

❖ The Heisenberg's Uncertainty Principle

In quantum mechanical world, the Heisenberg's uncertainty principle (or simply the uncertainty principle) is one of a variety of mathematical inequalities asserting a fundamental limit to the precision with which certain pairs of physical properties of a particle, known as complementary variables or canonically conjugate variables such as position x and momentum p , can be known. The concept was first introduced in 1927, by a German physicist Werner Heisenberg.

The Heisenberg's uncertainty principle states that the more precisely the position of some particle is determined, the less precisely its momentum can be known, and vice versa.

The formal inequality relating the standard deviation of position Δx and the standard deviation of momentum Δp_x was derived by Earle Hesse Kennard later that year and by Hermann Weyl in 1928:

$$\Delta x \cdot \Delta p_x \geq \frac{h}{4\pi} \quad (37)$$

or

$$\Delta x \cdot \Delta p_x \geq \hbar/2 \quad (38)$$

Where \hbar is the reduced Planck's constant, which is obviously equal to the Planck's constant divided by 2π . Besides the equation (37), there is also an energy-time uncertainty relation given by W. Heisenberg which states that higher the lifetime of a quantum mechanical state, less uncertain would be the energy value. Mathematically, it can be shown as:

$$\Delta E \cdot \Delta t \geq \frac{h}{2\pi} \quad (39)$$

Where ΔE and Δt represent the uncertainties in the energy and time respectively.

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➤ **Position Momentum Uncertainty**

Among various kinds of uncertainties, the position-momentum uncertainty is one of the popular kind that arises as a consequence of wave-particle duality. In order to understand the relation, we first need to study the effect of wave behavior on the simultaneous measurement of position about x -coordinate and the linear momentum component along the x -axis for a microscopic particle.

Consider a beam of particles traveling with a momentum “ p ” along the y -direction, and this beam finally strikes a narrow slit of width “ w ”. Now, from the principles of optics, we know that the uncertainty in the position of the particle along x -axis must be equal to the slit width. In other words, as the width of the slit is along x -axis, any particle that strikes the detector must have crossed the Δx region i.e. w , the slit width available. However, we exactly don't know where it does cross from. It could be along the center of the slit, or along a line slightly above or below the central trajectory. Therefore, the slit width ($w = \Delta x$) would be equal to a crossing domain that we are uncertain about. However, a diffraction pattern will be observed in the case of microscopic particles because of their wave-like character. The amplitude of the wave at a particular point on the detector represents the number of the particles reaching that point. Now because of this diffraction, the incident beam does not strike only at the central point O but also at the above and below to it. It means that some particles do reach upward and downward to O , suggesting that the part of their linear momentum is transferred along x -axis also.

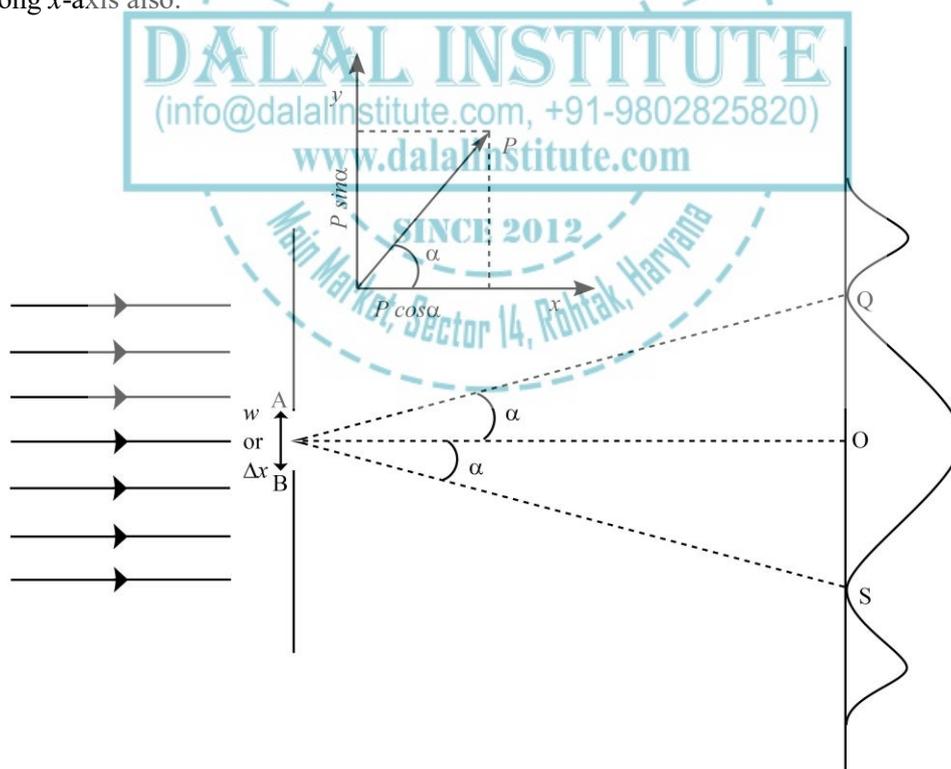


Figure 4. The diffraction of electron waves by single slit systems.

The x -component of linear momentum of the wave (aka particle) diffracted at an angle α can be obtained by the rectangular resolution of the linear momentum vector. The particles diffracted upward and downward at an angle α will yield the x -component as $P \sin\alpha$ and $-P \sin\alpha$, respectively. Now because a large number of particles reach the plate in between $+\alpha$ to $-\alpha$ i.e. in between the first minimums, half of the momentum spread in the central diffraction peak should give the uncertainty in the momentum along x -axis. Mathematically, we can say that

$$\Delta p_x = P \sin\alpha \quad (40)$$

Multiplying the above equation by the uncertainty in the position i.e. width of the slit used for the measurement purpose, we get

$$\Delta x \cdot \Delta p_x = w \cdot P \sin\alpha \quad (41)$$

Here, it is very important to recall the fact that the condition which must be satisfied to obtain the first minima is that the path difference between the waves reaching the minima point should be an integral multiple of $\lambda/2$.

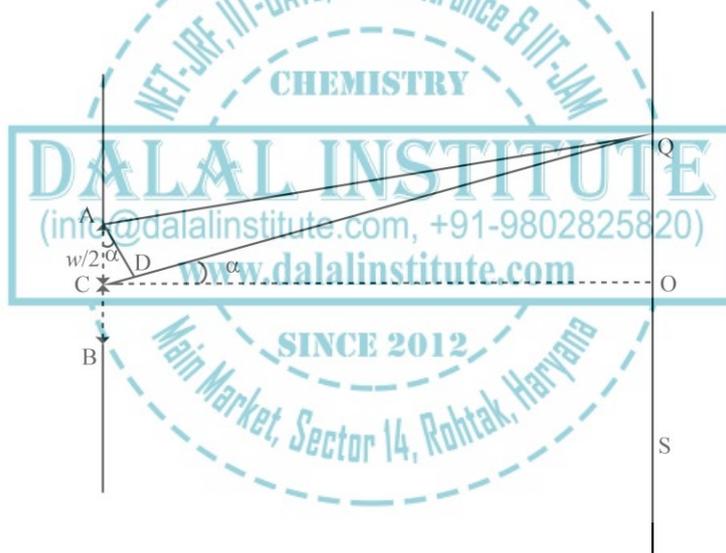


Figure 5. The calculation for 1st order diffraction for electron wave in single slit systems.

Hence we have the following equalities from the diagram given above.

$$AQ = DQ \quad (42)$$

$$CQ = \text{difference in the path length} \quad (43)$$

Now because the distance of the detector is very large as compared to the slit width, AQ and CQ can be considered parallel to each other i.e. $AQ \parallel DQ$. Hence, we can say that

$$\angle ADC = 90^\circ \quad (44)$$

$$\angle CAD = \alpha \quad (45)$$

also

$$AC = \frac{w}{2} \quad (46)$$

$$CD = \frac{\lambda}{2} \quad (47)$$

From the trigonometric relations, we get

$$\frac{CD}{AC} = \sin \alpha \quad (48)$$

$$CD = AC \sin \alpha \quad (49)$$

Putting the values of AC and CD from equation (46) and (47) in equation (49), we get

$$\frac{\lambda}{2} = \frac{w}{2} \sin \alpha \quad (50)$$

$$\lambda = w \sin \alpha \quad (51)$$

Now, after putting the value of w from equation (51) in equation (41), we get

$$\Delta x \cdot \Delta p_x = \frac{\lambda}{\sin \alpha} \cdot P \sin \alpha \quad (52)$$

$$\Delta x \cdot \Delta p_x = \lambda \cdot P \quad (53)$$

Using the de Broglie relation ($\lambda = h/p$) in equation (53), we get

$$\Delta x \cdot \Delta p_x = \frac{h}{p} \cdot P \quad (54)$$

$$\Delta x \cdot \Delta p_x = h \quad (55)$$

Now because we didn't define the uncertainty very precisely, we should not use the "equal" sign. Therefore, the above equation can be reduced to the following.

$$\Delta x \cdot \Delta p_x \approx h \quad (56)$$

This eventually means that decreasing the uncertainty in the position of the incident particle (decreasing the slit width) would result in a higher uncertainty in the momentum along x -axis; while the higher slit width does give more precise momentum but small precision in the calculation of the position of the incident particle.

➤ **Energy Time Uncertainty**

The uncertainty principle doesn't limit itself to position-momentum only but can also be applied to some other pairs of conjugate variables. All the variable pairs whose products have the same dimension as the Planck's constant h (Js) are said to be a conjugate pair. Besides the position-momentum, another famous uncertainty is relation energy-time because the product of these two quantities (energy \times time) also has the unit of h (Js).

$$\Delta E \cdot \Delta t \approx h \quad (57)$$

Where ΔE and Δt are uncertainties in energy and time, respectively. This popular relation can be derived directly from the concept of wave-particle duality. In the quantum mechanical world, a particle is supposed to possess a wave packet. Now, let us consider that this wave packet occupies the Δx region along the direction x -direction and travels with a velocity v . The time it needs to pass a certain point in x -direction has an uncertainty magnitude of Δt , and can be formulated as:

$$\Delta t = \frac{\Delta x}{v} \quad (58)$$

Now because this wave packet occupies the region Δx , the momentum uncertainty along x -axis can be given by the following relation.

$$\Delta p_x = \frac{h}{\Delta x} \quad (59)$$

or

$$\Delta x = \frac{h}{\Delta p_x} \quad (60)$$

Putting the value of Δx from equation (60) in equation (58), we get

$$\Delta t = \frac{h}{v\Delta p_x} \quad (61)$$

Moreover, we also know that

$$E = \frac{p_x^2}{2m} \quad (62)$$

Differentiating the above equation w.r.t p_x , we get

$$\frac{dE}{dp_x} = \frac{\Delta E}{\Delta p_x} = \frac{p_x}{m} = \frac{mv}{m} = v \quad (63)$$

$$\Delta E = \frac{dE}{dp_x} \Delta p_x = v \cdot \Delta p_x \quad (64)$$

Multiplying equation (63) and (64), we get

$$\Delta E \cdot \Delta t = v \Delta p_x \cdot \frac{h}{v \Delta p_x} \quad (65)$$

$$\Delta E \cdot \Delta t \approx h \quad (66)$$

The physical interpretation of the above relation can be viewed in terms of fluctuating energy level with a total ΔE uncertainty if the system does not stay in it longer than Δt interval of time i.e. lifetime of the state.

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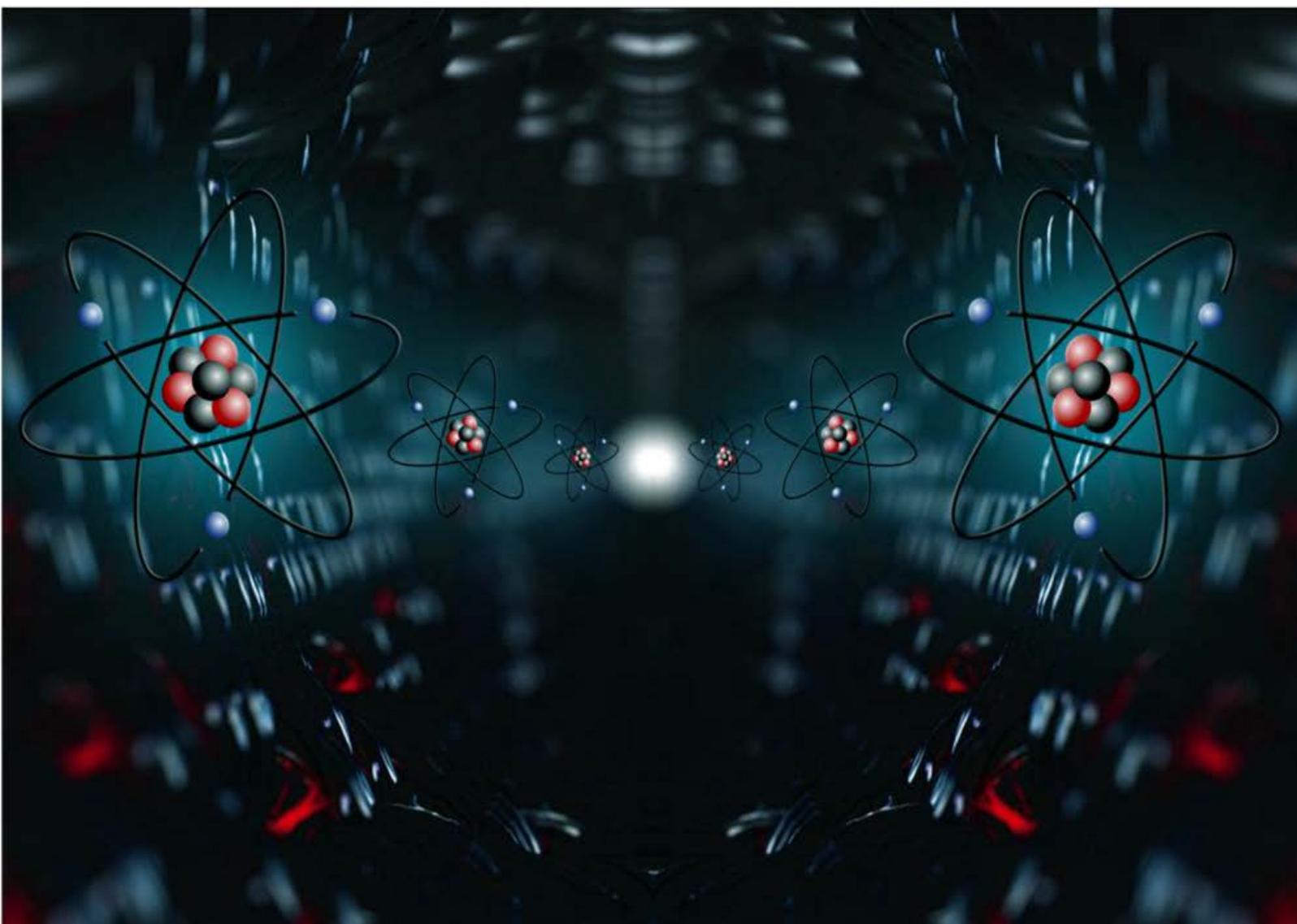
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A TEXTBOOK OF PHYSICAL CHEMISTRY

Volume I

MANDEEP DALAL



First Edition

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Table of Contents

CHAPTER 1	11
Quantum Mechanics – I	11
❖ 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
CHAPTER 2	84
Thermodynamics – I	84
❖ 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

CHAPTER 3	113
Chemical Dynamics – I.....	113
❖ 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
CHAPTER 4	160
Electrochemistry – I: Ion-Ion Interactions	160
❖ 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 (Λ) 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
CHAPTER 5	211
Quantum Mechanics – II	211
❖ 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
CHAPTER 8	390
Electrochemistry – II: Ion Transport in Solutions	390
❖ 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
INDEX	427



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