

### ❖ Partial Molar Quantities (Free Energy, Volume, Heat Concept)

So far we have discussed the variation of various thermodynamic properties with respect to temperature and pressure while the composition of the system was kept constant (closed system). In 1907, G.N. Lewis started the study of open systems i.e. the variation of various thermodynamic properties with respect to the composition of one or more components. In other words, he studied the behavior of a particular thermodynamic property of the system when a component is removed from or added to the system under consideration. Now since a variation like this is observable only for an extensive property, the general definition of partial molar properties can be given as given below.

*A partial molar property may simply be defined as a thermodynamic quantity which indicates how an extensive property of a solution or mixture changes with the variation in the molar composition of the mixture at constant temperature and pressure.*

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Basically, it is the partial derivative of the extensive property with respect to the number of moles of the component under consideration. All extensive properties of a mixture have corresponding partial molar properties. In this section, we will discuss some very important partial molar quantities like partial molar free energy ( $\bar{G}_i$ ), partial molar volume ( $\bar{V}_i$ ) and partial molar enthalpy ( $\bar{H}_i$ ).

➤ **Partial Molar Free Energy or Chemical Potential**

In order to derive the expression for partial molar free energy, consider a system that comprises of  $n$  types of constituents with  $n_1, n_2, n_3, n_4 \dots$  moles. So, being an extensive property, the partial molar free energy depends upon not only the temperature and pressure but also on the number of moles of different components. Mathematically, we can say that

$$G = f(T, P, n_1, n_2, n_3 \dots) \quad (160)$$

Now let us assume a small change in the temperature, pressure and amount of different components, this would impart a variation in partial molar free energy as given below.

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P, n_1, n_2, \dots} dT + \left(\frac{\partial G}{\partial P}\right)_{T, n_1, n_2, \dots} dP + \left(\frac{\partial G}{\partial n_1}\right)_{T, P, n_2, n_3, \dots} dn_1 + \dots \quad (161)$$

The first term on the right-hand side gives the change in the free energy with temperature at constant pressure and compositions; while the second term gives the change in the free energy with pressure at constant temperature and compositions. The terms afterward represent the variation in free energy with the amount of one component while the temperature, pressure and all other compositions are kept constant.

However, if the temperature and pressure of the system are kept constant i.e.  $dT = 0$ ,  $dP = 0$ , the equation (161) takes the form

$$(dG)_{T, P} = \left(\frac{\partial G}{\partial n_1}\right)_{T, P, n_2, n_3, \dots} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T, P, n_1, n_3, \dots} dn_2 + \left(\frac{\partial G}{\partial n_3}\right)_{T, P, n_1, n_2, \dots} dn_3 \dots \quad (162)$$

Every term on the right-hand side of the equation (162) is partial molar free energy and is symbolized by a “bar” over it i.e.

$$(dG)_{T, P} = \bar{G}_1 dn_1 + \bar{G}_2 dn_2 + \bar{G}_3 dn_3 \dots \quad (163)$$

For the  $i$ th component, we can say that

$$\bar{G}_i = \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_2, n_3, \dots} \quad (164)$$

The equation (164) gives the general expression for “partial molar free energy” or the “chemical potential” of the  $i$ th species.

➤ **Partial Molar Volume**

In order to derive the expression for partial molar volume, consider a system that comprises of  $n$  types of constituents with  $n_1, n_2, n_3, n_4 \dots$  moles. So, being an extensive property, volume depends upon not only the temperature and pressure but also on the number of moles of different components. Mathematically, we can say that

$$V = f(T, P, n_1, n_2, n_3 \dots) \quad (165)$$

Now let us assume a small change in the temperature, pressure and amount of different components, this would impart a variation in partial molar volume as given below.

$$dV = \left(\frac{\partial V}{\partial T}\right)_{P, n_1, n_2, \dots} dT + \left(\frac{\partial V}{\partial P}\right)_{T, n_1, n_2, \dots} dP + \left(\frac{\partial V}{\partial n_1}\right)_{T, P, n_2, n_3, \dots} dn_1 + \dots \quad (166)$$

The first term on the right-hand side gives the change in the volume with the temperature at constant pressure and compositions; while the second term gives the change in the volume with pressure at constant temperature and compositions. The terms afterward represent the variation in volume with the amount of one component while the temperature, pressure and all other compositions are kept constant.

However, if the temperature and pressure of the system are kept constant i.e.  $dT = 0, dP = 0$ , the equation (166) takes the form

$$(dV)_{T, P} = \left(\frac{\partial V}{\partial n_1}\right)_{T, P, n_2, n_3, \dots} dn_1 + \left(\frac{\partial V}{\partial n_2}\right)_{T, P, n_1, n_3, \dots} dn_2 + \left(\frac{\partial V}{\partial n_3}\right)_{T, P, n_1, n_2, \dots} dn_3 \dots \quad (167)$$

Every term on the right-hand side of the equation (167) is partial molar volume and is symbolized by a “bar” over it i.e.

$$\bar{V}_1 = \left(\frac{\partial V}{\partial n_1}\right)_{T, P, n_2, n_3, \dots} \quad (168)$$

$$\bar{V}_2 = \left(\frac{\partial V}{\partial n_2}\right)_{T, P, n_1, n_3, \dots} \quad (169)$$

After putting the values from equations like (168 – 169) in equation (167), we get

$$(dV)_{T, P} = \bar{V}_1 dn_1 + \bar{V}_2 dn_2 + \bar{V}_3 dn_3 \dots \quad (170)$$

For the  $i$ th component, we can say that

$$\bar{V}_i = \left(\frac{\partial V}{\partial n_i}\right)_{T, P, n_2, n_3, \dots} \quad (171)$$

The equation (171) gives the general expression for the “partial molar volume” of the  $i$ th species.

➤ **Partial Molar Enthalpy or Partial Molar Heat Content**

In order to derive the expression for partial molar enthalpy, consider a system that comprises of  $n$  types of constituents with  $n_1, n_2, n_3, n_4 \dots$  moles. So, being an extensive property, volume depends upon not only the temperature and pressure but also on the number of moles of different components, i.e.,

$$H = f(T, P, n_1, n_2, n_3 \dots) \quad (172)$$

Now let us assume a small change in the temperature, pressure and amount of different components, this would impart a variation in molar enthalpy as given below.

$$dH = \left(\frac{\partial H}{\partial T}\right)_{P, n_1, n_2, \dots} dT + \left(\frac{\partial H}{\partial P}\right)_{T, n_1, n_2, \dots} dP + \left(\frac{\partial H}{\partial n_1}\right)_{T, P, n_2, n_3, \dots} dn_1 + \dots \quad (173)$$

The first term on the right-hand side gives the change in the enthalpy with the temperature at constant pressure and compositions; while the second term gives the change in the enthalpy with pressure at constant temperature and compositions. The terms afterward represent the variation in enthalpy with the amount of one component while the temperature, pressure and all other compositions are kept constant.

However, if the temperature and pressure of the system are kept constant i.e.  $dT = 0, dP = 0$ , the equation (173) takes the form

$$(dH)_{T, P} = \left(\frac{\partial H}{\partial n_1}\right)_{T, P, n_2, n_3, \dots} dn_1 + \left(\frac{\partial H}{\partial n_2}\right)_{T, P, n_1, n_3, \dots} dn_2 + \left(\frac{\partial H}{\partial n_3}\right)_{T, P, n_1, n_2, \dots} dn_3 \dots \quad (174)$$

Every term on the right-hand side of the equation (174) is partial molar enthalpy and is symbolized by a “bar” over it i.e.

$$\bar{H}_1 = \left(\frac{\partial H}{\partial n_1}\right)_{T, P, n_2, n_3, \dots} \quad (175)$$

$$\bar{H}_2 = \left(\frac{\partial H}{\partial n_2}\right)_{T, P, n_1, n_3, \dots} \quad (176)$$

After putting the values from equations like (175 – 176) in equation (174), we get

$$(dH)_{T, P} = \bar{H}_1 dn_1 + \bar{H}_2 dn_2 + \bar{H}_3 dn_3 \dots \quad (177)$$

For the  $i$ th component, we can say that

$$\bar{H}_i = \left(\frac{\partial H}{\partial n_i}\right)_{T, P, n_2, n_3, \dots} \quad (178)$$

The equation (178) gives the general expression for the “partial molar enthalpy” of the  $i$ th species.

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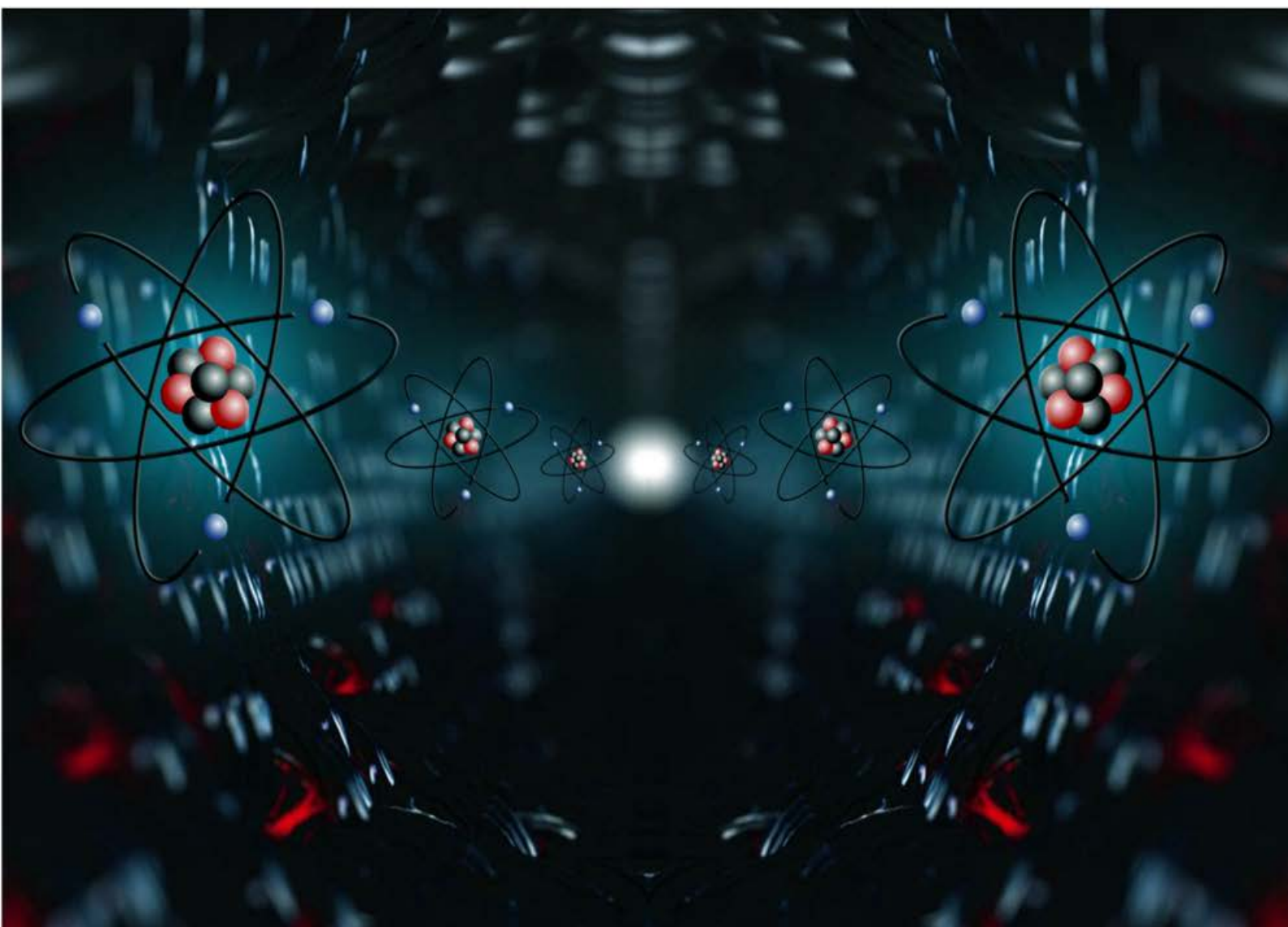
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**Volume I**

**MANDEEP DALAL**



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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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