



# CHEMISTRY

8961435



# CHEMISTRY

## An Introduction to Matter and Energy

**DONALD I. HAMM**

SOUTHWESTERN STATE COLLEGE



E8961435



New York

**APPLETON-CENTURY-CROFTS**

DIVISION OF MEREDITH PUBLISHING COMPANY

Copyright © 1965 by

MEREDITH PUBLISHING COMPANY

All rights reserved. This book, or parts thereof, must not be used or reproduced in any manner without written permission. For information address the publisher, Appleton-Century-Crofts, Division of Meredith Publishing Company, 440 Park Avenue South New York, N. Y. 10016

645 - 1

Library of Congress Card Number: 65-14499

PRINTED IN THE UNITED STATES OF AMERICA

E 40650



# **CHEMISTRY**

**An Introduction to  
Matter and Energy**

**To my Mother and Father**

# Preface

In his "Love of Two Chemists" Max Shulman has Dobie Gillis enrolled—apparently only temporarily—in a freshman chemistry course. Mr. Fitzhugh introduces the subject in the following manner.

"This course is dedicated to the idiotic proposition that you can be taught the fundamentals of organic chemistry, inorganic chemistry, qualitative analysis, quantitative analysis, physical chemistry, and biochemistry all in one semester. The odds against any of you passing this course would be staggering to contemplate if there were any time for contemplation. However, there is not. Get out your notebooks."<sup>1</sup> Gillis subsequently describes the lecture.

"For the next hour Mr. Fitzhugh, speaking a little faster than Clem McCarthy when he is announcing the Kentucky Derby, delivered a lecture about matter, elements, mixtures, compounds, reagents, the periodic table, atomic weights, ionization, valence, and other improbable topics. At the end of the hour I had nineteen pages of notes, all illegible."<sup>2</sup>

To those students who use this text I would point out that Mr. Shulman is a writer of fiction, not history. To their teachers I submit that were the picture drawn here completely unrelated to fact, it would be the more humorous.

The first course in chemistry cannot be all things for all people. We shall have to continue offering courses in organic chemistry, physical chemistry, and biochemistry to convey the ideas fostered by these disciplines. The ideas regarded as the properties of these disciplines will continue to be more easily perceived when they are laid upon a foundation of those "more noble" ideals which pervade the whole of chemistry.

Accordingly I have followed the precept of Bagehot that "to illustrate a principle you must exaggerate much and you must omit much. . ." To pay more attention to that most pervasive of all "chemical" ideas—atomic-molecular theory—some of what is ordinarily found in beginning texts has been omitted. Since the atomic-molecular theory as we know it today has evolved so slowly, it is presented historically. Those of us who have devoted our lives to acquiring some sophistication in thinking about atoms and molecules become impatient when our students do not perceive that which we would have them understand. We err here, of course, for they require time to arrive at this understanding. Because atomic-molecular theory accounts for the phenomena of heat, electricity, and light, as well as for the particulars of chemical change, rather more attention has been devoted to the former topics than is ordinarily the case in beginning texts. Hopefully, this will assist the prospective chemist in seeing chemistry and physics in

---

<sup>1</sup>From *The Many Loves of Dobie Gillis*; copyright 1945, 1946, 1948, 1950, 1951, by Max Shulman. Reprinted by permission of the Harold Matson Company and Doubleday and Company, Inc.

<sup>2</sup> *Ibid.*, pp. 105-106.

one light rather than two. If this is achieved, then surely the synthesis he or she later encounters in physical chemistry will be grasped more easily. At the present the physicists place the heavier claim on the study of the nucleus. That many chemists would have it no other way we may deduce from the circumstance that textbooks of organic chemistry frequently ignore the nucleus altogether. Nonetheless, the atomic-molecular theory of yesterday is in fact atomic-molecular-nuclear theory today. Hence the chemistry and physics of the nucleus is considered here at some length.

I hope that neither the exaggerations nor the omissions will be regarded as being too severe.

One cannot hope to acknowledge fully one's debt in affairs of learning. Nevertheless, I wish to convey my appreciation to certain of my teachers, colleagues, and collaborators in this endeavor. To my teachers Dr. H. C. Brown, Dr. C. D. Kochakian, Dr. Grace Jencke, and Mrs. Charles Goodwin I owe a considerable debt. My colleagues the Mssrs. G. E. Castleberry, Al Ossinger, Ed Neparko, E. A. Reynolds, and G. L. Cunningham (now at Eastern Illinois University) have helped me with many suggestions. However, my wife Jean, Dr. H. F. Timmons, the consulting editor Dr. Therald Moeller of the University of Illinois, and Truman Hall of Appleton-Century-Crofts have suffered the most; I can but hope that they find their influence on this work some reward.

Many authors and publishers have permitted the inclusion of their material herein. I should like to express my appreciation to them as well.

D. H.



# THE CHEMICAL ELEMENTS



Element	Symbol	Atomic Number	Atomic Weight
Actinium	Ac	89	[227]
Aluminum	Al	13	26.9815
Americium	Am	95	[243]
Antimony	Sb	51	121.75
Argon	Ar	18	39.948
Arsenic	As	33	74.9216
Astatine	At	85	[210]
Barium	Ba	56	137.34
Berkelium	Bk	97	[249]
Beryllium	Be	4	9.0122
Bismuth	Bi	83	208.980
Boron	B	5	10.811
Bromine	Br	35	79.909
Cadmium	Cd	48	112.40
Calcium	Ca	20	40.08
Californium	Cf	98	[251]
Carbon	C	6	12.01115
Cerium	Ce	58	140.12
Cesium	Cs	55	132.905
Chlorine	Cl	17	35.453
Chromium	Cr	24	51.996
Cobalt	Co	27	58.9332
Copper	Cu	29	63.54
Curium	Cm	96	[247]
Dysprosium	Dy	66	162.50
Einsteinium	Es	99	[254]
Erbium	Er	68	167.26
Europium	Eu	63	151.96
Fermium	Fm	100	[253]
Fluorine	F	9	18.9984
Francium	Fr	87	[223]
Gadolinium	Gd	64	157.25
Gallium	Ga	31	69.72
Germanium	Ge	32	72.59
Gold	Au	79	196.967
Hafnium	Hf	72	178.49
Helium	He	2	4.0026
Holmium	Ho	67	164.930
Hydrogen	H	1	1.00797
Indium	In	49	114.82
Iodine	I	53	126.9044
Iridium	Ir	77	192.2
Iron	Fe	26	55.847
Krypton	Kr	36	83.80
Lanthanum	La	57	138.91
Lawrencium	Lw	103	[257]
Lead	Pb	82	207.19
Lithium	Li	3	6.939
Lutetium	Lu	71	174.97
Magnesium	Mg	12	24.312
Manganese	Mn	25	54.9380
Mendelevium	Md	101	[256]

Element	Symbol	Atomic Number	Atomic Weight
Mercury	Hg	80	200.59
Molybdenum	Mo	42	95.94
Neodymium	Nd	60	144.24
Neon	Ne	10	20.183
Neptunium	Np	93	[237]
Nickel	Ni	28	58.71
Niobium	Nb	41	92.906
Nitrogen	N	7	14.0067
Nobelium	No	102	[254]
Osmium	Os	76	190.2
Oxygen	O	8	15.9994
Palladium	Pd	46	106.4
Phosphorus	P	15	30.9738
Platinum	Pt	78	195.09
Plutonium	Pu	94	[242]
Polonium	Po	84	[210]
Potassium	K	19	39.102
Praseodymium	Pr	59	140.907
Promethium	Pm	61	[147]
Protactinium	Pa	91	[231]
Radium	Ra	88	[226]
Radon	Rn	86	[222]
Rhenium	Re	75	186.2
Rhodium	Rh	45	102.905
Rubidium	Rb	37	85.47
Ruthenium	Ru	44	101.07
Samarium	Sm	62	150.35
Scandium	Sc	21	44.956
Selenium	Se	34	78.96
Silicon	Si	14	28.086
Silver	Ag	47	107.870
Sodium	Na	11	22.9898
Strontium	Sr	38	87.62
Sulfur	S	16	32.064
Tantalum	Ta	73	180.948
Technetium	Tc	43	[99]
Tellurium	Te	52	127.60
Terbium	Tb	65	158.924
Thallium	Tl	81	204.37
Thorium	Th	90	232.038
Thulium	Tm	69	168.934
Tin	Sn	50	118.69
Titanium	Ti	22	47.90
Tungsten	W	74	183.85
Uranium	U	92	238.03
Vanadium	V	23	50.942
Xenon	Xe	54	131.30
Ytterbium	Yb	70	173.04
Yttrium	Y	39	88.905
Zinc	Zn	30	65.37
Zirconium	Zr	40	91.22

Atomic weight values are based on carbon-12. Values listed in brackets denote mass numbers; these values are given for either the longest-lived or the best-known isotope.



PERIODIC TABLE OF THE ELEMENTS

I A IIA IIIB IVB VB VIB VIIB VIIIIB IB IIB IIIA IVA VA VIA VIIA VIIIA																		
1 H 1.00797																		2 He 4.0026
3 Li 6.939	4 Be 9.0122																	
11 Na 22.9898	12 Mg 24.312																	
19 K 39.102	20 Ca 40.08	21 Sc 44.956	22 Ti 47.90	23 V 50.942	24 Cr 51.996	25 Mn 54.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.9216	34 Se 78.96	35 Br 79.909	36 Kr 83.80	
37 Rb 85.47	38 Sr 87.62	39 Y 88.905	40 Zr 91.22	41 Nb 92.906	42 Mo 95.94	43 Tc (99)	44 Ru 101.07	45 Rh 102.905	46 Pd 106.4	47 Ag 107.870	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.9044	54 Xe 131.30	
55 Cs 132.905	56 Ba 137.34	57 La 138.91	72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 196.967	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.980	84 Po (210)	85 At (210)	86 Rn (222)	
87 Fr (223)	88 Ra (226)	89 Ac (227)																

Atomic weight values listed in parentheses are approximate.

# Contents

Preface .....	vii
---------------	-----

## 1. An Introduction To Chemistry

The nature of science .....	1
The study of science .....	2
The nature of chemistry .....	3
The fruits of chemistry .....	5

## 2. Elements, Compounds, And Mixtures

Composition .....	9
Elements .....	13
Compounds and mixtures .....	14
Resolution of mixtures .....	15
Resolution of compounds .....	17
Variable composition of mixtures .....	18
The law of definite proportions .....	18
The law of conservation of matter .....	20
Indirect analysis .....	22
Samples with identical compositions .....	24

## 3. Dalton's Theory Of The Atom

Dalton's atomic theory .....	29
The theoretical explanation of the law of conservation of matter .....	29

The theoretical explanation of the law of definite proportions .....	30
The concept of atomic weights .....	32
The law of multiple proportions .....	34
The theoretical explanation of the law of multiple proportions .....	35
The determination of atomic weights .....	38
Symbols and formulas .....	41
The concept of valence .....	42
Multiple valence .....	43

#### 4. Composition Calculations. Equations. Nomenclature Of Binary Compounds

The determination of elemental weight fractions and weight percent values from formulas. Molecular weights .....	48
Determination of formulas from analytical data .....	50
Gram atoms and gram moles .....	51
Empirical and molecular formulas .....	53
Molecular weights and formula weights .....	54
Calculation of weight of element present in a given weight of compound .....	55
Calculation of weight of compound which can be formed from a given weight of element .....	56
Chemical equations .....	56
The experimental aspects of chemical equations .....	58
Calculation of reaction weights from equations .....	60
Nomenclature of binary compounds .....	62
Radicals .....	63

#### 5. The Alkali Metals

Elemental groups .....	67
Formation of binary compounds .....	67
Reactions of the alkali metals with water .....	70
Reactions of the binary compounds with water .....	70
Other reactions of the binary compounds .....	73
Ternary compounds .....	74
Some electrical properties of alkali metal compounds .....	75
Electrolysis .....	77
Preparation of the alkali metals from their compounds .....	77
Reactivity .....	78
Heats of reaction .....	79

Heats of fusion, vaporization, sublimation, and atomization. Melting and boiling points .....	81
Lattice energies .....	84
Atomic radii .....	86
Atomic weight-property relations .....	87

## 6. The Behavior Of Gases. Avogadro's Modification Of Dalton's Theory

Gay-Lussac's law of combining volumes .....	92
The variation of gas volume with pressure. Boyle's law .....	93
The variation of gas volume with temperature. Charles' law .....	96
The Kelvin temperature scale .....	97
The variation of gas pressure with temperature. Gay-Lussac's law .....	98
The variation of gas volume with pressure and temperature. The combined gas law .....	99
Avogadro's modification of the Daltonian theory .....	99
The ideal gas law .....	107
Avogadro's number .....	109
Limiting gas densities .....	110
Graham's law of effusion .....	111
The law of partial pressures. Vapor pressure .....	112
Gram molecular weight calculations .....	114

## 7. Laws, Theories, And Hypotheses

The nature of laws .....	121
The nature of theories .....	125
The nature of hypotheses .....	128

## 8. An Introduction To The Study Of Heat. Effects Of Pressure And Temperature On Physical And Chemical Change

Temperature and thermometry .....	134
Distribution of heat .....	135

Heat capacity	137
Melting and freezing	140
Heat of fusion	140
Vapor pressure	142
Boiling	143
Condensation. Heat of vaporization	144
The effect of pressure on changes of state	147
The effects of pressure and temperature on the solubility of gases	150
The effects of pressure and temperature on chemical reactions	150
Heats of reaction	152
Experimental measurement of heats of reaction	153
Laws of thermochemistry	156
Heat contents	159
Studies on heat capacities	159

## 9. The Nature Of Heat And The Kinetic-Molecular Theory

The caloric theory	167
The conservation of energy	169
The kinetic-molecular theory	171
Absolute zero	173
Average kinetic energy	174
The solid state	174
Conduction	175
Temperature measurement	176
Melting and freezing	178
Boiling and condensation	178
Vapor pressure	179
The qualitative description of gaseous behavior	181
The quantitative description of gaseous behavior	182
Deviations from ideal gas behavior	185

## 10. Early Developments In Electrochemistry. Electron-Transfer Reactions

On elements and compounds	190
The invention of the battery	191

The use of electrolysis in the isolation of elements	192
Faraday's studies of electrolysis	193
Equivalent weights	195
Equivalent weights of compounds and radicals	199
Variable equivalent weights	200
Theoretical explanations of electricity	200
Ions and radicals	202
Electron-transfer reactions	202
The theoretical explanation of Faraday's laws	204
Relative and absolute ionic charges	206
Generation of electric current from chemical change	207
Oxidation and reduction	209
Ionic and covalent compounds	210
Expanded definitions of the mole and the equivalent	211

## 11. Standard Oxidation Potentials

Cell potentials	216
The measurement of cell potentials	218
Standard oxidation potentials	218
Oxidation state	223
Balancing electron-transfer reactions	226
Prediction of spontaneous reactions	228
Maximum work and the free energy	229

## 12. Concentration

Density	234
The concentration of solutions	234
Solution concentration indexes	235
Preparation of solutions	238
Temperature dependence	238
Dilution calculations	239
Reaction equivalency calculations	240
Other concentration indexes	241
Sample calculations	242

### 13. The Alkaline Earth Metals. Factors Which Govern The Reactivity of Metals

Formation of binary compounds .....	247
Reactivities of the alkaline earth metals .....	252
Born-Haber cycles .....	255
Factors regulating reactivity in the formation of ionic solids .....	256
Heats of atomization .....	256
Ionization energies .....	257
Lattice energies .....	258
Lattice energies as a function of ionic radius .....	260
Lattice energies as a function of charge-to-radius ratios .....	261
Reactions of the alkaline earth metals with water .....	262
Hydrolysis reactions of the binary compounds .....	263
Hydrate formation .....	263
Tendencies of the ions to hydrate .....	265
Hydration energies in the reactions of the metals with water .....	266
Hydration energies in the solubility of ionic solids .....	267
Lattice and hydration energies in reactions involving a pair of solutions .....	268
Acid-base reactions .....	270
Preparation of the metals .....	271
Occurrence .....	272

### 14. Reaction Energetics. I. Equilibrium

The concept of equilibrium .....	278
The effect of concentration of reactants on rates of reaction .....	279
The scope of an equilibrium .....	282
The law of mass action .....	283
The dependence of equilibrium upon temperature .....	284
The dependence of equilibrium upon pressure .....	286
The effect of pure substances on equilibrium .....	289
Why reactions come to particular equilibrium positions .....	291
The free energy .....	293
Free energy change and the equilibrium constant .....	299
Variation of cell potential with concentration .....	302
Alternative paths to changes in free energy. Heat content and entropy .....	303
Some representative equilibria .....	307
Activities .....	315
Sample calculations .....	316



## 15. Reaction Energetics. II. Rates Of Reactions

The variables in rate behavior .....	322
Molecularity and order of reactions .....	323
The experimental determination of reaction order and of rate constant values .....	325
The dependence of rate constants on temperature .....	330
The energy of activation .....	334
Multistep processes and rate-controlling steps .....	335
Catalysis .....	336
The effect of catalysis on equilibrium .....	339
Summary .....	340

## 16. Acids And Bases. I. The Arrhenius Theory

Acids and bases .....	344
Acids as hydrogen compounds of the nonmetals .....	346
Bases as metal hydroxides .....	346
Element-compound relationships .....	346
Nomenclature of the hydrogen acids .....	348
Nomenclature of the hydroxide bases .....	350
Nomenclature of salts .....	350
Acid and base strengths .....	354
Effect of concentration on acid and base strength .....	355
The acidity and basicity of solutions of salts .....	356
Effects of solutes on solvents .....	357
Conductivities of solutions .....	359
The theory of electrolytic dissociation .....	361
Partial dissociation .....	363
Ionization constants .....	364
The ionization constant of water .....	366
The neutralization reaction .....	367
The reaction of acids with metals .....	369
The buffer effect .....	370
Buffer solutions .....	371
An evaluation of Arrhenius' theory .....	371

## 17. Acids And Bases. II. Proton-Transfer Reactions

The Debye-Hückel theory of interionic attraction .....	376
The Brønsted-Lowry theory of acids and bases .....	378

Conjugate acid-base pairs .....	380
Neutralization .....	381
Water as an acid and a base .....	382
A comparison of the Arrhenius and Brønsted-Lowry theories .....	383
Electrolyte solutions as mixtures .....	384
Strengths of acids and bases .....	385
Quantitative measures of acid and base strengths .....	387
The leveling effect .....	389
The strengths of the "strong" acids .....	391
The acidity and alkalinity of salt solutions .....	391
Other amphiprotic substances .....	393
Energetics of neutralization reactions .....	394

## 18. The Periodic Classification Of The Elements

Early attempts at classification .....	399
The periodic law .....	401
Periodic tables .....	402
The utility of the periodic table .....	405

## 19. The Halogens

Occurrence .....	414
Physical properties .....	415
The formation of the halide ions .....	416
The formation of covalent halides .....	417
The hydrogen halides .....	418
The hydrogen bond .....	421
The hydrohalic acids .....	424
Other binary halides .....	430
The geometry of the binary halides .....	441
Oxyhalogen compounds .....	445
The halic acids .....	448
The perhalic acids .....	449
Preparation of the halogens .....	450