

HI O SILVER

Roald Hoffmann

The life-giving ideas of chemistry are not reducible to physics. Or, if one tries to reduce them, they wilt at the edges, lose not only much of their meaning, but interest too. And, most importantly, they lose their chemical utility—their ability to relate seemingly disparate compounds to each other, their fecundity in inspiring new experiments. I'm thinking of concepts such as the chemical bond, a functional group and the logic of substitution, aromaticity, steric effects, acidity and basicity, electronegativity and oxidation-reduction. As well as some theoretical ideas I've been involved in personally—through-bond coupling, orbital symmetry control, the isolobal analogy.

Consider the notion of oxidation state. If you had to choose two words to epitomize the same-and-not-the-same nature of chemistry, would you not pick ferrous and ferric? The concept evolved at the end of the 19th century (not without confusion with "valency"), when the reality of ions in solution was established. As did a multiplicity of notations—ferrous iron is iron in an oxidation state of +2 (or is it 2+?) or Fe(II). Schemes for assigning oxidation states (sometimes called oxidation numbers) adorn every introductory chemistry text. They begin with the indisputable: In compounds, the oxidation states of the most electronegative elements (those that hold on most tightly to their valence electrons), oxygen and fluorine for example, are -2 and -1, respectively. After that the rules grow ornate, desperately struggling to balance wide applicability with simplicity.

The oxidation-state scheme had tremendous classificatory power (for inorganic compounds, not organic ones) from the beginning. Think of the sky blue color of chromium(II) versus the violet or green of chromium(III) salts, the four distinctly colored oxidation states of vanadium. Oliver Sacks writes beautifully of the attraction of these colors for a boy starting out in chemistry. And not only boys.

But there was more to oxidation states than just describing color. Or balancing equations. Chemistry is transformation. The utility of oxidation states dovetailed with the logic of oxidizing and reducing agents—molecules and ions that with ease removed or added electrons to other molecules. Between electron transfer and proton transfer you have much of reaction chemistry.

I want to tell you how this logic leads to quite incredible compounds, but first let's look for trouble. Not for molecules—only for the human beings thinking about them.

Those Charges are Real, Aren't They?

Iron is not only ferrous or ferric, but also comes in oxidation states ranging from +6 (in BaFeO_4) to -2 (in $\text{Fe}(\text{CO})_4^{2-}$, a good organometallic reagent).

Is there really a charge of +6 on the iron in the first compound and a -2 charge in the carbonylate? Of course not, as Linus Pauling told us in one of his many correct (among some incorrect) intuitions. Such large charge separation in a molecule is unnatural. Those iron ions aren't bare—the metal center is surrounded by more or less tightly bound "ligands" of other simple ions (Cl^- for instance) or molecular groupings (CN^- , H_2O , PH_3 , CO). The surrounding ligands act as sources or sinks of electrons, partly neutralizing the formal charge of the central metal atom. At the end, the net charge on a metal ion, regardless of its oxidation state, rarely lies outside the limits of +1 to -1.

Actually, my question should have been countered critically by another: How do you define the charge on an atom? A problem indeed. A Socratic dialogue on the concept would bring us to the unreality of dividing up electrons so they are all assigned to atoms and not partly to bonds. A kind of tortured pushing of quantum mechanical, delocalized reality into a classical, localized, electrostatic frame. In the course of that discussion it would become clear that the idea of a charge on an atom is a theoretical one, that it necessitates definition of regions of space and algorithms for divvying up electron density. And that discussion would devolve, no doubt acrimo-

Roald Hoffmann is Frank H. T. Rhodes Professor of Humane Letters at Cornell University. Address: Baker Laboratory, Cornell University, Ithaca, NY 14853-1301.



Figure 1. Distinctive colors reveal the oxidation states of vanadium (V) in certain aqueous solutions: V^{+2} (violet), V^{+3} (green), V^{+4} (blue) and V^{+5} (yellow). But there is more to oxidation chemistry than meets the eye.

niously, into a fight over the merits of uniquely defined but arbitrary protocols for assigning that density. People in the trade will recognize that I'm talking about "Mulliken population analysis" or "natural bond analysis" or Richard Bader's beautifully worked out scheme for dividing up space in a molecule.

What about experiment? Is there an observable that might gauge a charge on an atom? I think photoelectron spectroscopies (ESCA or Auger) come the closest. Here one measures the energy necessary to promote an inner-core electron to a higher level or to ionize it. Atoms in different oxidation states do tend to group themselves at certain energies. But the theoretical framework that relates these spectra to charges depends on the same assumptions that bedevil the definition of a charge on an atom.

An oxidation state bears little relation to the actual charge on the atom (except in the interior of the sun, where ligands are gone, there is plenty of energy, and you can have iron in oxidation states up to +26). This doesn't stop the occasional theoretician today from making a heap of a story when the copper in a formal Cu(III) complex comes out of a calculation bearing a charge of, say, +0.51.

Nor does it stop oxidation states from being just plain useful. Many chemical reactions involve electron transfer, with an attendant complex of changes in chemical, physical and biological properties. Oxidation state, a formalism and not a representation of the actual electron density at a metal center, is a wonderful way to "book-keep" electrons in the course of a reaction. Even

if that electron, whether added or removed, spends a good part of its time on the ligands.

But enough theory, or, as some of my colleagues would sigh, anthropomorphic platitudes. Let's look at some beautiful chemistry of extreme oxidation states.

Incredible, But True

Recently, a young Polish postdoctoral associate, Wojciech Grochala, led me to look with him at the chemical and theoretical design of novel high-temperature superconductors. We focused on silver (Ag) fluorides (F) with silver in oxidation states II and III. The reasoning that led us there is described in our forthcoming paper. For now let me tell you about some chemistry that I learned in the process. I can only characterize this chemistry as incredible but true. (Some will say that I should have known about it, since it was hardly hidden, but the fact is I didn't.)

Here is what Ag(II), unique to fluorides, can do. In anhydrous HF solutions it oxidizes Xe to Xe(II), generates $C_6F_6^+$ salts from perfluorobenzene, takes perfluoropropylene to perfluoropropane, and liberates IrF_6 from its stable anion. These reactions may seem abstruse to a non-chemist, but believe me, it's not easy to find a reagent that would accomplish them.

Ag(III) is an even stronger oxidizing agent. It oxidizes MF_6^- (where M=Pt or Ru) to MF_6 . Here is what Neil Bartlett at the University of California at Berkeley writes of one reaction: "Samples of AgF_3 reacted incandescently with metal surfaces when frictional heat from scratching or grinding of the AgF_3 occurred."

Ag(II), Ag(III) and F are all about equally hungry for electrons. Throw them one, and it's not at all a sure thing that the electron will wind up on the fluorine to produce fluoride (F^-). It may go to the silver instead, in which case you may get some F_2 from the recombination of F atoms.

Not that everyone can (or wants to) do chemistry in anhydrous HF, with F_2 as a reagent or being produced as well. In a recent microreview, Thomas O'Donnell says (with some understatement), "... this solvent may seem to be an unlikely choice for a model solvent system, given its reactivity towards the usual materials of construction of scientific equipment." (And its reactivity with the "materials of construction" of human beings working with that equipment!) But, O'Donnell goes on to say, "... with the availability of spectroscopic and electrochemical equipment constructed from fluorocarbons such as Teflon and Kel-F, synthetic sapphire and platinum, manipulation of and physicochemical investigation of HF solutions in closed systems is now reasonably straightforward."

For this we must thank the pioneers in the field—generations of fluorine chemists, but especially Bartlett and Boris Žemva of the University of Ljubljana. Bartlett reports the oxidation of AgF_2 to AgF_4^- (as $KAgF_4$) using photochemical

irradiation of F_2 in anhydrous HF (made less acidic by adding KF to the HF). And Žemva used Kr^{2+} (in KrF_2) to react with AgF_2 in anhydrous HF in the presence of XeF_6 to make $XeF_5^+AgF_4^-$. What a startling list of reagents!

To appreciate the difficulty and the inspiration of this chemistry, one must look at the original papers, or at the informal letters of the few who have tried it. You can find some of Neil Bartlett's commentary in the article that Wojciech and I wrote, and in an interview with him.

Charge It, Please

Chemists are always changing things. How to tune the propensity of a given oxidation state to oxidize or reduce? One way to do it is by changing the charge on the molecule that contains the oxidizing or reducing center. The syntheses of the silver fluorides cited above contain some splendid examples of this strategy. Let me use Bartlett's words again, just explaining that "electronegativity" gauges in some rough way the tendency of an atom to hold on to electrons. (High electronegativity means the electron is strongly held, low electronegativity that it is weakly held.)

Bartlett writes:

It's easy to make a high oxidation state in an anion because an anion is electron-rich. The electronegativity is lower for a given oxidation state in an anion than it is in a neutral molecule. That in turn, is lower than it is in a cation. If I take silver and I expose it to fluorine in the presence of fluoride ion, in HF, and expose it to light to break up F_2 to atoms, I convert the silver to silver(III), AgF_4^- . This is easy because the $Ag(III)$ is in an anion. I can then pass in boron trifluoride and precipitate silver trifluoride, which is now a much more potent oxidizer than AgF_4^- because the electronegativity in the neutral AgF_3 is much higher than it is in the anion. If I can now take away a fluoride ion, and make a cation, I drive the electronegativity even further up. With such a cation, for example, AgF_2^+ , I can steal the electron from PtF_6^- and make $PtF_6...$ This is an oxidation that even $Kr(II)$ is unable to bring about.

Simple, but powerful reasoning. And it works.

A World Record?

Finally, a recent oxidation-state curiosity: What is the highest oxidation state one could get in a neutral molecule? Pekka Pyykkö and coworkers suggest cautiously, but I think believably, that octahedral UO_6 , that is $U(XII)$, may exist. There is evidence from other molecules that uranium $6p$ orbitals can get involved in bonding, which is what they would have to do in UO_6 .

What wonderful chemistry has come—and still promises to come—from the imperfect logic of oxidation states!

Acknowledgments

I am grateful to Wojciech Grochala, Robert Fay and Debra Rolison for corrections and comments. Thanks to Stan Marcus for suggesting the title of this column.

Bibliography

- Bartlett, N. 2000. Interview with Istvan Hargittai. *The Chemical Intelligencer*. April 2000, pp. 7–15.
- Grochala, W., and R. Hoffmann. 2001. Real and hypothetical intermediate-valence fluoride Ag^{2+}/Ag^{3+} and Ag^{2+}/Ag^{1+} systems as potential superconductors. *Angewandte Chemie*, in press.
- Jørgensen, C. K. 1969. *Oxidation States and Oxidation Numbers*. Berlin: Springer.
- O'Donnell, T. 2001. On the commonality of speciation of inorganic solutes in superacids, strong bases, molten salts, and water. *European Journal of Inorganic Chemistry* 2001:21–34.
- Pyykkö, P., N. Runeberg, M. Straka and K. G. Dyll. 2000. Could uranium(XII)hexoxide, $UO_6(O_h)$ exist? *Chemical Physics Letters* 328:415–419.
- Sacks, O. 2001. *Uncle Tungsten: Memories of a Chemical Boyhood* (to be published, New York: Knopf). An excerpt appeared as "Brilliant Light." *The New Yorker* Dec. 20, 1999, pp. 56–73.
- Žemva, B., K. Lutar, A. Jesih, W. J. Casteel, Jr., A. P. Wilkinson, D. E. Cox, R. B. Von Dreele, H. Borrmann and N. Bartlett. 1991. Silver trifluoride: Preparation, crystal structure, some properties, and comparison with AuF_3 . *Journal of the American Chemical Society* 113:4192–4198.

