

❖ Hard and Soft Acids and Bases

Most of the Lewis acids can be distributed into two categories; class *a* and class *b* acids. Generally speaking, class *a* acids prefer to bind with Lewis bases with donor atom from second row non-metal (i.e. F, O or N); whereas class *b* acids prefer to bind with Lewis bases with donor atom coming from third or below row (i.e. Br, I, S or P). An American chemist Ralph Pearson then developed a model where Lewis acids and bases can be characterized by strength and softness. To understand the concept, consider a typical acid-base reaction i.e.



Where *A* is the acid, \ddot{B} is the base and *A:B* represents the complex. The equilibrium constant for the reaction (21) can be written as

$$\log K = S_A S_B + \sigma_A \sigma_B \quad (22)$$

Where S_A and S_B represent the strength of acid *A* and base *B*, respectively. The symbol σ_A and σ_B represent the softness of acid *A* and base *B*, respectively. The experimental data showed that class *a* metals form stable complexes with ligands having N, O, or F as the donor site; whereas class *b* metals form stable complexes with ligands having P, S, or Cl like donor atoms. Therefore, Ralph Pearson articulated his observation as given below.

This trend is explainable by the hard-soft acid-base principle which states that hard acid prefers a hard base while soft acid prefers a soft base for binding to yield stable systems.

The typical classification of different species based on hardness or softness is quite useful in the understanding of the chemical reactivity of organic reactions.

➤ Hard and Soft Acids

Metals such as Li^{1+} , Ba^{2+} , Mg^{2+} , and Al^{3+} , which have large negative reduction potential have a lesser tendency to attract electrons, and hence, form stable complexes with highly electronegative groups like N, F, or O so that they become unable to draw the unwanted electron density due to polarization. However, Metals like Pd^{2+} or Pt^{2+} which have large positive reduction potential have a greater tendency to accept electrons and hence form stable complexes with less electronegative groups like P so that they can easily grab the electron density by polarizing the surrounding.

A typical hard acid has a small size, high polarizing power, less distortable outer cloud, and high positive oxidation sometimes. On the other hand, a typical soft acid has a large size, low polarizing power, a highly distortable outer cloud, and zero or low positive oxidation sometimes.

Borderline cases are also identified: borderline acids are trimethylborane, sulfur dioxide and ferrous Fe^{2+} , cobalt Co^{2+} cesium Cs^+ and lead Pb^{2+} cations. It is also very important to mention that the borderline list may vary from book to book it is also medium-dependent.

Table 1. The class *a*, class *b*, and borderline metals.

Hard acid	Soft acid	Borderline acids
H^+ , Li^+ , Na^+ , K^+	Cu^+ , Ag^+ , Au^+ , Tl^+	
Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+}	Hg^{2+} , Pd^{2+} , Pt^{2+}	Mn^{2+} , Fe^{2+} , Co^{2+} , Sr^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+}
Al^{3+} , Ga^{3+} , In^{3+} , Cr^{3+} , Mn^{3+} , Fe^{3+} , Co^{3+} , La^{3+} , Ce^{3+} , Gd^{3+}	Tl^{3+}	
In^{4+} , Zr^{4+} , Hf^{4+} , Th^{4+} , U^{4+} , Pu^{4+}	Pt^{4+}	

➤ **Hard and Soft Bases**

The base becomes more and more soft as the donor atom is selected from the lower part of a particular group in the periodic table. For instance, F^- is the hardest, and I^- is the softest base in its group.

A typical soft base has the donor atom of low polarizability, high electronegativity, high negative charge density, and tightly held electron cloud. On the other hand, a typical soft base the donor atom of high polarizability, low electronegativity, less negative charge density, and loosely held electron cloud.

Borderline cases are also identified: borderline bases are aniline, pyridine, nitrogen N_2 , and the azide, chloride, bromide, nitrate, and sulfate anions. It is also very important to mention that the borderline list may vary from book to book it is also medium-dependent.

Table 2. The hard, soft, and borderline bases.

Hard bases	Soft bases	Borderline bases
F^- , OH^- , F^- , CH_3COO^- , H_2O , SO_4^{2-}	RSH , R_2S , R_3P	$C_6H_5NH_2$
NO_3^- , Cl^- , ROH , R_2O , RO^-	RS^- , I^- , SCN^- , H^- , $(RO)_3P$, CN^- , Alkenes, R^-	N_3^- , Br^- , NO_2^- , N_2
N_2H_4 , NH_3 , RLi , $RMgX$ $RCOOR$, RNH_2		SO_2^{2-}

It is also worthy to mention that hard nucleophiles or hard bases have the highest occupied molecular orbitals (HOMO) of higher energy whereas soft nucleophiles or soft bases have HOMOs of lower energy.

LEGAL NOTICE

This document is an excerpt from the book entitled “A Textbook of Organic 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

CSIR UGC – NET JRF, IIT-GATE, M.Sc Entrance, IIT-JAM, IIT-JEE, NEET, 11th and 12th

Want to study chemistry for CSIR UGC – NET JRF + IIT-GATE; IIT-JAM + M.Sc Entrance; IIT-JEE + NEET + 11th +12th; and all other postgraduate, undergraduate & senior-secondary level examinations 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; IIT-JAM + M.Sc Entrance; IIT-JEE + NEET + 11th +12th; and all other postgraduate, undergraduate & senior-secondary level examinations where chemistry is a paper?
[READ MORE](#)

Postgraduate Level

Senior-Secondary Level

Undergraduate Level

CSIR UGC – NET JRF & IIT-GATE

First Chemistry Batch
(1st January – 31st May)

Second Chemistry Batch
(1st July – 30th November)

11TH, 12TH, NEET & IIT-JEE

First Chemistry Batch
(1st April – 31st August)

Second Chemistry Batch
(1st October – 28th February)

M.SC ENTRANCE & IIT-JAM

First Chemistry Batch
(1st February – 30th June)

Second Chemistry Batch
(1st August – 31st December)

Regular Program

Online Course

Result

Regular Program

Online Course

Result

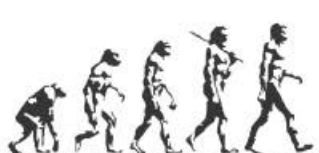
Regular Program

Online Course

Result

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](#)



JOIN THE REVOLUTION FROM BEAST TO

BUDDHA

D DALAL INSTITUTE

.....Chemical Science Demystified.....

Main Market, Sector 14, Rohtak, Haryana 124001, India
(+91-9802825820, info@dalalinstitute.com)
www.dalalinstitute.com

..... India's Best Coaching Center for Academic and Competitive Chemistry Exams
(CSIR UGC – NET JRF + IIT-GATE; IIT-JAM + M.Sc Entrance; IIT-JEE + NEET + 11th +12th; and all other postgraduate, undergraduate & senior-secondary level examinations where chemistry is a paper)

International
Edition



A TEXTBOOK OF ORGANIC CHEMISTRY

Volume I

MANDEEP DALAL



First Edition

DALAL INSTITUTE

Table of Contents

CHAPTER 1	11
Nature of Bonding in Organic Molecules	11
❖ Delocalized Chemical Bonding	11
❖ Conjugation	14
❖ Cross Conjugation	16
❖ Resonance	18
❖ Hyperconjugation	27
❖ Tautomerism	31
❖ Aromaticity in Benzenoid and Nonbenzenoid Compounds	33
❖ Alternant and Non-Alternant Hydrocarbons	35
❖ Huckel's Rule: Energy Level of π -Molecular Orbitals	37
❖ Annulenes	44
❖ Antiaromaticity	46
❖ Homoaromaticity	48
❖ PMO Approach	50
❖ Bonds Weaker Than Covalent	58
❖ Addition Compounds: Crown Ether Complexes and Cryptands, Inclusion Compounds, Cyclodextrins	65
❖ Catenanes and Rotaxanes	75
❖ Problems	79
❖ Bibliography	80
CHAPTER 2	81
Stereochemistry	81
❖ Chirality	81
❖ Elements of Symmetry	86
❖ Molecules with More Than One Chiral Centre: Diastereomerism	90
❖ Determination of Relative and Absolute Configuration (Octant Rule Excluded) with Special Reference to Lactic Acid, Alanine & Mandelic Acid	92
❖ Methods of Resolution	102
❖ Optical Purity	104
❖ Prochirality	105
❖ Enantiotopic and Diastereotopic Atoms, Groups and Faces	107
❖ Asymmetric Synthesis: Cram's Rule and Its Modifications, Prelog's Rule	113
❖ Conformational Analysis of Cycloalkanes (Upto Six Membered Rings)	116
❖ Decalins	122
❖ Conformations of Sugars	126
❖ Optical Activity in Absence of Chiral Carbon (Biphenyls, Allenes and Spiranes)	132
❖ Chirality Due to Helical Shape	137
❖ Geometrical Isomerism in Alkenes and Oximes	140
❖ Methods of Determining the Configuration	146

❖ Problems.....	151
❖ Bibliography.....	152
CHAPTER 3.....	153
Reaction Mechanism: Structure and Reactivity	153
❖ Types of Mechanisms.....	153
❖ Types of Reactions	156
❖ Thermodynamic and Kinetic Requirements.....	159
❖ Kinetic and Thermodynamic Control	161
❖ Hammond's Postulate.....	163
❖ Curtin-Hammett Principle	164
❖ Potential Energy Diagrams: Transition States and Intermediates	166
❖ Methods of Determining Mechanisms.....	168
❖ Isotope Effects	172
❖ Hard and Soft Acids and Bases.....	174
❖ Generation, Structure, Stability and Reactivity of Carbocations, Carbanions, Free Radicals, Carbenes and Nitrenes.....	176
❖ Effect of Structure on Reactivity	200
❖ The Hammett Equation and Linear Free Energy Relationship.....	203
❖ Substituent and Reaction Constants.....	209
❖ Taft Equation.....	215
❖ Problems.....	219
❖ Bibliography.....	220
CHAPTER 4.....	221
Carbohydrates	221
❖ Types of Naturally Occurring Sugars	221
❖ Deoxy Sugars	227
❖ Amino Sugars.....	229
❖ Branch Chain Sugars	230
❖ General Methods of Determination of Structure and Ring Size of Sugars with Particular Reference to Maltose, Lactose, Sucrose, Starch and Cellulose.....	231
❖ Problems.....	239
❖ Bibliography.....	240
CHAPTER 5.....	241
Natural and Synthetic Dyes	241
❖ Various Classes of Synthetic Dyes Including Heterocyclic Dyes	241
❖ Interaction Between Dyes and Fibers	245
❖ Structure Elucidation of Indigo and Alizarin	247
❖ Problems.....	252
❖ Bibliography.....	253
CHAPTER 6.....	254
Aliphatic Nucleophilic Substitution	254
❖ The S_N2 , S_N1 , Mixed S_N1 and S_N2 , S_Ni , S_N1' , S_N2' , S_N1'' and SET Mechanisms.....	254

❖ The Neighbouring Group Mechanisms.....	263
❖ Neighbouring Group Participation by π and σ Bonds	265
❖ Anchimeric Assistance	269
❖ Classical and Nonclassical Carbocations	272
❖ Phenonium Ions.....	283
❖ Common Carbocation Rearrangements.....	284
❖ Applications of NMR Spectroscopy in the Detection of Carbocations	286
❖ Reactivity – Effects of Substrate Structure, Attacking Nucleophile, Leaving Group and Reaction Medium	288
❖ Ambident Nucleophiles and Regioselectivity	294
❖ Phase Transfer Catalysis.....	297
❖ Problems.....	300
❖ Bibliography	301
CHAPTER 7	302
Aliphatic Electrophilic Substitution	302
❖ Bimolecular Mechanisms – SE_2 and SE_i	302
❖ The SE_1 Mechanism	305
❖ Electrophilic Substitution Accompanied by Double Bond Shifts	307
❖ Effect of Substrates, Leaving Group and the Solvent Polarity on the Reactivity	308
❖ Problems.....	310
❖ Bibliography	311
CHAPTER 8	312
Aromatic Electrophilic Substitution	312
❖ The Arenium Ion Mechanism.....	312
❖ Orientation and Reactivity	314
❖ Energy Profile Diagrams	316
❖ The Ortho/Para Ratio.....	317
❖ <i>ipso</i> -Attack	319
❖ Orientation in Other Ring Systems	320
❖ Quantitative Treatment of Reactivity in Substrates and Electrophiles	321
❖ Diazonium Coupling.....	325
❖ Vilsmeier Reaction	326
❖ Gattermann-Koch Reaction	327
❖ Problems.....	329
❖ Bibliography	330
CHAPTER 9	331
Aromatic Nucleophilic Substitution	331
❖ The $ArSN_1$, $ArSN_2$, Benzyne and S_RN_1 Mechanisms.....	331
❖ Reactivity – Effect of Substrate Structure, Leaving Group and Attacking Nucleophile.....	336
❖ The von Richter, Sommelet-Hauser, and Smiles Rearrangements	339
❖ Problems.....	343
❖ Bibliography	344

CHAPTER 10	345
Elimination Reactions	345
❖ The E ₂ , E ₁ and E ₁ CB Mechanisms	345
❖ Orientation of the Double Bond.....	348
❖ Reactivity – Effects of Substrate Structures, Attacking Base, the Leaving Group and The Medium	352
❖ Mechanism and Orientation in Pyrolytic Elimination.....	355
❖ Problems.....	358
❖ Bibliography.....	359
CHAPTER 11	360
Addition to Carbon-Carbon Multiple Bonds	360
❖ Mechanistic and Stereochemical Aspects of Addition Reactions Involving Electrophiles, Nucleophiles and Free Radicals.....	360
❖ Regio- and Chemoselectivity: Orientation and Reactivity	370
❖ Addition to Cyclopropane Ring	374
❖ Hydrogenation of Double and Triple Bonds	375
❖ Hydrogenation of Aromatic Rings.....	377
❖ Hydroboration	378
❖ Michael Reaction.....	379
❖ Sharpless Asymmetric Epoxidation	380
❖ Problems.....	382
❖ Bibliography	383
CHAPTER 12	384
Addition to Carbon-Hetero Multiple Bonds.....	384
❖ Mechanism of Metal Hydride Reduction of Saturated and Unsaturated Carbonyl Compounds, Acids, Esters and Nitriles	384
❖ Addition of Grignard Reagents, Organozinc and Organolithium Reagents to Carbonyl and Unsaturated Carbonyl Compounds.....	400
❖ Wittig Reaction.....	406
❖ Mechanism of Condensation Reactions Involving Enolates: Aldol, Knoevenagel, Claisen, Mannich, Benzoin, Perkin and Stobbe Reactions	411
❖ Hydrolysis of Esters and Amides.....	433
❖ Ammonolysis of Esters.....	437
❖ Problems.....	439
❖ Bibliography.....	440
INDEX.....	441



Mandeep Dalal

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

Founder & Educator, Dalal Institute

E-Mail: dr.mandeep.dalal@gmail.com

www.mandeepdalal.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 of "Dalal Institute" (India's best coaching centre for academic and competitive chemistry exams), the organization that is committed to revolutionize the field of school-level and 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: 978-81-952427-3-3



9 788195 242733 >

MRP: Rs 800.00

**D DALAL
INSTITUTE**

..... Chemical Science Demystified

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

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

www.dalalinstitute.com