis:-The phenomenin in which one reaction induces another reaction is known as induced catalysis

6.17 Industrial catalysts

Much fundamental and applied research is done by industrial companies and university research laboratories to find out how catalysts work and to improve their effectiveness. If catalytic activity can be improved, it may be possible to lower the temperature and/or the pressure at which the process operates and thus save fuel which is one of the major costs in a large-scale chemical process. Further, it may be possible to reduce the amount of reactants that are wasted forming unwanted by-products.

Thus, a catalyst increases the rate of a reaction by providing a pathway whose activation energy is lower than the activation energy of the uncatalysed reaction.

Table 6.1 Examples of industrial processes using heterogeneous catalysis.



Process	Catalyst	Equation
Making ammonia	Iron	$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
Making synthesis gas (carbon monoxide and hydrogen)	Nickel	$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$
Catalytic cracking of gas oil	Zeolite	Produces: a gas (e.g. ethene, propene) a liquid (e.g.petrol) a residue (e.g. fuel oil)
Reforming of naphtha	Platinum and rhenium on alumina	$CH_3CH_2CH_2CH_2CH_2CH_3(g) \rightarrow$ (g) + $H_2(g)$
Making epoxyethane	Silver on alumina	$C_2H_4(g) + ½O_2(g) \rightarrow$ O H_2C—CH_2 (g)
Making sulfuric acid	Vanadium(V) oxide on silica	$SO_2(g) + ½O_2(g) \rightarrow SO_3(g)$
Making nitric acid	Platinum and rhodium	$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$

Some of the large chemical processes that use catalysis

6.17.1 Water-gas shift (WGS) reaction

The water gas shift reaction was first used industrially in the beginning of the 20th century. Today the WGS reaction is used primarily to produce hydrogen that can be used for further production of methanol and ammonia.

WGS reaction:

(1) $CO + H_2O \leftrightarrow H_2 + CO_2$

The reaction refers to carbon monoxide (CO) that reacts with water (H_2O) to form carbon dioxide (CO_2) and hydrogen (H_2). The reaction is exothermic with $\Delta H = -41.1$ kJ/mol and have an adiabatic temperature rise of 8–10 °C per percent CO converted to CO_2 and H_2.

The most common catalysts used in the water-gas shift reaction are the high temperature shift (HTS) catalyst and the low temperature shift (LTS) catalyst. The HTS catalyst consists of iron oxide stabilized by chromium oxide, while the LTS catalyst is based on copper. The main purpose of the LTS catalyst is to reduce CO content in the reformate which is especially important in the ammonia production for high yield of H_2. Both catalysts are necessary for thermal stability, since using the LTS reactor alone increases exit-stream temperatures to unacceptable levels.

The equilibrium constant for the reaction is given as:

(2) $K_p=(p_{H2} \text{ x } p_{CO2})/ (p_{CO} \text{ x } p_{H2O})$

(3) $K_p=e^{((4577.8K/T-4.22))}$

Low temperatures will therefore shift the reaction to the right, and more products will be produced. The equilibrium constant is extremely dependent on the reaction temperature, for example the Kp is equal to 228 at 200 °C, but only 11.8 at 400 °C. The WGS reaction can be performed both homogenously and heterogeneously, but only the heterogeneously way is used commercially.

1. High temperature shift (HTS) catalyst

The first step in the WGS reaction is the high temperature shift which is carried out at temperatures between 320 °C and 450 °C. As mentioned before, the catalyst is a composition of iron-oxide, Fe_2O_3(90-95%), and chromium oxides Cr_2O_3 (5-10%) which have an ideal activity and selectivity at these temperatures. When preparing this catalyst, one of the most important step is washing to remove sulfate that can turn into hydrogen sulfide and poisons the LTS catalyst later in the process. Chromium is added to the catalyst to stabilize the catalytic activity over time and to delay sintering of iron oxide. Sintering will decrease the active catalyst area, so by decreasing the sintering rate the lifetime of the catalyst will be extended. The catalyst is usually used in pellets form, and the size play an important role. Large pellets will be strong, but the reaction rate will be limited.

In the end, the dominate phase in the catalyst consist of Cr^{3+} in α-Fe_2O_3 but the catalyst is still not active. To be active α-Fe_2O_3 must be reduced to Fe and CrO_3 must be reduced to Cr in presence of H_2. This usually happens in the reactor start-up phase and because the reduction reactions are exothermic the reduction should happen under controlled circumstances. The lifetime of the iron-chrome catalyst is approximately 3–5 years, depending on how the catalyst is handled.

2. Low temperature shift (LTS) catalyst

The low temperature process is the second stage in the process, and is designed to take advantage of higher hydrogen equilibrium at low temperatures. The reaction is carried out between 200 °C and 250 °C, and the most commonly used catalyst is based on copper. While the HTS reactor used an iron-chrome based catalyst, the copper-catalyst is more active at lower temperatures thereby yielding a lower equilibrium concentration of CO and a higher equilibrium concentration of H_2. The disadvantage with a copper catalysts is that it is very sensitive when it comes to sulfide poisoning, a future use of for example a cobaltmolybdenum catalyst could solve this problem. The catalyst mainly used in the industry today is a copper-zinc-alumina ($Cu/ZnO/Al_2O_3$) based catalyst.

Also the LTS catalyst has to be activated by reduction before it can be used. The reduction reaction $CuO + H_2 \rightarrow Cu + H_2O$ is highly exothermic and should be conducted in dry gas for an optimal result.

4. Carbon Monoxide

CO must be produced for the WGS reaction to take place. This can be done in different ways from a variety of carbon sources such as:

-passing steam over coal:

$C + H_2O = CO + H_2$

-steam reforming methane, over a nickel catalyst:

$CH_4 + H_2O = CO + 3H_2$

-or by using biomass. Both the reactions shown above are highly endothermic and can be coupled to an exothermic partial oxidation. The products of CO and H_2 are known as syngas

When dealing with a catalyst it is common to assume that the intermediate CO-Metal is formated before the intermediate reacts further into the products. The strength of interaction between the CO molecule and the metal should be strong enough to provide a sufficient concentration of the intermediate, but not so strong that the reaction will not continue.

6.18 Enzyme kinetics

Enzymes are protein catalysts that, like all catalysts, speed up the rate of a chemical reaction without being used up in the process.

They achieve their effect by temporarily binding to the substrate and, in doing so, lowering the activation energy needed to convert it to a product.

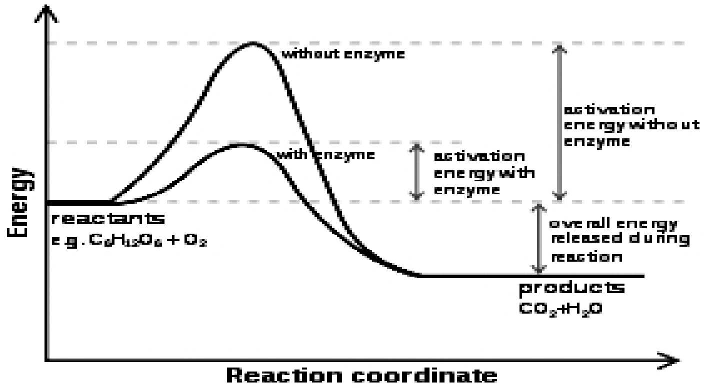


Fig. 6.30 enzymatic rate of reaction

The rate at which an enzyme works is influenced by several factors, e.g.,

1 the concentration of substrate molecules (the more of them available, the quicker the enzyme molecules collide and bind with them). The concentration of substrate is designated **[S]** and is expressed in units of molarity.

2 the temperature. As the temperature rises, molecular motion — and hence collisions between enzyme and substrate — speed up. But as enzymes are proteins, there is an upper limit beyond which the enzyme becomes denatured and ineffective.

3 the presence of inhibitors.

- competitive inhibitors are molecules that bind to the same site as the substrate — preventing the substrate from binding as they do so — but are not changed by the enzyme.
- noncompetitive inhibitors are molecules that bind to some other site on the enzyme reducing its catalytic power.

4 pH. The conformation of a protein is influenced by pH and as enzyme activity is crucially dependent on its conformation, its activity is likewise affected.

The study of the rate at which an enzyme works is called enzyme kinetics. Let us examine enzyme kinetics as a function of the concentration of substrate available to the enzyme.

1 We set up a series of tubes containing graded concentrations of substrate, **[S]**.

2 At time zero, we add a fixed amount of the enzyme preparation.

3 Over the next few minutes, we measure the concentration of product formed. If the product absorbs light, we can easily do this in a spectrophotometer.

4 Early in the run, when the amount of substrate is in substantial excess to the amount of enzyme, the rate we observe is the initial velocity of $\mathbf{V_i}$. Plotting $\mathbf{V_i}$ as a function of **[S]**, we find that

- At low values of **[S]**, the initial velocity,$\mathbf{V_i}$, rises almost linearly with increasing **[S]**.
- But as **[S]** increases, the gains in $\mathbf{V_i}$ level off (forming a rectangular hyperbola).
- The asymptote represents the maximum velocity of the reaction, designated $\mathbf{V_{max}}$
- The substrate concentration that produces a $\mathbf{V_i}$ that is one-half of $\mathbf{V_{max}}$ is designated the Michaelis-Menten constant, $\mathbf{K_m}$

(named after the scientists who developed the study of enzyme kinetics).

K_m is (roughly) an inverse measure of the affinity or strength of binding between the enzyme and its substrate. The lower the **K_m**, the greater the affinity (so the lower the concentration of substrate needed to achieve a given rate).

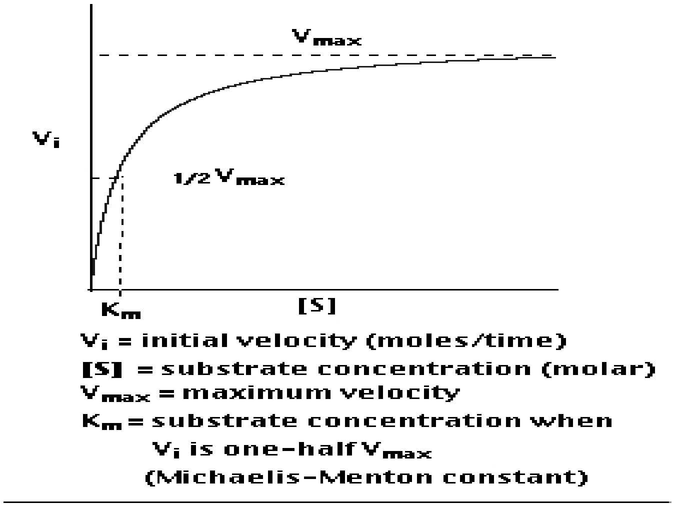


Fig 6.31 Vi as function of S

6.18 .1 The Effects of Enzyme Inhibitors

Enzymes can be inhibited

- **competitively**, when the substrate and inhibitor compete for binding to the same active site or
- **noncompetitively**, when the inhibitor binds somewhere else on the enzyme molecule reducing its efficiency.

The distinction can be determined by plotting enzyme activity with and without the inhibitor present.

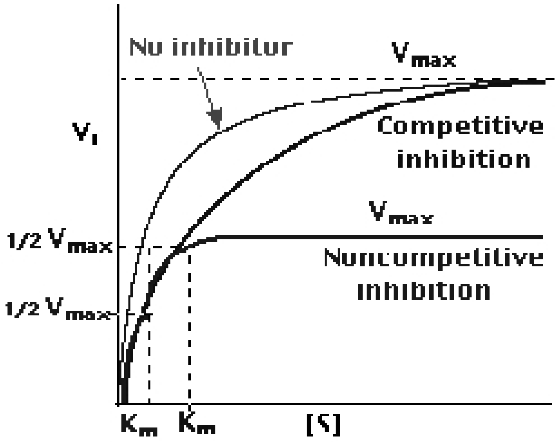


Fig.6.32(a) Lineweaver-Burk plot

1. **Competitive Inhibition**

In the presence of a competitive inhibitor, it takes a higher substrate concentration to achieve the same velocities that were reached in its absence. So while $\mathbf{V_{max}}$ can still be reached if sufficient substrate is available, one-half $\mathbf{V_{max}}$ requires a higher **[S]** than before and thus $\mathbf{K_m}$ is larger.

2. **Noncompetitive Inhibition**

With noncompetitive inhibition, enzyme molecules that have been bound by the inhibitor

are taken out of the game so enzyme rate (velocity) is reduced for all values of **[S]**, including

- $\mathbf{V_{max}}$ and one-half $\mathbf{V_{max}}$ but
- $\mathbf{K_m}$ remains unchanged because the active site of those enzyme molecules that have not been inhibited is unchanged.

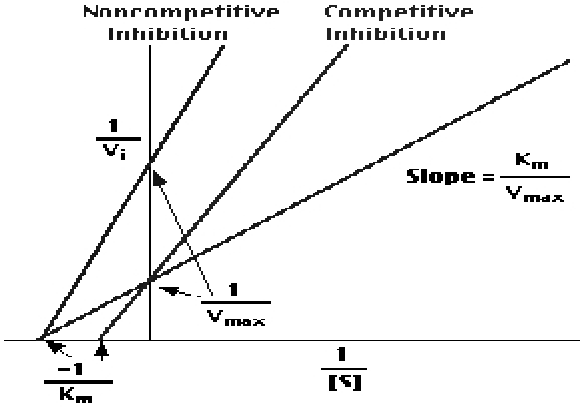


Fig. 6.32 (b) Lineweaver-Burk plot

6.18 Summary

Chemical kinetics is the study of chemical reactions with respect to reaction rates, effect of various variables, rearrangement of atoms and formation of intermediates. The rate of a reaction is concerned with decrease in concentration of reactants or increase in the concentration of products per unit time. It can be expressed as instantaneous rate at a particular instant of time and average rate over a large interval of time. A number of factors such as temperature, concentration of reactants, catalyst, affect the rate of a reaction. Mathematical representation of rate of a reaction is given by rate law. It has to be determined experimentally and cannot be predicted. Order of a reaction with respect to a reactant is the power of its concentration which appears in the rate law equation.

The order of a reaction is the sum of all such powers of concentration of terms for different reactants. Rate constant is the proportionality factor in the rate law.Rate constant and order of a reaction can be determined from rate law or its integrated rate equation. Temperature dependence of rate constants is described by Arrhenius equation ($k = Ae^{-Ea/RT}$). Ea corresponds to the activation energy and is given by the energy difference between activated complex and the reactant molecules, and A (Arrhenius factor or pre-exponential factor) corresponds to the collision frequency. The equation clearly shows that increase of temperature or lowering of Ea will lead to an increase in the rate of reaction and presence of a catalyst lowers the activation energy by providing an alternate path for the reaction. According to collision theory, another factor P called steric factor which refers to the orientation of molecules which collide, is important and contributes to effective collisions, thus, modifying the Arrhenius equation to $k = PZ_{AB}e^{-Ea/RT}$

6.19 Terminal Question

1. Discuss following method of determination of order of reaction.

(i) isolation method (ii) Half life method

2. Derive integrated rate equation for the second order reaction having same reactant.

3. What information can be drawn from the magnitude of the equilibrium constant?

4. The following data were obtained during the first order thermal decomposition of N2O5 (g) at constant volume:

$2N_2O_5\,(g) \rightarrow 2N_2O_4\,(g) + O_2\,(g)$

S.No.	Time/s	Total Pressure/(atm)
1.	0	0.5
2.	100	0.512

Calculate the rate constant

5. The rate constants of a reaction at 500K and 700K are $0.02s^{-1}$ and $0.07s^{-1}$ respectively. Calculate the values of Ea and A.

6.20 Answers

1. A kinetics experiment consists of measuring the concentrations of one or more reactants or products at a number of different times during the reaction. In the present section, we will look at the methods that allow us to use the experimental data to determine the reaction orders with respect to each reactant, and therefore the rate law.

(i) Isolation method

The isolation method is a technique for simplifying the rate law in order to determine its dependence on the concentration of a single reactant. Once the rate law has been simplified, the differential or integral methods discussed in the following subsections may be used to determine the reaction orders.

The dependence of the reaction rate on the chosen reactant concentration is isolated by having all other reactants present in a large excess, so that their concentration remains essentially constant throughout the course of the reaction. As an example, consider a reaction A + B → P, in which B is present at a concentration 1000 times greater than A. When all of species A has been used up,the concentration of B will only have changed by 1/1000, or 0.1%, and so 99.9% of the original B will still be present. It is therefore a good approximation to treat its concentration as constant throughout the reaction.This greatly simplifies the rate law since the (constant) concentrations of all reactants present in large excess may be combined with the rate constant to yield a single *effective rate constant*. For example, the rate law for the reaction considered above will become:

$$\nu = k\,[A]^a[B]^b \approx k\,[A]^a[B]_0{}^b = k_{\text{eff}}[A]^a \quad \text{with} \quad k_{\text{eff}} = k[B]_0{}^b$$

When the rate law contains contributions from a number of reactants, a series of experiments may be carried out in which each reactant is isolated in turn.

(ii) Half lives

Another way of determining the reaction order is to investigate the behaviour of the half life as the reaction proceeds. Specifically, we can measure a series of successive half lives. $t = 0$ is used as the start time from which to measure the first half life, $t_{1/2(1)}$. Then $t_{1/2(1)}$ is used as the start time from which to measure the second half life, $t_{1/2(2)}$, and so on.

$$\textit{Zeroth order} \qquad t_{1/2} = \frac{[A]_0}{2k}$$

Since at $t_{1/2(1)}$, the new starting concentration is ½$[A]_0$, successive half lives will decrease by a factor of two for a zeroth order reaction.

$$\textit{First order} \qquad t_{1/2} = \frac{\ln 2}{k}$$

There is no dependence of the half life on concentration, so $t_{1/2}$ is constant for a first order reaction.

$$\textit{Second order} \qquad t_{1/2} = \frac{1}{k[A]_0}$$

The inverse dependence on concentration means that successive half lives will double for a second order reaction.

2. Case 1: A + A → P

$$2A \longrightarrow P$$

The rate at which A decreases can be expressed using the **differential rate equation**.

$$-\frac{d[A]}{dt} = k[A]^2$$

The equation can then be rearranged:

$$\frac{d[A]}{[A]^2} = -kdt$$

Since we are interested in the change in concentration of A over a period of time, we integrate between t = 0 and t, the time of interest.

$$\int_{[A]_o}^{[A]_t} \frac{d[A]}{[A]^2} = -k\int_0^t dt$$

To solve this, we use the following rule of integration:

$$\int \frac{dx}{x^2} = -\frac{1}{x} + constant$$

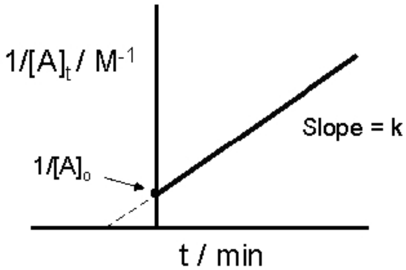
We then obtain the **integrated rate equation**.

$$\frac{1}{[A]_t} - \frac{1}{[A]_o} = kt$$

Upon rearrangement of the integrated rate equation, we obtain an equation of the line:

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_o}$$

The crucial part of this process is not understanding precisely how to derive the integrated rate law equation, rather it is important to understand how the equation directly relates to the graph which provides a linear relationship. In this case, and for all second order reactions, the linear plot of 1/[*A*]*t* versus time will yield the graph below.



This graph is useful in a variety of ways. If we only know the concentrations at specific times for a reaction, we can attempt to create a graph similar to the one above. If the graph yields a straight line, then the reaction in question must be second order. In addition, with this graph we can find the slope of the line and this slope is k, the reaction constant. The slope can be found be finding the "rise" and then dividing it by the "run" of the line. For an example of how to find the slope, please see the example section below. There are alternative graphs that could be drawn.

The plot of $[A]t$ versus time would result in a straight line if the reaction was zeroth order. It does, however, yield less information for a second order graph. This is because both the graphs of a first or second order reaction would look like exponential decays. The only obvious difference, as seen in the graph below, is that the concentration of reactants approaches zero more slowly in a second-order, compared to that in a first order reaction.

3. The magnitude of the equilibrium constant provides information about the relative rate constants of the forward and reverse reactions and the relative amounts of reactants and products at equilibrium.

- $\boldsymbol{K} >> 1$

A large value of $\boldsymbol{K}$ ($\boldsymbol{K} >> 1$) means that at equilibrium, the concentration of products is much larger than the concentration of reactants. The rate constant for the forward reaction is much larger than the reverse reaction rate constant ($\boldsymbol{k}_{\text{forward}} >> \boldsymbol{k}_{\text{reverse}}$), and at equilibrium the system contains mostly products. This is called a product-favored reaction. For example, consider the product-favored reaction between gaseous iodine and chlorine:

$$I_2(g) + Cl_2(g) \rightleftharpoons 2\ ICl(g) \qquad \boldsymbol{K} = 2.1 \times 10^5 \text{ at } 25\ °C$$

This is a product-favored reaction, and at equilibrium there will very little I_2 or Cl_2 in the reaction flask.

- $\boldsymbol{K} << 1$

A small value of $\boldsymbol{K}$ ($\boldsymbol{K} << 1$) means that at equilibrium, the concentration of reactants is much larger than the concentration of products. The rate constant for the reverse reaction is much larger than the forward reaction rate constant ($\boldsymbol{k}_{\text{reverse}} >> \boldsymbol{k}_{\text{forward}}$), and at equilibrium the system contains mostly reactants. This is called a reactant-favored reaction. For example, consider the reaction of acetic acid with water:

$$CH_3CO_2H(aq) + H_2O(\ell) \rightleftharpoons CH_3CO_2^-(aq) + H_3O^+(aq)\ \boldsymbol{K} = 1.8 \times 10^{-5} \text{ at } 25\ °C$$

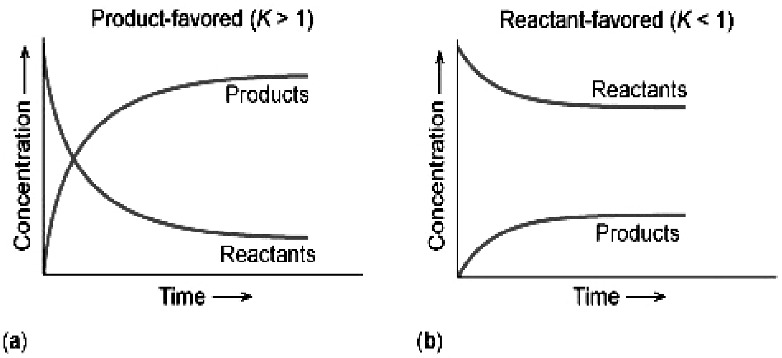
This is a reactant-favored reaction, and at equilibrium there will very little $CH_3CO_2^-$ or H_3O^+ in the reaction flask.

- $K \approx 1$

A value of $\boldsymbol{K}$ very close to 1 ($\boldsymbol{K} \approx 1$) means that at equilibrium, significant amounts of both reactants and product are found in the reaction vessel. The rate constants for the forward and reverse reactions are comparable ($\boldsymbol{k}_{\text{forward}} \approx \boldsymbol{k}_{\text{reverse}}$), and at equilibrium the system contains a mixture of both reactants and products. For example, consider the dimerization of nitrogen dioxide to form dinitrogen tetraoxide:

$2\,NO_2(g) \rightleftharpoons N_2O_4(g) \qquad \boldsymbol{K} = 1.4$ at 50 °C

The equilibrium constant has a value close to 1, so at equilibrium significant amounts of both NO_2 and N_2O_4 will be found in the reaction flask.



Graphical representations of (a) product-favored and (b) reactant-favored chemical reactions.

4

Let the pressure of $N_2O_5(g)$ decrease by 2x atm. As two moles of N_2O_5 decompose to give two moles of $N_2O_4(g)$ and one mole of O_2 (g), the pressure of N_2O_4 (g) increases by 2x atm and that of O_2 (g) increases by x atm.

	$2N_2O_5(g)$	$\rightarrow$	$2N_2O_4(g)$	+	$O_2(g)$
Start $t = 0$	0.5 atm		0 atm		0 atm
At time t	(0.5 – 2x) atm		2x atm		x atm

$$p_t = p_{N_2O_5} + p_{N_2O_4} + p_{O_2}$$

$$= (0.5 - 2x) + 2x + x = 0.5 + x$$

$$x = p_t - 0.5$$

$$p_{N_2O_5} = 0.5 - 2x$$

$$= 0.5 - 2\,(p_t - 0.5) = 1.5 - 2p_t$$

At $t = 100$ s; $p_t = 0.512$ atm

5.

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

$$\log\frac{0.07}{0.02} = \left(\frac{E_a}{2.303 \times 8.314\,JK^{-1}mol^{-1}}\right)\left[\frac{700-500}{700 \times 500}\right]$$

$$0.544 = E_a \times 5.714 \times 10^{-4}/19.15$$

$$E_a = 0.544 \times 19.15/5.714 \times 10^{-4} = 18230.8 \text{ J}$$

Since $k = Ae^{-E_a/RT}$

$$0.02 = Ae^{-18230.8/8.314 \times 500}$$

$$A = 0.02/0.012 = 1.61$$

Reference Books

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4. Reaction Kinetics by M. J. Pilling and P. W. Seakins