

## IV

# The Chemistry of Bug-Eyed Silicon Monsters

### 1. The Rise and Fall of an Analogy

Carbon and silicon were not always regarded as isovalent analogs of one another. The great Swedish chemist, Jöns Jakob Berzelius (figure 1), who was the first to isolate silicon as a simple substance in 1823, thought that it most resembled boron (1, 2). This assignment was based on the fact that both elements formed acidic, nonvolatile oxides which could act as glass formers, and on a similarity in the appearance of the simple substances themselves, both of which had been prepared only as highly-impure, amorphous, nonmetallic powders. This analogy was further reinforced by errors in the determination of their atomic weights, which assigned the analogous formulas,  $\text{BO}_3$  and  $\text{SiO}_3$ , to their respective oxides, in sharp contrast to the formulas,  $\text{CO}$  and  $\text{CO}_2$ , assigned to the oxides of carbon. With the gradual correction of atomic weights and the equally gradual substitution of “stoichiometric type” or valence, in place of acidity and electronegativity, as the preferred basis for chemical classification, silicon was reassigned as an analog of carbon.

In 1857, the German chemist, Friedrich Wöhler (figure 2), discovered silicon tetrahydride ( $\text{SiH}_4$ ), the stoichiometric and structural analog of methane ( $\text{CH}_4$ ), and the logical starting point for speculations on an alternative organic chemistry based on silicon rather

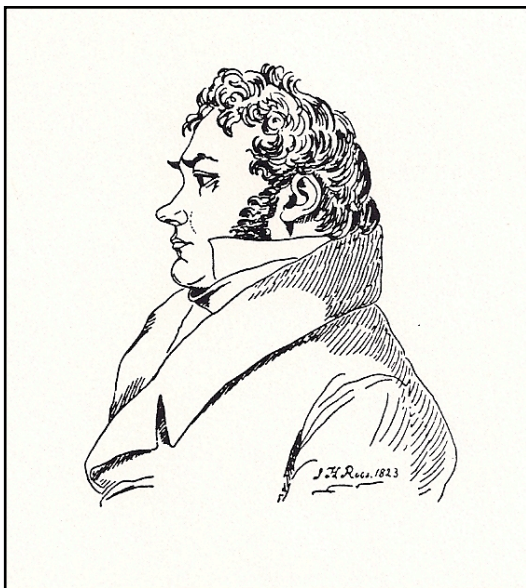


Figure 1. Jöns Jakob Berzelius (1779-1848).

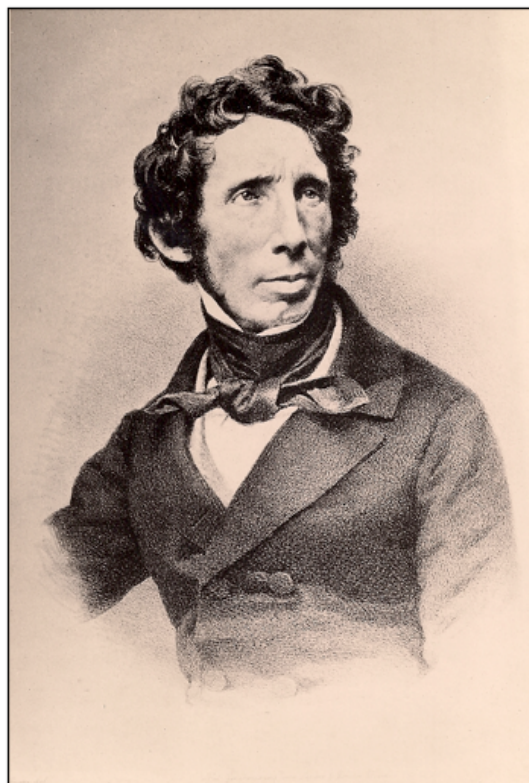


Figure 2. Friedrich Wöhler (1800-1882).

than carbon (3). Ironically, however, Wöhler did not consider this possibility until 1863 and then only as a result of a faulty interpretation of his experimental data. Having obtained, via the hydrolysis of magnesium silicide, a series of apparent compounds of silicon, hydrogen and oxygen, he found it very difficult to assign them exact formulas. Possibilities suggested by his analytical data for one of these compounds included  $\text{Si}_8\text{H}_4\text{O}_6$ ,  $\text{Si}_6\text{H}_3\text{O}_4$ ,  $\text{Si}_{12}\text{H}_6\text{O}_8$ , etc. Since the only compounds that Wöhler knew of having equally complex formulas were the organic compounds of carbon, he concluded that, regardless of which of these choices ultimately proved correct, it would correspond to (4):

*... a result of great interest in that it can be viewed as a compound constructed after the manner of an organic substance in which silicon plays the role of carbon in the organic material. Perhaps it can serve as the type for an entire series of similar bodies, and there would then exist the prospect of a special chemistry of silicon, similar to that which exists in the case of carbon.*

With the gift of hindsight, we would suspect that Wöhler's organic analogs were in fact nothing more than poorly characterized samples of silicic acid in various stages of dehydration.

Though the preparation and isolation of the pure silicon hydrides would show little further progress until the work of Alfred Stock in the 1920s, other classes of silicon compounds were soon discovered which proved to be more promising sources of inspiration for an alternative organosilicon chemistry than were Wöhler's poorly-characterized silicate sludges. Already in 1844, the French chemist, Jacques-Joseph Ebelmen, had successfully prepared a number of alkoxide derivatives of silicon having the general formula  $\text{Si}(\text{OR})_4$  (5), and in 1863 the French-American team of Charles Friedel and James Mason Crafts synthesized the first alkyl derivative – tetraethylsilane,  $\text{Si}(\text{C}_2\text{H}_5)_4$  (6). This work was continued by Friedel (figure 3), and especially by the German chemist, Albert Ladenburg (figure 4), throughout the last quarter of the 19th century, so that by 1916 the Swedish chemist, Artur Bygden, could list several hundred organosilicon compounds in his monograph *Silicium als Vertreter des Kohlenstoffs' organischer Verbindungen* (7).

In summarizing the early work on organosilicon chemistry, it is important to realize that the carbon-silicon analogy was used in two different ways by 19th- and early 20th-century chemists. The first of these usages, which we will call the “strong analogy,”

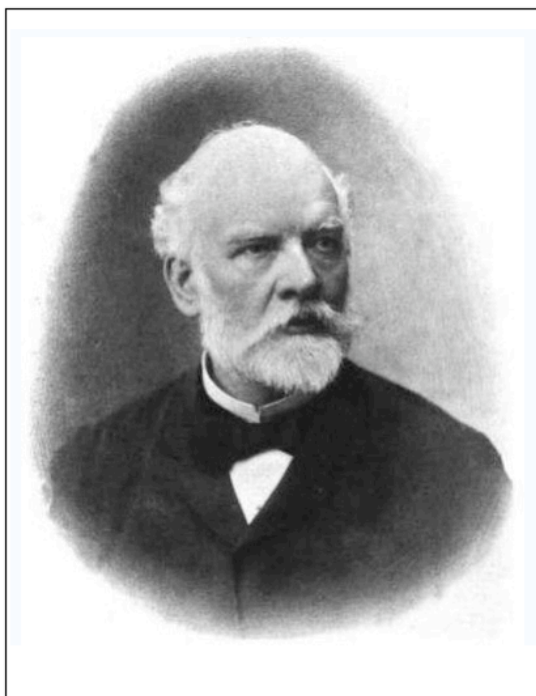


Figure 3. Charles Friedel (1832-1899).



Figure 4. Albert Ladenburg (1842-1911).

was the claim that it should be possible to build up a silicon analog of organic chemistry containing no carbon whatsoever. In other words, just as one constructs conventional organic chemistry from the hydrocarbons by preparing an almost limitless number of oxygen and nitrogen derivatives, so one should also be able to prepare large numbers of homocatenated polysilanes and their corresponding oxygen and nitrogen derivatives (or, for the more adventuresome, their isovalent sulfur and phosphorus derivatives). This is, in fact, the prospect hinted at by Wöhler, and discussion of the possibility of silicon-based life in the popular science literature and among science-fiction writers is always based, either explicitly or implicitly, on claims for the validity of this strong analogy.

The second usage, which we will call the “weak analogy,” was the more modest claim that it should be possible to modify or perturb conventional carbon-based organic compounds by substituting isolated carbon centers with silicon. Here, quite naturally, the emphasis was placed on the substitution of key carbon atoms corresponding to optically-active centers, functional groups, etc. The question of Si-Si chains arose in this context only in connection with the analogs of those functional groups corresponding to C-C multiple bonds.

Examination of Bygden's monograph shows that virtually all of the work on organosilicon chemistry

done in the 19th and early 20th centuries was based on the weaker of these two claims. The vast majority of the compounds listed by Bygden were simple substitution products of the tetralkylmonosilanes, and in almost all cases they were assigned structures based solely on the assumption that an analogous stoichiometry with a corresponding carbon compound automatically implied an analogous structure. Yet among popular writers, this work was often quoted as evidence for the validity of the stronger analogy.

The English-speaking reader can best catch the spirit of this tactic by reading a popular lecture given by the Irish chemist, James Emerson Reynolds, in 1873, summarizing the early results obtained by Friedel and Ladenburg. Reynold's provocative title, "On Alcohols from Flint and Quartz," not only reveals how literally the strong carbon-silicon analogy was taken, but also that the art of attracting an audience with a less than forthright seminar title has an ancient and honorable history (8).

In 1899 the British organic chemist, Frederick Stanley Kipping (figure 5), began an intensive study of organosilicon compounds (in the sense of the weak analogy just outlined) that would eventually span nearly four decades. Perhaps the most important contribution to come out of this work was Kipping's discovery of a new class of organosilicon oxygen derivatives known as the silicones. Like his predecessors, Kipping, in his early work, naively assumed that analogous stoichiometry automatically implied analogous structure. Consequently when he prepared a class of compounds having the general formula  $R_2SiO$ , he naturally thought that he had discovered the alkyl silane analogs of the ketones  $R_2CO$  – hence his use of the name "silicones" – a term equaled in the annals of chemical nomenclature for its misleading implications only by Lavoisier's equally naive assumption that the composition of sugars and starches implied that they were literally hydrates of carbon (9).

However, by the time Kipping delivered his 1936 Bakerian Lecture on "Organic Derivatives of Silicon," summarizing his life's work, time and experience had considerably dampened his earlier enthusiasm for the possibility of a silicon-modified organic chemistry (10):

*Even after a very short experience, it was evident that corresponding derivatives of the two elements in question showed very considerable differences in their chemical properties; it may now be said that the principal, if not the only, case in which they exhibit a really close resemblance is that of the paraffins and those particular silicohydrocarbons containing a silicon atom directly united to four alkyl radicals. But of far greater importance in any general comparison of car-*

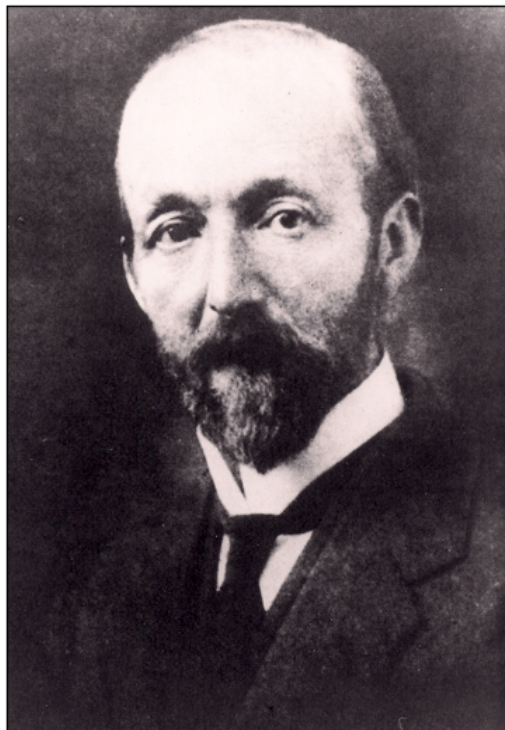
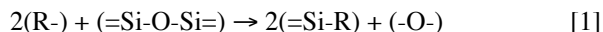


Figure 5. Frederick Stanley Kipping (1863-1949).

*bon compounds with the organic derivatives of silicon is the fact that many, if not most, of the more important types of the former are not represented among the latter. Apparently this is not merely a consequence of the insufficient experimental investigation of silicon derivatives but is due to the fundamental differences in the properties of the atoms of silicon and carbon ...*

In other words, after 40 years of research, Kipping had come to the conclusion that even the weak form of the analogy was defective, and subsequent work would soon show that his pessimism was fully justified.

As it turns out, the structures and chemistry of the silicones, silicols and other oxygen derivatives of the alkyl and arylsilanes are best viewed from the standpoint of inorganic chemistry as progressively depolymerized derivatives of silica in which one or more bridging Si-O-Si bonds per silicon center have been formally replaced by terminal or capping R- or RO-groups:



rather than from the standpoint of organic chemistry as simple substitutional analogs of the ketones, alcohols, etc. Indeed, this process parallels that observed in the purely inorganic realm when one depolymerizes silica via reaction with metal oxides, a process which leads

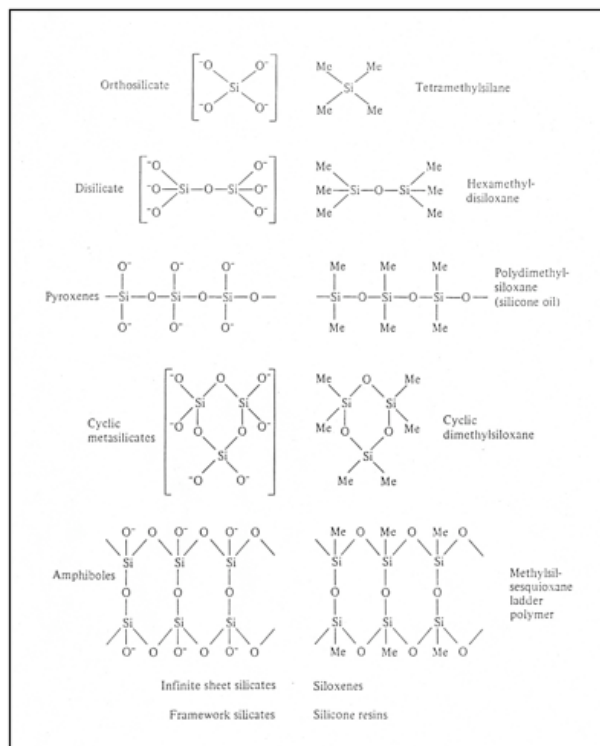
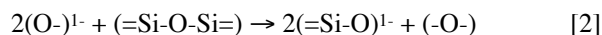


Figure 6. The analogy between the depolymerization of silica via capping with  $O^-$ , as found in the silicates, versus capping with alkyl groups, as found in the alkylsiloxanes.

to the formation of layer, chain, ring and isolated silicate anions, as well as silicate glasses of varying viscosity (figure 6). This may be “formally” viewed as the replacement of oxygen bridges by terminal  $(O^-)^-$  groups, which are isolobal with the alkyl and aryl groups used in relation 1:



Though silicon has an extremely interesting and highly diversified chemistry, that chemistry is uniquely its own and is not just a simple (please, excuse the pun) carbon copy of that of carbon.

By 1946, when Eugene Rochow’s (figure 7) classic monograph, *An Introduction to the Chemistry of the Silicones*, appeared, not only had these facts concerning the organosilicon oxygen derivatives been established, but the work of the Braggs in X-ray crystallography had shown the total absence, in the purely inorganic domain, of any similarity between the structures of carbon dioxide and the carbonates, on the one hand, and the structures of silicon dioxide and the silicates, on the other; and Alfred Stock’s (figure 8) work on the silanes in the period 1916-1923 had totally undermined the strong form of the analogy by showing that the

hydrides of silicon were highly sensitive to air and moisture and strictly limited in their propensity to undergo homocatenation – in short, that they were about as unlike the alkanes as one could imagine (11). The chemist’s naive faith in a simple silicon analog of organic chemistry in both its weak and strong forms was dead, and Rochow provided the funeral oration (12):

*In these and in the many other ways in which silicon differs markedly from carbon, the differences arise from the larger size of the silicon atom, with the correspondingly greater screening of its nuclear charge. Therefore, any attempt to force silicon into the framework of classical organic chemistry or to predict the reactions of silicon purely by analogy with those of carbon compounds is likely to fail because of this fundamental difference ... If the reader has any doubt about this point, let him attempt to predict the behavior of the hydrides of silicon from a consideration of the hydrocarbons.*

That more recent authors still agree with this evaluation is apparent from the remarks of the American chemist, Grant Urry, made nearly a quarter of a century after the publication of Rochow’s monograph (13):



Figure 7. Eugene George Rochow (1909-2002).

*It is perhaps appropriate to chide the polysilane enthusiast for milking the horse and riding the cow in attempting to adapt the successes of organic chemistry in the study of polysilanes. A valid argument can be made for the point of view that the most effective chemistry of silicon arises from the differences with the chemistry of carbon compounds rather than the similarities.*

## 2. From Silicon Chemistry to Silicon Life

Based on this brief outline of the rise and fall of the chemist's belief in the possibility of a silicon-based organic chemistry strictly analogous to that of carbon, to what extent did chemists further speculate on the possibility of a silicon-based biochemistry capable of serving as the basis of a silicon life-form? Quite surprisingly, given the widespread belief among science fiction fans that this was a common fantasy of chemists, I have found few examples of such speculations in the chemical literature and none before the turn of the 20th century. The earliest example I could locate occurs as an appendix in a monograph entitled *Researches on the Affinities of the Elements and on the Causes of the Chemical Similarity and Dissimilarity of Elements and Compounds* published in 1905 by the British chemist, Geoffrey Martin, who later in his career would, interestingly enough, become a coworker of Frederick Stanley Kipping (14).

The major premise of Martin's monograph was that the pattern of properties for the elements in the periodic table was pressure and temperature dependent and that it was possible to "equalize" the properties of two elements, especially if they were in the same group, by comparing them under widely different physical conditions. In particular, Martin postulated a "critical temperature and pressure" for each element's chemical compounds. This corresponded to an upper limit on their stabilities and represented the conditions under which they displayed a maximum in their reactivity. After first observing that carbon-based life was limited to a small temperature-pressure range, Martin wrote (14):

*I suggest that the temperature range of animal life is probably nothing more or less than the range of the critical temperature of decomposition of a series of certain very complex carbon compounds which are grouped together under the name "protoplasm," the external pressure of the atmosphere coinciding roughly with their critical pressures of decomposition.*

Given this assumption, the next step was obvious:

*We are therefore justified in asking whether there is any other element which at some other temperature could*



Figure 8. Alfred Eduard Stock (1876-1946).

*play the part now played by carbon at ordinary temperatures in living organic matter?*

as was Martin's answer to his rhetorical question:

*Silicon is such an element ... There probably exists for silicon, as well as for carbon, a transition or critical temperature range whereat a large number of unstable silicon compounds are capable of momentary existence, a higher temperature rendering their existence impossible, while a lower temperature would make the compounds stable. At this transitional temperature the complex compounds would be capable of a continual metathesis, and thus give rise to the phenomenon of life; only in this case all forms of life would have as the determining element not carbon, but silicon. Seeing that in the case of carbon this temperature occurs when many of its compounds are in a semi-fluid condition, and near their decomposing point, we should expect the corresponding temperature for silicon compounds to occur when they, too, are in a pasty or semi-fluid condition.*

Last, but not least, Martin connected his speculations with the geological history of the earth, which he assumed had been formed via the gradual cooling of an originally molten mass:

*Have we any evidence which supports the view that living matter did not start originally with carbon, hydrogen, oxygen, and nitrogen as its fundamental elements, but started with elements of far higher atomic weights, such as silicon, phosphorus, and sulphur, of which only vestiges now remain in the protoplasm? It must be remembered that our evidence could only be indirect; such life could have thrived to an enormous extent in the white hot molten siliceous matter which covered the earth's surface in by-gone ages, and yet have left no traces of its existence behind; for when such forms of life died, their bodies would but blend again into the molten rock, in the same way that a jelly-fish dies and blends into the ocean of salt water without leaving a vestige behind ...*

Similar ideas were expressed four years later by the Irish chemist, James Emerson Reynolds, whom we encountered earlier, in a popular lecture entitled “Recent Advances in Our Knowledge of Silicon and Its Relations to Organized Structures” (15):

*We can conceive of the existence of similar groupings of other analogous elements forming other protoplasm capable of existing within much greater ranges of temperature than any plants or animals now known to us have to withstand. For example, we might imagine a high temperature protoplasm in which silicon takes the place of carbon, sulfur of oxygen and phosphorus of nitrogen, either wholly or in part.*

Reynolds had made no reference to such musings in his 1873 lecture on silicon analogs of organic compounds, mentioned earlier, nor in his 1893 lecture on the same subject, which he presented to the Chemical Section of the British Association for the Advancement of Science as part of his presidential address for that year (16), and their appearance in his 1909 lecture leads to some interesting historical speculation. For though Reynolds failed to raise the issue of silicon life forms in 1893, a young British biology teacher, who summarized Reynolds’ presidential address for the *Saturday Review* in 1894, did (17):

*... at very much higher temperatures this immobility of silicon compounds might be exchanged for a vigorous activity ... [and] at temperatures above the points of decomposition of the majority of the carbon-nitrogen compounds, a silicon-aluminium series may conceivably have presented cycles of complicated syntheses, decompositions, and oxidations essentially parallel to those that underlie our own vital phenomena ... And if we are to admit the possibility that the chemical accompaniments of life were rehearsed long ago and at*



Figure 9. A young H. G. Wells (1866-1946).

*far higher temperatures by elements now inert, it is not such a very long step from this to the supposition that vital, subconscious, and conscious developments may have accompanied such a rehearsal. One is startled toward fantastic imaginings by such a suggestion: visions of silicon-aluminium organisms – why not silicon-aluminium men at once? – wandering through an atmosphere of gaseous sulphur, let us say, by the shores of a sea of liquid iron some thousand degrees or so above the temperature of a blast furnace.*

The name of the young biology teacher was Herbert George Wells, or H. G. Wells (figure 9), as he is now universally known. He had recently abandoned the teaching of biology for the more lucrative career of a free-lance writer and would publish his first major science fiction novel, *The Time Machine*, the very next year. Did Wells send Reynolds a copy of his review and did it play a role in shaping Reynolds’ explicit discussion of hypothetical silicon life forms in his 1909 lecture? Unfortunately, we can only speculate on this possibility, though it is of interest to note that Wells himself never saw fit to make his “fantastic imaginings” on this subject the theme of one of his science fiction stories.

### 3. The High-Temperature Fallacy

The early speculations of Martin, Wells, and Reynolds are typical examples of what I call the “high temperature fallacy.” This approach uses the stoichiometric analogy of one class of compounds (the hydrides) to argue that silicon can take the place of carbon in organic chemistry (the chemistry of the hydrocarbons and their derivatives) in the strong sense of the carbon-

silicon analogy, and then proceeds to substitute a second unrelated class of compounds (the silicates) in place of the original, while continuing to assume that the analogy remains unimpaired. More particularly, this fallacy, by taking silicon dioxide or silica, rather than silicon tetrahydride or monosilane, as its archetype for the behavior of silicon compounds, comes to the conclusion that, if silica can withstand higher temperatures than carbon-based materials, then the same must be true of all other silicon compounds, and that consequently silicon-based life, if its exists, can do so only at high temperatures.

Yet another example of this approach can be found in the poem, "The Silicon Man," which appeared in a popular 1915 text by Elwood Hendrick, entitled *Everyman's Chemistry*. Since this is not the most sterling example of English poetry to see the light of day, I've taken the liberty of editing out most of the less inspired verses (18):

*I saw a glowing silicon man  
Within my chamber fire,  
And heard him cry in agony  
"More fuel, or I expire!"*

*"I am," said he, "John Silicon,  
And I am so constructed  
That silicon's my substitute;  
My carbon's all deducted."*

*"My tissues, nerves, and viscera  
Show this phenomenon:  
That just as you of carbon are  
I am of silicon."*

*At ordinary temperature  
His soul was frozen dead  
And only resurrected when  
The flames were blazing red.*

*"My needs," said he, "are very few;  
I want no meat nor bread,  
And if you feed the fire well  
You'll never find me dead."*

Though Stock's work on the polysilanes, which destroyed the major premise of this flawed syllogism, should have put an end to this view of possible silicon life-forms, it is, in fact, still alive and well among writers on popular science, where it is now reinforced by the revised interpretation of the silicones as organic derivatives of silica, despite the fact that this revision invalidates their original interpretation as analogs of carbon-based organic compounds (19). This persis-



Figure 10. Lawrence Joseph Henderson (1878-1942).

tence is, in my opinion, ultimately traceable, not just to a misuse of the analogy between silicon and carbon in the periodic table, but to an ancient and deep-seated human fascination with blurring the lines separating living and nonliving matter – with the time-honored superstition that minerals, rocks, and even the earth itself, may be primitive living organisms with infinitely slow metabolic rates.

#### 4. The Biologist and Biochemist Also Disagree

If one turns from the writings of the chemist to the speculations of the biologist and biochemist on the origins of life and looks for comments on the possibility of silicon-based life, one finds that the statements take on a decidedly negative tone. Examination of twenty 20th-century books on this subject (20-39) showed that either the authors did not consider this possibility worthy of discussion or were quite skeptical of such suggestions (40). Much more attune to the requirements of metabolism, transport, replication and repair necessary to sustain a living organism, they were much less inclined to be enamored of superficial analogies of stoichiometry and valence implied by an excessively naive reading of the periodic table.

A good example of this critical attitude is the classic 1913 volume, *The Fitness of the Environment*, by the Harvard physiologist, Lawrence J. Henderson (figure 10), which was written one year before the nonmo-

lecular structure of quartz was established by Bragg using X-ray crystallography. Commenting on the problems inherent in imagining the use of silicon compounds in living systems, Henderson wrote (41):

*From time to time loose discussion has arisen among chemists as to the possibility of substituting another element for carbon in the organic cycle. Such speculations have never been serious, but they have at least demonstrated that very few elements, probably only silicon and perhaps boron can even be imagined in such a role. It has moreover just been shown [i.e., earlier in the book] that only carbon among the elements, and carbon itself only in conjunction with hydrogen, has the power to form the skeletons of compounds numerous, complex, and varied like those of organic chemistry. But apart from this conclusion, it is certain that silicon and boron cannot be mobilized like carbon. Quartz, the oxide of silicon, is the most inert and immobile of rocks; the oxide of boron is only less available as a movable constituent of the environment, and there is no other stable compound of either element that can be compared with carbonic acid [i.e., carbon dioxide] for its mobility.*

What Henderson is emphasizing here is the fact that all known living organisms are dynamic, open systems which require a continuous flow of matter and energy for their maintenance. Transport (or mobility, to use Henderson's phrase) of the material components always involves the use of solutions or gases and it is the negligible solubility and volatility of the oxides of silicon and boron, as compared to that of carbon dioxide, that almost immediately eliminates these elements from practical consideration as carbon substitutes.

### 5. The Silicon Monster in Science Fiction

Henderson's observations about the lack of mobility of silicon dioxide versus carbon dioxide form the basis of one of the earliest and most famous examples of a silicon-based life form in the annals of science fiction – Stanley G. Weinbaum's short story, "A Martian Odyssey," which was first published in 1934, about 20 years after Henderson's book (42). Its author was a 32-year old chemical engineer (figure 11) trained at the University of Wisconsin who had begun writing science fiction only a few months earlier and who would tragically die 15 months later of throat cancer at age 33 (43).

The story itself concerns Dick Jarvis, a chemist connected with a successful space mission to Mars, who runs into trouble when his one-man scouting rocket develops engine trouble and he is forced to walk 1800 miles back to the mother ship. Of course, he is

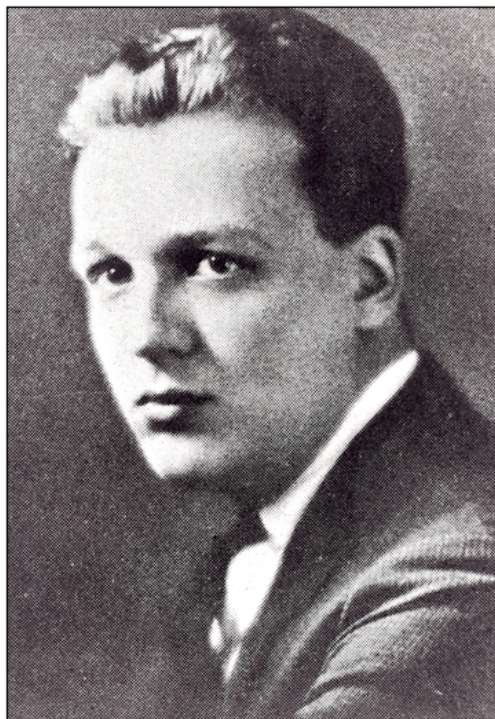


Figure 11. Stanley Grauman Weinbaum (1902-1935).

rescued by another member of the crew before he covers this distance but not before he meets an intelligent bird-like alien named "Tweel" and the two of them encounter a variety of curious life forms in their trek across Mars (figure 11).

In the course of their journey they come upon a series of brick pyramids of ever-increasing size. In each case the capstone is broken off and the pyramid is empty. Eventually, however, they encounter one with the cap in place. As they are examining it, the top tier of bricks begins to shake and heave, and (42):

*A long silvery-grey arm appeared, dragging after it an armored body. Armored, I mean, with scales, silver-grey and dull-shiny. The arm heaved the body out of the hole; the beast crashed to the sand, It was a nondescript creature [figure 12] – body like a big grey cask, arm and a sort of mouth-hole at one end; stiff, pointed tail at the other – and that's all, No other limbs, no eyes, ears, nose – nothing! The thing dragged itself a few yards, inserted its pointed tail in the sand, pushed itself upright and just sat. Tweel and I watched it for ten minutes before it moved. Then, with a creaking and rustling – oh like crumpling stiff paper – its arm moved to the mouth-hole and out came a brick! The arm placed the brick carefully in the sand and the thing was still again. Another ten minutes – another brick. Just one of Nature's brick layers.*





Figure 12. Jarvis and Tweel on their trek across Mars.

Jarvis soon realizes that he has encountered a silicon life-form (42):

*The beast was made of silica! There must have been pure silicon in the sand, and it lived on that. Get it? We, and Tweel and those plants out there, and even the bipods are carbon life; this thing lived by a different set of chemical reactions, It was silicon life ... We're carbon and our waste is carbon dioxide, and this thing is silicon and its waste is silicon dioxide – silica. But silica is a solid, hence the bricks. And it builds itself in, and when it is covered, it moves over to a fresh place to start over.*

At one point in the story the ship's biologist questions Jarvis' conclusions, asking him how he knew it really was a silicon-based creature, and Jarvis snaps back, "Because I'm a chemist!" This may be, but it is also apparent from Jarvis' description of the creature as taking nourishment through its so-called tail and removing its waste products through its so-called mouth, that he is no biologist since his description of the creature is obviously (and I hope you will excuse my vulgarity, but the phrase is so appropriate that I cannot pass it up) "ass-backwards" and that he has actually encountered a species that has to shit the proverbial brick every ten minutes.

Though one of the first science fiction stories to sport a silicon-based life form, Weinbaum's tale still remains one of the best – at least in the sense of having

some contact with the realities of chemistry. In sharp contrast, in many stories which have appeared since the publication of Weinbaum's classic, the chemistry is either unspecified or just down right wrong. Indeed, one of the best examples of the wrong category is the short story "The Devil in the Dark," which served as an episode of the original Star Trek series (44). This featured a silicon life-form called a "Horta" (figure 14) which spends its time instantaneously cutting man-sized tunnels through silicate rock by spitting out its own blood. This, in turn, supposedly consists of a rather improbable mixture of *aqua regia* and hydrofluoric acid, which the author of the story not only imagines is capable of instantaneously dissolving rock but also, when necessary, human bodies. Quite obviously, neither the author nor the screen writer had ever done a silicate analysis as they have no concept of the either the volume of liquid required (the creature is about half the size of a man) nor the rate at which hydrofluoric acid and silica react. Likewise, no attention is given to the enormous volumes of silicon tetrafluoride gas which are necessarily produced by the creature as a result of its tunneling operations in what appears to be a normal oxygen - water environment suitable for human beings, Under these conditions, the silicon tetrafluoride should partly hydrolyze back to hydrogen fluoride and silicon dioxide:

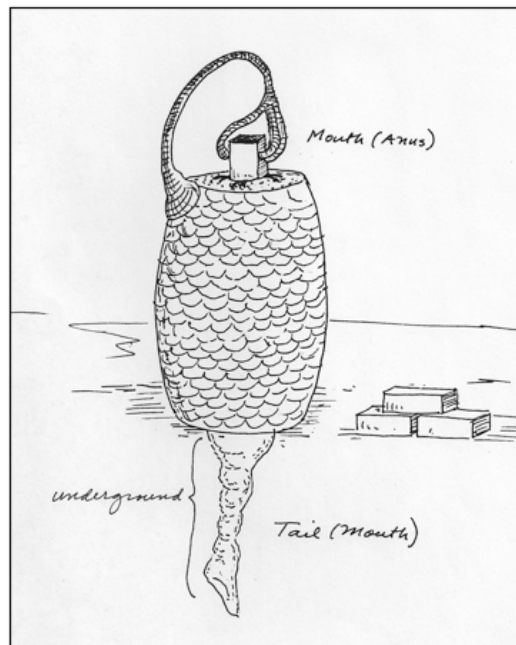
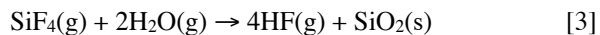


Figure 13. The author's interpretation of Weinbaum's "brick layer."



Figure 14. Captain Kirk confronts the Horta.

Yet Captain Kirk, Mr. Spock, and Bones run around in the resulting  $\text{HF-SiF}_4$  clouds with no apparent ill effects. Other elementary errors also abound: at one point Spock announces that teflon is made by reacting fluorine with silicon, the author repeatedly confuses the terms silicon and silica, and part of the resolution of the story rests on the mistaken impression that *aqua regia* doesn't dissolve platinum.

Another defect common to most stories dealing with silicon creatures is a failure on the part of the author to postulate both a geochemical history and a contemporary environment that are compatible with the evolution of such life forms. Thus Weinbaum assumed a pure silicon layer beneath the sandy surface of Mars, even though he also assumed an oxygen-rich atmosphere – a rather unlikely thermodynamic combination to survive the rigors of planet formation – and no explanation is given for where the Horta gets the materials necessary to generate the enormous volumes of hydrofluoric, nitric, and hydrochloric acids needed for its tunneling operations.

Finally, few authors appreciate the delicate interplay between form and function in living organisms and consequently they make no allowance for growth, repair and replication of their silicon creatures. What they are really describing are manufactured items made of the sorts of materials that an engineer would select in building a robot or android. Thus we are told that the Horta's internal organs are made of teflon – nice to hold acids, but lacking any type of chemical functionality and hence any mechanism for repair, growth or replication.

## 6. Yet More Chemistry

In closing, I would like to return again to the question of why silane chemistry is not the simple parallel of

organic hydrocarbon chemistry in the strong sense of the carbon-silicon analogy implied by science fiction writers and by a naive freshman chemistry reading of the periodic table. In explaining the observed differences, at least four points of are interest (45-48):

1. Comparison of the hydrogen derivatives of carbon and silicon shows that the silicon hydrides or silanes are thermodynamically unstable with respect to disproportionation to their elements at STP but are kinetically metastable up to about  $500^\circ\text{C}$  (52). Cycloalkanes, alkenes, alkynes, and aromatic derivatives of carbon are likewise thermodynamically unstable but kinetically metastable with respect to disproportionation, whereas the alkanes and their oxygen derivatives are thermodynamically stable. This point is emphasized in the graph in figure 15 which clearly shows the metastability of the cycloalkanes, alkenes, alkynes, and aromatics, and the corresponding thermodynamic stability of the alkanes and oxygen derivatives of the hydrocarbons.
2. The hydrocarbons and their derivatives are all thermodynamically unstable but kinetically metastable with respect to oxidation and hydrolysis at STP. Silanes, on the other hand, are both thermodynamically

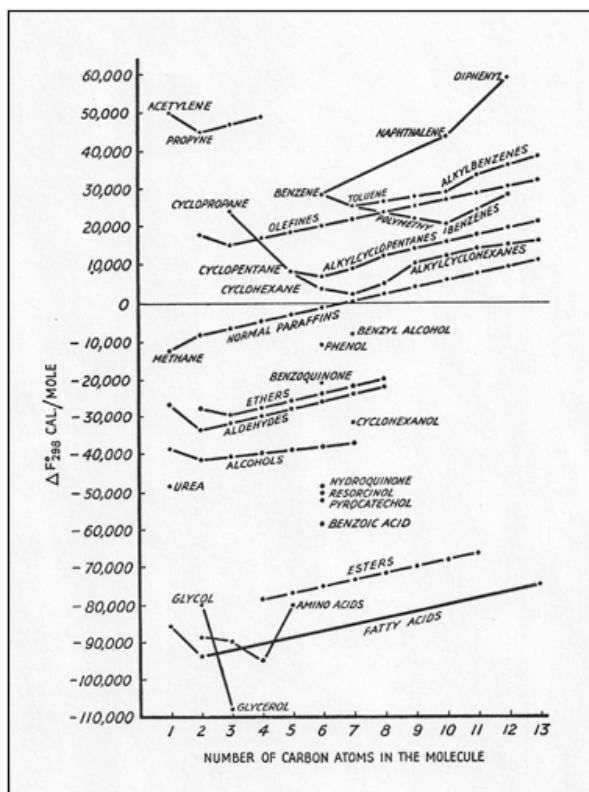


Figure 15. The thermodynamic stability of the hydrocarbons and their derivatives at STP.

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and kinetically unstable. With the exception of pure monosilane, the silanes spontaneously ignite on contact with air and all of them rapidly hydrolyze in slightly basic water.

3. It has not been possible to synthesize derivatives of unsubstituted silanes containing functional groups strictly analogous to those found among the derivatives of the hydrocarbons, most notably those containing analogs of either C=C multiple bonds or C=O multiple bonds, both of which play a key role in the synthetic reactions used to build up complex carbon chains.

4. Most conventional electronegativity scales give the order  $C > H > B > Si$ , which means that the polarity of the C-H bond is the reverse of that of the B-H and Si-H bonds. In effect, boranes and silanes are hydrides, whereas hydrocarbons are "carbides." Consequently alkanes and silanes generally respond differently to substituent effects and to attacking reagents (12).

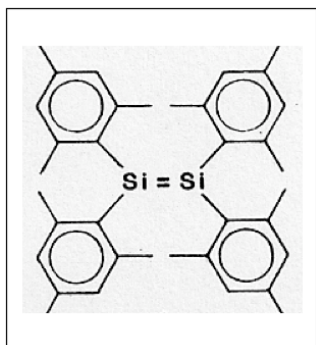
The role of C=C multiple bonds in point 3 can be further emphasized by comparing the energy change which accompanies the conversion of a C=C double bond into the equivalent number of C-C single bonds:

$$E_{C=C} - 2E_{C-C} = -82 \text{ kJ/mol} \quad [4]$$

a result which clearly suggests that C=C double bonds are kinetically metastable. Presumably not only are Si=Si double bonds thermodynamically unstable relative to the equivalent number of Si-Si single bonds, they are kinetically labile as well, since to date no one has succeeded in making a simple unsubstituted silene:

$$E_{Si=Si} - 2E_{Si-Si} < 0 \text{ kJ/mol} \quad [5]$$

This surmise is further supported by the well-publicized synthesis of the first Si=Si double bond in 1981 by West, Fink and Michl using large sterically hindering mesityl groups to induce kinetic metastability (49):



In a similar manner, the role of C=O double bonds in point 3 can be further emphasized by comparing the energy changes which accompany the conversion of C=O versus Si=O double bonds into the equivalent number of single bonds (45):

$$E_{C=O} - 2E_{C-O} = +88 \text{ kJ/mol} \quad [7]$$

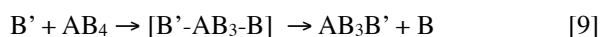
$$E_{Si=O} - 2E_{Si-O} = -282 \text{ kJ/mol} \quad [8]$$

As may be seen, the C=O double bond is thermodynamically stable with respect to the C-O single bond, whereas the reverse is true of its silicon analog, and it is this key difference which, in turn, accounts for the difference in the molecularity of carbon dioxide versus silicon dioxide, for the difference in their transport properties emphasized more than 80 years ago by Henderson, for the waste disposal problems encountered by Weinbaum's Martian "brick layer," and for the high temperature fallacy which characterized early speculations on silicon life-forms.

All of these facts converge to a single question:

*Why are most hydrocarbons and their derivatives kinetically metastable at STP with respect to such reactions as disproportionation, oxidation, hydrolysis and polymerization, whereas the corresponding silicon analogs are not?*

The usual answer involves the assumption of an associative transition state for these reactions in which the coordination sphere of carbon and silicon is expanded to five:



This, in turn, is assumed to require octet expansion on the part of carbon and silicon and the use of outer d-orbitals. Since these are energetically much more accessible in silicon than in carbon, this fact supposedly accounts for the lower activation energies observed for the silicon compounds and for their lack of kinetic metastability (45).

However, in 1982 Dewar and Healy published a paper giving the results of a detailed MNDO calculation for  $S_N2$  displacement reactions at tetrahedral carbon and silicon centers (50). Their results showed an activation barrier corresponding to the formation of the pentacoordinate intermediate for carbon, but none for silicon, even though no outer d-orbitals were included in the basis set. Indeed, the pentacoordinate intermediate for silicon actually appeared as an energy minimum (figure 16). As a result of these calculations, the authors concluded that the activation barrier for carbon

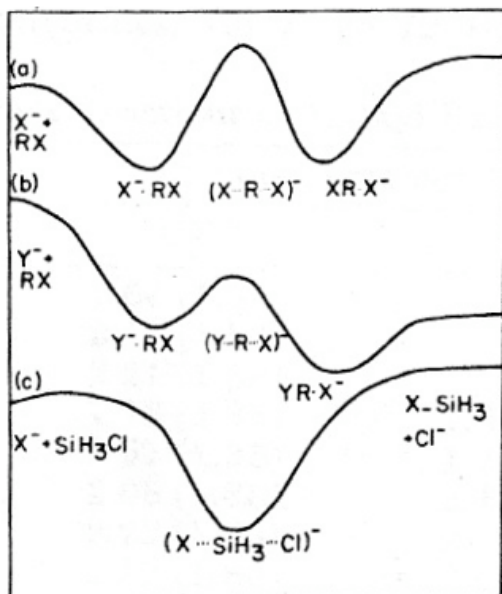


Figure 16. Energy profiles for S<sub>N</sub>2 displacement reactions at carbon (a and b) and at silicon (c).

came largely from the increase in the ligand-ligand repulsions which accompanied the expansion of the carbon coordination sphere from four to five. On the other hand, these repulsions were found to be much less important in the case of silicon because of its larger size, and, indeed, were actually outweighed in this case by the favorable energy changes which accompanied the formation of the new bond to the incoming ligand. Other theoreticians, most notably Werner Kutzelnig, have also opted for this explanation in the case of the closely-related problem of the so-called hypervalent compounds formed by the heavier p-block elements (e.g., PCl<sub>5</sub>, SF<sub>6</sub>, etc.), preferring a model based on multicentered 3c-4e bonds and reduced steric crowding to one which uses traditional 2c-2e bonds and outer d-orbitals for octet expansion (46, 51). Thus, we have ironically come full circle, and have arrived again at Rochow's 1946 statement.

Put colloquially then, the reason for the observed differences in the reactivity of carbon and silicon compounds can be ultimately traced to a difference in the size of their respective atoms. The small size of carbon results in kinetic metastability, which can be manipulated via changes in reaction temperature, solvent environment and the use of catalytic agents, and which leads to the isolation of a wide range of "metastable" compounds with reactive functional groups. By way of contrast, the larger size of silicon results in kinetic lability, leading to thermodynamic control of its reactions and to the isolation of only a few highly stable

compounds which are best characterized as relatively unreactive "thermodynamic sinks."

Of course, in light of the work of West, Fink and Michl on the Si=Si double bond, mentioned earlier, one might argue that one could engineer both the necessary kinetic control and the necessary functional groups into the chemistry of silicon via the use of large sterically hindering ligands, and indeed an increasing number of examples of this technique have been discovered, including many cases of the successful substitution of single, sterically-protected, carbon centers with silicon in conventional organic compounds, dyes, and natural products (52). However, this approach is best characterized as a perturbation on conventional carbon-based organic chemistry (i.e., our original weak analogy). As such, it does not correspond to the literal, naive silicon parallelism of an organic chemistry sans carbon (i.e., our original strong analogy) which inspired the silicon-life forms of the science fiction writer in the first place,

As compensation for this loss of innocence, it is at least worth pondering the irony that so large a difference as that which differentiates a living organism from a dead rock should find its ultimate explanation in so small a difference as that which differentiates the size of a carbon atom from that of a silicon atom.

## 7. References and Notes

1. An invited lecture first given at the 203rd National ACS Meeting, San Francisco, CA, on 05-10 April 1992, and on numerous occasions since.
2. J. J. Berzelius, *Lehrbuch der Chemie*, 4th ed, Vol. 1, Arnold: Dresden and Leipzig, 1835, p. 328 and *ibid.*, Vol. 2, p. 124. See also E. Turner, *Elements of Chemistry*, 7th ed., Thomas and Cowperthwait: Philadelphia, PA, 1846, pp. 208-212.
3. F. Wöhler, H. Buff, "Ueber eine Verbindung von Silicium mit Wasserstoff," *Ann. Chem.*, **1857**, *103*, 218-229; F. Wöhler, "Ueber das Silicium-Mangan," *ibid.*, **1858**, *106*, 54-59; and F. Wöhler, "Ueber das Siliciumwasserstoffgas," *ibid.*, **1858**, *107*, 112-119.
4. F. Wöhler, "Ueber Verbindungen des Silicium mit Sauerstoff und Wasserstoff," *Ann. Chem.*, **1863**, *127*, 257-274. Quote on page 268.
5. J. J. Ebelmen, "Sur les ethers siliciques," *Comptes rendus*, **1844**, *19*, 398-400.
6. C. Friedel, J. M. Crafts, "Ueber einige neue organische Verbindungen des Silicium," *Ann. Chem.*, **1863**, *127*, 28-32.
7. A. Bygden, *Silicium als Vertreter des Kohlenstoffs' organischer Verbindungen*, Almqvist & Wikseks: Uppsala, 1916.
8. J. E. Reynolds, "On Alcohols from Flint and Quartz,"

## THE CHEMISTRY OF BUG-EYED SILICON MONSTERS

*Notices Proc. Roy. Instit.*, **1873-1875**, 7, 106-115. Reprinted in W. L. Bragg, G. Porter, Eds., *The Royal Institution Library of Science: Physical Sciences*, Vol. 2, Elsevier: Amsterdam, 1970, pp. 383-392.

9. F. S. Kipping, L. L. Lloyd, "Triphenylsilicol and Alkyloxysilicon Chlorides," *J. Chem. Soc.*, **1901**, 79, 449-459. Actually Kipping appears to have hedged his bets. At one point he notes that  $\phi_2\text{SiO}$  "bears little, if any, resemblance to benzophenone, and is possibly a polymeride of high molecular weight," whereas later he lists it as a silicon ketone or silicone in a manner which suggests the assumption of a complete analogy.

10. F. S. Kipping, "Organic Derivatives of Silicon," *Proc. Roy. Soc.*, **1937**, 159A, 139-148.

11. A. Stock, *Hydrides of Boron and Silicon*, Cornell University Press: Ithaca, NY, 1933, Chapter 2.

12. E. G. Rockow, *An Introduction to the Chemistry of the Silicones*. Wiley: New York, NY, 1946, pp. 3-4. The second part of this quote appears as a footnote.

13. G. Urry, "Systematic Synthesis in the Polysilane Series," *Acc. Chem. Res.*, **1970**, 3, 306-312.

14. G. Martin, *Researches on the Affinities of the Elements and on the Causes of the Chemical Similarity or Dissimilarity of Elements and Compounds*, Churchill: London, 1905, pp. 247, 251-252, 253. In his introduction Martin indicates that the appendix on silicon life was based on the articles, "Life Under Other Conditions" and "The Nature of Life," which originally appeared in the periodical *Science Gossip* in March, April, May and June of 1900.

15. J. E. Reynolds, "Recent Advances in our Knowledge of Silicon and of Its Relations to Organized Structures," *Notices Proc. Roy. Instit.*, **1909-1910**, 19, 642-650. Reprinted in W. L. Bragg, G. Porter, Eds., *The Royal Institution Library of Science: Physical Sciences*, Vol. 7, Elsevier: Amsterdam, 1970, pp. 54-63.

16. J. E. Reynolds, "Opening Address. Section B (Chemistry)," *Nature*, **1893**, 48, 477-481.

17. H. G. Wells, "Another Basis for Life," *Saturday Review*, **1894**, 78 (Dec. 22), 676-677. Reprinted in R. M. Philmus, D. Y. Hughes, Eds., *H. G. Wells: Early Writings in Science and Science Fiction*, University of California Press: Berkeley, CA, 1975, pp. 144-147. Curiously, Wells attributes all of these speculations on high-temperature silicon-aluminum life forms to Reynolds, though no mention of them appears in the printed version of his lecture given in reference 16.

18. E. Hendrick, *Everyman's Chemistry*, Harper: New York, NY, 1917, pp. 131-133.

19. See, for example, I. Asimov, *Please Explain*, Dell: New York, NY, 1973, pp. 210-211; I. Asimov, "The One and Only" in *The Tragedy of the Moon*, Abelard-Schuman: London, 1973, pp. 79-91; I. Asimov, "Not as We Know It" in *View From a Height*, Doubleday: Garden City, NJ, 1963, pp. 47-60; and G. Feinberg, R. Shapiro, *Life Beyond Earth: The*

*Intelligent Earthling's Guide to Life in the Universe*, Morrow: New York, NY, 1980, pp. 252-256.

20. F. Le Dantec, *The Nature and Origin of Life*, Barnes: New York, NY, 1906.

21. B. Moore, *The Origin and Nature of Life*, Holt: New York, NY, 1912.

22. L. J. Henderson, *The Fitness of the Environment: An Inquiry into the Biological Significance of the Properties of Matter*, Macmillan: New York, NY, 1913.

23. A. I. Oparin, *The Origin of Life*, Macmillan: New York, NY, 1938.

24. H. F. Blum, *Time's Arrow and Evolution*, Princeton University Press: Princeton, NJ, 1955.

25. A. I. Oparin, *The Origin of Life on Earth*, 3rd. ed., Academic Press: New York, NY, 1957.

26. A. I. Oparin, V. Fesenkov, *Life in the Universe*, Twayne: New York, NY, 1961.

27. A. I. Oparin, *Life: Its Nature, Origin, and Development*, Academic Press: New York, NY, 1962.

28. P. G. Seybold, *A Survey of Exobiology*, Memorandum RM-3178-PR, The Rand Corporation: Santa Monica, CA 1963.

29. I. Keosian, *The Origin of Life*, Reinhold: New York, NY, 1964.

30. A. Dauvillier, *The Photochemical Origin of Life*, Academic Press: New York, NY, 1965.

31. J. Marquand, *Life: Its Nature, Origins and Distribution*, Norton: New York, NY, 1968.

32. M. Calvin, *Chemical Evolution: Molecular Evolution Towards the Origin of Living Systems on the Earth and Elsewhere*, Oxford University Press: Oxford, 1969.

33. H. S. Hein, *On the Nature and Origin of Life*, McGraw-Hill, New York, NY, 1971.

34. C. Ponnampertuma, *The Origins of Life*, Dutton: New York, NY, 1972.

35. S. L. Miller, L. E. Orgel, *The Origins of Life on the Earth*, Prentice Hall: Englewood Cliffs, NJ, 1974.

36. C. E. Folsome, *The Origin of Life: A Warm Little Pond*, Freeman: San Francisco, CA, 1979.

37. F. Dyson, *Origins of Life*, Cambridge University Press: Cambridge, 1985.

38. S. Fox, *The Emergence of Life*, Basic Books: New York, NY, 1988.

39. An excellent historical treatment of the debates surrounding the origins of life can be found in J. Farley, *The Spontaneous Generation Controversy from Descartes to Oparin*, Johns Hopkins: Baltimore, MD, 1977.

40. Excluded from this statement are the speculations of the British chemist, A. G. Cains-Smith, that silicate minerals may have served as templates for the evolution of early carbon-based life on earth. See, A. G. Cains-Smith, *Genetic Takeover and the Mineral Origins of Life*, Cambridge University Press: Cambridge, 1982 and earlier books cited therein. This hypothesis is quite distinct from that of a life

form composed solely of silicon compounds. For further reviews relating to the history of this hypothesis and the role of silicon in conventional carbon-based life, see R. K. Her, *The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties, and Biochemistry*, Wiley: New York, NY, 1979, Chapter 7, and M. G. Voronkov, G. L. Zlechan, E. Ya. Lukevitz, *Silizium und Leben*, Akademie Verlag: Berlin, 1975. Her indicates that the latter book, which I have not seen, contains a summary of "all the beliefs and hypotheses of the last 2000 years" on the subject of silicon-based life forms.

41. Reference 22, pp. 264-266.
42. S. G. Weinbaum, "A Martian Odyssey," in S. G. Weinbaum, *A Martian Odyssey and Other Science Fiction Tales*, Hyperion, Westport, CT, 1974, pp. 1-27.
43. S. Moskowit, "Dawn of Fame: The Career of Stanley G. Weinbaum," *ibid.*, unpaginated introduction to reference 42.
44. G. L. Coon, "The Devil in the Dark," in J. Blish, Ed., *The Star Trek Reader II*, Dutton: New York, NY, 1977, pp. 163-183.
45. J. D. Smith, "The Chemistry of Silicon," *Sci. Prog. Oxf.*, **1972**, *60*, 189-204.
46. R. Janoschek, "Kohlenstoff und Silicium - wie verschieden können homologe Elemente sein?," *Chem. unserer Zeit*, **1988**, *22*, 128-138.
47. P. Jutzi, "Die klassische Doppelbindungsregel und ihre vielen Ausnahmen," *Chem. unserer Zeit*, **1981**, *15*, 149-154.
48. In actual practice, the higher silanes disproportionate into a mixture of the lower silanes and polysilanes rather than all the way to the elements. See reference 12, p. 5.
49. R. West, M. J. Fink, J. Michl, "Tetramesityldisilene: A Stable Compound Containing a Silicon-Silicon Double Bond," *Science*, **1981**, *214*, 1343-1344.

50. M. J. S. Dewar, E. Healy, "Why Life Exists," *Organometal.*, **1982**, *1*, 1705-1708.

51. W. Kutzelnigg, "Chemical Bonding in Higher Main Group Elements," *Angew. Chem., Internat. Ed.*, **1984**, *23*, 272-295. For a good review of the current quantum mechanical status of the role of d-orbital participation in silicon chemistry, see the introduction to A. E. Reed, F. Weinhold, "On the Role of d-Orbitals in SF<sub>6</sub>," *J. Am. Chem. Soc.*, **1986**, *108*, 3586-3593.

52. For a popular account, see E. G. Rochow, *Silicon and Silicones*, Springer Verlag: Berlin, 1987, Chapter 8.

## 2010 Update

For updates on the history of the debate over octet expansion and its current quantum mechanical status, see:

1. F. Weinhold, C. Landis, *Valency and Bonding*, Cambridge University Press: Cambridge, 2005, Chapter 3.
2. W. B. Jensen, "The Origins of the Term 'Hypervalent'," *J. Chem. Educ.*, **2006**, *83*, 1751-1752.

Recent theoretical calculations have also called into question the existence of a classical double bond in the silenes strictly analogous to that found in the carbon-based alkenes, indicating instead that the actual bond order is closer to 1.2 and that there is some lone pair electron density on each of the Si atoms leading to a nonplanar arrangement of the attached ligands. See:

1. N. O. J. Malcom, R. J. Gillespie, P. A. Popelier, "A Topological Study of Homonuclear Multiple Bonds Between the Elements of Group 14," *Chem. Soc., Dalton Trans.*, **2002**, 3333-3341.