

11.5: Reaction to Gillespie's Six Great Ideas in Chemistry - Another Great Idea

I wish to respond to an article by Ronald J. Gillespie published in The Journal on the content of the general chemistry sequence (1). While I agree with his major premise, I strongly disagree with a number of his specific recommendations. Operating under the assumption that the teaching of chemistry is enriched by lively debate and critical analysis, I would like to share my observations with the readership of The Journal. In what follows, text in italic font is taken directly from Professor Gillespie's paper. I will follow the italicized text with my comments and observations.

Critique

We must remember that the general chemistry course is not (or should not be) designed as a first step in the training of future professional chemists.

I agree with this sentiment, but I have reservations about its implementation. In attempting to reach and educate all of the constituencies of general chemistry in a single course, we should not oversimplify the course simply for the benefit of the non-major, and thereby teach things which must be retracted at some later point in the education of the chemistry major. Teaching simple models that students can easily digest is tempting, but these easily digestible models are frequently scientifically incorrect. In my opinion Gillespie presents several models of this kind of simplicity that are incorrect and, if taught, would have to be untaught, or retracted, at some later time in the education of the chemistry major or others who study chemistry beyond the general chemistry sequence. We should follow Einstein's advice in our teaching and "make things as simple as possible, but no simpler."

Elements are a kind of matter that consists of atoms of only one kind.

Besides being casual in tone, the definition is not correct. It is clear from reading this paper and its footnote, that it is a transcription of a talk given at a national ACS meeting. However, The Journal is a peer reviewed scientific journal and by not correcting this statement it appears to be sanctioning this rather informal and inaccurate definition.

All chemical bonds are formed by electrostatic attractions between positively charged cores and negatively charged valence electrons. Electrostatic forces are the only important force (sic) in chemistry.

At this point I will simply observe that there is only one electrostatic force - Coulomb's Law. There are, however, many types of electrostatic interactions: ion-ion, ion-dipole, dipole-dipole, etc. In other words, there are a large number of ways charge is distributed in matter, and therefore a large number of ways these charge distributions can interact with one another. However, whatever its form, the electrostatic interaction is ultimately calculated using one equation - Coulomb's Law. If this fact was more widely appreciated the grammatical error in the second sentence wouldn't have occurred.

(Overlap of atomic orbitals) distracts attention from the real reason for bond formation: the electrostatic attraction between electrons and nuclei.

Unfortunately this simple idea is simply false, but it is easy to teach (see earlier remark). To put it bluntly, if the electrostatic force was all that was important, the electrons would reside inside the nuclei and never in the region between them or anywhere else. A simple electrostatic calculation will show that placing an electron exactly between two positive charges is not the most energetically favorable configuration of charges (see appendix). Solely on the basis of Coulomb's law the electron would be drawn toward one nucleus or the other; unless like Buridan's mule the electron is immobilized by its inability to distinguish between two identically attractive alternatives.

Orbitals and the LCAO-MO method are indeed only models, but at least they give a scientifically respectable picture of the covalent bond. Using the orbital model it can be shown that constructive interference due to overlap of atomic orbitals leads to charge build up in the internuclear region. This build up of charge, which is frequently described as the glue that holds atoms together, is funded by a decrease in kinetic energy due to the delocalization of electron density as Ruedenberg's insightful analysis of the chemical bond showed more than forty years ago (2). The potential energy actually increases during this process, as the exercise outlined in the appendix shows.

I am not recommending that we teach general chemistry students full-blown quantum mechanics, I am simply saying that Gillespie's simplistic electrostatic model is incorrect, and therefore shouldn't be taught to anyone, especially general chemistry students who are most vulnerable to specious arguments. We are accustomed to making simplifying approximations in chemistry, but Gillespie's model is not acceptable because it neglects a fundamental physical property, electron kinetic energy, which is essential to the understanding of atomic and molecular phenomena.

Moreover, the orbital model gives students the incorrect impression that chemistry is a difficult, abstract, mathematical subject based on a mysterious concept that is not and cannot be satisfactorily explained at the introductory level.

As a matter of fact chemistry is difficult and abstract, and students find this out long before they get to orbitals and quantum numbers. Furthermore, if quantum theory and the orbital concept are mysterious it is because the nano-scale world of electrons, nuclei, atoms, and molecules is mysterious. The fact that nano-world of atoms and molecules is not simply a miniature of the macro-world is one of the most important discoveries in the history of science. The classical principles that work in the macro-world are inadequate in the nano-world and need to be supplemented by the de Broglie hypothesis (see later, 7th great idea). In other words, the need for quantum theory is ‘data driven,’ to use a slogan currently in vogue within the community of chemical educators. Marvin Chester (3) put this most cogently when he wrote, “The mathematical predictions of quantum mechanics yield results that are in agreement with experimental findings. That is the reason we use quantum theory. That quantum theory fits experiment is what validates the theory, **but why experiment should give such peculiar results is a mystery** (emphasis added).”

This aspect of chemistry (molecular geometry) receives too little emphasis in the introductory course, although it is one that can stimulate and excite students by showing that chemistry is practical, useful, and challenging, not dull, theoretical, mathematical, and abstract.

I agree that structural and synthetic chemistry deserve more attention and are exciting and interesting areas of contemporary chemistry, but the last part of this sentence is simply a cheap shot. Theory is also exciting, useful, and challenging, especially when taught by those who understand its significance. Theory is an essential part of 20th Century chemistry and should be taught in a positive manner to students at all levels. In addition, it should be noted that theory has always been an essential part of chemistry. To describe chemistry simply as an experimental science, is to use a halftruth to describe a discipline that is much richer than a single-sentence definition can capture. I will return to the role of theory in science teaching in my conclusion.

Molecular modeling programs now make it even easier for students to understand and become familiar with the shapes of molecules.

This is indeed true, but molecular modeling programs (except for molecular mechanics calculations) are built on quantum mechanics and mainly exploit the orbital approximation, which Professor Gillespie has previously criticized as a “mysterious concept that is not and cannot be satisfactorily explained at the introductory level.” Is he proposing we hide this fact from the students and treat the molecular modeling programs as black boxes? If so this is not a valid or honest pedagogy.

By kinetic theory I do not mean the derivation of $PV = \frac{1}{3}nm\overline{c^2} = nRT$...

This equation cannot be derived from kinetic theory as Dewey Carpenter showed some thirty-five years ago in this Journal (4). Temperature is not a mechanical concept; it lies outside the kinetic molecular theory. The kinetic theory yields $PV = \frac{1}{3}nm\overline{c^2}$, which when compared to the empirically based ideal gas law, $PV = nRT$, leads to the conclusion that the average molecular kinetic energy is proportional to the absolute temperature: $\langle KE \rangle = \frac{1}{2}M\overline{c^2} = \frac{3}{2}RT$.

Everyone can understand the concept of disorder and that is really all there is to entropy.

While this erroneous belief is uncritically accepted by many, there is no scientific justification for its widespread use in teaching, as McGlashan showed so many years ago on these very pages (5a). More recently, Lambert has incisively exposed the error in equating entropy with disorder (5b). On Ludwig Boltzmann’s tombstone in Vienna is inscribed his famous formula, $S = k \log W$. With this simple, but powerful equation, Boltzmann connected the macro-world with the nano-world. S is entropy and W stands for the German word, *wahrscheinlichkeit*, which in English means likelihood or more formally probability. Probability is not an overly difficult concept so why not use it here. In addition it is so much more accurate and powerful than the more comfortable and casual, but scientifically vague, concept of disorder.

A Seventh Great Idea

The fact that atomic and molecular structure and stability, and the physical nature of the chemical bond cannot be understood with the six great ideas Gillespie promotes is evidence to me that another great idea is essential in the general chemistry curriculum. This seventh great idea, the corner stone of quantum mechanics, is de Broglie’s hypothesis that matter has wave-like properties and is, therefore, subject to interference phenomena (constructive and destructive) normally associated with wave-like phenomena. This is especially important for the light-weight electron and is the idea that is necessary to explain the chemical bond, and atomic and molecular stability, and atomic and molecular structure, and atomic and molecular spectroscopy.

From de Broglie's wave equation, $\lambda = \frac{h}{mv}$, it follows that in the nano-world kinetic energy is $\frac{h^2}{2m\lambda^2}$, which means that if the space an electron occupies is restricted, its kinetic energy is quantized and increased significantly. Thus, kinetic energy behaves like an outward force that counter balances the inward electrostatic force and prevents the electron from collapsing into the nucleus under the electrostatic attraction that Gillespie says is all that is needed to explain chemical phenomena. As Ruedenberg has pointed out there are no ground states or quantized energy levels in the classical, macroscopic world. We need de Broglie's hypothesis to explain chemical phenomena at the atomic and molecular level.

We have just left the century which began with the quantum revolution of Planck, Einstein, and Bohr. We have also recently celebrated the 100th anniversary of the discovery of the electron, that fundamental particle whose behavior dictates chemistry. Today, as far as we can tell, the behavior of the electron is accurately described by the principles of quantum mechanics. At some rudimentary level we should be teaching this important theory to all of our students.

Here is what I try to do. In my general chemistry course I teach de Broglie's wave equation and its implications. I concentrate on the consequences of confinement and delocalization at the atomic and molecular level. I outline the origin of quantized energy levels and quantum numbers from de Broglie's fundamental idea. I regard it as one of the most astonishing, provocative, and creative ideas of the 20th Century, and I want my students, majors and non-majors, to be aware of its existence and importance.

A survey of the current general chemistry texts will reveal that all of them present deBroglie's hypothesis. My point is that it should be elevated to an essential part of the introductory chemistry curriculum. If we are going to select a small number of essential ideas or principles, deBroglie's wave-particle duality for matter should be among them.

Conclusion

Chemistry is a great intellectual adventure and we must present the spirit of that adventure to all of our students, no matter what their academic major or their particular career objectives. If we are going to teach an honest first course in chemistry we have to describe both its experimental and theoretical features. I am offended and disturbed by Gillespie's gratuitous attack on mathematics and theory in the general chemistry sequence. He misrepresents chemistry because chemistry is not simply an experimental science, nor has it ever been so. I believe every scientific discipline involves a lively exchange between theory and experiment, and this is what we should tell our students. There is no hierarchy here, both theory and experiment are essential, on a day to day basis, for all practitioners of the art and science of chemistry. More than 20 years ago Roald Hoffmann wrote eloquently and incisively about the "symbiosis of theory and experiment." He spoke then of "... a vital interweaving of experiment inspired by theory, theory motivated by experiment, binding in a truly interdisciplinary way chemistry, physics, and engineering (5)."

According to Peter Medawar we can think of science as an on-going dialogue between what might be and what is actually so.

Scientific reasoning is an explanatory dialogue that can always be resolved into two voices or episodes of thought, imaginative (theoretical) and critical (experimental), which alternate and interact (6).

Hoffmann and Medawar, both Nobel Laureates, offer a much richer and more accurate description of science than the negative dichotomous view (experiment/theory, good/bad) that permeates Gillespie's paper.

Appendix

When asked what motivated the creation of his model of the atom Bohr replied "the stability of matter, a pure miracle when considered from the standpoint of classical physics." The following simple calculation will demonstrate what Bohr meant by this statement. This calculation will be carried out in atomic units where the charge on the electron is -1, the charge on the nucleus +1, and distances are measured in bohr, a_0 .

Two nuclei ($Z = 1$) are placed at $x = 0.0$ and 2.0 , respectively. An electron is located exactly between them at $x = 1.0$, where we instinctively, but incorrectly, think it would want to be on the basis of electrostatic considerations. The potential energy consists of three interactions (nuclear-nuclear repulsion and two electron-nuclear attractions) and is calculated to be:

$$V = \frac{(+1)(+1)}{2} + \frac{(-1)(+1)}{1} + \frac{(-1)(+1)}{1} = 1.5$$

Now move the electron 0.5 bohr closer to one of the nuclei.

$$V = \frac{(+1)(+1)}{2} + \frac{(-1)(+1)}{0.5} + \frac{(-1)(+1)}{1.5} = -2.17$$

And so it goes, on the basis of electrostatic considerations, until the electron is inside one nucleus or the other. While the electron was treated as a point charge in this calculation, a rigorous quantum mechanical calculation tells the same story - moving charge to

the internuclear region increases electrostatic potential energy.

The failure of classical physics to explain the stability and structure of matter and its interaction with electromagnetic radiation must be emphasized in the undergraduate curriculum at all levels. Again, the need for quantum mechanics is data driven, and it should be taught at an elementary level initially (see above) and at more sophisticated levels as science students progress through the undergraduate curriculum. Perhaps by the time they graduate chemistry and physics majors might be able to appreciate what Peter Atkins is saying here (8).

In a sense, the difference between classical and quantum mechanics can be seen to be due to the fact that classical mechanics took too superficial a view of the world: it dealt with appearances. However, quantum mechanics accepts that appearances are the manifestation of a deeper structure (the wavefunction, the amplitude of the state, not the state itself), and that all calculations must be carried out on this substructure.

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