The Proper Place for Hydrogen in the Periodic Table

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The Mystery

A puzzling mystery attends this title. Quite remarkable, after more than 130 years of construction, the place of hydrogen in the periodic table is still the subject of doubt, confusion, and inadequate explanation that appears to be little more than numerology. In 1956 and 1964, with additional comments in 1985 and 1987, R. T. Sanderson has pointed out the essential elements of this puzzle *(1)*.

> Electronically, or by valence, hydrogen belongs in both groups I and VII. Its electronegativity, however, corresponds to a chemistry intermediate between the two extremes. Hydrogen is, therefore, placed above the other elements and just to the left of carbon *(1a)*. In recognition of its fundamental electronic dissimilarity to both the alkali metals and the halogens, and of its similarity in electronegativity to the elements of group M4, especially carbon, hydrogen is placed over that group but in a separate independent position. Thus hydrogen, whose outer shell is half filled, is close to carbon whose outer shell is half filled. These two, alone of all the elements, have neither outer valency nor outer electrons left over when all possible covalent bonds have been formed *(1b)*.

Since 1964, these questions about the placement of hydrogen have continued without resolution as demonstrated in the following quotes:

> There have from time to time been discussions about the position of hydrogen in the periodic table. It has been quite usual to show it in two positions, both above the alkali metals and above the halogens. A closer examination shows that resemblance to either group I or group VII elements is somewhat superficial. In thermodynamic properties (ionization energy, electron affinity) hydrogen has most similarity to carbon and the other group IV elements. There is as much justification for showing hydrogen above group IV, therefore, as there is for placing it above the alkali metals or the halogens, and no single place is satisfactory *(2)*.
>
> Although its electron configuration (ls^1) links it to the alkali metals, its analogy with the halogens is strong. As hydrogen forms halides as do the alkali metals, and since there is sometimes great disparity between alkali hydrides and halides, it seems proper to place it in the first column of the periodic system rather than in the seventh column. When hydrogen was liquefied for the first time, many scientists expected the liquid to have metallic properties *(3)*.

"Hydrogen has a genuine claim to a place in any of the groups M1, M4, M7 as the following experiments show". "Hydrogen will, under enormous pressure, adopt metallic structures" and "carbon forms very unstable ions whereas hydrogen forms stable cations and anions"*(4a)*. There are also references to the properties of halides and hydrides in conflict with placement in groups 1, 4, or 7. Finally, "It cannot therefore be fitted satisfactorily into any one group of the periodic table. It is best placed above and a little to the left of carbon, since it is slightly less electronegative than the latter" *(4a);* however, more recently one author *(4b)* has placed hydrogen as the number one element simultaneously in both groups 1 and 7 in direct conflict with the assertion that "because hydrogen has no other electrons in its structure there are sufficient differences from each of the two groups (alkali metals and halogens) to justify placing hydrogen outside either" *(5a)*.

In 1989 a 3D periodic table was constructed because, "It is argued that electronegativity is the third dimension of the periodic table" *(6)*. In this 3D table, hydrogen was placed as the first element in the alkali metal family of elements; however, its appearance in this family was as out of place as a piglet in a litter of kittens.

It has been said that "the periodic table is also deeply reassuring in that it accounts for and assigns a specific position to every element" *(7)*. However, contrary to that sanguine sentiment, the search for an appropriate chemical family for hydrogen seems to have been abandoned altogether. "The properties of hydrogen, for example, are so unique that this element cannot be properly assigned to any family" *(8)*. "Hydrogen is formally a member of group 1, but its chemistry is usually dealt with separately from the other elements" *(9)*.

The typical periodic table in textbooks and in the usual chemistry classrooms charts *(10)* places hydrogen above the alkali metals. Sometimes it carries a slightly different color, perhaps a blush of embarrassment for such an awkward and inappropriate arrangement. Its chemistry is quite obviously not metallic and is treated quite separately from that of the alkali metals *(5b, 8, 9, 11)*.

So there is poor hydrogen, denied a chemical family to call its own, thrust like an unwanted orphan into a foster home where its chemistry cannot even be discussed in the same breath with the alkali metals where it now resides. How could this be so? For in the beginning, of both time and the periodic table, there was hydrogen. Still the most abundant element in the entire universe, about 88.67% *(5c)* of all atoms, its fusion brightening our days from time to time, while its oxidation product fills in the rest, and not just April. It is the third most abundant element of the earth's crust, about 15.47% of all crustal atoms *(5d)*. This little element with only one electron can claim, above all other elements, to be a constituent of the largest number, by a minuscule margin, of all compounds both natural and synthetic *(5e)*.[1]

Numerology versus Chemistry

Why has such a wealth of chemistry been ignored repeatedly in discussions of hydrogen's place in the periodic table? It would appear that the most persistent error in the assignment of hydrogen to its place is a kind of numerology, the belief that simply the number of electrons, absent context, determines the chemistry of an element. The fallacy of this belief is most readily exposed in a classic non sequitur: helium, because it has two outer shell electrons, should therefore be placed above beryllium in the periodic table.

The assignment of hydrogen to the alkali-metal family of elements, because it has one electron in its outer shell, is no less absurd than it would be to place helium over beryllium because it has two outer electrons. Both statements omit context for these electrons and belong to numerology and not chemistry. As Sanderson pointed out *(1)*, the context for hydrogen is that of a half-filled shell while for helium it is, of course, that of the filled valence shell which places it as the first member of the noble gases.

A very simple and clear indicator of the difference between hydrogen's electron and those of the alkali metals is to be found in the depth of their respective energy wells, with ionization potentials of 13.6 eV for hydrogen and 5.3 eV for lithium *(12a)*. Furthermore, an analysis by Edwards and Sienko *(13)* of the nature of the metallic and nonmetallic states of the elements has demonstrated that hydrogen is, in fact, one of the most nonmetallic of all the elements. It is even less metallic than oxygen and most of the halogens. Hydrogen is clearly no more metallic than mashed potatoes.

This misplacement of hydrogen at the head of the family of alkali metals has led to vivid bouts of unbridled imagination. After hydrogen was made conductive under high pressure *(14)*, it was reported that "this is a testament to the inherent similarities of hydrogen and the other alkali metals" *(15)*. Furthermore, it only needed "the use of additives, which would bond to the hydrogen molecules and atoms while they were under ultra high pressure...[and]...solid metallic hydrogen could be used to build lightweight automobiles" *(16)*. The properties of these additives would, no doubt, require a new type of superglue that would have the most fantastic properties indeed!

Even when the search for metallic properties among the nonmetallic elements is unrestrained by earthbound reality, there is no reason to consider hydrogen any more metallic than a considerable number of other nonmetals. Boron *(17)*, oxygen, sulfur, selenium, tellurium *(18)*, and phosphorus *(19)* have all been made conductive under pressure. Both boron *(17)* and oxygen *(18)* would seem to be better metallic candidates than hydrogen since both have already been pressured into superconductivity, while putting the squeeze on nitrogen has produced a semiconductor *(20)*.

The metallization of hydrogen under pressure prompted inquires such as: "What is a metal?" and "When is a metal?" *(15)*. A more appropriate question might have been: Where does a nonmetal act like a metal? There are three likely places:

1. In a sliver of space in an ultra high-pressure laboratory.
2. In a large gas bag, such as Jupiter.
3. In the general neighborhood of a neutron star *(20)*.

On such a star you might wish
more elements to squish.
But go there perhaps not,
lest you find yourself no larger than this •

Chemistry of Hydrogen

The agreed upon function of the periodic table has been to reflect a periodicity of physical and chemical properties of the elements with their increasing atomic number; however, there has been a surprising lack of any direct comparison of the chemistry of hydrogen and carbon, even though the relevant physical properties (ionization potential, electron affinity, electronegativity) place them in a close family relationship. The relationship of hydrogen to the carbon, silicon family of elements is clearly observable in a comparison of the chemistry of H−H, C−H, and Si−H bonds. The intrafamily nature of this bonding is disclosed by the chemistry of CH_4 in the same way that intrafamily compounds such as NaK and ClF demonstrate their own familial affinities.

The covalent bonding energies D°_{298} (kJ mol^{-1}) for the alkali metals are so weak they give way to the metallic state: Li−Li, 110.21; Na−Na, 73.08; K−K, 54.63; Li−K, 82.0; Na−K, 65.99. Hydrogen and carbon, in contrast, form very strong covalent bonds: H−H, 435.99; H_3C-H, 438.9; H_3C-CH_3, 376.0; and an isolated C−H, 338.4 *(12b)*. Unlike the alkali metals with their readily formed cations, M^{n+}, in crystals and solutions, hydrogen is always covalent and is never a free cation, H^+, in any condensed medium. The proton is free only in a vacuum.[2]

The reaction of hydrogen with chlorine produces a covalent gaseous product, HCl, obviously not an ionic crystal. Similarly, methane plus chlorine can give CH_3Cl, a covalent gaseous product, and HCl. With oxygen, hydrogen gives water and methane can give methanol. The pK_a of water is 15.74 while that of methanol is 15.5 (in water; ref *22)*. In combination with nitrogen a similar pattern emerges. The pK_a of NH_4^+ is 9.24 while that of $(CH_3)_3NH^+$ is 9.79 *(22)*. In reaction with metals the hydride products LiH, NaH, et cetera, are closest in their chemistry to the methides $LiCH_3$, $NaCH_3$, et cetera *(23)*.

Similarity to the C, Si Family

Saillard and Hoffman in 1984 provided clear illustrations of the family ties that bind hydrogen and carbon, while Ceyer in 2001 has reinforced this observation.

> The breaking of the H−H bond in H_2 and a C−H bond in CH_4 on both discrete transition metal complexes and Ni and Ti surfaces is studied and the essential continuity and similarity of the physical and chemical processes in the two cases is demonstrated *(24a)*.
>
> Given that the energy level diagram of the carbon–Ni system is qualitatively similar to that of the hydrogen–Ni system, it is anticipated that bulk C will be shown to exhibit similarly unique chemistry as bulk H *(24b)*.

Two extensive reviews by Crabtree include analyses of both the similarities and differences in the chemical behavior of H−H, C−H, Si−H, and C−C bonds *(25)*.

One objection to the inclusion of hydrogen in the same family with carbon suggested that "carbon forms very unstable ions whereas hydrogen forms stable cations and anions" *(4a)*. It is not at all clear what ions were being described. Carbon does indeed form stable cations whose properties have been thoroughly examined *(26)*. As noted above, there is no such object as a free ranging H^+ in any condensed system. All too often textbook authors engage in the annoying habit of using the symbol H^+ as a substitute for H_3O^+ and other proton carriers.[2] Unfortunately, for some unformed student minds, seeing is believing. As for the anions of carbon and hydrogen, the hydrides and methides are quite similar in their chemistry, as previously noted *(23)*. The familial relationship of carbon and hydrogen is also apparent in the similarity of members of the oxonium family of ions that range from the hydroxonium ion, H_3O^+, through ROH_2^+ and R_2OH^+ to the carbon counterpart of the hydroxonium ion, R_3O^+ *(27)*.

There is no doubt that hydrogen's family relationship extends to silicon as well as to carbon. The trialkylsilyl group bears a striking relationship to hydrogen in the chemistry of $C{-}SiR_3$ bonding. "As a broad generalization, it is usually the case that when a $C{-}H$ bond can be cleaved by a particular ionic reagent, then the corresponding $C{-}Si(CH_3)_3$ bond will be cleaved by the same reagent even more readily"*(28)*. The similarity of $C{-}Si$ and $C{-}H$ bonds in oxidation processes is also evident *(29)*.

Equally indicative of their close family relationship is the chemistry of the oxygen bonded group, $O{-}SiR_3$, whose behavior parallels that of the corresponding $O{-}H$. "A valid assumption appears to be that silyl enol ethers have reactivities comparable to those of their derived enols" *(30)*. In an extensive array of reactions, the $-SiR_3$ group behaves rather like a large polarizable soggy proton *(28–31)*. Finally, there is even a parallel chemistry in the reduction of carbonyl groups by $H{-}H$ as found in the corresponding reduction by the $Si{-}H$ bond *(32)*.

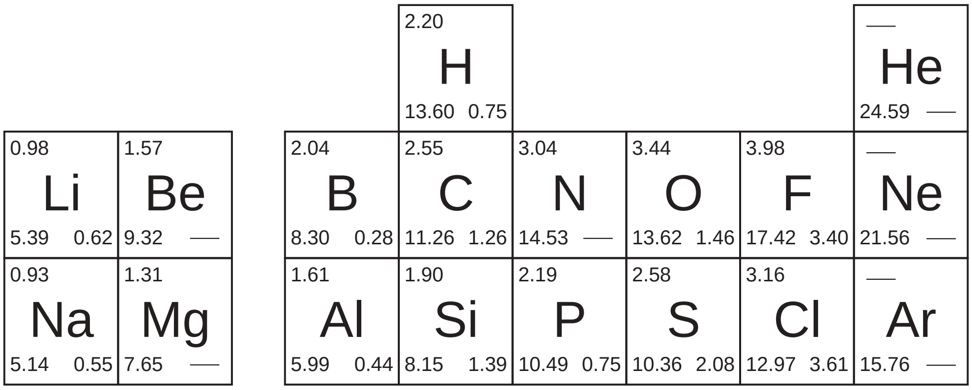
Within other families of elements in the periodic table there are differences in reactivity as the elements increase in atomic number and size: the extreme reactivity of fluorine compared with iodine in the halogens, the lack of reactivity of the smallest noble gases compared with compound formation in the larger members, the ubiquitous multiple bonding of carbon compared with the seldom encountered multiple bonding of silicon *(33)*, and the unique magnetic behavior and radical reactivity of the oxygen molecule with its two unpaired antibonding electrons.

As a consequence of having the smallest nuclear charge of any element, hydrogen also displays a singular chemical property. In addition to the chemical characteristics that it shares with the carbon, silicon family of elements, hydrogen, when bonded to more electronegative elements such as in $N{-}H$, $O{-}H$, $F{-}H$, $Cl{-}H$ *(34)*, and suitably substituted $C{-}H$ bonds *(35)*, can engage a nonbonded pair of electrons from a second atom with bond strengths and angular properties not found in typical electrostatic interactions. The deshielding influence of these elements on hydrogen is unique. No other element, while covalently bonded and with a filled valence shell, engages a nonbonded electron pair from a second atom in a similar fashion. "Li bonds and H bonds differ considerably. The geometrics are quite different. Li bonds are largely electrostatic, whereas H bonds result from charge-transfer, electrostatic, and electron correlative contributions" *(36)*. This very special type of bonding is, of course, responsible for the unusual physical properties of water, including the flotation of ice, and is essential for the structure, function, and genetic integrity of all living organisms *(37)*.

Never Let Sleeping Dogmas Die

There are those who have relied on chemists, for better *(38)* or for worse *(15, 16)*, to provide them with a coherent arrangement of the elements in such a way as to disclose the ties that bind within their physically and chemically related families. There should be no more excuses for such shoddy treatment of hydrogen as to deny its chemical lineage.

So, now we are ready for a new family photo op, not provided by the authority of any person or committee. As with all entries into the scientific lexicon, it comes courtesy of publicly available, sensible phenomena with their attendant logical consequences. Only three rows of the table are needed to illustrate this long overdue correction. Slide hydrogen over to the middle of the row above carbon (Figure 1). Notice how well the relevant physical properties display the genetic origins of the chemistry in each family group. Say "Chemistry" everyone. Click!



			2.20 H 13.60 0.75					— He 24.59 —
0.98 Li 5.39 0.62	1.57 Be 9.32 —	2.04 B 8.30 0.28	2.55 C 11.26 1.26	3.04 N 14.53 —	3.44 O 13.62 1.46	3.98 F 17.42 3.40		— Ne 21.56 —
0.93 Na 5.14 0.55	1.31 Mg 7.65 —	1.61 Al 5.99 0.44	1.90 Si 8.15 1.39	2.19 P 10.49 0.75	2.58 S 10.36 2.08	3.16 Cl 12.97 3.61		— Ar 15.76 —

Figure 1. Periodic table placing hydrogen in the C, Si family. Electronegativity values are shown in the upper left corner of each box, ionization potential values are shown in the lower left corner of each box, and electron affinity values are shown in the lower right corner of each box.

Acknowledgment

I want to thank the reviewers for their very useful comments. One reviewer stated: “Although I assign it to no specific group, the overhead transparency that I drew up to illustrate this idea does show H directly above C, Si….”

Notes

1. According to a search conducted by Ken Cada, Help Desk Editorial Consultant at the Chemical Abstracts Services, Columbus, Ohio, in February 2002, the total number of compounds in the CAS Registry containing hydrogen and carbon alone and with other elements numbered about 15 million. The number containing carbon with other elements, but no hydrogen, was about 47,000, while the number containing hydrogen and other elements, but no carbon, was slightly over 48,000. The difference between these two elements as a fraction of their total number was less than .01%. In compiling these totals such substances as polymers, alloys, minerals, isotopes, radical ions, and tabular inorganics, most of which are nonstoichiometric, were excluded, as were hydrates from the hydrogen count. The margin of difference is so slender and the yearly flood of entries into the registry so great, it would not be at all surprising to find that *numero uno* between hydrogen and carbon might fluctuate from month to month.

2. After the submission of this paper there appeared a report that described the preparation of a compound that reversed the charge distribution of Na^+H^- by the formation of “Inverse sodium hydride; a crystalline salt that contains H^+ and Na^-...” *(39)*. A closer reading discloses a rather misleading use of the H^+ symbol. The hydrogen in question is not a free proton, H^+, analogous to Na^+, but is the usual rather large and complex ammonium type of ion in which the positive charge is dispersed to nitrogens and their adjacent carbons with an adamanzane cage. In charge distribution it is analogous to NH_4^+ with its covalent hydrogens and all five atoms sharing the positive charge, unlike as isolated H^+. There is no voracious, omnivorous lion in the adamanzane cage, only the Cowardly Lion of Oz, a more appropriate metaphor for our imaginary proton.

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