

# PHYSICAL CHEMISTRY –I

## 18KP2CH06

### Unit – I

#### 2 Marks

1. What is symmetry?
2. What is order of group?
3. What is group?
4. What is abelian group
5. What is closure rule?
6. What is representation?
7. Write the symmetry elements of Naphthalene?
8. What is cycloc group?
9. What is rearrangement theorem?

#### 5 Marks

1. Define symmetry operation and symmetry element?
2. Show that the distinct operation generated by the symmetry elements  $C_4$  and E constitute mathematical group?
3. Show that the symmetry operation of water molecule form a abelian group?
4. Construct the group multiplication table for  $C_{3v}$  point group.

#### 10 Marks

1. State great orthogonality theorem and explain its consequences.
2. Find the symmetries of normal nodes of vibration of water molecule using group theory.
3. Deduce the hybridisation of carbon in methane by using group theory.

## **SYMMETRY ELEMENTS AND SYMMETRY OPERATIONS**

### **IMPORTANCE OF SYMMETRY**

Symmetry is a familiar concept in our world. Symmetry means that a certain portion of an object looks exactly like another portion of the same object.

Symmetry plays an important role in molecular spectroscopy, in quantum mechanics as well as in the determination of structure of molecules and understanding of stereochemistry. A thorough knowledge of the structure, shape and symmetry of molecules and an overall understanding of the symmetry and mechanisms of reactions leads to efficient designing of asymmetric syntheses which are vital in chemical, pharmaceutical and polymer industries.

The systematic discussion of symmetry is called group theory. This theory simple and direct method for arriving at useful conclusions with minimum calculations about the geometry and electronic structure of molecules. The frontier molecular orbital theory and the correlation method which are useful in predicting the 'allowedness' of the synthetically challenging pericyclic reactions are mainly based on group theory. The ligand field theory is also supported by group theory.

To understand the various symmetry elements present in a molecule, it is necessary to have some basic knowledge about the geometry of various molecules. This can be obtained from the Valence Shell Electron Pair Repulsion Theory (VSEPR).

### **SYMMETRY ELEMENTS**

Symmetry elements are defined as imaginary geometrical entities such as points, lines and planes that are present in a molecule, about which when symmetry operations are performed, the molecule presents an indistinguishable configuration. The nature of symmetry elements present in any molecule depends on its geometry.

#### **What are indistinguishable configurations?**

These are spatial arrangements which cannot be distinguished from one another. The two configurations are alike in all respects (but are not exactly identical) and it is difficult to predict if any change has been carried out or not. However, they can be differentiated by introducing

appropriate suffixes in the form of numbers or letters. For example, configurations I and II (Fig. 1.1) are indistinguishable but for the suffixes 1 and 2 on the B atoms.

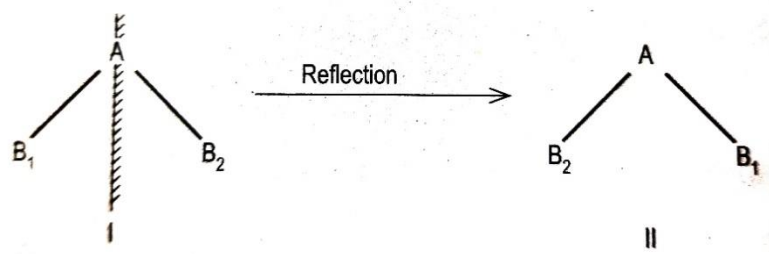


Fig 1.1

### Symmetry operations

These are simple geometric operations such as reflection, rotation or inversion which when performed on the molecule, give rise to an indistinguishable configuration of the same molecule. Thus, the presence of symmetry elements in a molecule can be identified by performing the appropriate symmetry operations (Table 1.2).

Types of symmetry elements and their corresponding symmetry operations

Symmetry element	Corresponding symmetry operation
Identity element (E) or (I)	doing nothing ( $360^\circ$ rotation)
Plane of symmetry ( $\sigma$ )	reflection
Centre of symmetry (i)	inversion of all coordinates
Proper axis of symmetry ( $C_n$ )	rotation through an angle of $\left(\frac{360}{n}\right)^\circ$ about an axis where n is the order of the axis
Improper axis of symmetry ( $S_n$ )	rotation through an angle of $\left(\frac{360}{n}\right)^\circ$ about an axis followed by reflection about a plane perpendicular to the original axis.

### Identity element (E)

The identity element is present in all molecules. Identity is the operation of not doing anything. When a molecule is not operated upon by any symmetry element, the system is left unchanged and the configuration of the molecule is identical with the original configuration. Thus, the molecule is said to possess the identity element. It is denoted by the symbol E. Though it may appear that this element does not have any significance, its mathematical relevance will be clear as we proceed further.

### **Plane of Symmetry ( $\sigma$ )**

When reflection is carried out about an imaginary plane in a molecule and if the molecule presents an indistinguishable configuration, the plane is called a plane of symmetry. It is represented by  $\sigma$ . A molecule may have one or several planes of symmetry or may not have any such plane. Let us identify the symmetry planes present in molecules possessing different geometries.

### **Centre of symmetry ( $i$ )**

When the coordinates  $(x,y,z)$  of every atom in a molecule are changed into  $(-x,-Y,-z)$  and even after that, if the molecule presents an indistinguishable configuration, then the point of origin  $(0,0,0)$  is called the *centre of symmetry* of the molecule. That is, if an imaginary line is drawn from an atom to the centre of the molecule and extended on the other side by the same distance and meets a similar atom, the molecule is said to possess a centre of symmetry or a centre of inversion. For example a cube, a sphere and an octahedron possess a centre of symmetry whereas a triangle and a pyramid do not.

Let us identify the centre of symmetry in molecules of different geometries. After inversion, atoms generally shift to their exact diagonally opposite positions. So, whenever diagonally opposite atoms are the same in a molecule, will have a centre of symmetry and vice versa.

### **Proper axis of symmetry ( $C_n$ )**

A proper axis of symmetry is defined as an imaginary axis present in a molecule about which, when the molecule is rotated through an angle of  $(360/n)^\circ$ , the molecule presents an indistinguishable configuration. Here,  $n$  represents the order of the axis and can take whole

number values. When  $n=2$ , the axis is referred to as the  $C_2$ , or the diad axis; when  $n = 3$ , the axis is referred to as the  $C_3$  or the triad axis and so on.

**Proper axis of symmetry (C)** A proper axis of symmetry is defined as an imaginary axis present in a molecule about which, when the molecule is rotated through an angle of  $(360/n)^\circ$ , the molecule presents an indistinguishable configuration. Here,  $n$  represents the order of the axis and can take whole number values. When  $n=2$ , the axis is referred to as the  $C_2$ , or the diad axis; when  $n = 3$ , the axis is referred to as the  $C_3$  or the triad axis and so on.

### **Improper axis of symmetry ( $S_n$ )**

When a molecule is rotated about an axis through an angle of  $360^\circ/n$ , followed by reflection about a plane perpendicular to the originally chosen axis, if it presents an indistinguishable configuration, it is said to possess an improper axis of symmetry. This axis is represented by  $S_n$ . Molecules having an improper axis of symmetry can be classified into two types.

- Molecules having both, an axis of symmetry ( $C_n$ ) and a perpendicular plane of symmetry ( $\sigma$ ).
- Molecules having neither an axis of symmetry nor a plane of symmetry but having only an improper axis of symmetry ( $S_n$ ).

## **PRODUCT OF SYMMETRY OPERATIONS**

The product of any two symmetry operations is also a symmetry operation. The product depends on the order in which the symmetry operations are carried out. Generally, the order in which symmetry operations are performed is represented from right to left.

For example, if the symmetry operation  $A$  is carried out first followed by  $B$ , it is represented as  $B \times A$ .

### **Determination of the Product of Symmetry Operations**

The product of symmetry operations can be determined either by choosing a point with its respective coordinates (Method 1) or an appropriate molecule (Method 2) or through a matrix (Method 3). All these methods can also be extended to determine the product of more than two symmetry operations.

## Commutative Symmetry Operations

Two symmetry operations A and B are said to be commutative when the product of these two symmetry operations remains the same irrespective of the order in which they are carried out.

That is,

$$A \times B = BA = C$$

To find out whether  $\sigma_{xz}$  and  $\sigma_{xy}$  are commutative, the two binary products  $\sigma_{xz} \times \sigma_{xy}$  and  $\sigma_{xy} \times \sigma_{xz}$  are determined. If the products are the same, then these two operations are said to be commutative.

## GROUP

A group is defined as any set or collection of elements which obey a certain set of mathematical rules and are related to each other by certain rules. The elements could be numbers, matrices, vectors, roots of an equation or symmetry elements.

- All positive and negative whole numbers together with zero form a group under the combining operation of addition.
- Elements 1, -1, i, -i (where  $i = \sqrt{-1}$ ) form a group under multiplication.
- All powers of two  $\dots 2^{-2}, 2^{-1}, 2^0, 2^1, 2^2 \dots$  form an infinite group under multiplication.

## MATHEMATICAL RULES FOR THE FORMATION OF A GROUP

- The combination of any two members of a group and the square of every member of a group should also be a member of that group (this is known as the closure property). Let A and B be the members of a group under the multiplication operation. If A multiplied by B gives C, A multiplied by A gives D, and B multiplied by B gives G, then C, D and G should also be members of the group. (C, D and G can also be the same as A or B.).
- The group must contain one and only one identity element (E) which has the property  $AE = E = A$  for all elements of the group.

- The associative law of combination should hold good.

That is,  $A(BC) = (AB)C$

The inverse of every element should also be a member of the group. The inverse of any element  $X$  is denoted by  $X^{-1}$  which when combined with the element itself results in the identity element. It can be represented by the following equation.

$$X^{-1}X = XX^{-1} = E$$

Let the inverse of  $\sigma$  be  $\sigma^{-1}$ . Therefore,  $\sigma, \sigma^{-1} = E$  according to the definition. Since it has already been proved that  $\sigma^{-2} = E, \sigma^{-1} = \sigma$ .

Similarly, we can prove that the inverse of  $i$  is  $i$  itself, and  $C_2$ , is  $C_2$  itself.

But the inverse of  $C_3$  is  $C_3^2$  since  $C_3^3 = E$ . In general, the inverse of any  $C_n$  is  $(C)^{n-1}$  and the inverse of any  $S_n$ , is  $(S_n)^{n-1}$  when  $n$  is even and  $(S_n)2^{n-1}$  when  $n$  is odd.

## DEFINITION AND CLASSIFICATION OF POINT GROUPS

A point group is a collection of the symmetry elements present in a molecule that obeys the mathematical rules for the formation of a group. During the application of various symmetry operations in a molecule, the centre of mass does not shift and therefore all the axes, points and planes of symmetry of the molecule intersect at one common invariant point (center of mass) and hence the term point group is used. The point groups are represented by *Schoenflies symbols*.

## GROUP MULTIPLICATION TABLE

A group multiplication table is a table which gives the binary product of any two members of the group and the square of every member of a group. The first row and first column of the group multiplication table list all symmetry operations of a particular point group one after another in the same order. The other rows and columns of the table indicate the binary product of the element in a row followed by the element in a column. Each point group has a group multiplication table that shows the interrelationships between the elements. This can be derived by determining the product of the symmetry elements as discussed in the last chapter. The group multiplication tables of point groups  $C_{2v}$  and  $C_{3v}$  are shown in Tables 2.4 and 2.5.

Tables 2.4 Group multiplication table for  $C_{2v}$

$C_{2v}$	E	$C_2$	$\sigma_{v1}$	$\sigma_{v2}$
E	E	$C_2$	$\sigma_{v1}$	$\sigma_{v2}$
$C_2$	$C_2$	E	$\sigma_{v2}$	$\sigma_{v1}$
$\sigma_{v1}$	$\sigma_{v1}$	$\sigma_{v2}$	E	$C_2$
$\sigma_{v2}$	$\sigma_{v2}$	$\sigma_{v1}$	$C_2$	E

Tables 2.5 Group multiplication table for  $C_{3v}$

$C_{3v}$	E	$C_3^1$	$C_3^2$	$\sigma_{v1}$	$\sigma_{v2}$	$\sigma_{v3}$
E	E	$C_3^1$	$C_3^2$	$\sigma_{v1}$	$\sigma_{v2}$	$\sigma_{v3}$
$C_3^1$	$C_3^1$	$C_3^2$	E	$\sigma_{v2}$	$\sigma_{v3}$	$\sigma_{v1}$
$C_3^2$	$C_3^2$	E	$C_3^1$	$\sigma_{v3}$	$\sigma_{v1}$	$\sigma_{v2}$
$\sigma_{v1}$	$\sigma_{v1}$	$\sigma_{v3}$	$\sigma_{v2}$	E	$C_3^2$	$C_3^1$
$\sigma_{v2}$	$\sigma_{v2}$	$\sigma_{v1}$	$\sigma_{v3}$	$C_3^1$	E	$C_3^2$
$\sigma_{v3}$	$\sigma_{v3}$	$\sigma_{v1}$	$\sigma_{v1}$	$C_3^2$	$C_3^1$	E

The total number of symmetry elements (non-redundant) present in a point group is called the order of a group. It is designated as 'h'. For example, the total number of symmetry elements present in a  $C_{3v}$  point group is 6 (E,  $C_3^1$ ,  $C_3^2$ ,  $\sigma_{v1}$ ,  $\sigma_{v2}$ ,  $\sigma_{v3}$ ) and thus the order,

If a symmetry element A can be transformed to another symmetry element B by means of a similarity transformation done with a third symmetry element C. all belonging to the same point group, then the symmetry elements A and B are referred to as conjugate elements. A complete set of elements that are conjugate to one another is called the class of the group. The number of classes present in a point group is indicated by 'k'.



The similarity transformation is a mathematical operation involving multiplication by an element on one side and by the inverse of the same element on the other side. For example, when a similarity transformation is done on symmetry element A by a symmetry element C, it can be represented as  $C^{-1}AC$ . If this ternary product leads to a different symmetry element B, then the elements A and B are referred to as conjugate elements, which can be mathematically represented as  $C^{-1}AC = B$ .

### Simple Method to identify the Classes Present in a Point Group

When a few simple rules are kept in mind and applied, the classes present in a point group can be easily identified.

- (i) E,  $\sigma_h$ , and  $i$  commute with all symmetry elements and as a result they form separate classes in every point group.
- (ii) The principal axis  $C_n$ , and its inverse  $C_n^{-1}$  belong to the same class, if a  $\sigma_h$  is present in the point group or a  $C_2$  axis perpendicular to  $C_n$  is present.
- (iii) The symmetry elements  $S_n$ , and  $S_n^{-1}$  are conjugate symmetry elements and can be clubbed into the same class if a  $\sigma_v$  is present in the molecule or a  $C_2$  axis perpendicular to  $S_n$  is present.

$$\text{That is, } \sigma_v^{-1} S_n \sigma_v = S_n n^{-1}$$

4. Other axes  $C_m$ , and  $C_m$  will belong to the same class if the atoms or groups present on  $C_m$  can be moved to corresponding positions on  $C_m$  by means of some other symmetry elements present in that point group.

### Subgroups

If a lesser number of symmetry elements of a group satisfy all the four mathematical rules for the formation of a group, they form a subgroup of the main group. A subgroup must satisfy the following conditions.

- (i) Order of a subgroup should be less than that of the main group.
- (ii) The ratio of the order of main group to the order of subgroup should be an integer.

### Abelian Group

An *abelian group* is a group where all the symmetry elements commute with each other. Diagonal elements are identity elements in such a group. For example, the  $C_{2v}$  group is an abelian group. Here, all the symmetry elements commute with each other and it is also seen that the diagonal elements are identity elements as indicated by the group multiplication table.

$C_{2v}$	E	$C_2$	$\sigma_{v1}$	$\sigma_{v2}$
E	E	$C_2$	$\sigma_{v1}$	$\sigma_{v2}$
$C_2$	$C_2$	E	$\sigma_{v2}$	$\sigma_{v1}$
$\sigma_{v1}$	$\sigma_{v1}$	$\sigma_{v2}$	E	$C_2$
$\sigma_{v2}$	$\sigma_{v2}$	$\sigma_{v1}$	$C_2$	E

## MATRICES

A matrix is an array of numbers arranged in rows and columns. A square matrix is a matrix that has an equal number of rows and columns. Consider A which is a 3 x 3 matrix.

$$A = \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix}$$

Here,  $a_{ij}$ , represents a matrix element in the  $i^{\text{th}}$  row and the  $j^{\text{th}}$  column. A is a notation used to represent the matrix A. For each square matrix A with entries that are real numbers, the determinant of A is denoted by  $\odot A \odot$  and is given by,

$$\det A = |A| = \sum \pm a_{1j_1} a_{2j_2} \dots a_{nj_n}$$

where, the sum is taken over all possible permutations on  $n$  elements and the sign is positive if the number of permutations is even and negative if the number of permutations is odd. For example,

The determinant of the 2 x 2 matrix  $A = \begin{pmatrix} a_1 & b_1 \\ b_1 & c_1 \end{pmatrix}$  is defined as  $|A| = a_1 b_2 - a_2 b_1$

and the determinant of a 3 x 3 matrix

$$B = \begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix} \text{ is defined as}$$

$$|B| = a_1 \begin{vmatrix} b_2 & c_2 \\ b_3 & c_3 \end{vmatrix} - b_1 \begin{vmatrix} a_2 & c_2 \\ a_3 & c_3 \end{vmatrix} + c_1 \begin{vmatrix} a_2 & b_2 \\ a_3 & b_3 \end{vmatrix}$$

$$= a_1 (b_2 c_3 - b_3 c_2) - b_1 (a_2 c_3 - a_3 c_2) + c_1 (a_2 b_3 - a_3 b_2)$$

A square matrix is called a *diagonal matrix* if all the elements other than those along the diagonal are zero. For example.

$$C = \begin{vmatrix} b_1 & 0 & 0 \\ 0 & b_2 & 0 \\ 0 & 0 & b_3 \end{vmatrix}$$

In every element of a diagonal matrix is 1, it is known as a *unit matrix*,  $E$ . For a matrix  $A$ , there exists a matrix  $A^{-1}$  (inverse of  $A$ ) such that  $AA^{-1} = E$ . The inverse does not exist if  $|A| = 0$ . Such materials are called *singular matrix*.  $A$  and  $A^{-1}$  commute.

## TRANSFORMATION MATRICES FOR SYMMETRY ELEMENTS

The changes produced by symmetry operations on a molecule have been illustrated by figures in Chapter 2. If the configurations are not carefully examined, it may lead to ambiguous conclusions. The most accurate method is to study the effect of operations on the coordinates and express the transformations in the form of a matrix. Such matrices are referred to as transformation matrices, since they indicate the net quantitative effect of the symmetry operations.

### Transformation Matrix for Identity Element

Consider a vector  $OP$  having the coordinates  $(x_1, y_2, z_3)$ . When the identity operation ' $E$ ' is performed on this vector let the coordinates be changed to  $(X_2, Y_2, Z_2)$ .

$$OP (X_1, Y_1, Z_1) \xrightarrow{E} OP (X_2, Y_2, Z_2)$$

Since by definition, the identity operation should not change any coordinates,

$$x_2 = x_1, Y_2 = y_1 \text{ and } z_2 = z_1$$

The new position of the vector can be defined in terms of the original coordinates of the vector and the relationship between  $(X_2, Y_2, Z_2)$  and  $(X_1, Y_1, Z_1)$  can be expressed as a set of mathematical equations.

$$x_2 = (0 \times x_1) + (0 \times y_1) + (0 \times z_1)$$

$$y_2 = (0 \times x_1) + (1 \times y_1) + (0 \times z_1)$$

$$z_2 = (0 \times x_1) + (0 \times y_1) + (1 \times z_1)$$

These equations can be combined to give the following matrix equation

$$\begin{pmatrix} x_2 \\ y_2 \\ z_2 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x_1 \\ y_1 \\ z_1 \end{pmatrix}$$

The matrix  $\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$  is the transformation matrix for  $E$  since it indicates the net quantitative

effect of  $E$  on the vector. A  $3 \times 3$  matrix is obtained since we started with three components (also called the basis elements) of a vector.

The above procedure gives an idea about the changes that have taken place with respect to the original coordinates that results in new coordinates. The character for the transformation matrix  $E$ ,

$$\chi_E = \text{Sum of diagonal elements (from left top to right bottom)}$$

$$= 3.$$

## CHARACTERISTICS OF MATRIX REPRESENTATIONS

Matrix representations of point groups should obey the following mathematical rules.

- (i) The product of any two matrices and the square of any matrix belonging to the point group, should also be a matrix that belongs to the point group.
- (ii) There should be one matrix, which when combined with any other matrix, leaves that matrix unchanged.
- (iii) Associative law should hold good.
- (iv) The inverse of every matrix of the point group should also be present in the representation for that point group.

Thus, the collection of matrices corresponding to each symmetry element of a point group which obeys all the four mathematical rules for the formation of a group, and produces a group multiplication table identical to that derived from the symmetry operations is called a matrix representation of a point group.

## CLASSIFICATION OF REPRESENTATIONS

Representations are classified into *reducible* and *irreducible* representations. Table 4.1 Reducible and irreducible representations

<b>Reducible Representation</b>	<b>Irreducible Representation</b>
If dimensions of representations can be reduced either using the similarity transformation method or the block factoring method, they are referred to as reducible representations.	Irreducible representations are those   representations whose dimensions cannot   be reduced by any of the mathematical methods like the block factoring or the similarity transformation methods.
They can be expressed as a combination of various irreducible representations that are possible for a group	They cannot be expressed as combinations of any other representations.
Reducible representations are derived for the combination for fundamental bases	Irreducible representations are derived for the product or. of fundamental bases.

## SIGNIFICANCE OF THE ORTHOGONALITY THEOREM

Every matrix element of a representation is a vector since it indicates the magnitude and direction of transformation of a component of the base chosen; meaning, the Cartesian coordinates or an orbital. Thus, if we choose a representation of dimension ' $l$ ' (where  $l$  indicates the presence of  $l$  number of rows and columns) it will contain  $l^2$  matrix elements or  $l^2$  vectors for every symmetry element of the group. Combination of corresponding matrix elements (matrix elements belonging to the same row and the same column) chosen from each symmetry element of a group forms a  $h$  dimensional vector where  $h$  is the order of the group. Such  $h$  dimensional vectors collectively represent the transformation of a particular component of the base chosen due to the influence of the symmetrical environment of the group. The nature of such  $h$  dimensional vectors is well defined by the orthogonality theorem.

## UNIT –II

### 2marks

1. Write BET isotherm equation.
2. What is secondary salt effect?
3. Distinguish Physisorption and chemisorption.
4. Write Michaelis – Menten law.
5. Give the Bronsted relations for Acid – base catalysis.
6. How does PH effect enzyme catalysis?
7. Mention the expression for Gibbs adsorption isotherm.
8. Define salt effect,

### 5marks

1. Derive Gibbs adsorption isotherm.
2. Explain the mechanism of catalytic hydrogenation of ethylene.
3. Discuss the effect of PH on enzyme catalysis.
4. Explain the mechanism of semiconductor catalysis.
5. Discuss on Langmuir – Rideal mechanism.

### 10marks

1. Discuss in detail the mechanism and kinetics of enzyme catalysed reactions.
2. Derive Langmuir adsorption isotherm.
3. Langmuir – Hinshel wood mechanism.

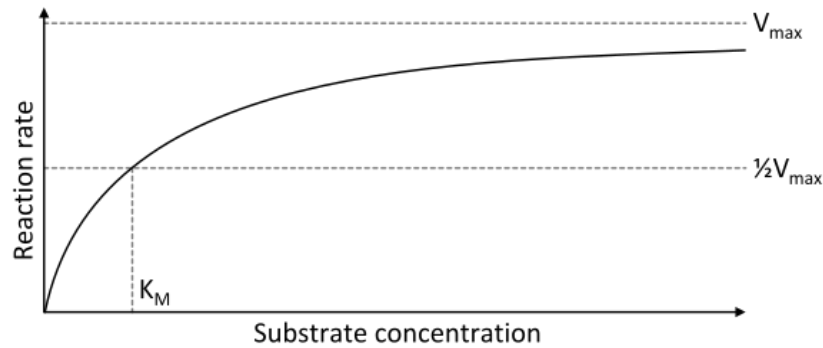
Write notes on (i) Effect of temperature

(ii) Effect of PH

## SURFACE PHENOMENA

### Michaelis–Menten Law

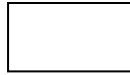
Michaelis–Menten kinetics is one of the best-known models of enzyme kinetics. It is named after German biochemist Leonor Michaelis and Canadian physician Maud Menten. The model takes the form of an equation describing the rate of enzymatic reactions, by relating reaction rate to the concentration of a substrate S. Its formula is given by



Applying the law of mass action, which states that the rate of a reaction is proportional to the product of the concentrations of the reactants (i.e.  $[E][S]$ ) gives a system of four non-linear ordinary differential equations that define the rate of change of reactants with time  $t$

$$\begin{aligned}\frac{d[\mathbf{E}]}{dt} &= -k_f [\mathbf{E}] [\mathbf{S}] + k_r [\mathbf{ES}] + k_{\text{cat}} [\mathbf{ES}] \\ \frac{d[\mathbf{S}]}{dt} &= -k_f [\mathbf{E}] [\mathbf{S}] + k_r [\mathbf{ES}] \\ \frac{d[\mathbf{ES}]}{dt} &= k_f [\mathbf{E}] [\mathbf{S}] - k_r [\mathbf{ES}] - k_{\text{cat}} [\mathbf{ES}] \\ \frac{d[\mathbf{P}]}{dt} &= k_{\text{cat}} [\mathbf{ES}].\end{aligned}$$

In this mechanism, the enzyme E is a **catalyst**, which only facilitates the reaction, so that its total concentration, free plus combined,  $[\mathbf{E}] + [\mathbf{ES}] = [\mathbf{E}]_0$  is a constant (i.e.  $[\mathbf{E}]_0 = [\mathbf{E}]_{\text{total}}$ ). This conservation law can also be observed by adding the first and third equations above.<sup>[4][5][6]</sup>



### Equilibrium approximation

In their original analysis, Michaelis and Menten assumed that the substrate is in instantaneous **chemical equilibrium** with the complex, which implies

$$k_f [\mathbf{E}] [\mathbf{S}] = k_r [\mathbf{ES}].$$

From the enzyme conservation law, we obtain

$$[\mathbf{E}] = [\mathbf{E}]_0 - [\mathbf{ES}].$$

Combining the two expressions above, gives us

$$\begin{aligned}k_f ([\mathbf{E}]_0 - [\mathbf{ES}]) [\mathbf{S}] &= k_r [\mathbf{ES}] \\ k_f [\mathbf{E}]_0 [\mathbf{S}] - k_f [\mathbf{ES}] [\mathbf{S}] &= k_r [\mathbf{ES}] \\ k_r [\mathbf{ES}] + k_f [\mathbf{ES}] [\mathbf{S}] &= k_f [\mathbf{E}]_0 [\mathbf{S}] \\ [\mathbf{ES}] (k_r + k_f [\mathbf{S}]) &= k_f [\mathbf{E}]_0 [\mathbf{S}]\end{aligned}$$

$$\begin{aligned}[\mathbf{ES}] &= \frac{k_f [\mathbf{E}]_0 [\mathbf{S}]}{k_r + k_f [\mathbf{S}]} \\ [\mathbf{ES}] &= \frac{k_f [\mathbf{E}]_0 [\mathbf{S}]}{k_f \left( \frac{k_r}{k_f} + [\mathbf{S}] \right)}\end{aligned}$$

Upon simplification, we get

$$[\mathbf{ES}] = \frac{[\mathbf{E}]_0 [\mathbf{S}]}{K_d + [\mathbf{S}]}$$

where  $K_d = k_r/k_f$  is the **dissociation constant** for the enzyme-substrate complex. Hence the velocity  $v$  of the reaction – the rate at which P is formed – is<sup>[1]</sup>

$$v = \frac{d[\mathbf{P}]}{dt} = V_{\text{max}} \frac{[\mathbf{S}]}{K_d + [\mathbf{S}]}$$

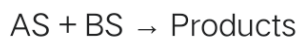
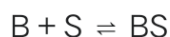
Where  $V_{\text{max}} = k_{\text{cat}} [\mathbf{E}]_0$  is the maximum reaction velocity.

### Langmuir–Hinshelwood mechanism



Reactions on surfaces are reactions in which at least one of the steps of the reaction mechanism is the adsorption of one or more reactants. The mechanisms for these reactions, and the rate equations are of extreme importance for heterogeneous catalysis. Via scanning tunneling microscopy, it is possible to observe reactions at the solid/gas interface in real space, if the time scale of the reaction is in the correct range. Reactions at the solid/gas interface are in some cases related to catalysis.

In this mechanism, suggested by [Irving Langmuir](#) in 1921 and further developed by [Cyril Hinshelwood](#) in 1926, two molecules adsorb on neighboring sites and the adsorbed molecules undergo a bimolecular reaction:



The rate constants are now  $k_1, k_{-1}, k_2, k_{-2}$  and  $k$  for adsorption/desorption of A, adsorption/desorption of B, and reaction. The rate law is:  $r = k\theta_A\theta_B C_S^2$

Proceeding as before we get  $\theta_A = \frac{k_1 C_A \theta_E}{k_{-1} + k C_S \theta_B}$ , where  $\theta_E$  is the fraction of empty

sites, so  $\theta_A + \theta_B + \theta_E = 1$ . Let us assume now that the rate limiting step is the reaction of the adsorbed molecules, which is easily understood: the probability of two adsorbed molecules colliding is low. Then  $\theta_A = K_1 C_A \theta_E$ , with  $K_i = k_i/k_{-i}$ , which is nothing but Langmuir isotherm for two adsorbed gases, with adsorption constants  $K_1$  and  $K_2$ .

Calculating  $\theta_E$  from  $\theta_A$  and  $\theta_B$  we finally get

$$r = k C_S^2 \frac{K_1 K_2 C_A C_B}{(1 + K_1 C_A + K_2 C_B)^2}$$

The rate law is complex and there is no clear order with respect to either reactant, but we can consider different values of the constants, for which it is easy to measure integer orders:

### **Effect on temp on enzyme catalyst**

Higher temperatures tend to speed up the effect of enzyme activity, while lower temperatures decrease the rate of an enzyme reaction. At higher temperatures, more molecules collide, increasing the chance that an enzyme will collide with its substrate. If the enzyme's shape changes, it cannot bind to the substrate.

### **Effect of enzyme catalyst**

Enzymes are also sensitive to pH . Changing the pH of its surroundings will also change the shape of the active site of an enzyme. . This contributes to the folding of the enzyme molecule, its shape, and the shape of the active site. Changing the pH will affect the charges on the amino acid molecules.

### **Kinetics of enzyme catalysed**

An enzyme attracts substrates to its active site, catalyzes the chemical reaction by which products are formed, and then allows the products to dissociate (separate from the enzyme surface). The combination formed by an enzyme and its substrates is called the enzyme–substrate complex.

### **Mechanism of semi conductor catalyst**

The process couples low-energy ultraviolet light with semiconductor particles as catalysts and is based on the principle of reduction by the photogenerated electrons. In contrast, photocatalytic reduction occurs when hole scavengers are adopted, and cathodic reactions occur with photogenerated electrons.

### **Mechanism of catalysed hydrogenation of ethylene**

Hydrogenation is a chemical reaction between molecular hydrogen (H<sub>2</sub>) and another compound or element, usually in the presence of a catalyst such as nickel, palladium or platinum. The process is commonly employed to reduce or saturate organic compounds. Hydrogenation typically constitutes the addition of pairs of hydrogen atoms to a molecule, often an alkene. Catalysts are required for the reaction to be usable; non-catalytic hydrogenation takes place only at very high temperatures. Hydrogenation reduces double and triple bonds in hydrocarbons.

Steps in the hydrogenation of a C=C double bond at a catalyst surface, for example Ni or Pt :

- (1) The reactants are adsorbed on the catalyst surface and H<sub>2</sub> dissociates.
- (2) An H atom bonds to one C atom. The other C atom is still attached to the surface.
- (3) A second C atom bonds to an H atom. The molecule leaves the surface.

### **Secondary Salt effect**

The term “**secondary kinetic salt effect**” is used to indicate a kinetic **salt effect** due to a change in concentration of the reacting molecules on account of a change in the inter-ionic forces.

### **Salt effect**

Salting in refers to the effect where increasing the ionic strength of a solution increases the solubility of a solute, such as a protein. This effect tends to be observed at lower ionic strengths. The solubility of proteins usually increases slightly in the presence of salt, referred to as salting

### Derivation of the Gibbs adsorption equation

For a two-phase system consisting of the  $\alpha$  and  $\beta$  phase in equilibrium with a surface  $S$  dividing the phases, the total Gibbs free energy of a system can be written as:

$$G = G^\alpha + G^\beta + G^S$$

where  $G$  is the Gibbs free energy.

The equation of the Gibbs Adsorption Isotherm can be derived from the “particularization to the thermodynamics of the Euler theorem on homogeneous first-order forms. The Gibbs free energy of each phase  $\alpha$ , phase  $\beta$ , and the surface phase can be represented by the equation:

$$G = U + pV - TS + \sum_{i=1}^k \mu_i n_i ,$$

where  $U$  is the internal energy,  $p$  is the pressure,  $V$  is the volume,  $T$  is the temperature,  $S$  is the entropy, and  $\mu_i$  is the chemical potential of the  $i$ -th component.

By taking the total derivative of the Euler form of the Gibbs equation for the  $\alpha$  phase,  $\beta$  phase and the surface phase:

$$dG = \sum_{\alpha, \beta, S} \left( dU + pdV + Vdp - TdS \right)$$

where  $A$  is the cross sectional area of the dividing surface, and  $\gamma$  is the surface tension.

For reversible processes, the first law of thermodynamics requires that:

$$dU = \delta q + \delta w ,$$

where  $q$  is the heat energy and  $w$  is the work.

$$\delta q + \delta w = \sum_{\alpha, \beta, S} (TdS - pdV - \delta w_{\text{non-P}})$$

Substituting the above equation into the total derivative of the Gibbs energy equation and by utilizing the result  $\gamma dA$  is equated to the non-pressure volume work when surface energy is considered:

$$dG = \sum_{\alpha, \beta, S} \left( Vdp - SdT + \sum_{i=1}^k \mu_i dn_i \right)$$

by utilizing the fundamental equation of Gibbs energy of a multicomponent system:

$$dG = Vdp - SdT + \sum_{i=1}^k \mu_i dn_i .$$

The equation relating the  $\alpha$  phase,  $\beta$  phase and the surface phase becomes:

$$\sum_{i=1}^k n_i^{\alpha} d\mu_i + \sum_{i=1}^k n_i^{\beta} d\mu_i + \sum_{i=1}^k n_i^S d\mu_i$$

When considering the bulk phases ( $\alpha$  phase,  $\beta$  phase), at equilibrium at constant temperature and pressure the Gibbs–Duhem equation requires that:

$$\sum_{i=1}^k n_i^{\alpha} d\mu_i + \sum_{i=1}^k n_i^{\beta} d\mu_i = 0.$$

The resulting equation is the Gibbs adsorption isotherm equation:

$$\sum_{i=1}^k n_i^S d\mu_i + A d\gamma = 0.$$

The Gibbs adsorption isotherm is an equation which could be considered an adsorption isotherm that connects surface tension of a solution with the concentration of the solute.

For a binary system containing two components the Gibbs Adsorption Equation in terms of surface excess is:

$$-d\gamma = \Gamma_1 d\mu_1 + \Gamma_2 d\mu_2.$$

### Chemisorption

Chemisorption is a kind of adsorption which involves a chemical reaction between the surface and the adsorbate. New chemical bonds are generated at the adsorbant surface. Examples include macroscopic phenomena that can be very obvious, like corrosion, and subtler effects associated with heterogeneous catalysis.

**Physical adsorption**, or physisorption, is a type of adsorption that occurs for most particles in contact with a solid or liquid surface. Condensation of water molecules sticking to a drinking glass is an example. In other words, the molecules desorb from the surface.

### Physical adsorption

Weak vander waals forces are present between the adsorbate molecules and the adsorbent. The enthalpy of adsorption is low (20 to 40 kJ/mol).

Occurs at low temperature and decreases with increase in temperature.

It is reversible.

No significant activation energy is required.

It forms multimolecular layers.

### **Chemisorption** (chemical adsorption)

Strong chemical forces similar to chemical bonds are present between the adsorbate molecules and the adsorbent. The enthalpy of adsorption is high (80 to 240 kJ/mol). Occurs at high temperature and increases with increase in temperature. Usually, high activation energy is required. It is irreversible. It forms unimolecular layers.

### **Kinetics of enzyme catalysis**

enzyme kinetics is the study of the chemical reactions that are catalysed by enzymes. In enzyme kinetics, the reaction rate is measured and the effects of varying the conditions of the reaction are investigated. Studying an enzyme's kinetics in this way can reveal the catalytic mechanism of this enzyme, its role in metabolism, how its activity is controlled, and how a drug or an agonist might inhibit the enzyme.

Enzymes are usually protein molecules that manipulate other molecules the enzymes' substrates. These target molecules bind to an enzyme's active site and are transformed into products through a series of steps known as the enzymatic mechanism



These mechanisms can be divided into single-substrate and multiple-substrate mechanisms. Kinetic studies on enzymes that only bind one substrate, such as triosephosphate isomerase, aim to measure the affinity with which the enzyme binds this substrate and the turnover rate. Some other examples of enzymes are phosphofructokinase and hexokinase, both of which are important for cellular respiration (glycolysis).

When enzymes bind multiple substrates, such as dihydrofolate reductase (shown right), enzyme kinetics can also show the sequence in which these substrates bind and the sequence in which products are released. An example of enzymes that bind a single substrate and release multiple products are proteases, which cleave one protein substrate into two polypeptide products. Others join two substrates together, such as DNA polymerase linking a nucleotide to DNA. Although these mechanisms are often a complex series of steps, there is typically one rate-determining step that determines the overall kinetics. This rate-determining step may be a chemical reaction or a conformational change of the enzyme or substrates, such as those involved in the release of product(s) from the enzyme.

Knowledge of the enzyme's structure is helpful in interpreting kinetic data. For example, the structure can suggest how substrates and products bind during catalysis; what changes occur during the reaction; and even the role of particular amino acid residues in the mechanism. Some enzymes change shape significantly during the mechanism; in such cases, it is helpful to determine the enzyme structure with and without bound substrate analogues that do not undergo the enzymatic reaction.

Not all biological catalysts are protein enzymes: RNA-based catalysts such as ribozymes and ribosomes are essential to many cellular functions, such as RNA splicing and translation. The main difference between ribozymes and enzymes is that RNA catalysts are composed of nucleotides, whereas enzymes are composed of amino acids.

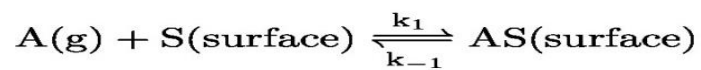
Ribozymes also perform a more limited set of reactions, although their reaction mechanisms and kinetics can be analysed .

## 1 Langmuir Isotherm

Assumptions used for the Langmuir isotherm

1. Gaseous molecules behave ideally
2. Only one monolayer forms
3. All sites on the surface are equivalent
4. No adsorbate - adsorbate interactions
5. An adsorbed molecule is immobile

Then, for the following reaction



we can say

$$\text{rate of adsorption} = k_1 P N (1-\theta)$$

$$\text{rate of desorption} = k_{-1} N \theta$$

where  $P$  is the pressure above the surface,  $N$  is the total number of sites, and

$$\theta = \frac{\text{number of sites occupied}}{\text{number of sites available}} = \frac{n_a}{n_m}$$

$n_a$  is the number of molecules adsorbed, and  $n_m$  is the number of molecules in one monolayer.  $N(1-\theta)$  is the number of empty sites and  $N\theta$  is the number of occupied sites.

We can then say that the rate of change of  $\theta$  is

$$\begin{aligned} \frac{d\theta}{dt} &= \text{rate of adsorption} - \text{rate of desorption} \\ &= k_1PN(1 - \theta) - k_{-1}N\theta \end{aligned}$$

At equilibrium  $\frac{d\theta}{dt}=0$  so

$$\begin{aligned} \theta &= \frac{k_1PN}{k_1PN + k_{-1}N} \\ &= \frac{KP}{KP + 1} \end{aligned}$$

where  $K = \frac{k_1}{k_{-1}}$  is the binding equilibrium constant with units of  $P^{-1}$ .

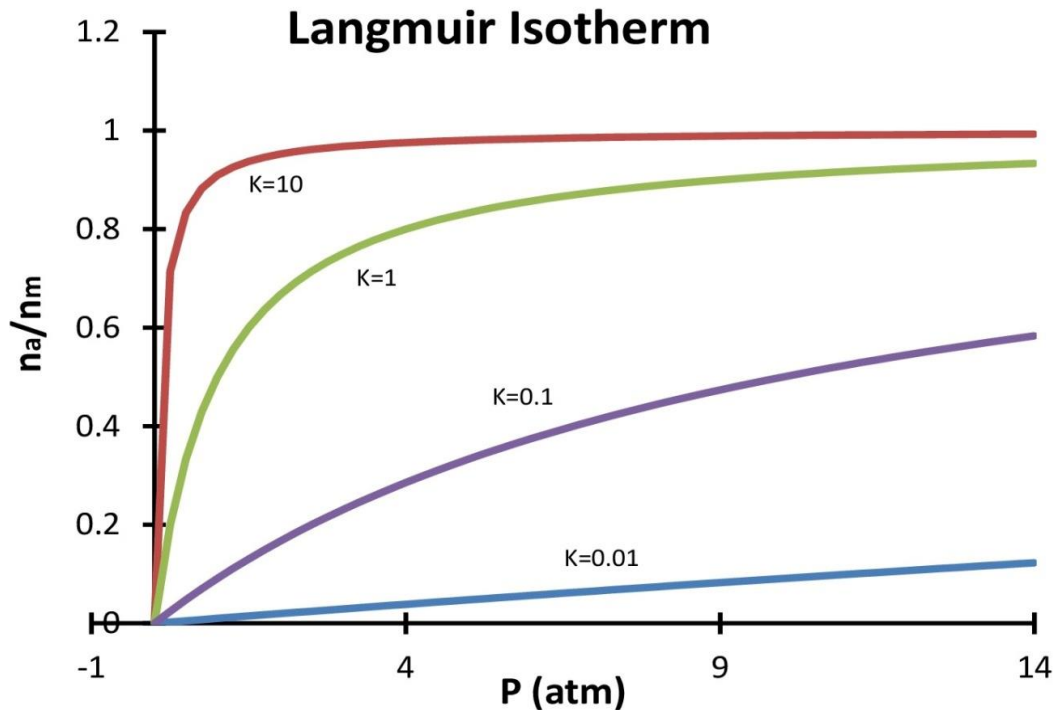


Figure 1: Langmuir isotherm plot of  $n_a/n_m$  vs  $P$  (atm) for several different values of the equilibrium binding constant,  $K$ .

Figure 1 shows a graph of  $n_a/n_m$  as a function of pressure in atmospheres for several different values of  $K$ , the binding equilibrium constant. Figure 2 shows a cartoon representation of how the alumina surface is being filled. For the Langmuir isotherm the alumina surface can be treated as being made of

# BET Isotherm

## Assumptions

While the Langmuir isotherm provides a simple picture for looking at surface adsorption, it is not an accurate representation of how nitrogen actually adsorbs to the surface. This is because more than one nitrogen molecule can adsorb to each site on the alumina. A better approximation for this process is to use the BET Isotherm (named for its inventors, Brunauer, Emmett, and Teller) which allows for multiple nitrogen molecules to adsorb to each alumina site.

The assumptions used to derive the BET isotherm are

1. Gas molecules behave ideally
2. Multiple nitrogen molecules can be adsorbed to each site
3. Each adsorbed molecule provides a site for the adsorption of the molecule in the layer above it
4. All sites on the surface are equivalent
5. No adsorbate - adsorbate interactions
6. An adsorbed molecule is immobile
7. Nitrogen in the second and higher layers are assumed to be liquid like



## 2.2 Derivation

Figure 3 shows a cartoon of what an alumina surface would look like under the BET isotherm assumptions. We define  $\theta_0, \theta_1, \theta_2, \theta_n \dots$  where

$$\theta_n = \frac{\# \text{ of sites with } n \text{ adsorbed molecules}}{\# \text{ of sites total}} \quad (1)$$

(Note the definition is the number of sites with  $n$  adsorbed molecules, not with “at least”  $n$  adsorbed molecules, see Figure 3.) We can also define

$k_n$  - rate of condensation to form the  $n^{\text{th}}$  layer

$k_{-n}$  - rate of evaporation to form the  $n^{\text{th}}$  layer

$P$  - pressure above the surface

$N$  - total number of sites

For this cartoon...

$$\theta_0 = 3/14$$

$$\theta_1 = 4/14$$

$$\theta_2 = 4/14$$

$$\theta_3 = 2/14$$

$$\theta_4 = 1/14$$

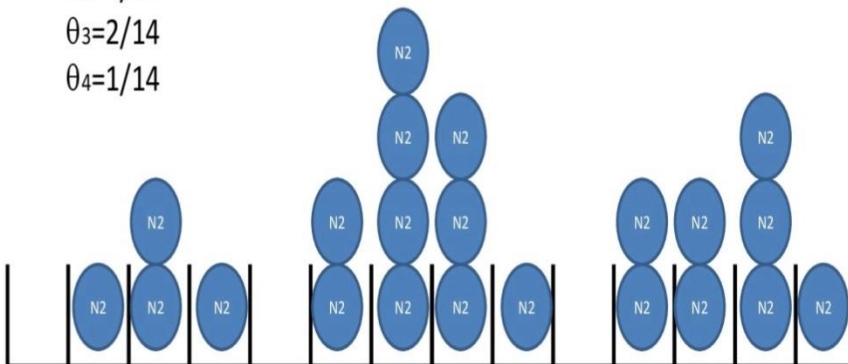


Figure 3: Cartoon of nitrogen adsorbing onto an alumina surface assuming a BET isotherm.

At equilibrium

$$\frac{d\theta_n}{dt} = 0 \quad (2)$$

for all n. For the bare surface we can write

$$\begin{aligned} \frac{d\theta_0}{dt} &= \text{rate of evaporation from 1}^{\text{st}} \text{ layer} - \text{rate of condensation onto bare surface} \\ 0 &= Nk_{-1}\theta_1 - Nk_1P\theta_0 \\ \theta_1 &= P\frac{k_1}{k_{-1}}\theta_0 \end{aligned} \quad (3)$$

where  $N\theta_1$  is the number of sites with 1 layer of nitrogen on it and  $N\theta_0$  is the number of sites with no nitrogen adsorbed. (Note this is the same answer as for the Langmuir isotherm where  $\theta_1=(1-\theta_0)$ .)

For surface sites with only one molecule adsorbed we can write

$$\begin{aligned} \frac{d\theta_1}{dt} &= \text{rate of condensation onto bare surface} + \text{rate of evaporation from 2}^{\text{nd}} \text{ layer} \\ &\quad - \text{rate of condensation onto the 1}^{\text{st}} \text{ layer} - \text{rate of evaporation from the 1}^{\text{st}} \text{ layer} \\ 0 &= k_1P\theta_0N + k_{-2}N\theta_2 - k_2PN\theta_1 - k_{-1}N\theta_1 \end{aligned} \quad (4)$$

combining equations 3 and 4 gives

$$\begin{aligned} k_{-2}\theta_2 &= k_2P\theta_1 \\ \theta_2 &= P\frac{k_2}{k_{-2}}\theta_1 = P^2\frac{k_2}{k_{-2}}\frac{k_1}{k_{-1}}\theta_0 \end{aligned} \quad (5)$$

For the second layer

$$\begin{aligned} \frac{d\theta_2}{dt} &= \text{rate of condensation onto 1}^{\text{st}} \text{ layer} + \text{rate of evaporation from 3}^{\text{rd}} \text{ layer} \\ &\quad - \text{rate of condensation onto the 2}^{\text{nd}} \text{ layer} - \text{rate of evaporation from the 2}^{\text{nd}} \text{ layer} \\ 0 &= k_2P\theta_1N + k_{-3}N\theta_3 - k_3PN\theta_2 - k_{-2}N\theta_2 \end{aligned} \quad (6)$$

Plugging equation 5 into 6 gives

$$\begin{aligned} k_{-3}\theta_3 &= k_3P\theta_2 \\ \theta_3 &= P\frac{k_3}{k_{-3}}\theta_2 = P^3\frac{k_3}{k_{-3}}\frac{k_2}{k_{-2}}\frac{k_1}{k_{-1}}\theta_0 \end{aligned} \quad (7)$$

Generalizing to the  $i^{\text{th}}$  layer gives

$$\begin{aligned} k_{-i}\theta_i &= k_i\theta_{i-1}P \\ \theta_i &= \frac{k_i}{k_{-i}}P\theta_{i-1} \\ &= \frac{k_i}{k_{-i}} \frac{k_{i-1}}{k_{-(i-1)}} \frac{k_{i-2}}{k_{-(i-2)}} \dots \frac{k_1}{k_{-1}} P^i \theta_0 \end{aligned} \quad (8)$$

Since for  $i > 1$  the BET isotherm assumes the nitrogen is liquid like, we can also say that

$$\begin{aligned} k_2 \simeq k_3 \simeq k_4 \simeq k_i \neq k_1 \\ k_{-2} \simeq k_{-3} \simeq k_{-4} \simeq k_{-i} \neq k_{-1} \end{aligned}$$

where  $k_i$  is the rate of adsorption onto a liquid nitrogen surface and  $k_{-i}$  is the rate of desorption off a liquid nitrogen surface. So if we define  $x = P \frac{k_i}{k_{-i}}$  we can write

$$\theta_i = x^{i-1} P \frac{k_1}{k_{-1}} \theta_0 = x^i \frac{1}{x} P \frac{k_1}{k_{-1}} \theta_0; i \neq 0, 1 \quad (9)$$

and if we define  $c = \frac{Pk_1}{xk_{-1}}$ , we can say

$$\theta_i = x^i c \theta_0; i \neq 0, 1 \quad (10)$$

If we then define the total surface coverage,  $\theta$ , such that

$$\theta = \frac{n_a}{n} = \frac{\text{total \# of molecules adsorbed}}{\text{total \# of sites}}$$

we can write

$$n_a = \sum_{i=0}^{\infty} i \theta_i N$$

because each site has  $i$  molecules on it and

$$n = \sum_{i=0}^{\infty} \theta_i N$$

so that

$$\theta = \frac{\sum_{i=0}^{\infty} i \theta_i N}{\sum_{i=0}^{\infty} \theta_i N} = \frac{\sum_{i=1}^{\infty} i \theta_i}{\theta_0 + \sum_{i=1}^{\infty} \theta_i} = \frac{c \theta_0 \sum_{i=1}^{\infty} i x^i}{\theta_0 + c \theta_0 \sum_{i=1}^{\infty} x^i}$$

If we use

$$\sum_{i=1}^{\infty} x^i = \frac{x}{1-x}$$

then

$$\sum_{i=1}^{\infty} ix^i = x \sum_{i=1}^{\infty} ix^{i-1} = x \sum_{i=1}^{\infty} \frac{d}{dx} x^i = x \frac{d}{dx} \sum_{i=1}^{\infty} x^i = x \frac{d}{dx} \frac{x}{1-x} = \frac{x}{(1-x)^2}$$

plugging this in for  $\theta$  we obtain

$$\theta = \frac{c\theta_0 \frac{x}{(1-x)^2}}{\theta_0 + c\theta_0 \frac{x}{1-x}} = \frac{\frac{cx}{(1-x)^2}}{\frac{1-x+cx}{(1-x)}} = \frac{cx}{1-x} \frac{1}{1-x+cx} = \frac{cx}{(1-x)(1+(c-1)x)}$$

## 2.4 Limitations of the BET Isotherm

The BET isotherm is accurate when  $P/P_o$  is between  $\sim 0.05$  and  $\sim 0.3$ , pressures at which only a few complete layers have formed. At low pressures the BET isotherm does not do a good job at describing adsorption because in deriving the isotherm it was assumed that all the sites on the alumina surface are equivalent. This is not really the case and when only a few molecules have adsorbed, effects from inhomogeneities in the surface become more important. As more molecules adsorb these inhomogeneities average out. At high pressures, the cracks and roughness of the surface cause the BET isotherm to fail. This is especially true for very porous materials where the indents have a width of only a few monolayers. This is because the cracks can only hold a few monolayers and as the cracks fill up, the effective surface area of the solid where the nitrogen adsorbs can change.

### Bronsted relations for acid base catalyst

The Brønsted catalysis equation or law of correlation gives the relationship between acid strength and catalytic activity in general acid catalysis.

A plot of the common logarithm of the reaction rate constant  $k$  versus the logarithm of the ionization constant  $K_a$  for a series of acids (for example a group of substituted phenols or carboxylic acids) gives a straight line with slope  $\alpha$  and intercept  $C$ . The

Brønsted equation is a free-energy relationship. The relationship implies that the Gibbs free energy for proton dissociation is proportional to the activation energy for the catalytic step. When the relationship is not linear, the chosen group of catalysts do not operate through the same reaction mechanism.

Specific and general catalysis is also found in base catalysed reactions and base Brønsted equation also exists with constant  $\beta$ .

The Brønsted equation gives information about a reaction mechanism. Reactions that have low values for proportionality constants  $\alpha$  or  $\beta$  are considered to have a transition state closely resembling the reactant with little proton transfer. With a high value, proton transfer in the transition state is almost complete. In a study of a group of phenalene compounds it was concluded from Brønsted analysis that phenalene acidity is very different from either indene acidity or phenylene acidity 1.

In acid catalysis and base catalysis, a chemical reaction is catalyzed by an acid or a base. By Brønsted–Lowry acid–base theory, the acid is the proton (hydrogen ion,  $H^+$ ) donor and the base is the proton acceptor. Typical reactions catalyzed by proton transfer are esterifications and aldol reactions. In these reactions, the conjugate acid of the carbonyl group is a better electrophile than the neutral carbonyl group itself. Depending on the chemical species that act as the acid or base, catalytic mechanisms can be classified as either specific catalysis and general catalysis. Many enzymes operate by specific catalysis.