

On the ‘true position’ of hydrogen in the Periodic Table

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Abstract Several attempts have recently been made to point to ‘the proper place’ for hydrogen (sometimes also helium) in the Periodic Table of the elements. There are altogether five different types of arguments that lead to the following conclusions: (1) hydrogen should be placed in group 1, above lithium; (2) hydrogen should be placed in group 17, above fluorine; (3) hydrogen is to be placed in group 14, above carbon; (4) hydrogen should be positioned above both lithium and fluorine and (5) hydrogen should be treated as a stand-alone element, in the center of the Periodic Table. Although all proposals are based on arguments, not all of them sound equally convincing. An attempt is made, after critical reexamination of the arguments offered, to hopefully point to the best possible choice for the position of hydrogen. A few words are also mentioned on the structure of the Periodic Table and the (novel) attempts to reorganize it.

Keywords Hydrogen · Position of · Periodic Table · Trends · Hydrogen bonding

Introduction

In the beginning of the new millennium, several authors made attempts to answer the question that has persisted for many decades: what is the true position of hydrogen in the Periodic Table (PT) of the elements?

Let us mention in the very beginning that we understand perfectly that:

- this question is a difficult one;

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- depending on the arguments offered, various choices may appear to seemingly lead to the ‘best possible choice’, and
- people are usually biased/predetermined to one of the possible choices.

The latter necessarily leads to non-objectiveness, meaning that people put ‘high weights’ on their own arguments while being in the same time highly critical of arguments offered by others.

For several years we followed with interest the discussions (sometimes monologues) of various authors, heavily based on their own arguments. We ourselves were not particular supporters of any of the offered proposals. This is (perhaps) kind of an advantage that allows us to judge the offered arguments more critically and objectively than the authors themselves.

Let us rephrase slightly the task that is to be completed: the problem is, how to classify hydrogen? In other words, to which group(s) in the PT should it be properly assigned?

Hydrogen is the first element in the PT. It seems obvious (without offering a formal proof) that *if it is to be classified* to some group, it should be one of the eight groups, formerly called ‘main groups’ of the PT, i.e. groups 1–2 and 13–18, and not groups 3–12 (containing transition metals).

The italicized text in the previous paragraph is intended to point to an important issue that is often forgotten: every classification is a human activity. It is not just a mere indisputable fact that exists in nature waiting to be discovered. Classifications are (or might be) more or less arbitrary. Indeed, there are many criteria according to which the elements of a given set could be classified. The above holds especially when speaking about chemical elements: chemical elements might be classified according to the state of aggregation, boiling and melting temperatures, color, electrical conductivity etc., etc. It may not be quite clear why someone would classify the elements on the basis of their electrical conductivity, unless it is done for a very specific (hence limited) interest. Yet, even such a classification is possible.

The standard approach nowadays (and for many decades back) is to list the elements in a series of ascending atomic numbers, and then search for similarities. This approach is today somewhat different from Mendeleev’s (Mendeleev 1869), but has the advantage of being on a better scientific ground. The result is the well-known classification of the elements in the PT, comprising 7 periods and 18 groups, accounting for all *s*-, *p*- and *d*-elements, except hydrogen and (to a lesser extent) helium. Other approaches exist too, resulting in somewhat different schemes of the elements in the PT and will be briefly mentioned in what follows.

Brief review of previous work

In the somewhat extensive literature sources that were available to us, there are those devoted to the discovery of the PT (Mendeleev 1869; Brooks 2002; Kaji 2003; Hendry 2005; Scerri 2012a, b; Weinstein 2016), its reception (Kaji 2003), the contribution of physics to the periodic law (Ostrovsky 2001; Habashi and Tsimmerman 2013), the definitions of the term element (Scerri 2004, 2012a; Hendry 2005; Sharlow 2006; Earley 2009; Leach 2013) and jubilees (centennial) of the death of Mendeleev (Stewart 2007). The definition of *element* is in, a way, dual: it relies on a concept of element as an observable (elemental, or simple substance), but also on a concept of element as “a ‘basic substance,’ something

that can survive chemical change and is the common component of different compound substances” (Hendry 2005). It is the latter notion, of elements as basic substances, that is more important. It seems that the distinction between the two concepts was known as early as the discovery of the PT (Sharlow 2006).

Closely related to the previous are publications aimed (among other things) at the best possible demonstration of the periodicity (including triads) and the periodic law selecting “the best possible choice of a PT” (Katz 2001; Laing 2005; Scerri 2007, 2010; Marks and Marks 2010; Nelson 2013; Rayner-Canham 2013). Some critics that the PT as “misleading, incomplete and unduly neglected” have claimed (Allen 1991), pointing to the configuration energies, *CE*, as very important complementary information for the elements/atoms in question. Regarding the possible formats/presentations of PT, we will mention only few (let’s call those ‘typical representatives’) of the huge number of possibilities (Figs. 1, 2, 3, 4, 5):

			Ti = 50	Zr = 90	? = 180
			V = 51	Nb = 94	Ta = 182
			Cr = 52	Mo = 96	W = 186
			Mn = 55	Rh = 104,4	Pt = 197,4
			Fe = 56	Ru = 104,4	Ir = 198
			Ni = Co = 59	Pd = 106,6	Os = 199
			Cu = 63,4	Ag = 108	Hg = 200
H = 1			Zn = 65,2	Cd = 112	
	Be = 9,4	Mg = 24	? = 68	Ur = 116	Au = 197?
	B = 11	Al = 27,4	? = 70	Sn = 118	
	C = 12	Si = 28	As = 75	Sb = 122	Bi = 210
	N = 14	P = 31	Se = 79,4	Te = 128?	
	O = 16	S = 32	Br = 80	J = 127	
	F = 19	Cl = 35,5	Rb = 85,4	Cs = 133	Tl = 204
Li = 7	Na = 23	K = 39	Sr = 87,6	Ba = 137	Pb = 207
		Ca = 40	Ce = 92		
		? = 45	La = 94		
		?Er = 56	Di = 95		
		?Yt = 60	Th = 118?		
		?In = 75,6			

(a)

Reihen	Gruppe I. — R ⁰	Gruppe II. — R ⁰	Gruppe III. — R ⁰	Gruppe IV. RR' R ⁰	Gruppe V. RR' R ⁰	Gruppe VI. RR' R ⁰	Gruppe VII. RR' R ⁰	Gruppe VIII. — R ⁰
1	H = 1							
2	Li = 7	Be = 9,4	B = 11	C = 12	N = 14	O = 16	F = 19	
3	Na = 23	Mg = 24	Al = 27,3	Si = 28	P = 31	S = 32	Cl = 35,5	
4	K = 39	Ca = 40	— = 44	Ti = 48	V = 51	Cr = 52	Mn = 55	Fe = 56, Co = 59, Ni = 59, Cu = 63.
5	(Cu = 63)	Zn = 65	— = 68	— = 72	As = 75	Se = 78	Br = 80	
6	Rb = 85	Sr = 87	?Yt = 88	Zr = 90	Nb = 94	Mo = 96	— = 100	Ru = 104, Rh = 104, Pd = 106, Ag = 108.
7	(Ag = 108)	Cd = 112	In = 113	Sb = 118	Sb = 122	Te = 125	J = 127	
8	Cs = 133	Ba = 137	?Di = 138	?Ce = 140	—	—	—	
9	(—)	—	—	—	—	—	—	
10	—	—	?Er = 178	?La = 180	Ta = 182	W = 184	—	Os = 195, Ir = 197, Pt = 198, Au = 199.
11	(Au = 199)	Hg = 200	Tl = 204	Pb = 207	Bi = 208	—	—	
12	—	—	—	Th = 231	—	U = 240	—	

(b)

Fig. 1 a The original Mendeleev PT (1869) and b his short-period table (Laing 2005)

Periodic Table of the Elements

The image shows a standard periodic table with 118 elements. The elements are color-coded by groups: Alkali Metals (purple), Alkaline Earths (pink), Transition Metals (blue), Basic Metals (green), Semimetals (yellow), Nonmetals (orange), Halogens (red), Noble Gases (grey), Lanthanides (light blue), and Actinides (dark blue). The f-block elements (Lanthanide and Actinide series) are shown separately below the main body of the table. The groups are labeled at the top: 1 IA, 2 IIA, 3-10 IIB-VIIB, 11 IB, 12 IIB, 13-18 IIIA-VIIIA.

Fig. 2 The standard medium-long PT format with the *f*-elements shown separated from the main body of the table (<https://sciencenotes.org/periodic-table-wallpaper-2/> 2017)

The image shows a proposed periodic table by Kaesz and Atkins (2003). It features a unique placement for hydrogen (H) at the top center, between the first and second columns. The rest of the table is a standard 18-column format with elements colored in shades of orange and yellow. The groups are labeled at the top: 1, 2, 3-12, 13-18.

Fig. 3 PT proposed by Kaesz and Atkins (2003)

The above format presentations will be discussed in relation to the central question of the present contribution: what is the true (if any) place of the element hydrogen, in the PT. For that reason, the references primarily devoted to this question (Kaesz and Atkins 2003; Cronyn 2003; Scerri 2004; Rich 2005; Sacks 2006; Laing 2007; Novaro 2008; Ramírez-Solís and Novaro 2014; Hernández and Novaro 2014; Labarca and Sri-vaths 2016; Cvetković and Petruševski 2017; Silvera and Dias 2017) will be reviewed under the next heading. It would be fair to also mention here that the position of some

Where to place hydrogen in the PT?

The first one that assigned hydrogen in the PT was, of course, Mendeleev (Mendeleev 1869). In 1869 he originally positioned it (cf. Fig. 1a) in the same group (row) with copper, silver and mercury. In view of his excellent knowledge of the chemical properties which weighed so much on the positioning of the elements it is reasonable to allow that he meant it to be separated from all other elements. Two years later (i.e. in 1871) he placed it in the first group, next to the alkali metals (Sacks 2006). Since this is the short format of PT, this group contained also Cu, Ag and Au but arguments could be offered even for such similarities (Rayner-Canham 2013). Group 1 is even nowadays the most ‘popular’ place for H (Katz 2001; Scerri 2004, 2007; Rich 2005; Laing 2007), as demonstrated by the most common ‘shape’ of the PT (cf. Fig. 2). The arguments stem from the fact that H is univalent (exactly as the alkali metals), and forms compounds with the same general formula. Further, from the point of view of physics, the atomic term of hydrogen ($^2S_{1/2}$) is identical with that of alkali metals. One more reason would be that under very high pressures (≈ 500 GPa) there are strong experimental indications that metallic hydrogen is formed (Silvera and Dias 2017). If this is proven to be true, it would be a serious argument for those inclined to put H above Li. The trends of electronegativities is qualitatively correct, albeit the value for H is much higher (the variation of the electronegativity from Li to Cs occurs in much smaller steps). On the other hand, there are really strong arguments against this assignment. We would only like to mention here that no alkali metal forms M^- anions (unlike the stable H^- , the hydride anion). Also, all MX salts (where M is an alkali metal, and X is halogen) are ionic solids. All HX compounds are covalent and gaseous. More arguments will be offered in the subsequent paragraph.

Hydrogen could be placed in Group 17 (halogens) above F (cf. Fig. 4). A solid argument for this is that it forms covalent compounds with all nonmetals, but ionic compounds with alkali metals and most of alkaline earths (exactly as the halogens). Hydrogen as a simple substance, just like the halogens, exists in the form of diatomic molecules. It cannot form free H^+ ions, due to the extremely high polarizability of the naked proton. Invoking Sacks (2006), “A Coulombic model, in which all compounds of hydrogen are treated as hydrides, places hydrogen exclusively as the first member of the halogen family and forms the basis for reconsideration of fundamental concepts in bonding and structures. The model provides excellent descriptive and predictive ability for structures and reactivities of a wide range of substances... Although unique in many respects, both physical and chemical properties of the element conform best—if not perfectly—with other halogens”. Scerri has also supported this view (Scerri 2010), in contrast to his previous opinion (Scerri 2004, 2007), first of all as a result of treating the elements as basic (and not simple) substances, but also because if such a scheme is adopted, the PT benefits from one more perfect triad (triad of atomic numbers). Hernández and Novaro also give arguments against placing hydrogen in Group 1 (Hernández and Novaro 2014), but without saying explicitly that it should lead the halogens group. Although H above F seems a better option than H above Li, it too suffers from several shortcomings. The atomic term of all halogen atoms is $^2P_{3/2}$, and this is a compelling argument against its assignment to this group, at least for physicists. Also, the trend of electronegativities in the series H, F, Cl, Br, I is counterintuitive (one would expect the first element in a group to be the one with highest value for the electronegativity and this is true for all groups of *s*- and *p*-elements, providing hydrogen is left aside). Further, all alkali metals react vigorously (some of them even explosively) with water, giving MOH and hydrogen gas. The products with the analogous X_2O are MX and M_2O , if an excess

alkali metal is used. It would not be possible to prevent the formation of MOH under similar experimental conditions, for if that was possible, Davy could not have generated potassium and sodium by electrolysis of molten MOH! Alkali hydrides are hydrolyzed in water giving H_2 and MOH. No reaction is possible between MX and X_2O , at least for $X = F, Cl$! Finally, considering the ionization energies one comes to the conclusion that hydrogen is 'incompatible' with both Group 1 and Group 17.

Hydrogen has also been placed in group 4, above carbon (Cronyn 2003; Rich 2005), on the basis of several arguments: (a) Its valence electron shell ($1s^1$) is half filled, as is the shell of carbon ($1s^22p^2$); (b) Its electronegativity is between the electronegativities of C and Si; (c) The types of compounds hydrogen forms are closely related to the compounds with methyl (CH_3) instead of H; (d) The H–H and C–H bonds are of comparable strengths etc. While the above is true, it is highly unusual to put a univalent element in a group of tetravalent ones. Neither the atomic terms of the elements in the carbon family (3P_1) have anything in common with the term for hydrogen ($^2S_{1/2}$). In our opinion, this is the weakest proposal of all offered so far.

A step forward is the PT of Labarca and Srivaths (2016) (cf. Fig. 5), where H is positioned above both Li and F, thus pointing to a resemblance of H with both Group 1 and Group 17. To further advocate this approach, one should be aware that there are no real arguments, apart from a belief, that 'every element in PT belongs to *one and one only* of the existing groups of elements'. Simplified, that would read: 'Every *s*- or *p*-element in the PT belongs to one of the eight groups headed by the elements of period 2'. Admittedly the latter works perfectly for all *s*- and *p*-elements except for hydrogen. In relation to this, the Labarca and Srivaths approach seems to be successful. The questions are: can one do better than that? Namely, within the frame of Labarca and Srivaths PT scheme, the problems with the trends (electronegativity, ionization energy) discussed above remain. Also, there are peculiarities about hydrogen, that are specific for this element only. That is the phenomenon of hydrogen bonding (HB), where a hydrogen atom is shared between two (or, very seldom, three highly electronegative atoms). This unique type of bonding may vary in strength continuously: at one end, it may approach the 'bonding strength' of Van der Waals contacts; at the other, it may be indistinguishable from a true covalent bond, like in the case of $(F-H-F)^-$, where both FH and HF bonds are identical by symmetry. A whole continuum of HB strengths is possible. This has remarkable consequences on the XH stretching frequencies of a HB species $X-H\cdots Y$ (with X being proton donor and Y being proton acceptor): from some 3700 cm^{-1} for a 'free' O–H stretching, to some 500^{-1} for very strong O–H–O hydrogen bonds. No other element in the PT spans such a wide range of stretching vibration wavenumbers.

Bearing in mind the above, it might be understandable why we agree that H should be placed at a stand-alone position within the PT (Kaeszi and Atkins 2003). As the authors say: 'We do not support the duplication of hydrogen in the periodic table. Instead, we believe the symbol should appear only once in the table, in Period 1 but centered between the alkali metals and the halogens as illustrated in the figure. This position is consistent with the elements at the head of each group being significantly different from their congeners: hydrogen lies at the head of the entire table and as such can be expected to be strikingly different from all the elements, as is in fact the case' (cf. Fig. 3). However, the reasoning of Kaeszi and Atkins was criticized (Scerri 2004): "Our current inability to place hydrogen in the periodic table in an unambiguous manner should not lead us to exclude it from the periodic law altogether, as Atkins and Kaeszi seem to imply in removing hydrogen from the main body of the table. I suggest that hydrogen is as subject to the periodic law as all the other elements are". Now, the latter conclusion isn't quite true. Of course, hydrogen

was not ‘excluded’ from the PT. It is well within it. However, it is *not* placed in any of the groups in this table. We do not see why such an approach would not be a legitimate one? Especially, when one recalls that the leading elements (Li, Be, B, C, N, O and F) show a certain extent of ‘exotic behaviour’, when compared with those below them in the group. The diagonal relationships in the PT (Rayner-Canham 2011), that is similarities between Li and Mg; Be and Al; B and Si, and to a lesser extent of C and P, have been well known for a long time. These similarities might be, at least in part, related to the fact that atoms of the elements of the second period do not have (empty) *d*-orbitals of energy comparable to that of the valence electrons, unlike their heavier analogues. A similar, but much more pronounced ‘exotic behaviour’ could then be a priori expected for hydrogen, being a first period element (and thus having no energetically close *p*-orbitals). If the former is true, the logical consequence would be to give it a special position in the PT, exactly as Kaesz and Atkins did.

We will very briefly point to the similar dilemma about the true position of He in the PT (Novaro 2008; Marks and Marks 2010; Ramírez-Solís and Novaro 2014; Labarca and Srivaths 2016). Should it be placed above Be or above Ne? Actually, it is only the electron configuration and the atomic spectra of He that matches those of alkaline earths. The atomic term of helium is equal to the terms of both the alkaline earths and noble gases, namely 1S_0 . However, there is a lack of real chemistry of He (with a single exception, the synthesis of Na_2He under some really extreme experimental conditions, that has just recently been published (Dong et al. 2017)). The former is in line with the properties of noble gases (showing, once again, a pronounced trend of increasing reactivity when going from He to Xe). Chemically, helium has nothing in common with typical metals, as are alkaline earths and the latter fact fully justifies its position in the PT as the first noble gas (and the least reactive element in PT).

After we published our view (Cvetković and Petruševski 2017; Petruševski and Cvetković 2017), a reply followed almost immediately (Labarca and Srivaths 2017). The authors try to persuade the readers that they are, indeed, right. As the questions they raise have already been addressed earlier, we decline the possibility to answer now. However, after reading Scerri’s comment (2017), we have to say that he has a very strong point saying that the attempt of Srivaths and Labarca is ‘a blatant form of an ad hoc maneuver... one that does not solve the problem but rather surrenders to it fully’. Apart from our first reaction to Labarca and Srivaths paper that was basically positive, we have to admit that Scerri is right in his rigorous evaluation.

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