Physical Chemistry

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Preface

Oor universe is like an e'e
Turned in, man's benmaist hert to see,
And swamped in subjectivity.

But whether it can use its sicht
To bring what lies withoot to licht
To answer's still ayont my micht.

Hugh MacDiarmid
1926[*]

Like the last edition, this new edition of *Physical Chemistry* is the result of a substantial rewriting of the entire book. About 22 years ago, in the preface to the first edition, I said that this book was not designed to be a collection of facts, but rather an introduction to ways of thinking about the world. Actually this edition was written under the title *Foundations of Physical Chemistry*, and such a title expresses quite well the basic intention of the book. I have tried to emphasize critical discussions of definitions, postulates, and logical operations. The concepts of physical chemistry today are transient states in the progress of the science. The historical background in the book is intended to help the student reach this understanding, without which science becomes static and comparatively uninteresting.

For some students of physical chemistry the use of mathematics remains a major difficulty. We try to convince students that the scientist must learn mathematics while he studies science. It is neither necessary nor desirable to learn "pure mathematics" first and then to apply it to scientific problems. The level of mathematical difficulty in this edition is somewhat higher than previously, but as a compensation, more careful discussions of mathematical details have been given. Nevertheless, many students would find it worthwhile to acquire one of several excellent books on mathematics for the physical sciences, references to which are made in the text.

In this edition, the order of the subject matter has been changed in order to bring statistical mechanics into the text as early as possible, and then to use its methods in subsequent discussions. Examination of current textbooks of general chemistry and physics (universal prerequisites for the study of physical chemistry)

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[*] From "The Great Wheel" by Hugh MacDiarmid (C. M. Grieve) in *A Drunk Man Looks at the Thistle* (Edinburgh: Wm. Blackwood & Sons, 1926).

indicates that almost all contain sufficient atomic physics and elementary quantum theory to serve as an adequate foundation for the principles of statistical mechanics as given in my Chapter 5.

I have tried to follow the recommendations on nomenclature and units of the International Union of Pure and Applied Chemistry, except for the retention of the *atmosphere* as a unit of pressure, a relic of nonsystematic units, which also should disappear in due course. Probably within a decade, the SI system of units will be in general use by all scientists.*

There are not many worked out numerical problems in the text, but Professors William Bunger of Indiana State University and Theodore Sakano of Rose–Hulman Polytechnic Institute have prepared a manual of solutions to all the problems at the ends of chapters. In my experience students will learn most quickly if th obtain this manual as a companion to the text.

It is always a pleasant duty to thank my confreres who have contributed s generously with illustrations, corrections, and suggestions to improve the book. So many people have helped that I am sure to forget to mention some, but these also have my thanks. The publishers wisely enlisted Thomas Dunn to provide a general analysis of the book and Jeff Steinfeld to make a critical reading of the manuscript. Walter Kauzmann was a continual source of help, both in the extensive comments he sent me and in the excellent material I found in his clearly written books. By devious pathways, an exegesis of the third edition by George Kistiakowsky fell into my hands, which provided many valuable clarifications.

Apart from these major efforts on the total book, much work on individual chapters was done by Peter Langhoff, Edward Bair, Donald McQuarrie, Robert Mortimer, John Bockris, Donald Sands, Edward Hughes, John Ricci, John Griffith, Dennis Peters, Ludvik Bass, Albert Zettlemoyer and Dieter Hummel (who has made a German translation). Lucky is the author who has such good neighbors as these. Acknowledgments to scientists who sent illustrations are included in the text. At Prentice-Hall, Albert Belskie, Editor for Chemistry, was a solid source of support and good counsel at all times.

With all this help one may wonder why the book is still so far from an ideal state. The answer must have something to do with the fact that we are not working closer to absolute zero.† As always, I shall welcome comments from readers and try to correct all the mistakes that they will find.

W.J.M.

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*M. A. Paul, "The International System of Units (SI)—Development and Progress," *J. Chem. Doc. 11*, 3 (1971).

†A concise summary of thermodynamics has been given: (1) The First Law says you can't win; the best you can do is break even. (2) The Second Law says you can break even only at absolute zero. (3) The Third Law says you can never reach absolute zero.

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1

Physicochemical Systems

> *Nosotros (la indivisa divinidad que opera en nosotros) hemos soñado el mundo. Lo hemos soñado resistente, misterioso, visible, ubicuo en el espacio y firme en el tiempo; pero hemos consentido en su arquitectura tenues y eternos intersticios de sinrazón, para saber que es falso.*
>
> Jorge Luis Borges
> 1932*

On the planet Earth the processes of evolution created neural networks called *brains*. Reaching a certain degree of complexity, these networks generated electrical phenomena in space and time called *consciousness*, *volition*, and *memory*. The brains in some of the higher primates, *genus Homo*, devised a medium called *language* to communicate with one another and to store information. Some of the human brains persistently sought to analyze the input signals received from the world in which they had their existence. One form of analysis, called *science*, proved to be especially effective in correlating, modifying, and controlling the sensory input data.

Most of the structure of brains was laid down in conformity with information coded into the base sequence of the DNA molecules of the genetic material. Additional structuring was caused by a relatively uniform experience during their periods of growth and maturation. Thus, heredity and early environment combined to produce adult brains with rather stereotyped capabilities for analysis and communication.

Language was effective in communications that dealt with the content of sensory input data, but it did not allow the brains to talk about themselves or their relation to the world without breakdowns into paradox or contradiction. In particular, although it was possible to find thousands of books filled with results of science, to observe thousands of men at work in the fields of science, and to experience the earthshaking effects of science, it was not possible to explain in words what science was or even the mechanism by which it operated. Different views on these questions were eloquently put forth from time to time.

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*From "La Perpetua Carrera de Achilles e la Tortuga" in *Discusion* (Buenos Aires: M. Gleizer, 1932). "We (the undivided divinity that operates within us) have dreamed the world. We have dreamed it resistant, mysterious, visible, ubiquitous in space and firm in time; but we have allowed into its architecture tenuous and eternal interstices of unreason to let us understand that it is false."

1. What Is Science?

According to one view, called *conventionalism*, the human brains created or invented certain beautiful logical structures called *laws of nature* and then devised special ways, called *experiments*, of selecting sensory input data so that they would fit into the patterns ordained by the laws. In the conventionalist view, the scientist was like a creative artist, working not with paint or marble but with the unorganized sensations from a chaotic world. Scientific philosophers supporting this position included Poincaré,* Duhem,† and Eddington.‡

A second view of science, called *inductivism*, considered that the basic procedure of science was to collect and classify sensory input data into a form called *observable facts*. From these facts, by a method called *inductive logic*, the scientist then drew general conclusions which were the laws of nature. Francis Bacon, in his *Novum Organum* of 1620, argued that this was the only proper scientific method, and at that time his emphasis on observable facts was an important antidote to medieval reliance on a formal logic of limited capabilities. Bacon's definition accords most closely with the layman's idea of what scientists do, but many competent philosophers have also continued to support the essentials of inductivism, including Russell§ and Reichenbach.||

A third view of science, called *deductivism*, emphasized the primary importance of theories. According to Popper,♯ "Theories are nets cast to catch what we call 'the world': to rationalize, to explain, and to master it. We endeavor to make the mesh ever finer and finer." According to the deductivists, there is *no* valid inductive logic, since general statements can never be proved from particular instances. On the other hand, a general statement can be *disproved* by one contrary particular instance. Hence, a scientific theory can never be proved, but it can be disproved. The role of an experiment is therefore to subject a scientific theory to a critical test.

The three philosophies outlined by no means exhaust the variety of efforts made to capture science in the web of language. As we are studying the part of science called *physical chemistry*, we should pause sometimes (but not too often) to ask ourselves which philosophic school we are attending.

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*Henri Poincaré, *Science and Hypothesis* (New York: Dover Publications, Inc., 1952).

†Pierre Duhem, *The System of the World*, 6 Vols. (Paris: Librarie Scientifique Hermann et Cie., 1954).

‡Arthur Stanley Eddington, *The Philosophy of Physical Science* (Ann Arbor, Mich.: University of Michigan Press, 1958).

§Bertrand Russell, *Human Knowledge, Its Scope and Limits* (New York: Simon and Schuster, Inc., 1948).

||Hans Reichenbach, *The Rise of Scientific Philosophy* (Berkeley: University of California Press, 1963).

♯Karl R. Popper, *The Logic of Scientific Discovery* (New York: Harper Torchbooks, 1965).

2. Physical Chemistry

There appear to be two reasonable approaches to the study of physical chemistry. We may adopt a synthetic approach and, beginning with the structure and behavior of matter in its finest known state of subdivision, gradually progress from electrons to atoms to molecules to states of aggregation and chemical reactions. Alternatively, we may adopt an analytical treatment and, starting with matter or chemicals as we find them in the laboratory, gradually work our way back to finer states of subdivision as we require them to explain experimental results. This latter method follows more closely the historical development, although a strict adherence to history is impossible in a broad subject whose different branches have progressed at different rates.

Two main problems have been primary concerns of physical chemistry: the question of the position of chemical equilibrium, which is the principal problem of chemical thermodynamics; and the question of the rate of chemical reactions, which is the field of chemical kinetics. Since these problems are ultimately concerned with the interactions of molecules, their complete solutions should be implicit in the mechanics of molecules and molecular aggregates. Therefore, molecular structure is an important part of physical chemistry. The discipline that allows us to bring our knowledge of molecular structure to bear on the problems of equilibrium and kinetics is found in the study of statistical mechanics.

We shall begin our study of physical chemistry with thermodynamics, which is based on concepts common to the everyday world. We shall follow quite closely the historical development of the subject, since usually more knowledge can be gained by watching the construction of something than by inspecting the polished final product.

3. Mechanics: Force

The first thing that may be said of thermodynamics is that the word itself is evidently derived from *dynamics*, which is a branch of mechanics dealing with matter in motion.

Mechanics is founded on the work of Isaac Newton (1642–1727), and usually begins with a statement of the well-known equation

$$\mathbf{F} = m\mathbf{a}$$

with

$$\mathbf{a} = \frac{d\mathbf{v}}{dt} = \frac{d^2\mathbf{r}}{dt^2} \tag{1.1}$$

The equation states the proportionality between a vector quantity $\mathbf{F}$, called the *force* applied to a particle of matter, and the acceleration $\mathbf{a}$ of the particle, a vector in the same direction, with a proportionality factor m, called the mass. Equation (1.1) may also be written

$$\mathbf{F} = \frac{d(m\mathbf{v})}{dt} \tag{1.2}$$

where the product of mass and velocity is called the *momentum*.

In the International System of Units (SI), the unit of mass is the kilogram* (kg), the unit of time is the second† (s), and the unit of length is the metre‡ (m). The SI unit of force is the *newton* (N).

Mass might be introduced in Newton's Law of Gravitation,

$$F = \frac{Gm_1m_2}{r_{12}^2}$$

which states that there is an attractive force between two masses proportional to their product and inversely proportional to the square of their separation. If this gravitational mass is to be the same as the inertial mass of (1.1), the proportionality constant

$$G = 6.670 \times 10^{-11}\ \mathrm{m^3 \cdot s^{-2} \cdot kg^{-2}}$$

The weight of a body, W, is the force with which it is attracted toward the earth, and may vary slightly over the earth's surface, since the earth is not a perfect sphere of uniform density. Thus

$$W = mg$$

where g is the acceleration of free fall in vacuum.

In practice, the mass of a body is measured by comparing its weight by means of a balance with that of known standards ($m_1/m_2 = W_1/W_2$).

4. Mechanical Work

In mechanics, if the point of application of a force **F** moves, the force is said to *do work*. The amount of work done by a force **F** whose point of application moves a distance dr along the direction of the force is

$$dw = F\,dr \tag{1.3}$$

If the direction of motion of the point of application is not the same as the direction of the force, but at an angle θ to it, we have the situation shown in Fig. 1.1.

The component of **F** in the direction of motion is $F\cos\theta$, and the element of work is

$$dw = F\cos\theta\,dr \tag{1.4}$$

If we choose a set of Cartesian axes XYZ, the components of the force are

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*Defined by the mass of the international prototype, a platinum cylinder at the International Bureau of Weights and Measures at Sèvres, near Paris.

†Defined as duration of 9 192 631 770 periods of the radiation corresponding to the transition between the two hyperfine levels in the ground state of the cesium-133 atom.

‡Defined as the length equal to 1 650 763.73 wavelengths in vacuum of the radiation corresponding to the transition between the levels $2p_{10}$ and $5d_5$ of the krypton-86 atom.

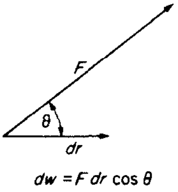

FIG. 1.1 Definition of differential element of work.

F_x, F_y, F_z and

$$dw = F_x\,dx + F_y\,dy + F_z\,dz \tag{1.5}$$

For the case of a force that is constant in direction and magnitude, (1.3) can be integrated to give

$$w = \int_{r_0}^{r_1} F\,dr = F(r_1 - r_0)$$

An example is the force acting on a body of mass m in the earth's gravitational field. Over distances that are short compared to the diameter of the earth, this $F = mg$. To lift a body against earth's gravitational attraction we must apply to it an external force equal to mg. What is the work done on a mass of 1 kg when it is lifted a distance of 1 m?

$$\begin{aligned} w = mgr_1 &= (1)(9.80665)(1)\ \mathrm{kg \cdot m \cdot s^{-2} \cdot m} = 9.80665\ \mathrm{kg \cdot m^2 \cdot s^{-2}} \\ &= 9.80665\ \text{newton metre } (\mathrm{N \cdot m}) = 9.80665\ \text{joule (J)} \end{aligned}$$

An application of (1.3) in which the force is not constant is to the stretching of a perfectly elastic spring. In accord with the law of Hooke, 1660, ***ut tensio sic vis***: the restoring force is directly proportional to the extension,

$$F = -\kappa r \tag{1.6}$$

where κ is called the *force constant* of the spring. Hence, the work dw done on the spring to extend it by dr is

$$dw = \kappa r\,dr$$

Suppose the spring is stretched by a distance r_1,

$$w = \int_0^{r_1} \kappa r\,dr = \frac{\kappa}{2} r_1^2$$

The work done on the spring is taken by convention to be positive.

In the general case, we can write the integral of (1.5) as

$$w = \int_a^b (F_x\,dx + F_y\,dy + F_z\,dz) \tag{1.7}$$

The components of the force may vary from point to point along the curve followed by the mass point. They are functions of the space coordinates x, y, z: $F_x(x, y, z)$, $F_y(x, y, z)$, and $F_z(x, y, z)$. It is evident that the value of the integral depends upon the exact path or curve between the two limits a and b. It is called a *line integral.*