THE ROLE AND STRUCTURE OF PHYSICAL CHEMISTRY IN THE UNDERGRADUATE CURRICULUM

BRUCE H. MAHAN
University of California, Berkeley, Calif. 94720

Like the other subjects in the science curriculum, the physical chemistry course is beset by a plethora of new findings, ideas, and areas of investigation which could, and in some cases should, be included in the course of study. However, this expansion of the breadth of the subject matter can lead to a superficial survey course which provides students with few skills and little insight which can be applied to other subjects. Abolition of the physical chemistry course and integration of its conceptual material with descriptive chemistry is one solution that has been offered for this problem. A preferable procedure is to examine carefully the meaning and use of physical chemistry, and accordingly to restructure the course so that it provides students with an introduction to and training in the use of those concepts and techniques which are of widest applicability and most lasting value.

I am addressing the problem of the role, position and nature of the instruction in physical chemistry in the undergraduate curriculum. Naturally, I would not be doing this unless I thought that something is now wrong, or at the very least that we are capable of much more effective instruction than we now provide. In the following, I shall state what I feel the problems are, then discuss some possible solutions, and attempt to predict their consequences.

Like the other subjects in the science curriculum, physical chemistry is becoming almost overwhelmed by new experimental findings and ideas. Many of these are more than just interesting, they are so general and important that each chemistry student should have a basic understanding of them. What has been the result of this information explosion? First, the textbooks have grown in length, and the pace of instruction has increased. Also, subjects of lesser current interest or generality have been discarded entirely, or appear in texts and are rarely taught. A number of topics such as ionic equilibria, ideal gas laws, and elementary electrochemistry, which were prominent in texts widely used as recently as 1955, have been relegated to the introductory general chemistry course. In still other instances, modern ideas have led to a generality and unity of presentation which has been accompanied by a most welcome saving in instructional time and, for the fortunate, a deeper understanding of the subject. However, I feel that despite these ameliorations, the overall result of the inclusion of a vastly increasing number of topics has been to make physical chemistry a shallow survey course. Many sophisticated ideas are presented so superficially that the only thing the student carries away is a feeling that he has heard of these concepts, but doesn't understand them. This is one problem which we must solve.

There is a second difficulty. The influence of the ideas and techniques of physical chemistry on the other branches of chemistry has increased enormously. Without doubt, people who are labelled as 'organic' and 'inorganic' chemists measure more rate constants and equilibrium constants, and take more infra-red, ultra-violet, and n.m.r. spectra than all physical chemists and chemical physicists together. The interpretation of all chemical phenomena is constantly becoming more quantitative, sophisticated and fundamental. For the undergraduate curriculum, the consequence has been the appearance in traditional organic and inorganic chemistry courses of short introductions to such things as atomic and molecular orbitals, infra-red and n.m.r. spectra, and group theory. Unless the organization of the total curriculum is kept well in hand, the result can be that the student receives the same elementary introduction to these subjects three or four times, and never progresses to a deeper understanding or more rigorous use of them. In the extreme, group theory may displace the descriptive chemistry in an inorganic chemistry course, and the ambitious undergraduate well trained in mathematics and physics may be all too ready to find the quantum theory professed by some organic chemists dull and lacking in rigour. Thus, not only must the physical chemistry instruction cope with an enormous volume of potential subject matter, but it must also provide the student with an understandable introduction to theoretical principles which he can draw upon and apply in his other chemistry courses and throughout his career.

One possible solution is to abandon the conventional separate physical chemistry course, and instead integrate the conceptual material with descriptive chemistry. While this plan evidently has the extremely attractive feature of introducing at the earliest possible time an exchange, and we should hope, a cross-fertilization of the ideas of theoretical and descriptive chemistry, I am not attracted to it. I firmly believe that certain subjects, in particular thermodynamics, quantum mechanics and statistical mechanics, are uniquely well organized, cohesive disciplines, which not only stand by themselves, but are indeed more fundamental and lasting than the rough and ready conceptual material that a practising chemist uses. To submerge and diffuse them in the sea of ill-defined (but often ingenious and useful) concepts and models that chemists use would be dangerously confusing to the student. I feel that we can make these subjects, along with molecular structure and chemical kinetics, into tools available for use in understanding descriptive chemistry without sacrificing their beautiful unity and organization.

To find a way to proceed, we must first recognize what physical chemistry is. I feel that it comprises the ideas and principles of chemistry which are fundamental, general, *quantitative* and, if anything is, permanent. We must identify a minimum set of these principles, teach them and a few of their important applications carefully, and insist that in subsequent descriptive chemistry courses knowledge of them be assumed, and that use of this knowledge be made.

I feel that the way in which the physical chemistry course must evolve is to a certain degree indicated by what has happened to the teaching of thermodynamics in the last twenty years. In a physical chemistry text published in 1948, thermodynamics was the single most important subject. However, the treatment was wordy, with halting use of mathematics. The level of sophistication was not much higher than that currently achieved by freshmen, in that such things as partial molal quantities and non-ideal systems were not treated. Today, the thermodynamics taught in physical chemistry is more concise, rigorous, mathematical and of greater scope. Much of this improvement predates the introduction of thermodynamics into the introductory or freshman course. How did the upgrading in instruction occur? With guidance from new texts, teachers simply came to realize that the college student in his second or third year had acquired all the mathematical and intellectual preparation he needed to understand a complete and precise treatment of thermodynamics. Moreover, it has become clear that this more mathematical approach is less confusing and difficult for the student than the earlier treatment, which relied too much on words, and too little on precise definitions and equations.

My suggestions for the rest of the physical chemistry course are quite modest. We must stop teaching the vague versions of quantum theory and quantum chemistry that abound today in texts and courses, and instead supply the second year college student with a course in quantum mechanics. This course should have as its aim the exposure of the postulates, principal mathematical techniques and major results of quantum mechanics in a concise and precise form, so that the student will be able to do the simplest quantum mechanical calculations, and understand what is involved in the more complicated ones. With a background in legitimate, somewhat formal quantum mechanics, the student is far better prepared to understand spectroscopic phenomena and chemical bonding, and will be much less inclined to accept without criticism or analysis the imprecise language and models that are so useful in correlating complicated chemical phenomena. We can even hope to suppress imprecise application and misuse of the subject in descriptive chemistry courses, and to remove the confusion that often accompanies talking about, rather than doing, quantum mechanics.

I believe that this can be accomplished given the current mathematical preparation of students and the traditional position of physical chemistry in the second and third years of college. In eighteen lectures, the postulates of quantum mechanics, box and barrier problems, the harmonic oscillator, rigid rotor and hydrogen atom problems can be presented, solved and the solutions studied in detail, particularly if operator techniques are used extensively. While it is possible in this time to discuss the polynomial method of solving the Schrödinger equation, the major emphasis should be on studying the nature of the wavefunctions, seeing their relation to the potential energy function, and learning to use them as calculation tools. By adopting the non-historical, postulatory approach and avoiding discussion of measurement processes, we complement rather than infringe upon the typical treatment of quantum mechanics which is presented in elementary physics courses.

Following this, twelve lectures could be used to introduce stationary and time dependent perturbation theory, and the variation method. These techniques should be applied to as many problems as possible, since they really are the basis for much of our intuitive or qualitative analysis of chemical phenomena. It has been my experience that such a course can be taught successfully in this time without using mathematics which is above the college sophomore level. The appearance of several new texts appropriate for such a course certainly confirms that others have had similar feelings and experience.

Following the thirty lectures on quantum mechanical methods, there should be a similar number devoted to the principal experimental methods for the study of molecular structure. The earlier exposure to quantum mechanics should make possible a fairly rigorous presentation of the various spectroscopic methods used by chemists. In turn, the students' understanding of quantum mechanics should be strengthened by seeing it applied repeatedly to problems of molecular structure and spectra. The principles, power limitations of x-ray and electron diffraction, often neglected or badly handled, should also be treated. Throughout the course, the guiding theme could well be to discern what each experimental method has contributed to our understanding of chemical bonding and molecular reactivity.

It is to be expected that an introduction to symmetry group theory and its uses in molecular structure and spectroscopy problems should be an important component of this course. This extremely valuable subject has traditionally had no well-defined place in the undergraduate curriculum. Its inclusion in a required course in molecular structure would ensure that each undergraduate would be given a chance to learn its usefulness.

I will not discuss the details of the subject material further, since existing texts and several other pieces of evidence make it clear that molecular structure courses of this type exist now at many colleges. However, they are usually offered to students as an option after they have completed the conventional physical chemistry course. My proposal is simply that they be made part of the physical chemistry course taken by all students.

The major topics which would remain to be covered include thermodynamics, statistical mechanics, and chemical kinetics in its broadest sense. There has been considerable debate over whether one should teach a pure thermodynamics course, or a mixture of statistical mechanics and thermodynamics. Although I have never done it, I believe I would favour the latter approach. It does have the advantage of offering an immediate molecular interpretation of the all too often mysterious state variables of thermodynamics, and does in fact closely represent how most chemists think about and work with the thermal properties of matter. The more philosophically minded will argue that it is important for students to see thermodynamics as a set of laws that are independent of assumptions about molecular models, and that this can only be accomplished by teaching a pure macroscopic thermodynamics course. In the first instance they are right, in the second I believe they are wrong. I would, therefore, follow the lectures on quantum mechanics and molecular structure with a series of thirty or forty hours on statistical thermodynamics.

We now have to deal with chemical dynamics. I am a specialist in this area, and am aware of the usual tendency of such people to be over-critical of what has been traditionally taught by others. Even after allowing for such tendencies, I feel that in the area of chemical dynamics, the poorest job of instruction has been done. There are good reasons for this. Much of the theory and general organizing principles of chemical dynamics are rather new, or are only recently understood clearly by a relatively small group of chemists. The part of the theory which is and has been well understood for some time has not been taught to chemists, and, in addition, there is a dearth of authoritative reference material on the fundamentals of the subject. Fortunately, all this is changing rapidly.

What has been done wrong in the past? First, too much time has been spent on phenomenological chemical kinetics, integrating rate laws, deducing activation energies from experimental data, and so on. This is important material, but much of it could be and has been relegated to the introductory chemistry course, and to the physical chemistry laboratory. Secondly, we have failed to present the simple, well-understood dynamical processes like transport in ideal gases in a manner which is sophisticated, general or even clear. There has been too much emphasis on the hard sphere and mean free path, and too little on such things as the basic idea of what a collision is, that transport is a non-equilibrium phenomenon which implies departures from the Maxwell–Boltzmann distribution of velocities, and that careful study of transport processes does tell us what intermolecular forces are like. Thirdly, we have tended to ignore analysis from the molecular point of view of transport processes in condensed phases. The general understanding of this subject is increasing rapidly, and it should be treated more thoroughly. Finally, in the realm of reaction kinetics, we have been leaning for theoretical guidance on the ultra-simplified version of collision theory, or on murky, imprecise formulations of absolute rate theory. The presentations of this material that I have found in texts tend to leave one with the feeling that theories of reaction kinetics are insecurely based and impossible to use precisely.

In place of what we have been doing, I propose that we present a careful treatment of classical collision theory, followed by a discussion, based on Boltzmann's *H*-theorem and transport equation, of how collisions lead to and maintain the Maxwell–Boltzmann velocity distribution. Then one could present a treatment of the kinetic theory of gases. A discussion of transport theory based on the relaxation time approximation to the Boltzmann equation would follow, and while emphasizing dilute gas phenomena, the treatment could be extended to include the transport and electrical properties of liquids and solids.

Conventional treatments of chemical kinetics rightly emphasize the idea of elementary processes, and present, usually not very successfully, some of the theory of unimolecular, bimolecular and termolecular processes in gases. The very important physical processes of vibrational, rotational, and electronic energy exchange are often ignored totally. With the suggested background of quantum mechanics and molecular structure, students should be able to understand the simple collision theories of these processes, and to gain an appreciation that the solution to the more complicated problems of chemical reaction lies in the application of collision theory. In addition, the importance of these energy transfer processes in maintaining the population of the states of a reacting system in an approximately Boltzmann distribution will become clearer.

In treating chemical reactions, we can now make use of the relatively detailed results of molecular beam experiments to remove at least part of the mystery of how reactants are converted to products. Examples of reactions which proceed by very short-lived collision complexes formed principally by head-on or by grazing collisions now abound in the literature, and examples of long-lived collision complexes are being found in increasing numbers. Computer calculations of the classical trajectories of reacting molecules provide an explicit and clear exposition of the reaction process. Acquaintance with the details of gas phase reaction dynamics should make discussions of certain aspects of condensed phase reactions clearer. In a similar manner, recent experimental work has greatly increased our understanding of unimolecular dissociation and rearrangements. There have only been relatively half-hearted attempts to discuss the theory of these processes in physical chemistry texts. A greater attempt should be made to reduce the existing very effective theory to its simplest terms for presentation at the undergraduate level, since the ideas could have important impact on the business of predicting and understanding reaction paths in complicated systems.

The physical chemistry course I have outlined is similar to and I should hope shares the virtues of the organization used in the undergraduate physics curriculum, where following an introductory general physics course, the student takes intermediate courses in classical mechanics, electricity and magnetism, quantum mechanics and thermal physics. The physical chemistry sequence of quantum mechanics, molecular structure, statistical thermodynamics and chemical kinetics involves approximately one-third more lecture time than the conventional ninety-hour lecture course. This extra time need not burden the already bulging curriculum, since the proposed course would allow elimination of one of the optional advanced level courses which students frequently take following the conventional treatment of physical chemistry. The inclusion of the material I have outlined in a *required* sequence starting in the second year of study would allow lecturers in the predominantly descriptive chemistry courses to use the ideas of quantum chemistry and molecular structure, spectroscopy, group theory, statistical thermodynamics and reaction kinetics without apology in discussion and analysis of chemical facts.

A possible objection to the course I propose is that it could tend to be relatively abstract. This is a matter largely in the hands of the individual instructor, who while emphasizing fundamentals must constantly refer to problems of interest to chemists. Another objection is that the mathematics required for quantum mechanics may exceed the preparation of the second year students. This certainly need not be true. With operator techniques the number of differential equations that must be solved could be two or three of the simplest variety. The use of mathematics in finding average values, minima and maxima, and the roots of equations is entirely appropriate for the second year of college. Finally, the articulation of the course with others in chemistry and physics might appear to be a problem. However, the postulational approach taken in the quantum mechanics section will most probably make it complementary to what is offered to the student in physics, and removes the necessity for waiting until the student has completed physics before beginning quantum mechanics. In summary, I think that these possible difficulties can be eliminated or minimized, and that this approach will have the overriding virtue of providing the student with the tools of, rather than just a look at, physical chemistry.

DISCUSSION

J. A. Campbell (*Harvey Mudd College, Claremont, California*)—The mathematical and physical background of many students is indeed now sufficient to teach quantum mechanics to second year college students. Our own experience, however, is that too little use is or can be made of this material in the third year courses in reaction (descriptive) chemistry. Also, more useful to second year students is a wide-ranging approach emphasizing the inter-relationships of reaction chemistry and physical chemistry, and more successful courses in quantum chemistry including symmetry theory can be given in the last year based on the reaction chemistry favoured by that time and in anticipation of graduate school where further use will be made of the subjects.

W. H. Eberhardt (*Georgia Institute of Technology, Atlanta*)—I am concerned about the tendency of chemists to try to teach all aspects of science and mathematics within their own discipline. Many aspects of mathematics and physics, especially the methods of mathematical physics and electromagnetic theory, may be taught more effectively by mathematicians or physicists dedicated to these disciplines. It is not evident that elementary and general courses in mathematics and physics are sufficient, especially for individuals who will ultimately work in physical chemistry. Rather, it is likely that advanced work in these areas taught by mathematicians and physicists may be of greater ultimate use to chemists than comparable courses taught by chemists themselves. Some space or flexibility must be kept in the chemistry curriculum for such advanced courses outside the chemistry department.