

### ❖ Law of Mass Action and Its Thermodynamic Derivation

According to the law of mass action, the rate of a chemical reaction is directly proportional to the product of the activities or simply the active masses of the reactants each term raised to its stoichiometric coefficients.

To understand the law of mass action in mathematical language, consider a reaction in which two reactants  $A$  and  $B$  react to form the product  $C$  and  $D$  i.e.



Then the law of mass action says the rate of the above conversion should be

$$\text{Rate} \propto [A]^a [B]^b \quad (34)$$

$$\text{Rate} = k[A]^a [B]^b \quad (35)$$

Where  $k$  is the constant of proportionality and is typically labeled as rate constant of the reaction.

However, the actual rate of the reaction may or may not be equal to what is suggested by the “law of mass action” because the actual rate law may have powers raised to the active masses different from their stoichiometric coefficients. Mathematically, the actual rate law for the reaction given by equation (33) is

$$\text{Rate} \propto [A]^\alpha [B]^\beta \quad (36)$$

$$\text{Rate} = k[A]^\alpha [B]^\beta \quad (37)$$

Now comparing equation (35) and equation (37); the law of mass action and actual rate law will give same results when  $a = \alpha$  and  $b = \beta$ ; whereas different results will be observed when  $a \neq \alpha$  and  $b \neq \beta$ .

#### ➤ Modern Definition of the Law of Mass Action

The law of mass action can be used to study the composition of a mixture in a reversible reaction under equilibrium conditions. To do so, consider a typical reversible reaction i.e.



Now, from the law of mass action, we know that the rate of forward reaction ( $R_f$ ) and rate backward reaction ( $R_b$ ) will be

$$R_f = k_f [A]^a [B]^b \quad (39)$$

$$R_b = k_b [C]^c [D]^d \quad (40)$$

Where  $k_f$  and  $k_b$  are the rate constants for the forward and backward reactions, respectively. After equilibrium is reached, we have

$$R_f = R_b \quad (41)$$

$$k_f[A]^a[B]^b = k_b[C]^c[D]^d \quad (42)$$

or

$$\frac{k_f}{k_b} = \frac{[C]^c[D]^d}{[A]^a[B]^b} \quad (43)$$

Since the  $k_f$  and  $k_b$  are also constant at equilibrium, the ratio of the two is also a constant and is typically labeled as  $K$  or the equilibrium constant. Therefore, equation (43) is modified as

$$K = \frac{k_f}{k_b} = \frac{[C]^c[D]^d}{[A]^a[B]^b} \quad (44)$$

All this leads to the modern definition of “law of mass action” that the ratio of the multiplication of molar concentrations of products raised to the power of their stoichiometric coefficients to the multiplication of the molar concentrations of the reactants raised to the power of their stoichiometric coefficients is constant at constant temperature and is called as “equilibrium constant”. It is also worthy to mention that equation (44) is also known as the “law of chemical equilibrium”.

➤ **Thermodynamic Derivation of the Law of Mass Action**

In order to derive the law of mass action thermodynamically, recall the general form of a typical reversible reaction under equilibrium conditions in which reactants and products are ideal gases i.e.



Now, as we know that the total free energy of the reactant ( $G_R$ ) can be formulated as

$$G_R = a\mu_A + b\mu_B \quad (46)$$

Where  $\mu_A$  and  $\mu_B$  are the chemical potentials of reactant  $A$  and  $B$ , respectively. Similarly, the total free energy of the products ( $G_P$ ) can also be formulated i.e.

$$G_P = c\mu_C + d\mu_D \quad (47)$$

It is also important to mention that the temperature and pressure are kept constant. Moreover, the free energy change of the whole reaction can be obtained by subtracting equation (46) from equation (47) i.e.

$$\Delta G_{reaction} = G_P - G_R \quad (48)$$

$$\Delta G_{reaction} = (c\mu_C + d\mu_D) - (a\mu_A + b\mu_B) \quad (49)$$

Recalling the fact that the free energy change at equilibrium is zero, equation (49) is reduced to

$$(c\mu_C + d\mu_D) - (a\mu_A + b\mu_B) = 0 \quad (51)$$

Now recall the expression of the chemical potential of the  $i$ th species in gas phase i.e.

$$\mu_i = \mu_i^0 + RT \ln p_i \quad (52)$$

Where  $p_i$  and  $\mu_i^0$  are the partial pressure and standard chemical potential of  $i$ th species, respectively. Now using equation (52) in equation (51), we get

$$[c(\mu_C^0 + RT \ln p_C) + d(\mu_D^0 + RT \ln p_D)] - [a(\mu_A^0 + RT \ln p_A) + b(\mu_B^0 + RT \ln p_B)] = 0 \quad (53)$$

or

$$c\mu_C^0 + cRT \ln p_C + d\mu_D^0 + dRT \ln p_D - a\mu_A^0 - aRT \ln p_A - b\mu_B^0 - bRT \ln p_B = 0 \quad (54)$$

$$c\mu_C^0 + RT \ln p_C^c + d\mu_D^0 + RT \ln p_D^d - a\mu_A^0 - RT \ln p_A^a - b\mu_B^0 - RT \ln p_B^b = 0 \quad (55)$$

$$RT \ln p_C^c + RT \ln p_D^d - RT \ln p_A^a - RT \ln p_B^b = -c\mu_C^0 - d\mu_D^0 + a\mu_A^0 + b\mu_B^0$$

or

$$RT \ln (p_C^c p_D^d) - RT \ln (p_A^a p_B^b) = -[c\mu_C^0 + d\mu_D^0 - a\mu_A^0 - b\mu_B^0] \quad (56)$$

$$RT \ln \frac{(p_C^c p_D^d)}{(p_A^a p_B^b)} = -[G_P^0 - G_R^0] \quad (57)$$

$$RT \ln \frac{(p_C^c p_D^d)}{(p_A^a p_B^b)} = -\Delta G_{reaction}^0 \quad (58)$$

Where  $\Delta G_{reaction}^0$  is the standard free energy change of the reaction can be simply abbreviated as  $\Delta G^0$  only. Therefore, the equation (58) can be rearranged as given below.

$$\ln \frac{(p_C^c p_D^d)}{(p_A^a p_B^b)} = -\frac{\Delta G^0}{RT} \quad (59)$$

$$\frac{p_C^c p_D^d}{p_A^a p_B^b} = e^{-\frac{\Delta G^0}{RT}} \quad (61)$$

Now because  $\Delta G^0$  is a function of temperature only and  $R$  is a constant quantity, the right-hand side can be put equal to another constant, say ' $K_p$ '.

$$e^{-\frac{\Delta G^0}{RT}} = K_p \quad (62)$$

From equation (61) and equation (62), we have

$$K_p = \frac{p_C^c p_D^d}{p_A^a p_B^b} \quad (63)$$

Which is again the modern statement of "law of mass action" but in terms of partial pressures.

Other forms of equation (63) can also be written depending upon the reactants and products involved. If the chemical potentials of the reactants and products are in mole fractions ( $x_i$ ) i.e.

$$\mu_i = \mu_i^0 + RT \ln x_i \quad (64)$$

Then equation (63) takes the form

$$K_x = \frac{x_C^c x_D^d}{x_A^a x_B^b} \quad (65)$$

Similarly, If the chemical potentials of the reactants and products are in molar concentrations ( $c_i$ ) i.e.

$$\mu_i = \mu_i^0 + RT \ln c_i \quad (66)$$

Then equation (63) takes the form

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad (67)$$

Which is the popular form of “law of mass action”.

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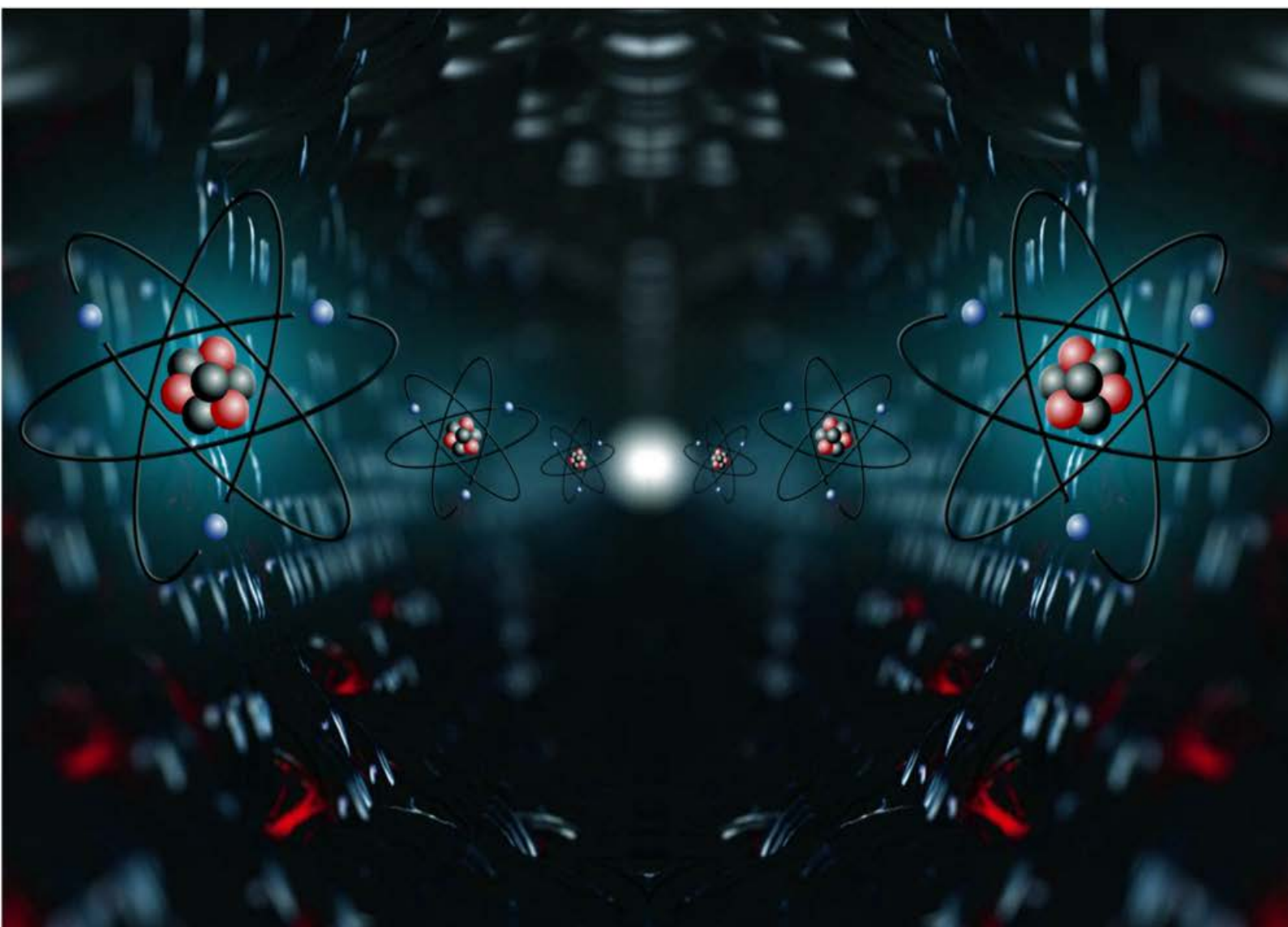
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# Table of Contents

<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 1st Order and 2nd Order.....	119
❖ Rate Law for Consecutive & Parallel Reactions of 1st 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
<b>CHAPTER 6 .....</b>	<b>289</b>
<b>Thermodynamics – II.....</b>	<b>289</b>
❖ 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
<b>CHAPTER 7 .....</b>	<b>344</b>
<b>Chemical Dynamics – II .....</b>	<b>344</b>
❖ 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>



*Mandeep Dalal*

*(M.Sc, Ph.D, CSIR UGC - NET JRF, IIT - GATE)*

*Founder & Director, Dalal Institute*

*Contact No: +91-9802825820*

*Homepage: [www.mandeepdalal.com](http://www.mandeepdalal.com)*

*E-Mail: [dr.mandeep.dalal@gmail.com](mailto:dr.mandeep.dalal@gmail.com)*

Mandeep Dalal is an Indian research scholar who is primarily working in the field of Science and Philosophy. He received his Ph.D in Chemistry from Maharshi Dayanand University, Rohtak, in 2018. He is also the Founder and Director of "Dalal Institute", an India-based educational organization which is trying to revolutionize the mode of higher education in Chemistry across the globe. He has published more than 40 research papers in various international scientific journals, including mostly from Elsevier (USA), IOP (UK) and Springer (Netherlands).

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