Letters to the Editor Писма до редакцията

ON THE PLACEMENT OF HYDROGEN AND HELIUM IN THE PERIODIC SYSTEM: A COMMENT

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Introduction

In the last two decades the question of the correct placement (i.e. assignment to particular group within the PT) of hydrogen and, more seldom, of helium, has often reappeared (Labarca & Srivaths, 2016 and the references therein).

We were tempted to write a few words about this brave attempt (Labarca & Srivaths, 2016), which includes assignation of hydrogen *between* Group 1 (alkali metals) and Group 17 (the halogens) and helium *between* Group 2 (alkaline earths) and Group 18 (noble gases). In such an approach, it appeared necessary to rearrange the PT in the following way (Fig. 1).

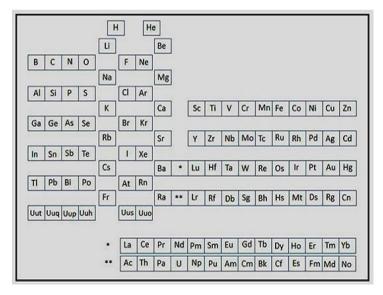


Figure 1. The Srivaths-Labarca PT

This approach apparently breaks with the traditional dogma of having "a single element in a single group of the PT". The Labarca & Srivaths approach places both elements "in the neighbourhood" that is considered similar enough, so one could feel that H might be assigned to both alkali metals and halogens, and He – to both alkaline earths and noble gases.

Having said the above, in the following short comment we will take the opportunity to reconsider few things and to (hopefully) offer better positions for both elements. We will draw our conclusions on the basis of some well-known chemistry facts. After all, the classification of Mendeleev (Mendeleev, 1869) was done following the rich chemistry facts for the elements and the similarity of behaviour in this respect. A more detailed elaboration will, hopefully, be published soon.¹⁾

Place for helium...

The entire (lack of a real) chemistry of helium is in accord with its placement in the Group 18 together with the other noble gases and in sharp disagreement with its placement in Group 2. True, its atomic configuration $1s^2$ is the same as the one in the alkaline earths (ns^2) with one crucial difference: it is in helium only that the first electron shell is completely filled (as in the rest of the noble gases, unlike any of the alkaline earth metals). Further, it is a gas (alkaline earths are solids). It is non-metal (alkaline earths are typical metals). The trend of "reactivity" is preserved when placed in Group 18. Thus, He and Ne have no real chemical compounds under 'mundane' conditions; Ar has a single one, HArF, stable at low temperatures (Khriachtchev et al., 2000); Kr has several and Xe has many). The atomic term of helium (${}^{1}S_{0}$) is the same as for both alkaline earths and noble gases, but that would be too weak an argument for insisting on its double assignment in groups 2 and 18. There is no *chemical* relation of helium to the alkaline earths whatsoever! One should accept therefore that the 'true place' of helium is in the Group 18 only.

...and for hydrogen

We start with a series of facts most of which picture the dissimilarities of hydrogen and the alkali metals/halogens:

(1) Hydrogen forms ionic compounds with typical metals (Group 1 and Group 2 elements). Surely, none of the alkali metals exhibits any similarity in this respect. This behaviour shows resemblance of hydrogen with the halogens. However, with the hydrogen in the anion (as H^- ion) there are marked differences from the (rest of) halides. First it is the reactivity of the ionic hydrides. They all react with water. Alkali fluorides, on the other hand, not only are water indifferent but *do not* react with OF_2 as well (OF_2 is the analogue of H_2O , if hydrogen was to be placed above the halogen group); neither do alkali chlorides react with Cl_2O etc. The behaviour is definitely different from the rest of both the alkali metals and the halogens.

- (2) The electronegativity of H is much higher than that of alkali metals, where it varies rather smoothly (in small steps) from Li to Cs. If put above fluorine, on the other hand, the trend of electronegativities in the group is seriously disturbed. H does not belong logically to either of the two groups. A similar reasoning works for the ionization energies, leading (once again) to the 'incompatibility' of hydrogen with the elements of the two groups.
- (3) Besides from forming stable hydrides with alkali metals, hydrogen forms very stable covalent compounds with the halogens.
- (4) Hydrogen is the only element that forms a specific type of bond (hydrogen bond) with highly electronegative donor and acceptor atoms. In this respect it is truly unique among all elements in the PT.
- (5) Most of the second period elements (particularly Li, Be, B and C) show a certain extent of 'exotic behaviour' and significant dissimilarities when compared to the rest of the group. For some of them (all of the above-mentioned) diagonal relationships have been identified: Li–Mg; Be–Al; B–Si and to a lesser extent C–P (Rayner-Canham, 2011). No clear-cut explanation exists so far for these dissimilarities, but part of it might be 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).
- (6) The electronic configuration and atomic term of hydrogen (${}^{2}S_{1/2}$) match those of alkali metals, but not of the halogens (${}^{2}P_{3/2}$).

Further, one should bear in mind that:

- (7) Classification is a human activity. It does not exist in nature as such. It might be useful: for most elements in the PT it indeed is and works very well; however, it can also pose problems if one insists on finding a place for every single element within this 'preselected' group scheme.
- (8) There are no real arguments, apart from a belief, that 'every element in PT belongs to some 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 the hydrogen! In relation to this, the Labarca & Srivaths approach is a real success. The questions are: can one do better than that? Hasn't this already been done earlier?
- (9) There are no simple criteria (like electron configuration, electronegativity, existence of triads) for classification of hydrogen to particular group of the PT, as already pointed out (Labarca & Srivaths, 2016).

Finally:

(10) We may be somewhat conservative, but we have to say that we prefer a form of the PT where all elements belonging to certain period are found in a single horizontal row (like in the traditional 'modern' form of PT). For practically all elements the number of the period they belong to corresponds to the number of 'electron shells' in its atom. By

electron shell we mean a set of electrons with a common value for n (n = the principal quantum number). Pd is the only exception! It is in the fifth period, but its fifth shell is empty, reading $5s^0$ and this exception can easily be explained by the minor energy differences between the 4d and 5s energy levels.

In a situation like this, relying heavily on chemistry arguments (some of which were mentioned above), we prefer to leave the hydrogen unassigned to any of the eight mentioned groups of the PT, as already done in the past (Kaesz & Atkins, 2003). Hydrogen is, simply, truly unique element: it is the only element with a single electron in the valence shell and no core electrons! We believe that this fact should be justified by giving it a special position in the PT.

NOTES

1. Petruševski, V. M. & Cvetković, J. (submitted to Contributions (Macedonia)).

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