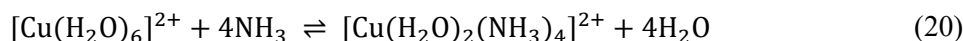


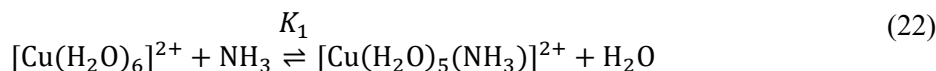
❖ Trends in Stepwise Constants

The values of stepwise equilibrium constants for the formation of a particular metal-complex decrease successively in most of the cases i.e. $K_1 > K_2 > K_3 > K_4 > K_5 > \dots > K_n$. This regular decrease in the values of stepwise formation constants may be attributed to the decrease in the number of coordinated H_2O ligands that are available for the replacement by the attacking ligands. Besides, the continuous decline in the values of successive stepwise stability constant values may also be attributed to the decreasing ability of metal ions with a progressive intake of ligands, Coulombic factors and steric hindrance. Consider the following ligand displacement reaction:



$$\beta_4 = \frac{[[\text{Cu}(\text{H}_2\text{O})_2(\text{NH}_3)_4]^{2+}][\text{H}_2\text{O}]^4}{[[\text{Cu}(\text{H}_2\text{O})_6]^{2+}][\text{NH}_3]^4} \quad (21)$$

The overall process can be supposed to take place through the following steps:

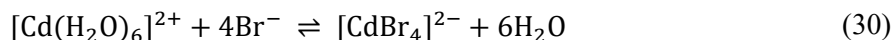


$$K_1 = \frac{[[\text{Cu}(\text{H}_2\text{O})_5(\text{NH}_3)]^{2+}][\text{H}_2\text{O}]}{[[\text{Cu}(\text{H}_2\text{O})_6]^{2+}][\text{NH}_3]} \quad (23)$$

LEGAL NOTICE

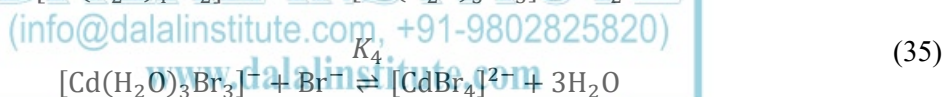
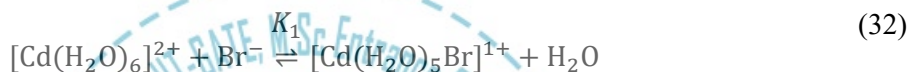
This document is an excerpt from the book entitled “A Textbook of Inorganic Chemistry – Volume 1 by Mandeep Dalal”, and is the intellectual property of the Author/Publisher. The content of this document is protected by international copyright law and is valid only for the personal preview of the user who has originally downloaded it from the publisher’s website (www.dalalinstitute.com). Any act of copying (including plagiarizing its language) or sharing this document will result in severe civil and criminal prosecution to the maximum extent possible under law.

Now although the decreasing trend in stepwise constants is pretty much common in most of the complex formation processes, still some exceptions do exist in which it is found that $K_{n+1} > K_n$. This weird behavior in stepwise equilibrium constants may be explained in terms of some unusual structural deviations and variations in the electronic structure of the metal center. The deviations in electronic configurations cause the change in crystal field stabilization energy (CFSE), and therefore, also affect the overall stability of the metal complex i.e. complex with a large magnitude of CFSE will be more stable and, consequently, will have higher value of the stepwise formation constants. Consider the following ligand displacement reaction:



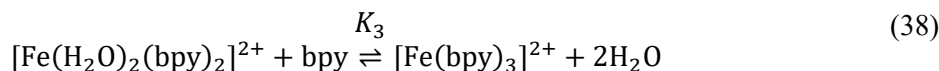
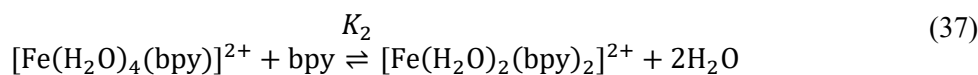
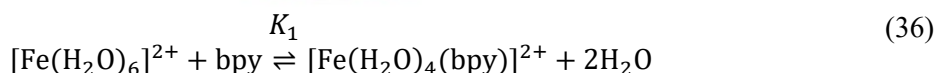
$$\beta_4 = \frac{[[\text{CdBr}_4]^{2-}][\text{H}_2\text{O}]^6}{[[\text{Cd}(\text{H}_2\text{O})_6]^{2+}][\text{Br}^-]^4} \quad (31)$$

The overall process can be supposed to take place through the following steps:



It has been observed that $\log K$ values follows the order $K_1 > K_2 > K_3 < K_4$, instead of $K_1 > K_2 > K_3 > K_4$. This unusually high value of K_4 is because the last step is actually pretty much favored by the release of three aquo ligands and some simultaneous structural and electronic changes.

Similarly, consider the formation of $[\text{Fe}(\text{bpy})_3]^{2+}$ complex:



It has been observed that $\log K$ values follow the order $K_1 > K_2 < K_3$, instead of $K_1 > K_2 > K_3$. This unusually high value of K_3 is because the complexes formed during first two steps are high spin due to weak H_2O ligands with a CFSE of $-0.4\Delta_o$ ($t_{2g}^4 e_g^2$), while the last complex $[\text{Fe}(\text{bpy})_3]^{2+}$ is low spin with a CFSE value of $-2.4\Delta_o$ ($t_{2g}^6 e_g^0$). Hence, large crystal field stabilization in the last step makes K_3 even greater than K_2 .

LEGAL NOTICE

This document is an excerpt from the book entitled “A Textbook of Inorganic Chemistry – Volume 1 by Mandeep Dalal”, and is the intellectual property of the Author/Publisher. The content of this document is protected by international copyright law and is valid only for the personal preview of the user who has originally downloaded it from the publisher’s website (www.dalalinstitute.com). Any act of copying (including plagiarizing its language) or sharing this document will result in severe civil and criminal prosecution to the maximum extent possible under law.



This is a low resolution version only for preview purpose. If you want to read the full book, please consider buying.

Buy the complete book with TOC navigation, high resolution images and no watermark.

Home

CLASSES

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM

Want to study chemistry for CSIR UGC - NET JRF, IIT-GATE, M.Sc Entrance, IIT-JAM, UPSC, ISRO, IISc, TIFR, DRDO, BARC, JEST, GRE, Ph.D Entrance or any other competitive examination where chemistry is a paper ?

[READ MORE](#)

BOOKS

Publications

Are you interested in books (Print and Ebook) published by Dalal Institute ?

[READ MORE](#)

VIDEOS

Video Lectures

Want video lectures in chemistry for CSIR UGC - NET JRF, IIT-GATE, M.Sc Entrance, IIT-JAM, UPSC, ISRO, IISc, TIFR, DRDO, BARC, JEST, GRE, Ph.D Entrance or any other competitive examination where chemistry is a paper ?

[READ MORE](#)

Home: <https://www.dalalinstitute.com/>

Classes: <https://www.dalalinstitute.com/classes/>

Books: <https://www.dalalinstitute.com/books/>

Videos: <https://www.dalalinstitute.com/videos/>

Location: <https://www.dalalinstitute.com/location/>

Contact Us: <https://www.dalalinstitute.com/contact-us/>

About Us: <https://www.dalalinstitute.com/about-us/>

Postgraduate Level Classes (NET-JRF & IIT-GATE)

Admission

[Regular Program](#)

[Test Series](#)

[Distance Learning](#)

[Result](#)

Undergraduate Level Classes (M.Sc Entrance & IIT-JAM)

Admission

[Regular Program](#)

[Test Series](#)

[Distance Learning](#)

[Result](#)

A Textbook of Inorganic Chemistry – Volume 1

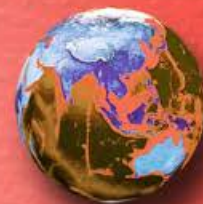
“A Textbook of Inorganic Chemistry – Volume 1 by Mandeep Dalal” is now available globally; including India, America and most of the European continent. Please ask at your local bookshop or get it online here.

[READ MORE](#)

Join the revolution by becoming a part of our community and get all of the member benefits like downloading any PDF document for your personal preview.

[Sign Up](#)

International
Edition



A TEXTBOOK OF INORGANIC CHEMISTRY

Volume I

MANDEEP DALAL



First Edition

DALAL INSTITUTE

Table of Contents

CHAPTER 1	11
Stereochemistry and Bonding in Main Group Compounds:.....	11
❖ VSEPR Theory	11
❖ $d\pi-p\pi$ Bonds	23
❖ Bent Rule and Energetic of Hybridization.....	28
❖ Problems	42
❖ Bibliography	43
CHAPTER 2	44
Metal-Ligand Equilibria in Solution:.....	44
❖ Stepwise and Overall Formation Constants and Their Interactions	44
❖ Trends in Stepwise Constants.....	46
❖ Factors Affecting Stability of Metal Complexes with Reference to the Nature of Metal Ion and Ligand.....	49
❖ Chelate Effect and Its Thermodynamic Origin.....	56
❖ Determination of Binary Formation Constants by pH-metry and Spectrophotometry.....	63
❖ Problems	68
❖ Bibliography	69
CHAPTER 3	70
Reaction Mechanism of Transition Metal Complexes – I:.....	70
❖ Inert and Labile Complexes.....	70
❖ Mechanisms for Ligand Replacement Reactions	77
❖ Formation of Complexes from Aquo Ions.....	82
❖ Ligand Displacement Reactions in Octahedral Complexes- Acid Hydrolysis, Base Hydrolysis....	86
❖ Racemization of Tris Chelate Complexes	89
❖ Electrophilic Attack on Ligands	92
❖ Problems	94
❖ Bibliography	95

CHAPTER 4	96
Reaction Mechanism of Transition Metal Complexes – II:	96
❖ Mechanism of Ligand Displacement Reactions in Square Planar Complexes.....	96
❖ The Trans Effect.....	98
❖ Theories of Trans Effect.....	103
❖ Mechanism of Electron Transfer Reactions – Types; Outer Sphere Electron Transfer Mechanism and Inner Sphere Electron Transfer Mechanism.....	106
❖ Electron Exchange.....	117
❖ Problems.....	121
❖ Bibliography.....	122
CHAPTER 5	123
Isopoly and Heteropoly Acids and Salts:	123
❖ Isopoly and Heteropoly Acids and Salts of Mo and W: Structures of Isopoly and Heteropoly Anions	123
❖ Problems.....	152
❖ Bibliography.....	153
CHAPTER 6	154
Crystal Structures:	154
❖ Structures of Some Binary and Ternary Compounds Such as Fluorite, Antifluorite, Rutile, Antirutile, Cristobalite, Layer Lattices - CdI ₂ , BiI ₃ ; ReO ₃ , Mn ₂ O ₃ , Corundum, Pervoskite, Ilmenite and Calcite.....	154
❖ Problems.....	178
❖ Bibliography.....	179
CHAPTER 7	180
Metal-Ligand Bonding:	180
❖ Limitation of Crystal Field Theory.....	180
❖ Molecular Orbital Theory – Octahedral, Tetrahedral or Square Planar Complexes.....	184
❖ π -Bonding and Molecular Orbital Theory	198
❖ Problems.....	212
❖ Bibliography.....	213

CHAPTER 8	214
Electronic Spectra of Transition Metal Complexes:	214
❖ Spectroscopic Ground States	214
❖ Correlation and Spin-Orbit Coupling in Free Ions for 1st Series of Transition Metals.....	243
❖ Orgel and Tanabe-Sugano Diagrams for Transition Metal Complexes ($d^1 - d^9$ States).....	248
❖ Calculation of Dq , B and β Parameters	280
❖ Effect of Distortion on the d -Orbital Energy Levels	300
❖ Structural Evidence from Electronic Spectrum	307
❖ Jahn-Teller Effect	312
❖ Spectrochemical and Nephelauxetic Series	324
❖ Charge Transfer Spectra	328
❖ Electronic Spectra of Molecular Addition Compounds.....	336
❖ Problems	340
❖ Bibliography	341
CHAPTER 9	342
Magnetic Properties of Transition Metal Complexes:	342
❖ Elementary Theory of Magneto-Chemistry	342
❖ Guoy's Method for Determination of Magnetic Susceptibility	351
❖ Calculation of Magnetic Moments	354
❖ Magnetic Properties of Free Ions.....	359
❖ Orbital Contribution: Effect of Ligand-Field	362
❖ Application of Magneto-Chemistry in Structure Determination	370
❖ Magnetic Exchange Coupling and Spin State Cross Over	375
❖ Problems	384
❖ Bibliography	385
CHAPTER 10	386
Metal Clusters:	386
❖ Structure and Bonding in Higher Boranes.....	386
❖ Wade's Rules.....	401

❖ Carboranes.....	407
❖ Metal Carbonyl Clusters- Low Nuclearity Carbonyl Clusters.....	412
❖ Total Electron Count (TEC).....	417
❖ Problems.....	424
❖ Bibliography.....	425
CHAPTER 11.....	426
Metal-II Complexes:	426
❖ Metal Carbonyls: Structure and Bonding.....	426
❖ Vibrational Spectra of Metal Carbonyls for Bonding and Structure Elucidation.....	439
❖ Important Reactions of Metal Carbonyls.....	446
❖ Preparation, Bonding, Structure and Important Reactions of Transition Metal Nitrosyl, Dinitrogen and Dioxygen Complexes.....	450
❖ Tertiary Phosphine as Ligand.....	463
❖ Problems.....	469
❖ Bibliography.....	470
INDEX.....	471



Mandeep Dalal

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

Founder & Director, Dalal Institute

Contact No: +91-9802825820

Homepage: www.mandeepdalal.com

E-Mail: 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) .

Other Books by the Author

A TEXTBOOK OF INORGANIC CHEMISTRY - VOLUME I, II, III, IV

A TEXTBOOK OF PHYSICAL CHEMISTRY - VOLUME I, II, III, IV

A TEXTBOOK OF ORGANIC CHEMISTRY - VOLUME I, II, III, IV

ISBN: 978-81-938720-0-0



9 788193 872000

MRP: Rs 800.00

**D DALAL
INSTITUTE**

Main Market, Sector 14, Rohtak, Haryana 124001, India

(+91-9802825820, info@dalalinstitute.com)

www.dalalinstitute.com