

# Marginalia

## Unstable

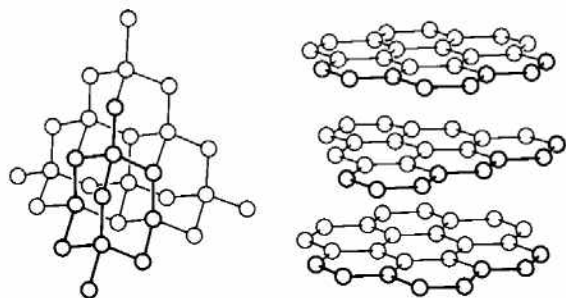
Roald Hoffmann

Words are our enemies, words are our friends. In science, we think that words are just an expedient for describing some inner truth, one that is perhaps ideally represented by a mathematical equation. Oh, the words matter, but they are not essential for science. We might admit there is a real question as to whether a poem is translatable, but we argue that it is irrelevant whether the directions for the synthesis of a molecule are in Japanese or Arabic or English—if the synthesis is described in sufficient detail, the same molecule will come out of the pot in any laboratory in the world.

Yet words are all we have, and all our precious ideas must be described in these history- and value-laden signifiers. Furthermore, most productive discussion in science takes place on the colloquial level, in simple conversation. Even if we know that a concept signaled by a word has a carefully defined and circumscribed meaning, we may still use that word colloquially. In fact, the more important the argument is to us, the more we want to be convincing, the more likely we are to use simple words. Those words, even more than technical terms, are unconsciously shaped by our experience—which may not be the experience of others.

I was led to reflect on this by the reaction of a friend of mine, a physicist, to my use of the word "stable." I had said that an as yet unmade form of carbon was unstable with respect to diamond or graphite by some large amount of energy. Still, I thought it could be made. My friend said, "Why bother thinking about it at all, if it's unstable?" I said, "Why not?" and there we were off arguing. Perhaps we should have pondered why the simple English word "stable" has different meanings for a physicist and a chemist.

First, a little background. Diamond (*left*) and graphite (*right*) are the two well-known modifications, or

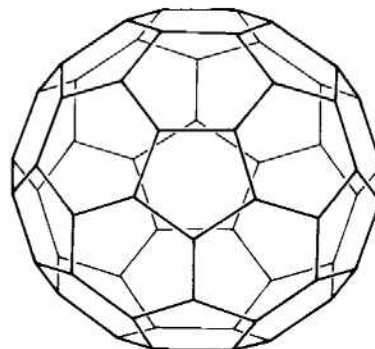


allotropes, of carbon. The carbon atoms are linked up in very different ways: in diamond each carbon atom is tetrahedrally surrounded by four neighbors, whereas in graphite a layer structure is apparent. Each layer is composed of "trigonal" carbons, three bonds going off each carbon at 120° angles. The graphite layers are held weakly, and not by real chemical bonds. They slip easily by each other, which is why graphite serves as a

lubricant. Isn't it nice that black graphite is more stable (thermodynamically, more on this in a moment) than pellucid, hard diamond? Not by much, but so it is for carbon on the surface of the

earth. Under high pressure, however, the stability sequence, which is determined by a combination of energy and entropy, changes; the denser diamond becomes more stable. This is what happens deep within the earth; it is also the basis of a commercial process for making industrial-grade diamonds.

There are other forms of carbon (1). The random and systematic incendiary activities of men and women have led to a multitude of pyrogenic materials, and most seem to be some form of graphite. A couple of rare, but well-established, allotropes of carbon are related to the diamond and graphite structures, and the existence of some others is disputed (1). Carbon also turns up in short chains in the tails of comets and in flames, and recently hefty clusters of between two and 100 carbon atoms have been produced in the gas phase. A most abundant cluster is one with 60 atoms, first detected by Richard Smalley and his co-workers at Rice University. They suggested the structure of a soccer ball for this remarkable molecule, and named it "buckminsterfullerene" (2).



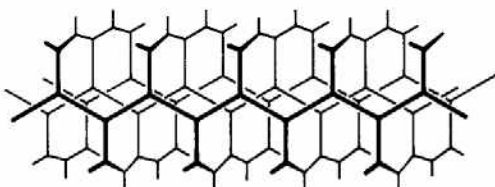
One day, I was trying to think up some alternatives to diamond and graphite. Why? For one thing, it was fun; for another, people have been squeezing elements which are not metals, trying to make them metallic. When you apply a megabar or so of pressure to almost anything, the atoms are forced so close together that their electron clouds overlap, and the material becomes a metal. Some of my friends at Cornell do this routinely—using diamond anvils! Xenon, iodine, and oxygen have been made metallic in this way (3), and there's an argument whether hydrogen has been so transformed.

The interesting thing about both diamond and graphite is that they are, so to speak, full of nothing. They're not dense at all; a close-packed structure such as that of a typical metal would be much denser. Of course, there is a good reason that the density of the known carbon allotropes is so low: carbon atoms form bonds, and there is a lot of energy to be gained by forming those bonds only directionally, trigonally, or tetrahedrally. Carbon, with its four valence electrons, has better things to do than to try to shuffle its bonding among its 12 or 14

different nearest neighbors, as it might be forced to do in a close-packed structure.

Could there be carbon networks filling space more densely than diamond or graphite, yet forming bonds along tetrahedral or trigonal directions? If such a structure could in principle exist, applying pressure to one of the known allotropes might be a way to produce it. To sum up a long story, many hypothetical alternative space-filling structures have been designed (4). But we haven't yet found one denser than diamond.

Peter Bird and I thought up an allotrope that is intermediate in density between diamond and graphite and is quite special. It fills space with perfect trigonal carbon atoms. In the jargon of our trade, these form polyacetylene chains, needles of conjugation, running in two dimensions, and no conjugation at all in the third.



The most remarkable thing about this structure, something which emerged from the calculations of Tim Hughbanks, is that it should be metallic—as it is, with no pressure applied to it (5).

Here then is a prediction of a metallic allotrope of carbon. If only one knew how to make it!

Proceeding from structural reveries to matters of stability, the relatively unreliable calculations at our disposal indicate our hypothetical substance to be *unstable* relative to graphite by a whopping 0.7 electron volt per carbon atom, or 17 kilocalories per mole of carbons. This is what made my physicist friend say, "Why bother thinking about this substance?" But this degree of instability didn't bother me at all.

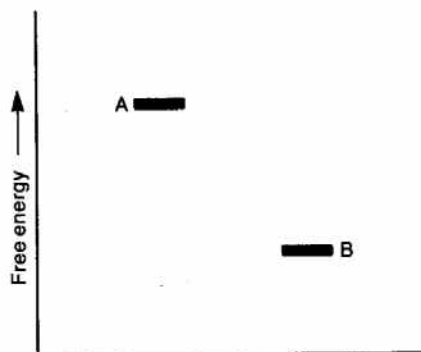
Why the different reactions? Because the common English words "stable" and "unstable" had different meanings for the two of us!

To get at the source of our misunderstanding, let me go back to a scientific definition on which both my friend and I could agree. Real stability has to do both with thermodynamics, the science of energy and entropy relationships, and with kinetics, the rates or speeds of imagined processes by which a system might be stabilized or destabilized. In chemistry we distinguish between thermodynamic and kinetic stability. Suppose we have two molecules, A and B, which have the potential of changing one into the other:

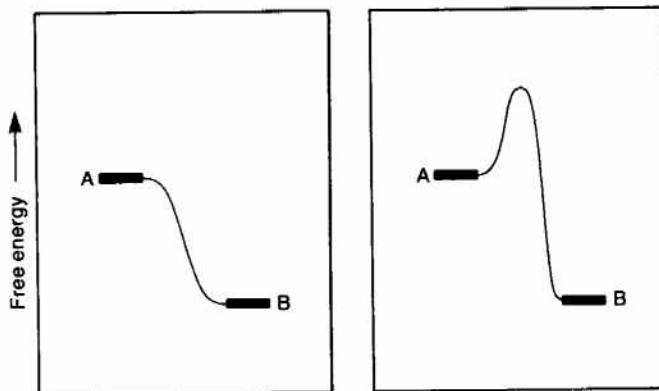


Their relative thermodynamic stability is gauged by a marvelous function called the Gibbs free energy, which contains in it terms for enthalpy (something very much like energy, but with specific conditions placed on it) and entropy. The natural, spontaneous direction in which matter moves is toward lower enthalpy and higher entropy, which means, in turn, greater disorder. A molecule which has the lower free energy is more stable, and a molecule with higher free energy will transform spontaneously into one with lower free energy. To be

specific: should it be that B has the lower free energy, then the spontaneous reaction will be  $A \rightarrow B$ . We can represent this in a graph in which the vertical axis is the free energy.



But life is not so simple. Thermodynamics says what *must* happen, but not how fast it *will* happen. To go from molecule A (say, my hypothetical metallic carbon) to molecule B (graphite) is no idle molecular promenade. Bonds have to break, many of them, and then to reform. Before poor A knows all the happiness waiting for it in those lovely rings of B, it's got to suffer a lot of electronic indignity in the form of broken bonds. It resists. In general, molecules have barriers to their transformation. The situation is typically not as shown at left, but as at right.



There's a hill in the way. It's like a book that wants to fall under the force of gravity, but has a shelf under it. We might say that A is metastable, or that A is a local minimum on some energy surface. Suddenly it is no longer a question of falling, but of climbing hills!

Will the reaction proceed after all? Yes, if you wait long enough. It depends on the size of the hill and on the temperature. Molecules don't sit still. In a gas or in solution they are bouncing around at great speed, buffeted randomly by collisions with the  $10^{20}$  other molecules in a typical flask. It's a crowded dance floor there. Some of the molecules acquire enough energy through collisions (this is where the temperature comes in, for the higher the temperature, the faster the molecules move) to pass over the hill. Others don't. If the hill is higher than about 30 kilocalories per mole, then at room temperature A will remain A. Unless you wait a thousand years, for it is only then you might begin to see a little B.

A chemist would say A is thermodynamically unstable and kinetically stable, whereas a physicist might call A metastable. These concepts are quite familiar to chemists and to physicists. So where is the problem? The difficulty is that our everyday discourse is perforce colloquial. We say "stable" and not "thermodynamically and/or kinetically stable." Some may label the colloquial characterization sloppy and say it should be more precise. I say that we wouldn't be human (and therefore have the potential of doing great science) unless we were often imprecise in just this way.

But now comes the crux of the matter. Into that word "stable" goes the history of what we are or have done. When a chemist says "stable," I think he or she means 90% kinetic and 10% thermodynamic. But a physicist, I would hazard a guess, means (not in the sense of making a rational choice, but unconsciously) just about the converse: 90% thermodynamic, 10% kinetic.

From the beginning of one's life in chemistry the importance of kinetic stability and the relative unimportance of thermodynamic stability are highlighted. Every organic molecule in the presence of air (a typical situation in the laboratory and real life) is thermodynamically unstable with respect to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Think of methane ( $\text{CH}_4$ , natural gas), the essence of stability, having survived unchanged under the earth for thousands of years. Every time you light a gas stove, you demonstrate methane's thermodynamic instability. But it takes the complicated autocatalytic reaction set off by a match to take those  $\text{CH}_4$  and  $\text{O}_2$  molecules and get them over the hill, giving off light and heat along the way. Otherwise, methane is stable as a rock. Speaking of rocks, modern air pollution shows that they are not particularly stable when strong acids come around.

One amusing way to define synthetic chemistry, the making of molecules that is at the intellectual and economic center of chemistry, is that it is the local defeat of entropy, the construction of complex thermodynamically unstable molecules. In chemistry, a molecule that is strained, or otherwise thermodynamically disfavored by 1 electron volt per molecule relative to another molecule, is not thought of as an occasion to throw up one's hands. It's a challenge to be made, ingeniously.

Thermodynamic stability is set more firmly in the physicist's mind, for a number of reasons. First, a typical course in elementary physics concentrates on mechanics, dynamics, and electromagnetism in the absence of barriers or obstacles. Motion in the presence of barriers is too difficult to solve explicitly, so such problems are not mentioned. No one ever puts a shelf of variable permeability under that falling weight in Physics 100. Barrier penetration is probably first encountered in quantum mechanics courses.

Second, in thinking about the transformation of matter, physicists most often begin with motions governed by central forces, masses, or charges moving around without hooks or directional valences. Entering the study of matter from the starting point of gases or close-packed metals, one encounters few activated processes, only collisions, or balls sliding frictionlessly past balls, to reach the thermodynamically most stable point. Friction, barriers, and the evolution in time of real systems are just as important in the end for physicists as

they are for chemists. But the subtle weighting of concepts which shapes the colloquial language of science is fixed in scientific infancy. The early experiences matter; this is why I think the words "stable" and "unstable" mean different things to chemists and physicists (6).

Meanwhile, our metallic carbon allotrope is still waiting to be synthesized. I think it will be pretty stable—sorry, enduring—when it is made. If it is made.

## References

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5. R. Hoffmann, T. Hughbanks, M. Kertesz, and P. H. Bird. 1983. *J. Am. Chem. Soc.* 105:4831.
6. For some fascinating observations on the language of physics see C. F. von Weizsäcker, 1974, *Die Einheit der Natur*, p. 61. Munich: DTV.



"This is a lovely old song that tells of a young woman who leaves her cottage, and goes off to work. She arrives at her destination, and places some solid  $\text{NH}_4\text{HS}$  in a flask containing 0.50 atm of ammonia, and attempts to determine the pressures of ammonia and hydrogen sulfide when equilibrium is reached."