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Educational review

ON THE 'TRUE POSITION' OF HYDROGEN IN THE PERIODIC TABLE*

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Several attempts are known lately intending 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 offered arguments sound equally convincing. An attempt is made, after critical reexamination of the offered arguments, to hopefully point to the best possible choice for the position of hydrogen. Few words are also mentioned on the structure of the Periodic Table and the (novel) attempts to reorganize it.

Key words: hydrogen; position of; Periodic Table; trends; hydrogen bonding

PROLOGUE

In addition to the numerous works in molecular spectroscopy (mostly hydrogen-bonded systems, particularly crystalline hydrates) it has to be recognized that our laureate was the first one that introduced modern courses of chemistry education for chemistry majors (in the early 1990's) at the Ss. Cyril and Methodius University. In thinking about a suitable topic that would reflect his main interests of study, it seemed more than appropriate to discuss, once again, the 'true position' of the element *hydrogen* in the Mendeleev's Periodic Table.

INTRODUCTION

In the beginning of the new millennium, several authors made attempts to answer the question that persists 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;
- 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 to 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 that is (perhaps) kind of an advantage that allows judging the offered arguments more critically and objectively than the authors themselves.

*Dedicated to academician Bojan Šoptrajanov on the occasion of his 80th birthday

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 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 would someone 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 the original Mendeleev’s [1], 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, but 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.

A word on the literature used: we listed all references [1–40] chronologically, and then refer to each of them simply by its number in the list.

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 [1, 6, 8, 11, 26, 36], its reception [8], the contribution of physics to the periodic law [4, 27], the definitions of the term element [10, 11, 15, 20, 25, 28] and jubilees (centennial) of the death of Mendeleev [17]. The definition of **element** is in, a way, dual: it relies on a concept of element as an observable (elemental, or simple sub-

stance), 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.*” [11]. 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 [15].

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” [5, 12, 18, 22, 23, 29, 30]. Regarding the possible formats/presentations of PT, we will mention only few (let’s call those ‘typical representatives’) of the huge number of possibilities (Figures 1–5).

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, primarily the references devoted to this question [7, 9, 10, 13, 14, 16, 19, 31, 32, 34, 37, 39] will be reviewed in the next heading.

Three references were devoted to noble gas chemistry: that of Ar [2, 3] (HArF was synthesized in 2000 and was proven to be stable at very low temperatures [2]) and the brand new publication reporting the synthesis of Na₂He under extreme pressures of some 100 GPa [38]. Reference 21 is about the notion of isoelectronic series, isodiagonality and diagonal relationships between the elements in PT [24], the order in which the 3*d* and 4*s* energy levels are populated [33] and the eka- elements and chemical pure possibilities [35].

WHERE TO PLACE HYDROGEN IN THE PT?

The first one that assigned hydrogen in the PT was, of course, Mendeleev [1]. In 1869 he originally positioned it (cf. Figure 1 a) 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. In two years (1871) he placed it in the first group, next to the alkali metals [14]. True, 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 [30]). Group 1 is even nowadays the most ‘popular’ place for H [5, 10, 13, 16, 18], as demonstrated by the most common ‘shape’ of the PT (cf. Figure 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 [39]. If this is proven to be true, that 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 is 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.

					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
					Zn = 65,2	Cd = 112	
					? = 68	Ur = 116	Au = 197?
					? = 70	Sn = 118	
					As = 75	Sb = 122	Bi = 210
					Se = 79,4	Te = 128?	
					Br = 80	J = 127	
					Rb = 85,4	Cs = 133	Tl = 204
					Sr = 87,6	Ba = 137	Pb = 207
					? = 45		
					Ce = 92		
					La = 94		
					Di = 95		
					Th = 118?		

(a)

Reihen	Gruppe I. — R ¹ O	Gruppe II. — R ⁰	Gruppe III. — R ⁰ 3	Gruppe IV. RH ⁴ R ⁰ 2	Gruppe V. RH ⁵ R ⁰ 6	Gruppe VI. RH ⁶ R ⁰ 2	Gruppe VII. RH R ⁰ 7	Gruppe VIII. — R ⁰ 4
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	Sn = 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)

Figure 1. (a) The original Mendeleev's PT [1] and (b) his short-period table (source: Lang [12]).

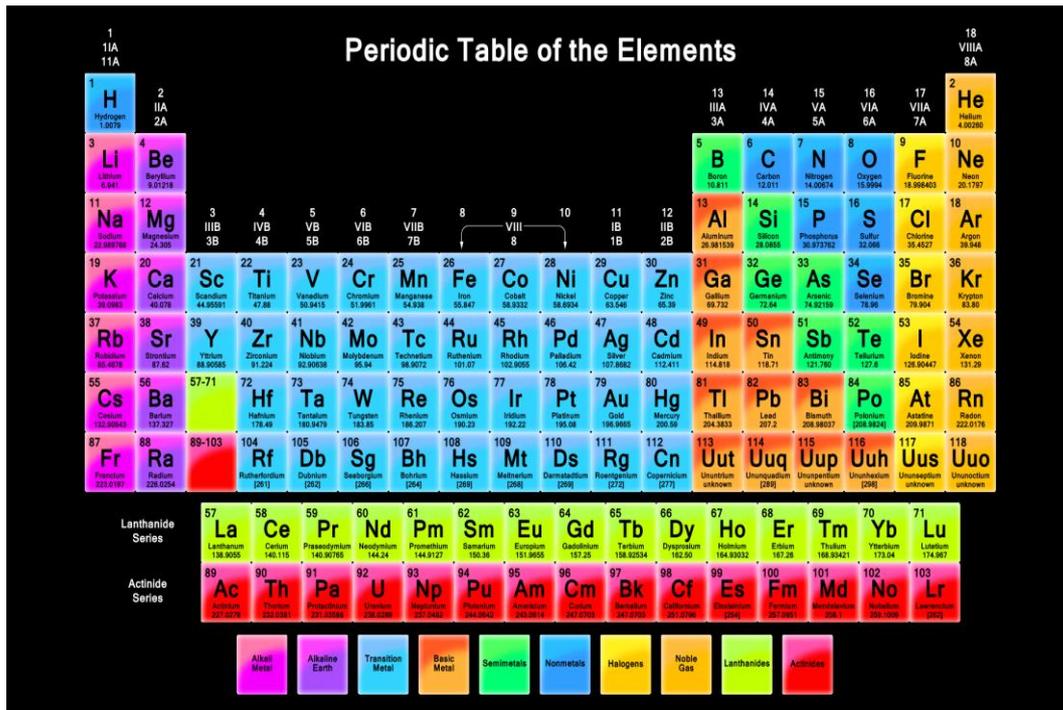


Figure 2. The standard medium-long PT format with the *f*-elements shown separated from the main body of the table [40].

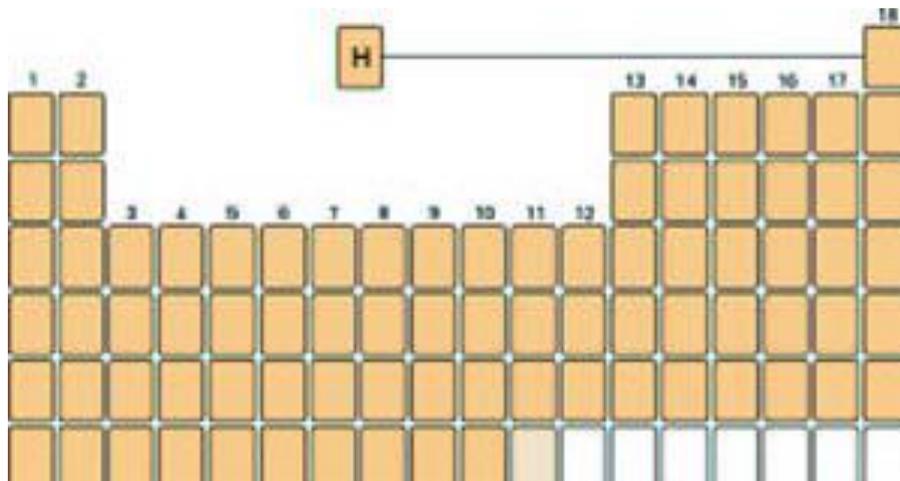


Figure 3. PT proposed by Kaesz & Atkins [7].

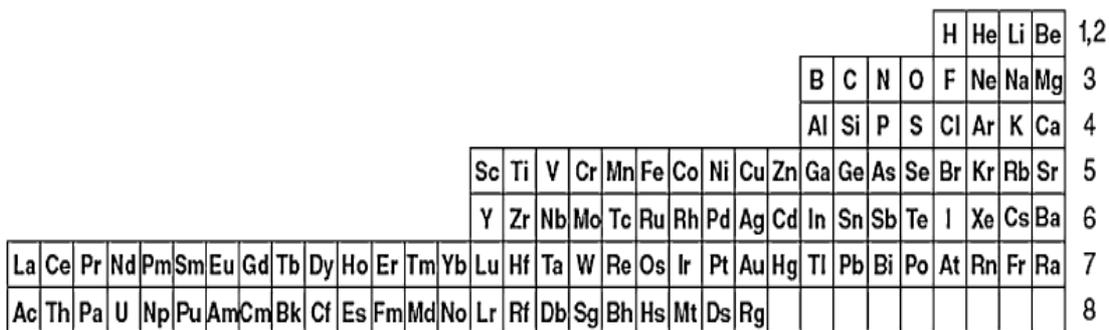


Figure 4. PT proposed by Scerri [22].

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 & Srivaths [34] (cf. Figure 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’. Yes, the latter works perfect for all *s*- and *p*- elements except for hydrogen! In relation to this, the Labarca & Srivaths approach is a real success. The questions are: can one do better than that? Namely, within the frame of Labarca & Srivaths PT scheme, the problems with the trends (electronegativity, ionization energy) discussed above remain. Also, there are pure peculiarities about hydrogen, 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: on one end, it may approach the ‘bonding strength’ of Van der Waals contacts; on 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.

Having in mind the above, it might be understandable why we agree with Kaesz & Atkins [7], that H should be placed at a stand-alone position within the PT. 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. Figure 3).

However, the reasoning of Kaesz and Atkins was criticized by Scerri: ‘*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 Kaesz 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 [24] (i.e. similarities between Li and Mg; Be and Al; B and Si, and to a lesser extent of C and P) are 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 & Atkins did!

To end this discussion, we will very briefly point to the similar dilemma about the true position of He in the PT [19, 23, 31, 34]: shall it be put 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 both terms of 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 [38]). 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).

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ЗА 'ВИСТИНСКОТО МЕСТО' НА ВОДОРОДОТ ВО ПЕРИОДНИОТ СИСТЕМ

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Во последно време се познати неколку обиди чија амбиција е да се укаже на "вистинското место" на водородот (понекогаш и хелиумот) во периодниот систем на елементите. Постојат вкупно пет различни вида аргументи кои доведуваат до следните заклучоци: (1) Водородот треба да се стави во првата група, над литиумот; (2) Водородот треба да се става во 17-тата група, над флуорот; (3) Водородот треба да се стави во 14-тата група, над јаглеродот; (4) Водородот треба да биде поставен над литиумот и флуорот и (5) водородот треба да се третира како уникатен елемент и да се смести централно во периодниот систем. Иако сите предлози се засноваат на аргументи, не сите понудени аргументи звучат подеднакво убедливо. По критичкото преиспитување на понудените аргументи, направен е обид да се избере најдобрата можна позиција за водород. Се споменуваат и неколку зборови и за структурата на Периодниот Систем маса и за обиди за неговото реорганизирање.

Клучни зборови: водород; местоположба; периоден систем; трендови; водородна врска