Teaching Chemistry - The Great Ideas

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Introduction

In this lecture I want to consider the organization of ideas in chemistry. So this is going to be the most general of general lectures in chemistry. It will be so general that at the end you'll be convinced that I said nothing at all. One thing I want to say in advance, however, is that the students among you should be delighted that they are studying chemistry because it is the central subject. Standing in the centre of chemistry, we are standing in the centre of science. We can look in one direction and we can see biology and reach out and touch it. And if we look into the other direction we can see physics and reach out from chemistry and touch physics. So we are at the pivot, at the centre point, the fulcrum of science.

An important thing that chemistry does is to establish the link between the imagined and the percieved. So it is very important for chemists to develop the sense that when you touch something tangible, you know what it is in microscopic terms that you are dealing with.

Another important thing that chemistry does is that it trains you to think in terms of a tug-of-war, but not just a boring one-dimensional tug-of-war with two opposing teams pulling on a single rope, but a multi-dimensional tug-of-war, with teams in every direction and it is up to us to decide which is a dominant influence, which team in this multi-dimensional game is going to win. Is it going to be electronegativity, or polarizability, or ionization energy?

It is a juggling act as well as a tug-of-war. Chemistry is a supreme device for the manipulation of matter. Chemists are conjurers, in the sense that they are able to turn one form of matter into another form of matter. That, I think, is the great justification for learning anything at all about chemistry. A chemist can make matter that has never been made anywhere else in the universe, and this is an extraordinary skill.

It is interesting to try to identify the differences between physical chemistry and inorganic chemistry. An inorganic chemist proceeds in a way that is quite distinct from how a physical chemist proceeds. An inorganic chemist seeks to identify the parameters that can account for a trend. So an inorganic chemist would look for trends that are related to electronegativity, ionization energy, ionic radius, and other parameters. An inorganic chemist works at the level of rationalization by parameter, whereas a physical chemist looks underneath the parameters for explanations in terms of more fundamental ideas.

I will try to identify the great ideas that provide the intellectual coherence of the subject. The ideas which are the bones that provide the skeleton of the subject, that stop it from falling over into a heap of flesh and that give it shape. I will try to show that chemistry consists of a few very simple ideas that develop enormously and that account for everything that one needs to know about chemistry. I will identify the two ideas of chemistry that, if I were to go to a desert island, I would like to take with me. Imagine you were invited to take just one tiny bag, big enough to hold only two ideas, from which, in principle, you could develop the whole of chemistry. Which two ideas would you take with you to this desert island?

I'm going to suggest what these two ideas should be and for what reasons. In order to be able to do this, I will present chemistry as a kind of network of ideas and we shall crawl along this network and meet ideas of different importance as we go. Some of these ideas are so great that they are almost trivial. But it is worth pointing out just the trivial ideas as well. I think that there are two, maybe three great but trivial ideas.

The Pauli principle

The existence of elements is perhaps the single great idea in this network that gives chemistry its coherence as an intellectual subject. The idea that there are elements is the foundation of structure and of our ability to manipulate matter. The specific role of elements is that they turn chemistry into a single, coherent subject by their organization as a periodic table. There is not just a collection of single elements, but each element, with its own personality, is a member of a family of elements. There is a great idea embedded in this that should never be lost sight of, which is that the world can be reduced to not more than a hundred elements. The fact that everything we touch can be developed in terms of these hundred entities is an enormously exciting thing. To be able to go out into the world and to say that whatever you encounter is composed of these entities, is something that is very familiar to us but should never be forgotten.

The existence of elements, of course, is just what we percieve. A little deeper underneath is something that we imagine: the existence of atoms. An atom is the quantum of matter that chemists deal with. They think of atoms as they discuss matter. One very important consequence of the existence of atoms is the fact that one can develop an arithmetic with elements, that brings in the possibility of making quantitative predictions in terms of stoichiometry.

The second great idea in this network is the existence of internal structure of atoms. Once one realizes that atoms have an internal structure one can begin to rationalize and predict. And I think the central idea in this connection, an idea that I would take to a desert island with me, one of the underlying principles that relate to the structure of atoms and therefore to the whole structure of chemistry, is the Pauli principle.

Imagine what the world would be like without the Pauli principle. If more than two electrons could fit into a single orbital, which is after all the central content of the Pauli principle as far as chemists are concerned, then there would be no specific matter. All matter would blend into a single cosmic block. So the Pauli principle saves the world from being infinitely small. It is responsible for the existence of individual species of matter and for the fact that matter has bulk and that it can form particular numbers of bonds, which is after all one of the central ideas of elementary chemistry.

An extremely important consequence of the Pauli principle is the building-up (Aufbau) principle. The building-up principle is one of the ways in which chemists interpret the Pauli principle. It is not a great principle in itself, it is rather the slave of the Pauli principle. But at the same time it is a great rationalization for chemistry, because it enables us to account for the periodic table and to talk in terms of atomic radii, ionization energies, electron affinities, electronegativities, polarizabilities and so on. It is the link between physics represented by the Pauli principle and chemistry represented by the periodic table.

Electron pair formation is another consequence of the Pauli principle. It is another great rationalizing principle of elementary chemistry. If we were to look for a God of electron pairing, we might think of G. N. Lewis and the Lewis theory of valency. But I believe that Lewis is a false God that we should not put too much emphasis on. In my view molecular orbital theory is a much more powerful God than Lewis, because Lewis is misleading in many respects. I would not want him to come to a desert island with me, because although Lewis is very good at elementary chemistry, he leads us to false surprises. For example, Lewis says: octet formation is the alpha and omega of bonding. But then we are supposed to be surprised when we encounter exceptions to the octet rule, such as three-centre bonds in the borides, for example, and bonds that involve only one electron. All those are false surprises. If Lewis had never lived and had never concentrated on octets, then we would not be surprised by the appearance of three-centre bonds and one-electron bonds. So in my view Lewis is a wonderful but also an evil and misleading presence in chemistry.

Electron pair formation leads us on to the identification of chemical reactions in terms of three very simple ideas: proton transfer, electron transfer and radical reactions. In other words: acid-base, redox and radical reactions. These three great types of reactions come down to electron pair formation and the exchange of partners. The great beauty of these three reaction types is that they illustrate that very simple processes can have consequences of profound importance. Photosynthesis for example is just the motion of an electron by a sunbeam. They are also very important in the sense that they illustrate another of chemistry's skills and another of its methods, i.e. they show how concepts are enlarged to capture ever larger domains of facts.

I think one should never teach chemistry historically. It is an evil waste of young minds to teach science by teaching history, except in perhaps two instances. One is acids and bases and another is quantum mechanics. The reason why it is good to teach acids and bases in terms of history is because one can show how a single concept gradually enlarges and captures an ever larger domain of the subject. Originally - let's pretend it was originally - there was Arrhenius and his simple ideas about what an acid was and what a base was. Then came Brønsted and Lowry, who enlarged the concepts of acid and base and captured a much greater area of chemistry. And then there was of course Lewis - yes, I think Lewis did well here - and he enlarged the concepts of acid and base to embrace not only Arrhenius but also Brønsted and Lowry.

There is, however, a little known chemist who has probably done even more to enlarge the concepts of acid and base and his name is Usanovich. In modern terms he made an extremely simple identification that accounts for the whole of chemistry: that an acid is a hole and a base is an electron. And it is possible to show that all chemical reactions are in fact the interaction of an electron with a hole. An electron occupying a vacancy - that is the most general description of a chemical reaction. It accounts, for example, for radical combination. If we take two radicals, each of them has an unwritten hole and an electron, and the electron on one radical falls into the hole of the other radical, and vice versa. It also accounts for Lewis theory, where a base has two electrons, and an acid has two holes, and each electron falls into a hole. This Lewis approach includes Brønsted acids and base reactions. And if there is a reducing agent and an oxidizing agent, then essentially the redox reaction is also an electron falling into a hole. So suddenly the whole of chemistry boils down to the transfer of electrons into holes, making every chemical reaction look like an acid base reaction.

Now maybe the Usanovich approach is just too general and it is better to concentrate on the Brønsted definitions. But at least we should be aware that the whole of chemistry can be reduced to a very simple single act.

The Boltzmann distribution

Let us go on to the third great idea, which is the existence of energy. No one knows what energy is. It is much easier to explain what entropy is than what energy is, but everyone knows that its existence is very important. And just as the existence of elements and the conservation of atoms gave us a sudden quantitative control over chemistry, the existence of energy, and specifically the conservation of energy expressed by the first law of thermodynamics, is also an enormous principle of chemistry. It is almost too grand a principle to have any consequences and therefore I am not going to say very much about it. But it does underlie everything that we do.

More important, I think, for direct practical applications, is the fact that energy is quantized. It is because energy is quantized, because systems are quantized, that there is any chemistry at all. If energy were not quantized, matter would be extremely responsive to its environment. There would be no rigidity, no personality if you like, in matter. Everything would respond to the slightest perturbation, whereas chemistry depends upon atoms retaining their personality, not responding to every little perturbation that comes along. Atoms need to be reasonably stiff systems, unresponsive to their environment.

Arising from this is the degradation of energy and in particular the second law of thermodynamics. That takes us into the kingdom of the great liberator of the human spirit. The second law of thermodynamics is not normally taught in that way, but in my view the second law liberates the human spirit from the grip of the past and I think it is the most important single principle in chemistry. It is the motive power of chemical change and it is an amazing feature of the world that all change stems from collapse into chaos.

Now it happens that chemists do not like things that fall upwards spontaneously. They think that everything should fall downwards, so they invented something called the free energy which effectively differs only in sign from the entropy. In terms of free energy everything falls downwards spontaneously. But free energy is not a very important concept in chemistry and it could be disregarded. However, an important consequence of entropy, the central concept in chemical thermodynamics which makes calculation feasible, is the chemical potential. It is a wonderful concept and it is beautifully named, because once you understand that the chemical potential conveys the potential for chemical change, then you suddenly have a calculational device of enormous power under your control and you can develop the whole of equilibrium thermodynamics. The central idea is that everything to do with chemical potential ultimately stems from the collapse of the world into chaos. There is no time now to develop that idea but I did that elsewhere[1].

Entropy is not in itself a terribly important aspect of the second law. There is a more fine-grained approach to entropy that is more interesting: the

Boltzmann distribution, which is a much more central component of chemistry because it gives a much more fine-grained account of the distribution of matter over the available energy states. Entropy is just a global measure of disorder, whereas the Boltzmann distribution really looks at the details of that distribution and therefore is a much richer concept. The content of the Boltzmann distribution can be summarized simply by drawing a diagram (Fig. 1) which conveys its

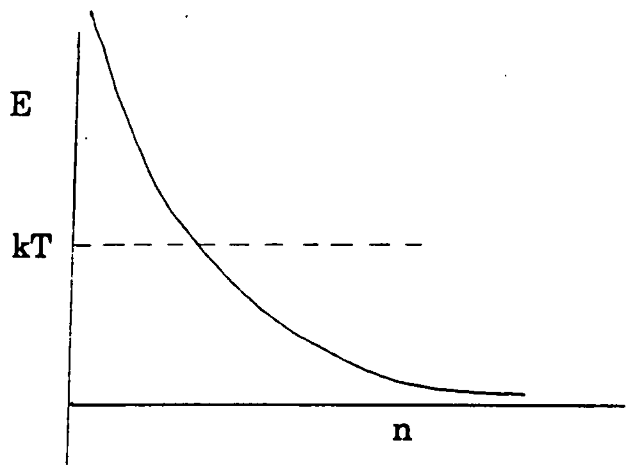

Fig. 1.

essence. It summarizes the whole of chemistry in a particularly refined way. Everything that is below kT is to do with stability and structure, whereas everything that is above kT is to do with change. And so we have the two wings of chemistry, the structural aspect of it, the stability of it and the ability of that stability to be lost and to admit change. The amazing thing about the Boltzmann distribution is that it is really rooted in chaos, that it is a purely statistical result, obtained simply by scattering molecules over available states. It is amazing to find a consequence of randomness at the centre of orderly change and of structure.

Chemistry is the outcome of the restrained collapse of matter into ultimate chaos in the sense that chaos is both the carrot and the cart of progress. Chaos drives the world forward through its increase in entropy but it also slows down the progress of change by insuring that very few molecules populate energy levels high in energy. So in my view randomness and the Boltzmann distribution jointly show that chemistry is a very slow collapse, a restrained collapse into chaos.

Conclusion

Chemistry is all about restraint. If reactions occurred rapidly the world would be over, but because reactions occur slowly and sometimes not at all, because the universe is very restrained in the way that it spreads into chaos, chemistry survives. Therefore, looking for the two major principles of chemistry, I would look for the principles that slow down collapse into chaos.

There are two of these principles. One is the Boltzmann distribution and the randomness of the distribution of molecules over the available energy states. This is a great restraint on the rate of collapse. And the other one, the other great, golden principle, I would say is the Pauli principle , because it also controls the rate at which collapse occurs. So the two principles that I would take with me to the desert island, would be the Pauli principle and the Boltzmann distribution, because these control the rate of collapse.

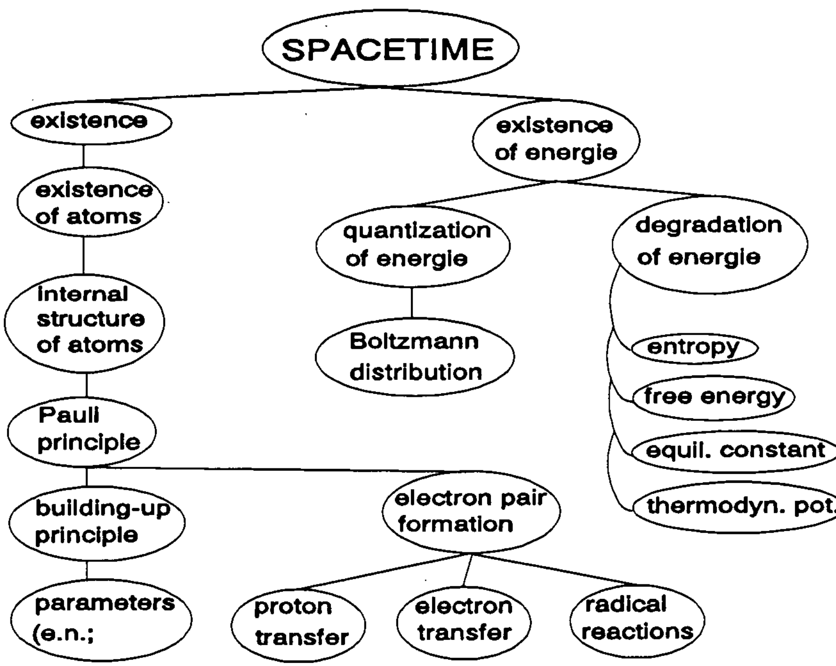

Fig. 2

Figure 2 summarizes what I said. It all comes down to spacetime in the end, which is something that we as chemists are not supposed to understand or to inquire into. But spacetime gives rise to matter and to energy which are the two wings of the development of our subject. I mentioned the existence of elements and the fact that there is an internal structure to atoms and the Pauli principle that governs the way that atoms can stick together. The building-up principle and electron pair formation are two great chemical applications of the Pauli principle. There are the particular versions of electron pair formation which we call the three different types of chemical reaction. Down the other wing of this chart is the existence of energy, its quantization and especially its degradation and the funny ways in which we sometimes talk about the simple concept of degradation in terms of entropy, free energy, equilibrium constant and so on.

That, I think, is the whole of chemistry on a single diagram. I'm sure there are omissions, although some of the concepts are so general that I can claim that whatever one can think of is actually embedded in the diagram. But looking for a structure for chemistry and for the organization of our subject in terms of very simple ideas and central concepts, I would choose these ideas and this network to find my way among them.