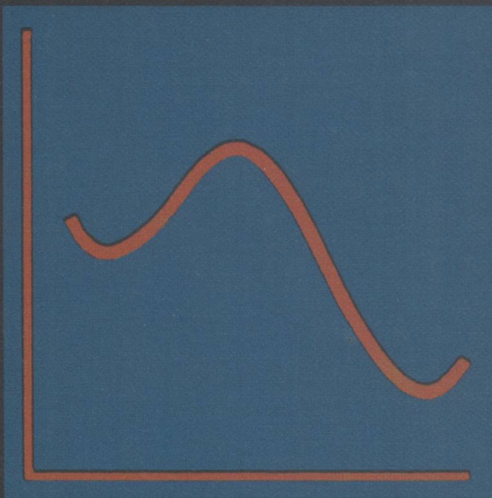

JOHN R. HOLUM

INTRODUCTION TO

PRINCIPLES OF CHEMISTRY

INTRODUCTION TO Principles of Chemistry

John R. Holum, Ph.D.
Professor of Chemistry, Augsburg College

JOHN WILEY & SONS, INC.
New York · London · Sydney · Toronto

10 9 8 7 6 5 4 3 2 1

Library of Congress Catalog Card Number: 77-84201

SBN 471 40850 6

Printed in the United States of America

INTRODUCTION TO PRINCIPLES OF CHEMISTRY

To Mary

and to our children,

Elizabeth

Ann

Kathryn

PREFACE

Matter, motion, spontaneity, permanence. Four of the most common and ordinary features of human experience. Things are, and things move. Events happen; some things endure. These four phenomena describe our world and us as we live and move and have our being. Their enthralling variety enriches our art and poetry, our music and dance, and it accounts for much of our simple love of life. Although the underlying laws of matter, motion, spontaneity, and permanence circumscribe what we can do, they also free us from the anarchy of chaos.

Part of the enjoyment of life is to wonder, to ask questions, to seek, to desire an understanding of as much of experience as possible. In mysteries confronted by philosophers and theologians—in issues about ultimate meaning, purpose, and destiny—are some questions that have not been settled to the mutual satisfaction of all. Religious and philosophical pluralism is a fact of history and of today. Yet, in the face of this pluralism, faith in the ultimate order and rationality of existence persists. Life is all of a piece, Tolstoy's Levin affirmed. There is a basic unity to it all, we fondly hope and believe. This faith is upheld by the spectacular success of efforts to answer questions less ultimate in nature, questions about what unity there may be in the bewildering variety of matter and motion, in the innumerable displays of spontaneity and permanence. This book is meant to provide a basis for studying at an elementary level these four common features of human experience while laying a foundation for additional studies in chemistry.

The analysis of motion in this book is much less thorough than that accorded it in physics textbooks, but I have very limited goals. Only part of the first chapter is devoted to the irreducible elements of all motions so that they may be used later to develop the concept of energy. An analysis of motion provides the almost equally important opportunity of introducing students to a useful approach to complex phenomena, namely reducing the phenomenon being studied to its fewest and most fundamental parameters. For example, what are the simplest elements in terms of which all motions can be described? Three have been found—position in space, position in time, and inertia. To measure these and express them quantitatively, we recognize three of nature's most fundamental dimensions, length (L), time (T) and mass (M), and we see clearly the need to make some decisions about units—yards or meters, moons or seconds, grains or grams. Useful functions or combinations of some or all of the basic dimensions naturally emerge—volume, density, force, and, most importantly, energy.

With the concepts of force, energy, and mass we can analyze the simplest elements for understanding matter and its behavior. What are the simplest and most universal features of all matter? Of all the spontaneous events in nature? Of situations that seem to be permanent (or in a state of equilibrium)? Subatomic particles, atoms, elements, compounds, chemical bonds, and certain classes of substances are the natural topics in an analysis of matter. To understand spontaneity and the direction of chemical events, the concepts of enthalpy, entropy, and free energy are extremely illuminating; they also help us to understand permanence (or equilibrium). We have too long been afraid to mention these topics in an introductory course, alleging them to be too difficult and abstract. If the credentials of calculus are demanded of all who approach the gates of thermodynamics, we effectively tell most who wish some understanding of nature at even a modest level that only the initiated can pass through. It is as if all visitors to Arizona's Grand Canyon were turned back from the rim view unless they agreed to hike the Bright Angel–Kaibab trail. This trek may well be an unforgettable experience, but for those who lack the time or the stamina the rim view is still awesome and rewarding. Calculus is not used in this text, but I do not believe that the demands of rigor, appropriate and essential though they may be for training future scientists, require us to deny students who will not become physicists or chemists an opportunity of learning something about the grand laws and concepts that are at the heart of an understanding of both spontaneity and permanence.

I hope that this text will help the student feel more at home on this hurtling planet; that it will open for him some windows to both the world of physical existence and the world of ideas; that it will awaken wonder even as it (incompletely) satisfies it.

At a less elevated but still important level, I hope this introduction to the fundamental principles of chemistry will prepare the student for further studies leading to a variety of occupations for which a college major in chemistry is not required. Students who have learned the material in this book should be ready to take a course in elementary analytical chemistry or elementary organic chemistry as part of their education for any of the paramedical vocations and for many of the positions in the food and fiber industries. In fact, this textbook is one product of a larger effort to survey a broader field, an effort that produced another book, *Principles of Physical, Organic, and Biological Chemistry* (John Wiley and Sons, New York, 1969). During the prepublication stages of review and revision of the longer book, it was suggested that its first eight chapters be issued as a separate book for teachers who wish to follow a survey of principles with topics other than organic and biological chemistry, or who need a brief book for a short, terminal course in chemistry.

I wish to thank Dr. Earl R. Alton of Augsburg College, Dr. Arne Langsjoen of Gustavus Adolphus College, and Dr. A. H. Blatt of Queens College for critical readings of all eight chapters. My gratitude extends also to many others not known to me by name who contributed valuable suggestions during the prepublication reviews.

Lastly, I am grateful to two of my students, Ronald Swanson, and Sandra Olmsted, for helping in many ways.

I invite those who have questions, comments, suggestions, and criticisms to write me. Teachers may obtain a booklet of answers to problems of a computational nature by writing on their departmental stationery to the publisher at 605 Third Avenue, New York, New York 10016.

John R. Holum

Augsburg College
Minneapolis, Minnesota 55404
January 1969.

CONTENTS

1 ENERGY 1

2 ATOMS AND ELEMENTS 27

3 SUBSTANCES AND CHANGE 72

4 SUBSTANCES AND STRUCTURE 106

5 SOLUTIONS AND COLLOIDAL DISPERSIONS 136

6 IMPORTANT IONIC REACTIONS 168

7 THE DIRECTION OF CHEMICAL CHANGES 189

8 IONIC EQUILIBRIA 215

APPENDICES

I EXPONENTIALS 241

II COMMON LOGARITHMS 244

INDEX 247

CHAPTER ONE

Energy

Dynamos, fullbacks, waterfalls, bees, hurricanes, and small boys indisputably have one characteristic in common, energy. Even though it is not an object like matter, occupying space, energy is so commonplace and apparently so well understood that the word is learned and used at an early age. We do not see energy, taste, smell, hear, or feel it, but we experience its effects. Man virtually had to invent the term so that he could better describe features common to a variety of his experiences with matter.

Energy is something like a talent. A person with a talent has an ability to do something and do it more or less well. But a talent is not a thing. It is a characteristic of certain things, people. Just as a talent is related to an ability, so too is energy. A person or other object that we say has energy has the ability or the potential to do something—to do work. In fact, the word "energy" comes from the Greek *en* plus *ergon,* "in work." But the word "work" is not a synonym for energy. Work is usually thought of as the doing of something in a purposeful way. Energy is needed, but not all expenditures of energy actually work. It is useful to think of energy as available in several forms: mechanical, thermal (heat), electric, electromagnetic (light), sound, chemical, and potential. The presence of chemical energy on this list makes this chapter necessary. Chemical energy can be converted into all the other forms, and it happens that analyzing mechanical energy is one of the better ways to begin a study of chemical energy.

THE ANALYSIS OF MOTION

Elements of Motion. If energy is used to move an object from one point to another, we say that "mechanical work" has been done. Any object in motion is said to possess mechanical energy. In fact, the whole modern notion of energy developed from attempts to analyze the motion that nature exhibits in almost endless variety. We see movements and motions everywhere, as we look out the window, ride along in a car or bus, or watch a football game. Although the list of motions in the universe seems infinite, a meaningful analysis is still possible. Certain features are apparently common to all kinds of motion.

For centuries the analysis of motion has occupied the attention of scientists in one branch of physics, those studying mechanics. It is often true in science, as elsewhere, that asking the right questions is an essential part of progress. The right questions in mechanics read something like this. What are the simplest elements or the simplest aspects in terms of which motion can be described? What are the simplest elements to which all forms of motion can be reduced? Two of the most helpful "elements" have to do with position—position of the object in space and position of the object in time. A description of a moving body has to state where it is and when. How an object moves can be described by showing how changes in these two positions relate to each other. The best description is an equation by means of which we may predict where the object will be at some future time or where it was at some previous time. The movements of stars, planets, and moons have been successfully fitted into such equations. The remarkable accuracy with which men and equipment are hurled into orbits and recovered is a dramatic illustration of how successful the analysis of motion has been.

References. The notion of position is meaningless without some set, agreed-upon reference position. When we describe the position of an object, we really specify the path we would take to reach it from some starting point. We may say "The car is over there," pointing. The reference is our position. Or we may say "It's along the north side of the building"; by implication one of our references is the North Star, or the north pole, and any agreed-upon system of latitude, longitude, city map, etc., that describes where the building is. For more exact descriptions the distance from the reference point has to be stated together with directions. Units for describing distance or length are obviously necessary.

The standard length universally used in scientific work, and in virtually all countries, is the *meter*. Until late in 1960 the world's standard meter was universally agreed to be the distance between two thin scratches on a long bar of platinum-iridium alloy stored in a locked subbasement at Sèvres, near Paris, France. When first proposed, it was meant to be one ten-millionth of the distance along the surface of the earth from the North Pole to the equator. In October 1960 the World Conference on Weights and Measures decided to replace the standard meter with a reference that would not be subject to corrosion, to thermal expansion, or to loss by any possible means, and one that was more portable. This new standard meter is defined as 1,650,763.73 wavelengths of the orange-red light given off by the electrically excited isotope krypton-86, a rare gas found in trace amounts in the atmosphere all over the world and available to all scientists (see Figure 1.1).

The meter is but one of the standards defined in the metric system of weights and measures. The great convenience of this system is the decimal relations of its units, relations always implied by adding a suitable prefix to the name of the unit itself. Table 1.1 contains a summary of the important prefixes in the metric system.

Figure 1.1 A National Bureau of Standards scientist adjusts a krypton-86 lamp in its liquid nitrogen bath. The wavelength of the orange-red light emitted by the lamp has been adopted as the international standard of length. (Courtesy of the National Bureau of Standards, Washington, D.C.)

To specify position in time, a unit of time is needed, and this unit is the *second.* The standard for the second has undergone change, the most recent being in 1964. For virtually all the affairs of most people, including navigators, the second may be taken as the *mean solar second,* which is 1/86,400 of the mean solar day—the average time it takes the earth to make one complete turn on its axis. If a perfect clock had been set on this basis in the year 1900, it would now be off about 30 seconds. This amount does not seem like much, but for physicists, astronomers, and space scientists such accuracy is not good enough. Therefore in 1964 another General Conference on Weights and Measures redefined the second in terms of the transition between two specific energy levels in cesium-133. Greater detail than this is unnecessary for our purposes.

Table 1.1 Prefixes in the Metric System

The names of multiples and submultiples of the units are formed with the following prefixes.*

Multiples			Submultiples		
Factor by Which Unit is Multiplied	Prefix	Symbol	Factor by Which Unit is Multiplied	Prefix	Symbol
10	deka	da	10^{-1}	deci	d
10^2	hecto	h	10^{-2}	**centi**	c
10^3	**kilo**	k	10^{-3}	**milli**	m
10^6	mega	M	10^{-6}	**micro**	μ
10^9	giga	G	10^{-9}	nano	n
10^{12}	tera	T	10^{-12}	pico	p
			10^{-15}	femto	f
			10^{-18}	atto	a

* The most common are indicated by boldface.

Kinematics. Thus far we have found two elements of motion, position and time. We have ignored what moves and, surprisingly, we can go on ignoring it for a while. Our analysis is simpler, up to a point, if we treat "what moves" as a geometric point and then proceed to think about how a point might move in both space and time. Our discussion, then, is of the geometry of motion, or kinematics. With just two elements of motion, kinematics gives us two extremely useful combinations of them, speed (and velocity) plus acceleration.

Suppose that a point moves in a straight line and that it passes some reference point, a "mile zero" so to speak. Let us start a stopwatch at "time zero." The following observations illustrate what would be observed if the motion were uniform.

The point was at	when the stopwatch read
0 cm	0 sec
4 cm	2 sec
7 cm	3.5 sec
10 cm	5 sec
14 cm	7 sec

A quick calculation at each reading shows that in the midst of this change in both location and time something remains unchanged—the ratio of distance traveled to time elapsed. Man has been fascinated by both change and permanency. He has found by experience that anything that remains unchanged in the midst of change bears looking into. Often he invents a name for it. This ratio of distance traveled to time elapsed is called the *speed* of the particle:

$$\text{Speed} = \frac{\text{distance traveled}}{\text{time elapsed}}$$

$$s = \frac{L}{T}$$

(1.1) $$s = LT^{-1}$$

Here we use L to represent distance or length and T to stand for time. (Later, in other contexts, T will stand for temperature, but the context will clearly indicate how the symbol is used.)

Thus just two elements of motion in one of their possible combinations give us a very useful property of a moving object, its speed. We can improve on this particular combination by specifying its direction, which is as important as its speed. When a hurricane warning or a tornado alert is sounded, we want to know both the speed and direction of the storm. When both speed and direction are specified, the quantity is called *velocity*.[1] By definition velocity has both magnitude and direction.

Actually, very few motions of real objects correspond to uniform motion in a straight line, for velocity is not usually constant throughout the movement. Either the speed or the direcion, or both, change. In one important situation the velocity changes smoothly with time, and we shall look into this, since it is obviously easier to examine than a velocity that changes erratically with time. To illustrate what is meant by smooth uniform change in velocity, the following values represent typical data:

The velocity of the point was	when the stopwatch read
0 cm/sec	0 sec
4 cm/sec	2 sec
6 cm/sec	3 sec
10 cm/sec	5 sec
18 cm/sec	9 sec

It is assumed that the motion is in some fixed direction. The velocity is clearly changing with time, but the ratio of velocity to elapsed time at any moment does not and is the same for all measurements, $\frac{2\ \text{cm/sec}}{\text{sec}}$ (2 cm per sec per sec). We say that the point is undergoing an *acceleration,* and we may define acceleration in terms of a ratio:

$$a = \text{acceleration} = \frac{\text{velocity}}{\text{time}}$$

$$a = \frac{L/T}{T}$$

$$a = LT^{-2} \tag{1.2}$$

Here, then, is another useful combination of but two of the elements of motion, a phenomenon well known to drag racers and astronauts and to anyone who has been pressed back into his seat when the car started or the plane took off.

Other combinations of L and T, although possible on paper, are not useful. For a more extensive analysis of motion we must change from a moving point to a real object, introducing a decidedly nongeometric property.

Inertia. Objects that look alike in shape, size, color, and volume can differ greatly in how easy it is to make them move or, if they are moving, to make them

[1] Velocity is therefore a *vector* quantity, speed a *scalar* quantity. We have no need for these distinctions in this book, but many readers will be familiar with vectors and scalars.

veer to one side or to stop. A cubic meter block of wood sheathed in thin lead foil looks exactly like a cubic meter block of pure lead, but imagine trying to move them. Suppose that they are suspended by some stout wire to reduce frictional problems. Making the block of solid lead swing would be much harder than making the other block perform the same motion. The block of solid lead possesses something that is profoundly important in any analysis of its possible movements. Whatever that something is, it is independent of the other elements of motion (at least when velocities are small compared with the velocity of light). That something is a new element of motion which we must consider if we are to move real objects or analyze their motions. It is called *inertia,* and it is an idea so important that the word is part of ordinary usage. Any person, any society, any object that resists change is said to have inertia. The solid block of lead has more inertia than the lead-coated wood. To continue our analysis of motion we must have a measure for inertia or differences in inertia.

Mass. As the science of motion developed, the quantitative measure of inertia came to be called *mass*. An object with a large mass, such as the block of pure lead, has a large inertia. The reference unit of mass in the metric system is the kilogram, the mass of a particular cylinder of platinum-iridium alloy, called the International Prototype Kilogram, which is preserved in the Sèvres (p. 2) vault by the International Bureau of Weights and Measures (Figure 1.2). In chemical work the gram (one-thousandth of the kilogram) and the milligram (one-thousandth of a gram) are the most common mass units.

With these three elements of motion—mass, distance, and time (M, L, and T), together with reference standards—a number of different motions of real objects have been successfully analyzed. Success here means finding an equation that includes nothing more than these three variables to describe the motion. With the right equations programmed into high-speed calculators, Jet Propulsion Laboratory scientists routinely put to the machines such questions as "If the lunar landing module was at point A in space at time T, traveling so many meters per second, where will it be at time T plus one hour?"

FORCE

Let us turn our attention to the effect of a push or a pull on an object. Human power is not the only source of pushes and pulls. Blowing wind pushes on the slanted vanes of a windmill, flowing water can be made to push on the paddles of a paddle wheel, and a harnessed horse pushes on its harness, thereby pulling a plow or a wagon. But a large block of lead with its huge mass would take a powerful push to overcome its inertia. If the block of lead is at rest, and if we push on it hard enough, it will go from a velocity of zero to some definite velocity. In other words, applying the push changes its velocity, which is another way of stating the first of the three laws of motion expressed by Isaac Newton:

> Newton's First Law of Motion. Every body continues in its state of rest, or in a state of uniform motion in a straight line, except insofar as it is compelled by forces to change that state.

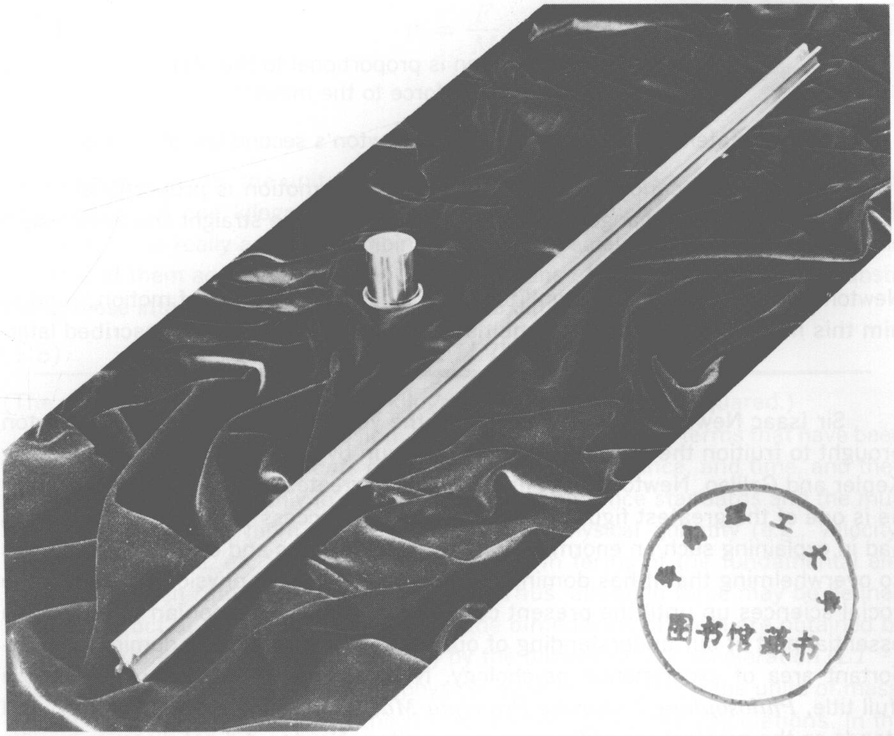

Figure 1.2 The United States standard of mass, Prototype Kilogram Number 20, the cylinder shown above, is a duplicate of the international standard kept in France. Also shown is Prototype Meter Number 27, a distance marked off on the platinum-iridium bar, which served the United States as its standard of length until the new standard, based on the krypton-86 lamp, was adopted. The bar will remain as a secondary standard because of the ease with which it can be used for certain types of measurements. (Courtesy of the National Bureau of Standards, Washington, D.C.)

This law gives us a qualitative definition of force. A force is what will cause a body to change its motion. (Force is a better term than push or pull because these two words imply living creatures at work; force is more general.)

We learned earlier that a change in velocity is called an acceleration. The greater the applied force, the greater the change in velocity—that is to say, the greater the acceleration. But if the mass of the object receiving this force is large, the change in velocity will not be great. Switching to simpler terms, mathematical terms, for expressing these ideas, we have

(1.3) $$a \propto F$$ The symbol $\propto$ means "is proportional to." Here "acceleration is proportional to the force" for a given mass.

(1.4) $$a \propto \frac{1}{M}$$ "Acceleration is inversely proportional to the mass," for a given force.

These may be combined:

(1.5) $$a \propto \frac{F}{M}$$ "Acceleration is proportional to the ratio of the applied force to the mass."

The first statement, equation 1.3, gives Newton's second law of motion:

> Newton's Second Law of Motion. Change in motion is proportional to the force, and the change occurs in the direction of the straight line along which the force acts.

Newton meant "change in motion" to mean "change in quantity of motion," and to him this meant momentum, a combination of M, L, and T to be described later.

Sir Isaac Newton (1642–1727). Born the year in which Galileo died, Newton brought to fruition the scientific revolution begun by Copernicus and continued by Kepler and Galileo. Newton is not just one of the greatest scientists who ever lived; he is one of the greatest figures in all history. The success that Newtonian physics had in explaining such an enormous variety of experiences and events in nature was so overwhelming that it has dominated thought not only in physics but also in the social sciences up until the present century. Even today Newtonian physics is an essential part of our understanding of our world and continues to dominate an important area of experimental psychology. Newton's monumental book, *Principia* (full title, *Philosophiae Naturalis Principia Mathematica*), published in 1687, still stands as the greatest scientific work ever written. Newton did not discover gravity, but it was his genius to recognize that gravity is universal, that what is said to act on an apple to impel it toward the earth extends not just to the top of the tree but all the way to the moon and beyond. On this assumption Newton derived equations for expressing the motion of the moon and other bodies, and the equations checked with observations. He never tried to speculate on the cause of gravity; he believed it enough to know that gravity does really exist. In addition to his contributions to mechanics, he made great discoveries in optics, including the ability of a prism to disperse white light into its colors.

The third proportionality, equation 1.5, can be converted to an equation by inserting a proportionality constant:

$$a \propto \frac{F}{M}$$

becomes

$$a = k \cdot \frac{F}{M}$$

where k is some constant.[2] Or we could ignore this proportionality constant by *defining* force with the simple equation

[2] The dot in the equation is one symbol we sometimes use to signify multiplication; the other is the more common times sign, $\times$.