

## ❖ Kinetics of (One Intermediate) Enzymatic Reaction: Michaelis-Menten Treatment

In 1901, a French Chemist, Victor Henri, proposed that enzyme reactions are actually initiated by a bond formed between the substrate and the enzyme. The concept was further developed by German researches Leonor Michaelis and Canadian scientist Maud Menten, who examined the kinetics of an enzymatic reaction mechanism of invertase. The final model of Michaelis and Menten's treatment was published in 1913 and gained immediate popularity among the scientific community.



Where  $E$  is the enzyme that binds to a substrate  $S$ , and forms a complex  $ES$ . This enzyme-substrate complex then turns into product  $P$ . The overall rate of product formation should be

$$+ \frac{d[P]}{dt} = r = k_2[ES] \quad (248)$$

Since  $[ES]$  is intermediate, the steady-state approximation can be applied i.e.

$$\text{Rate of formation of } [ES] = \text{Rate of decomposition of } [ES] \quad (249)$$

$$k_1[E][S] = k_{-1}[ES] + k_2[ES] \quad (250)$$

$$k_1[E][S] = (k_{-1} + k_2)[ES] \quad (251)$$

$$[ES] = \frac{k_1[E][S]}{k_{-1} + k_2} \quad (252)$$

Now, defining a new parameter named as Michaelis- Menten constant ( $K_m$ ) with the following expression,

$$K_m = \frac{k_{-1} + k_2}{k_1} \quad (253)$$

equation (252) takes the form

$$[ES] = \frac{[E][S]}{K_m} \quad (254)$$

Now, if we put the  $[ES]$  concentration given above into equation (248), we will get the rate of enzyme-catalyzed reaction in terms of substrate concentration and enzyme left unused i.e.  $[E]$ . This is again a problem that can be solved if we obtain the rate expression in terms of total enzyme concentration i.e.  $[E_0]$ ; which would make the calculation of catalytic efficiency much easier. In order to do so, recall the total enzyme concentration mathematically i.e.

$$[E_0] = [E] + [ES] \quad (255)$$

Where  $[E]$  is the enzyme concentration left unused whereas  $[ES]$  represents the enzyme concentration that is bound with the substrate. Rearranging equation (253), we get

$$[E] = [E_0] - [ES] \quad (256)$$

After using the value of  $[E]$  from equation (256) in equation (254), we have

$$[ES] = \frac{\{[E_0] - [ES]\}[S]}{K_m} \quad (257)$$

$$[ES] = \frac{[E_0][S] - [ES][S]}{K_m} \quad (258)$$

Rearranging for  $[ES]$  again

$$K_m[ES] = [E_0][S] - [ES][S] \quad (259)$$

$$K_m[ES] + [ES][S] = [E_0][S] \quad (260)$$

$$[ES] = \frac{[E_0][S]}{K_m + [S]} \quad (261)$$

After putting the value of  $[ES]$  from above equation into equation (248), we get

$$r = \frac{k_2[E_0][S]}{K_m + [S]} \quad (262)$$

If the rate of the enzyme-catalyzed reaction is recorded in the very initial stage, the substrate concentration can also be replaced by the initial substrate concentration i.e.  $[S_0]$ . Therefore, the initial enzyme-catalyzed rate ( $r_0$ ) should be

$$r_0 = \frac{k_2[E_0][S_0]}{K_m + [S_0]} \quad (263)$$

Which is the well-known Michaelis-Menten equation.

Although the equation (263) is the complete form of the Michaelis-Menten equation that has measurable quantities like  $[E_0]$  and  $[S_0]$ , the more popular form of the same includes the maximum initial rate. At very large initial substrate concentration, the  $K_m$  can simply be neglected in comparison to  $[S_0]$  in the denominator, which makes the equation (263) to take the form

$$r_{max} = \frac{k_2[E_0][S_0]}{[S_0]} = k_2[E_0] \quad (264)$$

After using the  $k_2[E_0] = r_{max}$  in equation (263), we have

$$r_0 = \frac{r_{max}[S_0]}{K_m + [S_0]} \quad (265)$$

Which is the most popular form of the Michaelis-Menten equation. The plot of the initial reaction rate for the enzyme-catalyzed reaction is given below.

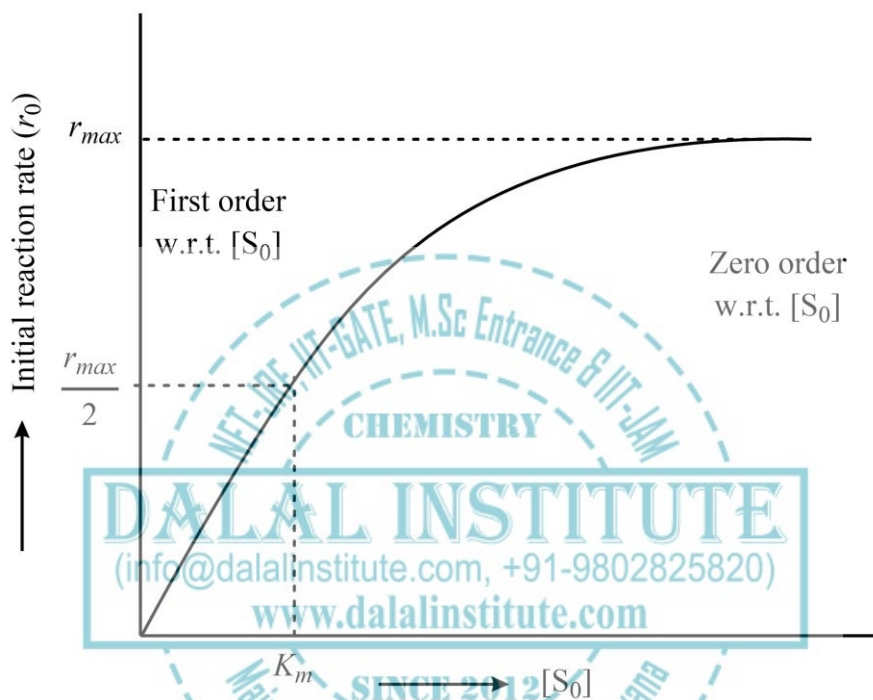


Figure 2. The variation of initial reaction rate as a function of substrate concentration for an enzyme-catalyzed reaction.

### ➤ Order of Enzyme Catalysed Reactions

The reaction kinetics of the enzyme-catalyzed reactions can be well understood by looking at the general form of Michaelis-Menten equation.

i) *At high  $[S_0]$* : When initial substrate concentration is very high,  $K_m$  can be neglected, and the equation (263) takes the form

$$r_0 = \frac{k_2[E_0][S_0]}{[S_0]} = k_2[E_0] \quad (266)$$

Hence, the reaction will be zero-order w.r.t. substrate concentration and first order w.r.t the total enzyme concentration.

ii) At low  $[S_0]$ : When initial substrate concentration is low,  $[S_0]$  can be neglected, and the equation (263) takes the form

$$r_0 = \frac{k_2}{K_m} [E_0][S_0] \quad (267)$$

Hence, the reaction will be the first-order w.r.t. substrate concentration and first order w.r.t the total enzyme concentration as well.

➤ **Calculation of Catalytic Efficiency**

The catalytic efficiency of enzyme-catalyzed reactions is simply the maximum overall reaction rate per unit of enzyme concentration. When initial substrate concentration is very high,  $K_m$  can be neglected, and the equation (263) takes the form

$$r_{max} = \frac{k_2 [E_0][S_0]}{[S_0]} = k_2 [E_0] \quad (268)$$

$$k_2 = \frac{r_{max}}{[E_0]} \quad (269)$$

Hence,  $k_2$  is simply equal to the catalytic efficiency of enzyme-catalyzed reactions.

➤ **Calculation of Michaelis-Menten Constant**

The Michaelis-Menten constant of enzyme-catalyzed reactions can simply be calculated once the maximum initial reaction rate is known. When initial substrate concentration is very high,  $K_m$  can be neglected, and the equation (263) takes the form

$$r_{max} = \frac{k_2 [E_0][S_0]}{[S_0]} = k_2 [E_0] \quad (270)$$

After using the  $k_2 [E_0] = r_{max}$  in equation (263), we have

$$r_0 = \frac{r_{max} [S_0]}{K_m + [S_0]} \quad (271)$$

When the initial reaction rate is half of the maximum initial rate i.e.  $r_0 = r_{max}/2$ , we have

$$\frac{r_{max}}{2} = \frac{r_{max} [S_0]}{K_m + [S_0]} \quad (272)$$

$$K_m + [S_0] = 2[S_0] \quad (273)$$

$$K_m = [S_0] \quad (274)$$

Hence, the concentration at which the initial rate is half of the maximum initial rate, will be equal to  $K_m$ .

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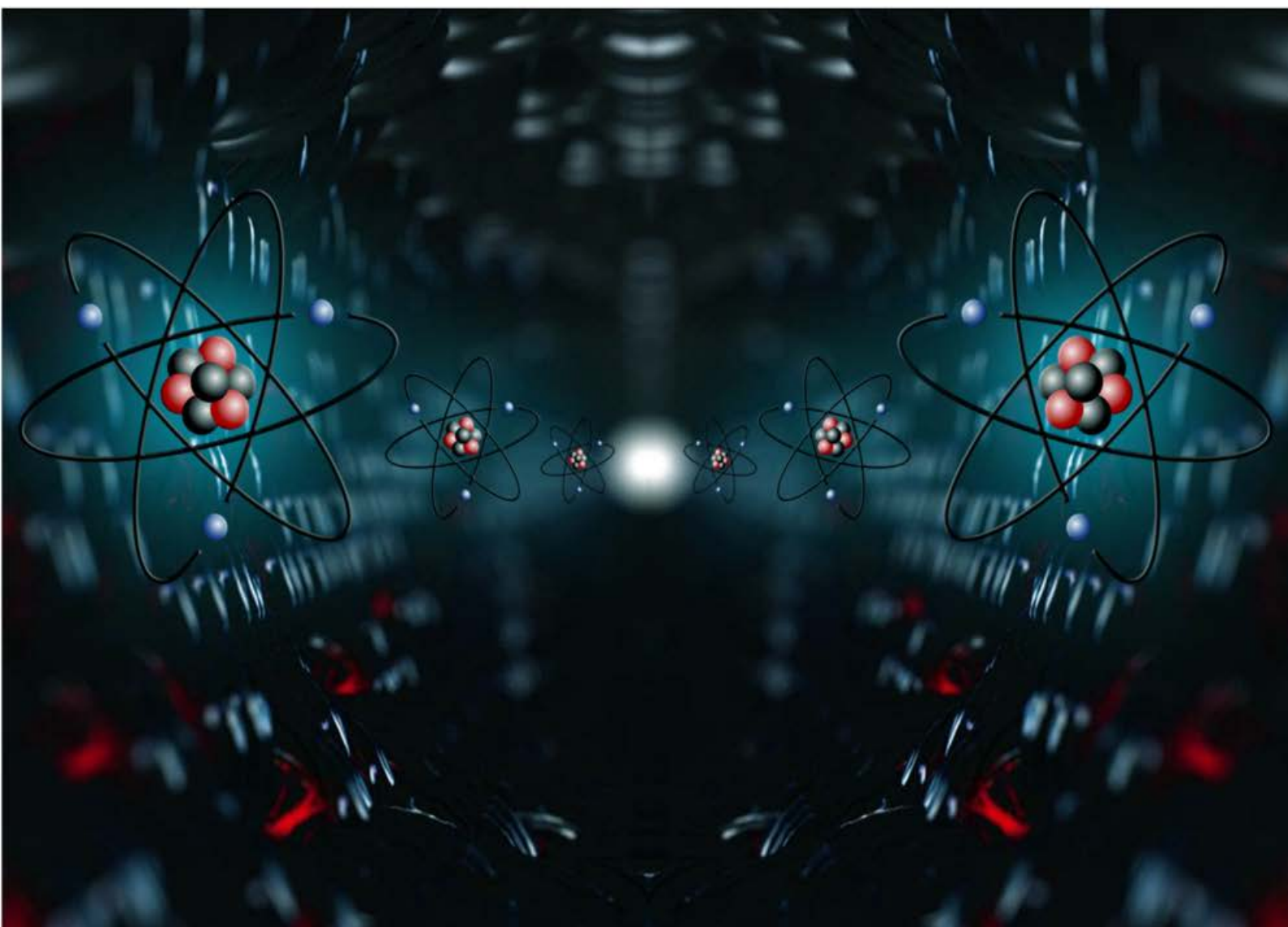
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# Table of Contents

<b>CHAPTER 1 .....</b>	<b>11</b>
<b>Quantum Mechanics – I .....</b>	<b>11</b>
❖ Postulates of Quantum Mechanics .....	11
❖ Derivation of Schrodinger Wave Equation.....	16
❖ Max-Born Interpretation of Wave Functions .....	21
❖ The Heisenberg's Uncertainty Principle.....	24
❖ Quantum Mechanical Operators and Their Commutation Relations.....	29
❖ Hermitian Operators – Elementary Ideas, Quantum Mechanical Operator for Linear Momentum, Angular Momentum and Energy as Hermitian Operator .....	52
❖ The Average Value of the Square of Hermitian Operators .....	62
❖ Commuting Operators and Uncertainty Principle ( $x$ & $p$ ; $E$ & $t$ ) .....	63
❖ Schrodinger Wave Equation for a Particle in One Dimensional Box.....	65
❖ Evaluation of Average Position, Average Momentum and Determination of Uncertainty in Position and Momentum and Hence Heisenberg's Uncertainty Principle.....	70
❖ Pictorial Representation of the Wave Equation of a Particle in One Dimensional Box and Its Influence on the Kinetic Energy of the Particle in Each Successive Quantum Level .....	75
❖ Lowest Energy of the Particle .....	80
❖ Problems .....	82
❖ Bibliography .....	83
<b>CHAPTER 2 .....</b>	<b>84</b>
<b>Thermodynamics – I .....</b>	<b>84</b>
❖ Brief Resume of First and Second Law of Thermodynamics.....	84
❖ Entropy Changes in Reversible and Irreversible Processes.....	87
❖ Variation of Entropy with Temperature, Pressure and Volume .....	92
❖ Entropy Concept as a Measure of Unavailable Energy and Criteria for the Spontaneity of Reaction .....	94
❖ Free Energy, Enthalpy Functions and Their Significance, Criteria for Spontaneity of a Process ...	98
❖ Partial Molar Quantities (Free Energy, Volume, Heat Concept).....	104
❖ Gibb's-Duhem Equation.....	108
❖ Problems .....	111
❖ Bibliography .....	112



<b>CHAPTER 3 .....</b>	<b>113</b>
<b>Chemical Dynamics – I.....</b>	<b>113</b>
❖ Effect of Temperature on Reaction Rates.....	113
❖ Rate Law for Opposing Reactions of Ist Order and IInd Order.....	119
❖ Rate Law for Consecutive & Parallel Reactions of Ist Order Reactions .....	127
❖ Collision Theory of Reaction Rates and Its Limitations .....	135
❖ Steric Factor.....	141
❖ Activated Complex Theory .....	143
❖ Ionic Reactions: Single and Double Sphere Models .....	147
❖ Influence of Solvent and Ionic Strength.....	152
❖ The Comparison of Collision and Activated Complex Theory.....	157
❖ Problems .....	158
❖ Bibliography .....	159
<b>CHAPTER 4 .....</b>	<b>160</b>
<b>Electrochemistry – I: Ion-Ion Interactions .....</b>	<b>160</b>
❖ The Debye-Huckel Theory of Ion-Ion Interactions .....	160
❖ Potential and Excess Charge Density as a Function of Distance from the Central Ion .....	168
❖ Debye-Huckel Reciprocal Length .....	173
❖ Ionic Cloud and Its Contribution to the Total Potential .....	176
❖ Debye-Huckel Limiting Law of Activity Coefficients and Its Limitations.....	178
❖ Ion-Size Effect on Potential.....	185
❖ Ion-Size Parameter and the Theoretical Mean - Activity Coefficient in the Case of Ionic Clouds with Finite-Sized Ions.....	187
❖ Debye-Huckel-Onsager Treatment for Aqueous Solutions and Its Limitations.....	190
❖ Debye-Huckel-Onsager Theory for Non-Aqueous Solutions.....	195
❖ The Solvent Effect on the Mobility at Infinite Dilution .....	196
❖ Equivalent Conductivity ( $\Lambda$ ) vs Concentration $C^{1/2}$ as a Function of the Solvent .....	198
❖ Effect of Ion Association Upon Conductivity (Debye-Huckel-Bjerrum Equation) .....	200
❖ Problems .....	209
❖ Bibliography .....	210
<b>CHAPTER 5 .....</b>	<b>211</b>
<b>Quantum Mechanics – II .....</b>	<b>211</b>
❖ Schrodinger Wave Equation for a Particle in a Three Dimensional Box .....	211

❖ The Concept of Degeneracy Among Energy Levels for a Particle in Three Dimensional Box ....	215
❖ Schrodinger Wave Equation for a Linear Harmonic Oscillator & Its Solution by Polynomial Method .....	217
❖ Zero Point Energy of a Particle Possessing Harmonic Motion and Its Consequence .....	229
❖ Schrodinger Wave Equation for Three Dimensional Rigid Rotator.....	231
❖ Energy of Rigid Rotator .....	241
❖ Space Quantization.....	243
❖ Schrodinger Wave Equation for Hydrogen Atom: Separation of Variable in Polar Spherical Coordinates and Its Solution .....	247
❖ Principal, Azimuthal and Magnetic Quantum Numbers and the Magnitude of Their Values.....	268
❖ Probability Distribution Function.....	276
❖ Radial Distribution Function .....	278
❖ Shape of Atomic Orbitals ( <i>s</i> , <i>p</i> & <i>d</i> ).....	281
❖ Problems .....	287
❖ Bibliography .....	288

## **CHAPTER 6 ..... 289**

### **Thermodynamics – II..... 289**

❖ Clausius-Clapeyron Equation.....	289
❖ Law of Mass Action and Its Thermodynamic Derivation .....	293
❖ Third Law of Thermodynamics (Nernst Heat Theorem, Determination of Absolute Entropy, Unattainability of Absolute Zero) And Its Limitation.....	296
❖ Phase Diagram for Two Completely Miscible Components Systems .....	304
❖ Eutectic Systems (Calculation of Eutectic Point).....	311
❖ Systems Forming Solid Compounds $A_xB_y$ with Congruent and Incongruent Melting Points .....	321
❖ Phase Diagram and Thermodynamic Treatment of Solid Solutions.....	332
❖ Problems .....	342
❖ Bibliography .....	343

## **CHAPTER 7 ..... 344**

### **Chemical Dynamics – II ..... 344**

❖ Chain Reactions: Hydrogen-Bromine Reaction, Pyrolysis of Acetaldehyde, Decomposition of Ethane.....	344
❖ Photochemical Reactions (Hydrogen-Bromine & Hydrogen-Chlorine Reactions).....	352
❖ General Treatment of Chain Reactions (Ortho-Para Hydrogen Conversion and Hydrogen-Bromine Reactions).....	358

❖ Apparent Activation Energy of Chain Reactions .....	362
❖ Chain Length .....	364
❖ Rice-Herzfeld Mechanism of Organic Molecules Decomposition (Acetaldehyde) .....	366
❖ Branching Chain Reactions and Explosions ( $H_2-O_2$ Reaction) .....	368
❖ Kinetics of (One Intermediate) Enzymatic Reaction: Michaelis-Menten Treatment .....	371
❖ Evaluation of Michaelis's Constant for Enzyme-Substrate Binding by Lineweaver-Burk Plot and Eadie-Hofstee Methods .....	375
❖ Competitive and Non-Competitive Inhibition .....	378
❖ Problems .....	388
❖ Bibliography .....	389
<b>CHAPTER 8 .....</b>	<b>390</b>
<b>Electrochemistry – II: Ion Transport in Solutions .....</b>	<b>390</b>
❖ Ionic Movement Under the Influence of an Electric Field .....	390
❖ Mobility of Ions .....	393
❖ Ionic Drift Velocity and Its Relation with Current Density .....	394
❖ Einstein Relation Between the Absolute Mobility and Diffusion Coefficient .....	398
❖ The Stokes-Einstein Relation .....	401
❖ The Nernst-Einstein Equation .....	403
❖ Walden's Rule .....	404
❖ The Rate-Process Approach to Ionic Migration .....	406
❖ The Rate-Process Equation for Equivalent Conductivity .....	410
❖ Total Driving Force for Ionic Transport: Nernst-Planck Flux Equation .....	412
❖ Ionic Drift and Diffusion Potential .....	416
❖ The Onsager Phenomenological Equations .....	418
❖ The Basic Equation for the Diffusion .....	419
❖ Planck-Henderson Equation for the Diffusion Potential .....	422
❖ Problems .....	425
❖ Bibliography .....	426
<b>INDEX .....</b>	<b>427</b>



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