On the position of helium and neon in the Periodic Table of Elements

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Abstract Helium and neon, the two lightest noble gases, have been traditionally positioned by IUPAC in the Group 18 of the Periodic Table of Elements, together with argon, and other unreactive or moderately reactive gaseous elements (krypton, xenon, radon), and oganesson. In this account we revive the old discussion on the possible placement of helium in the Group 2, while preserving the position of neon in Group 18. We provide quantum-chemical arguments for such scenario—as well as other qualitative and quantitative arguments—and we describe previous suggestions in the literature which support it or put it into question. To this author's own taste, He should be placed in Group 2.

Keywords Periodic Table · Hydrogen · Fluorine · Beryllium · Noble gases · Helium · Neon · Argon · Reactivity · Electronic structure · Ionization potential · Electron affinity

The traditional depiction of the periodic system, which has been taught to this author in primary school in the 1980s, has been the so-called short version (SPT), with the division to A (main group) and B (transition metal) Group elements (Fig. 1 top). This version follows to some extent the early formulation by Mendeleyev, and introduces Group VIII containing Fe, Co, Ni, and their heavier analogues. Here, noble gases stand out as Group 0, to emphasize lack of room for them in the original Mendeleyev's formulation; this happily coincides with their null (or weak at best) bond-forming ability. On the other hand, the Periodic Table recommended to this author during education in the comprehensive school

This work commemorates the 150th anniversary of the discovery of helium and the 120th of neon.

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Group 0	I a	II b	III b	IV b	V b	VI b	VII b	VIII
H 1								
He 2	Li 3	Be 4	B 5	C 6	N 7	O 8	F 9	
Ne 10	Na 11	Mg 12	Al 13	Si 14	P 15	S 16	Cl 17	
Ar 18	K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26, Co 27, Ni 28
	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	
Kr 36	Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	—	Ru 44, Rh 45, Pd 46
	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	
Xe 54	Cs 55	Ba 56	57–71*	Hf 72	Ta 73	W 74	Re 75	Os 76, Ir 77, Pt 78
	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	—	
Rn 86	—	Ra 88	Ac 89	Th 90	Pa 91	U 92		

group 1 1a																		18 VIIIa				
1s	1 H	2 He																				
2s, 2p	3 Li	4 Be															5 B	6 C	7 N	8 O	9 F	10 Ne
3s, 3p	11 Na	12 Mg	3 IIIb	4 IVb	5 Vb	6 VIb	7 VIIb	8 VIIIb	9 VIIIb	10 VIIIb	11 Ib	12 IIb	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar				
4s	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr				
3d, 4p																						
5s	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe				
4d, 5p																						
6s, 4f	55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn				
5d, 6p																						
7s, 5f	87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og				
6d, 7p																						

* 4f, 5d	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
* 5f, 6d	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Fig. 1 Top: Short version of the Periodic Chart. Bottom: Long version

a decade later was the so-called long version (LPT), with the transition metal elements clearly separated from the main group ones (Fig. 1 bottom, Roman numerals). Here, the A and B Groups still persisted. Finally, the freshman years of the 1990s brought another, more subtle, modification: the giant Periodic Table depicted in the Grand Aula of the Chemistry Faculty of the University of Warsaw corresponds to a long version, with noble gases placed in the last Group of the chart, the Group numbering now running from 1 to 18 in Arabic rather than Roman numbers (Fig. 1 bottom, Arabic numerals). Now, the old Group VIII encompasses three modern Groups: 8, 9 and 10. This version of the Table survived in the main didactic room to this day, except for a few elements being given their new IUPAC-recommended names (Francel 2009). It may seem that with the naming of the last superheavy elements in 2016, the history of the formulation of the Periodic Chart is closed, or at least it will rest until the new Period is opened due to a synthesis of a $Z > 118$ element (Seaborg 1969; Pykkö 2011).

In all versions routinely used today in the universities worldwide, helium, the $Z = 2$ element, is been placed together with other “noble” gases, i.e. neon, argon, krypton, xenon, radon (and Ununoctium, i.e. the recently named oganesson). However, this has not

necessarily been the case, if other historically important formulations of the Periodic Table are taken into consideration. Specifically, the so-called left-step form of the periodic table, LSPT (Janet 1928a, b, 1929; Tarantola 2000; Scerri 2005a; Stewart 2010) organizes elements according to the orbital filling (instead of theoretical maximum valence) and is sometimes used by physicists (Fig. 2 top and middle). This version strongly emphasizes the electronic structure of isolated atoms in the gas phase, and the fact of existence of the *s*, *p*, *d*, and *f* blocks of the Periodic Table. Scerri's modifications of the Table (both "symmetric traditional", and LSPT, for the latter see Fig. 2 bottom) seem to lose this feature while they position helium in a traditional way above neon (Scerri 2009). In addition, in these versions, hydrogen is placed together with halogens (we will return later to *pros* and *cons* of that).

Stowe's physicist's periodic table (PPT) goes even further than Janet into linking of the placement of elements with the modern understanding of the electronic structure of atoms, and it is three-dimensional with the three axes representing the principal quantum number, orbital quantum number, and orbital magnetic quantum number (Stowe 1989). Here, helium is again a Group 2 element, with neon falling into the same vertical Column as argon and heavier noble gases (Fig. 3 top). Similarly, the versions proposed by Le Cornec (Fig. 3 middle) (Le Cornec 2002), and Tarantola (Fig. 3 bottom) (Tarantola 2002), while they strive to take into account the first ionization potential of isolated atoms in the gas phase, they prefer placing helium above beryllium rather than above neon. This is also the case for all versions of the Chart proposed by Górski (not shown here) (Górski 2001). The selection between various forms of the Table is a matter of personal idiosyncrasies, as correctly noticed by many authors (for interesting comment, cf. Schwarz 2016¹).

A question naturally arises: *Is there any preferred placement of helium in the Periodic Table?* This question may, but does not need to be linked to an even more important one: *Is there any supreme ("most correct") version of the Table itself?* (cf. Scerri 2007).

Here, we will ponder mostly upon the first issue, while only touching on the second one. But before the answer is proposed, we must dwell a little into the physical and chemical properties of noble gases. As well as into some recent quantum mechanical calculations of noble gas containing molecules.

"Nobility" of certain elements has fascinated humans for millennia, gold serving as a base of monetary systems until the early XX century, but preserving its status as a reference measure of wealth to this day. The term "*noble gas*" has been coined at the end of the XIX century by Erdmann (cf. Renouf 1901) to describe the chemically inert gaseous elements known at that time (helium was discovered in 1868, argon in 1895, neon, krypton, and xenon in 1898, while radon in 1900) for which initially there was no room in the Mendeleev's Chart. For nearly one century since the discovery of helium chemists attempted to turn noble gases into chemical compounds, but they all failed, albeit some came very close. It was in the outburst of genius that Bartlett decided to react xenon with a small sample of PtF₆ which resulted in the isolation of the first noble gas compound (Bartlett 1962), what proved to be a mixture of several distinct compounds (Bartlett et al. 1976), as it was finally confirmed only half a century from the initial discovery (Graham et al. 2000; Craciun et al. 2010; Seppelt 2015). The noble gas chemistry—particularly that

¹ My impression was that you like the so-called left-step or Janet form of the Periodic Table (PT), which fulfills one of the three requirements on PTs (1. arrange the elements according to Z, 2. in a beautiful form, 3. exhibiting some chemical trends)—very well, namely symmetric beauty. A drawback of this form is that the physical origin and background of the chemical trends is less well reproduced. Of course, the final decision on the preferred form of the PT depends on the relative weights, one puts on the criteria of beauty and chemistry.

Charles Janet's
left-step periodic table, 1929

The top part of the figure shows Charles Janet's left-step periodic table from 1929. It is a single continuous block of elements arranged in rows and columns. The noble gases (He, Ne, Ar, Kr, Xe, Rn) are placed at the end of each row. The elements are color-coded: s-block (green), p-block (blue), d-block (yellow), and f-block (purple). The table is labeled with atomic numbers and element symbols.

The middle part of the figure shows a diagram of the periodic table with the s, p, d, and f blocks highlighted. The s-block is green, the p-block is blue, the d-block is yellow, and the f-block is purple. The diagram shows the relative positions of these blocks and the elements within them.

The bottom part of the figure shows Scerri's modification of the periodic table. It is a single continuous block of elements arranged in rows and columns, with the noble gases (He, Ne, Ar, Kr, Xe, Rn) placed at the end of each row. The elements are color-coded: s-block (green), p-block (blue), d-block (yellow), and f-block (purple). The table is labeled with atomic numbers and element symbols.

Fig. 2 Top and Middle: two left-step forms of the Periodic Chart. Bottom: Scerri's modification

of xenon and krypton, and including organoxenon chemistry (Naumann and Tyrre 1989; Frohn and Jakobs 1989)—has flourished since 1962 (Christe and Wilson 1982; Christe et al. 1991; Dixon et al. 2007), and even argon has proved to form a stable chemical compound, HArF, at sufficiently low temperatures (Khriachtchev et al. 2000)—it remains the only isolated chemical compound of noble gases, their chemistry has been extensively reviewed during the last three decades (Laszlo and Schrobilgen 1988; Lehmann et al. 2002; Schrobilgen and Moran 2003; Grochala 2007; Grochala et al. 2011; Brock et al. 2013; Hope 2013; Haner and Schrobilgen 2015). Moreover, the experimental and theoretical chemistry and physics of noble gas compounds at high pressure started to flourish (Kim et al. 2010; Kurzydłowski et al. 2011; Dong et al. 2017; Zhu et al. 2013, 2014; Hermann

<i>s</i>		<i>p</i>				<i>d</i>										<i>f</i>									
H	He																								
Li	Be	B	C	N	O	F	Ne																		
Na	Mg	Al	Si	P	S	Cl	Ar																		
K	Ca	Ga	Ge	As	Se	Br	Kr																		
Rb	Sr	In	Sn	Sb	Te	I	Xe																		
Cs	Ba	Tl	Pb	Bi	Po	At	Rn																		
Fr	Ra																								

Fig. 3 Top: Stowe's, Middle: Le Cornec's, and Bottom: Tarantola's versions of the Periodic Chart

																1	2																						
																H	He																						
																3	4	5	6	7	8	9	10																
																Li	Be	B	C	N	O	F	Ne																
																11	12	13	14	15	16	17	18																
																Na	Mg	Al	Si	P	S	Cl	Ar																
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36																						
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr																						
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54																						
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe																						
55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72																						
Cs	Ba	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf																						
73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90																						
Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn																										

Fig. 3 continued

and Schwerdtfeger 2014; Li et al. 2015; Dewaele et al. 2016; Kurzydłowski and Zaleski-Ejgierd 2016), following the preliminary exploration a decade ago (Grochala 2007). One particularly interesting case is that of Na_2He at very high pressures, which is called “stable” and “compound” by the authors (Dong et al. 2017), despite the fact that (1) high pressure is necessary to keep this species intact, and that (2) diverse bonding analyses point out to the lack of chemical bonding in this system. Peculiar Na_2He calls for making our definitions of “compound” more precise (more on that anon in the last section).

Despite these impressive developments, neon and helium have *not* been forced to form genuine chemical bonds in *neutral entities* to this day. The status of the ingenious but fruitless efforts as of 1990 has been summarized in the insightful review (Frenking et al. 1990). It is important to realize here that the genuine challenge in formation of noble gas species is connected with *electrically neutral systems*. This issue is similar in some aspects to the following one: what is the largest oxidation state which may be achieved for a given element? While this question is certainly very important, it should be specified that only *electrically neutral* isolable entities constitute real challenge in this matter; take uranium: it is not a major problem to generate U^{92+} cations by physical means. However, it is a paramount obstacle to go beyond the formal oxidation state of U^{6+} in neutral compounds of this element using chemical means. By a similar token, it is very easy to generate chemical bonds to helium, or to neon, letting alone argon and heavier noble gases—but one must use naked cations to bind them. To give an example: HAr^+ is an extremely common cationic species in gas spectrometry, which inevitably appears in every experiment conducted in the flow of “inert” argon gas. Similarly, HHe^+ —isoelectronic to H_2 —is very strongly bound, with the perfectly normal two-electron sigma bond, and the bond dissociation energy approaching 2 eV (as it has been calculated already in the early days of quantum mechanics over a century ago). HHe^+ is by no means elusive—it has been first observed in 1925. Indeed, a multitude of *helides*, i.e. MHe_n^{m+} cations, should be easy to prepare, as well, as they are usually very stable with respect to dissociation (Frenking et al. 1990; Wilson et al. 2002). Obviously, analogous cationic species containing neon or argon are even more facile to manufacture than those of helium, since Lewis basicity (measured by proton affinity) of light noble gas atoms increases in the order: He (1.84 eV) < Ne (2.06 eV) $\ll$ Ar (3.83 eV). Consequently, there is a vast literature on theoretical predictions of novel light noble gas-containing cations (Borocci et al. 2010; Rzepa 2010; Pan et al. 2016; these efforts were reviewed: Lewars 2008) and experimental reports, as well (Cunje et al. 2001; Roithová and Schröder 2009; Lockyear et al. 2010), to mention just a few examples. However, the neutral (solid state) analogues of helides (stabilized by counteranions) do not exist albeit their first xenon analogues were successfully prepared (Seppelt and Seidel 2000; Hwang et al. 2003).

Noticing the usual stability order of light noble gas species: cationic $\gg$ anionic > neutral (Grochala 2009a), it is not surprising that also some anions were predicted to constitute local minima on the potential energy surface (Liu et al. 2012). The most

remarkable cases are those of FNgO^- (Li et al. 2005) and of related $\text{F}^-(\text{NgO})_n$ (Liu et al. 2007) where $\text{Ng} = \text{He}, \text{Ar}, \text{and Kr}$. These species are bound on the singlet potential energy surface but the ground state of the system corresponds to triplet, $\text{F}^- + \text{Ng} + {}^3\text{O}$. An independent suggestion of metastable FNgO^- anions came later from theorizing a possible oxidation state of chemical elements is easier achieved in anionic than in neutral species (Grochala 2009a). Thus, FNgO^- may be viewed as a product of insertion of He into the O–F bond of the OF^- anion, itself a derivative of a metastable HOF acid.

Having understood that this is not difficult for noble gas atoms to form chemical bonds per se, but this is quite challenging to achieve bonding in *neutral moieties* (i.e. *chemical compounds*), we turn to the latter. Unfortunately, most of such connections are bound by weak forces and they may be classified as van der Waals complexes (Zou et al. 2013; Cappelletti et al. 2015). This is e.g. the case of adducts of Group 11 halide molecules with light noble gases—the binding energies do not surpass 0.25 eV (for ArAgF , Evans and Gerry 2000; Lovallo and Kłobukowski 2003; Belpassi et al. 2008), and they are calculated to be even smaller for Ne and He (Zou et al. 2009). Nevertheless, the adduct of Ne with AuF has been observed experimentally (Wang et al. 2013) and its dissociation energy has been estimated to be smaller than 0.1 eV. Regretfully, the infra-red absorption bands corresponding to $\text{Ne}\cdots\text{Au}$ stretching and $\text{Ne}\cdots\text{Au}\cdots\text{F}$ bending modes have not been observed.

These were Frenking and colleagues (Koch et al. 1986; Frenking et al. 1988) who were the first to theoretically study molecules bearing light noble gas atoms attached to coordinatively unsaturated metal centers, notably Be^{2+} , in neutral molecules. An analogous matrix species containing argon, ArBeO , was prepared (Thompson and Andrews 1994) following the above-mentioned theoretical proposal that the strong electric field outside the small, highly charged Be^{2+} cation of BeO could bind rare-gas atoms through their electric dipole polarizability. But the calculated Ar-Be bond energy is only 0.3 eV, and the bond can only be considered as anomalously strongly bound van der Waals complex rather than covalently bound moiety. This is also the case of the related NeBeS adduct which exhibits an even smaller value of the bonding energy (Wang and Wang 2013). No helium adducts of this kind were ever prepared, albeit they have been theorized. Similarly, isoelectronic adducts of the type RNBeNG (where R is an electronegative substituent) were studied theoretically (Antoniotti et al. 2003), with the conclusion that they might constitute viable experimental targets. Not surprisingly, for all complexes which are weakly bound via polarization forces, stability of helium adducts is somewhat smaller than that of the respective neon ones (helium has just two electrons, while neon has ten).

The neutral compounds of helium and neon bearing strong covalent bonds to noble gas atom were considered nearly half a century ago (Liebman and Allen 1970). These authors have noticed that the ${}^1\Sigma$ singlet states of NGF^+ ($\text{NG} = \text{He}, \text{Ne}$) cations exhibit short equilibrium bond lengths (1.33 Å for He; 1.65 Å for Ne, indicative of covalent bonding) and they are bound by over 1.2 eV (albeit helium species slightly more than the neon one!); these authors have speculated that salts of these cations might be prepared. These predictions were never confirmed in experiment. One major difficulty in obtaining such salts sits in immense oxidizing power of NGF^+ cations, and another in the fact that their ground state corresponds to a dissociative triplet state, and it is placed over 2 eV below the above-mentioned singlet. Thus—if preparable—these salts would likely be thermally unstable or even explosive. Following a similar line of reasoning it was pointed out that the ArH^+ salts in the solid state (letting alone the NeH^+ and HeH^+ ones!) are unlikely to be prepared since we currently do not have a Lewis acid powerful enough to withdraw F^-

anion from the neutral HArF molecule (Christe 2001). In other words, the salts bearing NGF^+ or NGH^+ cations ($\text{NG} = \text{Ar}, \text{Ne}, \text{He}$) would, by necessity, be thermodynamically unstable albeit possibly metastable (Frenking et al. 1989). For example, ArFSbF_6 was estimated to be unstable by over 1 eV with respect to Ar , F_2 and SbF_5 . It is completely unclear at this moment what reaction pathways could be used to generate such metastable species, since even more unstable precursors should possibly be used for a facile (downhill) reaction. For example, superhalogens were suggested as one possible substrate of this reaction (Samanta 2014) but this strategy has not yet been tested in theoretical calculations for the two lightest noble gases.

With HArF successfully isolated, HNeF and HHeF became obvious targets. The first theoretical study has indicated that HHeF is a local minimum at the potential energy surface, while its neon analogue is not (at the CCSD level of theory) (Wong 2000). However, the ZPE-corrected energy barrier for the highly exoenergetic dissociation (by nearly 7 eV!) to HF and He amounts to 25.3 kJ mol^{-1} which may not be sufficient for isolating of this molecule (Wong 2000). Subsequent studies using multireference methods have showed that the barrier is even smaller than initially thought, and the predicted lifetime of HHeF is only 157 fs (Takayanagi and Wada 2002). It was also suggested that HHeF cannot be sufficiently well stabilized by complexation (Giordani et al. 2010). Some authors considered placing (or in situ generating of) HHeF molecules in the helium matrix and applying high pressure (Bihary et al. 2002). Albeit the bonds to NG are stiffened at high pressure, this strategy has multiple problems, such as for example necessity to keep the HHeF molecules strictly isolated from one another. Moreover, subsequent calculations have showed that HHeF molecules are far from being thermodynamically stable even at huge pressure of 500 GPa (Grochala 2014). Last but not least, HNgCl molecules were also theoretically studied (McDowell 2001); the CISD results suggest that, just like in the case of fluoride derivative, the stoichiometry containing neon does not correspond to a minimum at the potential energy surface, while the helium species is a genuine minimum. Both authors (Wong 2000; McDowell 2001) tend to assign the lack of stability of neon species to a weaker electrostatic attraction between H^+ and F^- (or Cl^-) due to a larger radius of neon than that of helium (and thus a larger anion–cation separation). The HNgX molecules described in this section fall into category of push–pull systems, with the predominant resonance structure of the type: $[\text{H}^+ \leftarrow \text{Ng}] \cdots \text{X}^-$. In this way, NG atom with the stable doublet (He) or octet (Ne) electronic configuration avoids being pushed into a hypervalent bonding (for a critical discussion of a concept of hypervalence cf. Gillespie and Silvi 2002).

The last type of molecules containing covalently bound He, which have been theorized in the past, are the derivatives of helium monoxide, HeO, with small molecules which exhibit substantial dipole moment (Grochala 2009a, 2012). These include: $(\text{HeO})(\text{MF})$ where $\text{M} = \text{Cs}, \text{NMe}_4$, as well as $(\text{HeO})(\text{LiF})_2$. The $(\text{HeO})(\text{MF})$ systems may be viewed as derivatives of the previously discussed OHeF^- anion (Li et al. 2005) with the large and soft cation, which does not destroy the integrity of the anionic species. The proposed synthetic pathway towards $(\text{HeO})(\text{MF})$ systems relies on a photochemical reaction between He and MOF molecule, where the $\sigma \rightarrow \sigma^*$ excitation of the O–F bond would permit the insertion of noble gas atom and formation of the metastable target species (Grochala 2009a). This observation has led this author to postulate that neon is in fact the most noble of noble gases, and it should be the first member of the Group 18, with helium moved to the Group 2 of the Periodic Table (Grochala 2009a, b, 2013).

On the other hand, metastable $(\text{HeO})(\text{LiF})_2$ is best described as HeO molecule embedded into a ferroelectric cavity composed of two parallel LiF dipoles (Grochala

2012). This interesting minimum on the potential energy surface features a short covalent He–O bond at ~ 1.15 Å; the bond is slightly polarized with the electrons transferred *from helium to oxygen* ($\text{He}^{\delta+}\text{O}^{\delta-}$). This suggests that neutral helium atom is a lone pair donor towards an unusual Lewis acid: a singlet oxygen atom ($\text{He} \rightarrow {}^1\text{O}$). The $(\text{HeO})(\text{LiF})_2$ molecule is also different from other neutral species bearing helium by the fact that the noble gas atom has only one close neighbor and the *trans* position is free (this helps to avoid hypervalence at helium). Remarkably, the neon analogue does not correspond to a minimum (Grochala 2012) but the heavier noble gases form the minima on the singlet potential energy surface (Szarek and Grochala 2015). Moreover, there is a striking similarity between the molecular geometries of $(\text{HeO})(\text{LiF})_2$ and $(\text{BeO})(\text{LiF})_2$ (Fig. 4). Helium seems to show affinity to oxygen, just like beryllium does. This observation, again, led this author to reconsider the position of helium and neon in the Periodic Table (cf. parts S13–S15 of the electronic supplementary information; Grochala 2012). If such $\text{He} \sim \text{Be}$ analogy were pushed further, one might evaluate the ionic radius of He^{2+} to be about 0.06 Å (the ionic radius of Be^{2+} is quoted at 0.41 Å, while the bond length difference between Be–O and He–O bonds is computed to be about 0.35 Å, Fig. 4). The value obtained is reasonably close to the expected value of ~ 0.0 Å.

The striking relative inertness of neon—in cationic, anionic and neutral systems—has been noticed before by several authors independently (Frenking and Cremer 1990; Wong 2000; Lundell et al. 2000; McDowell 2001; Li et al. 2005; Liu et al. 2007; Borocci et al. 2008). Notably, a hypothetical $(\text{F}^{\cdots}\text{NeBN})$ anion remains the only metastable anionic species which contains chemically bound Ne atom—an analogous He species is predicted to be much more strongly bound (Antoniotti et al. 2007). The inertness of neon has been traditionally assigned to the Pauli repulsion involving $2p$ shell—note: helium lacks p electrons, hence Pauli repulsion is greatly reduced. Interestingly, none of these authors has suggested that this implies that neon is the most inert noble gas. It was finally Grandinetti who admitted such possibility (Grandinetti 2013), he failed, however, to specifically cite all earlier proposers (Bent 2006; Scerri 2007; Grochala 2009a, b, 2012), which resulted in an exchange of correspondence between Roald Hoffmann, Felice Grandinetti and the journal editor (Pichon 2013).

Let us reanalyze here different aspects of various placements of helium and neon in the Periodic Table (Fig. 5), as quantified by the first ionization potential and the first electron affinity of elements from Groups 1, 2, 17 and 18 (Fig. 6), issues of scientific priority aside. We have focused primarily on these two energy-related parameters of atoms, as they govern many physical and chemical properties of elements. To clearly observe the *trends of properties* we always normalize the absolute values to the value exhibited by the first (lightest) member of the series and we then draw the plots with respect to the period number of the Periodic Chart. Graphs on the left in Fig. 6 correspond to situation C) from Fig. 5, those in the middle to B), and those on the right to the traditional variant A).

Let us begin the discussion of the trends in the first ionization potential. Placement of H over Li and He over Be leads to the following picture: the normalized I_p drops considerably between H and Li and between He and Be (emphasizing the well-known substantial discrepancy between the properties of elements from Period 1 and Period 2), and then drops more smoothly for the subsequent periods (only Period 7 elements slightly bend this trend as compared to their Period 6 counterparts due to well-known relativistic effects). Similar trends is seen for Groups 17 and 18, albeit the fall of normalized I_p is not as dramatic (recall, we now start with Period 2 elements, F and Ne, as the first members of their series). Remarkably, Group 1 and Group 2 elements show (quantitatively) very similar behaviour, so do Group 17 and Group 18 elements. This emphasizes the fact that

Fig. 4 Comparison of the calculated molecular geometry of $(\text{HeO})(\text{LiF})_2$ and $(\text{BeO})(\text{LiF})_2$ (reproduced with permission from Grochala 2012)

(A)

1	2		17	18
H				He
Li	Be	...	F	Ne

(B)

1	2		17	18
			H	He
Li	Be	...	F	Ne

(C)

1	2		17	18
H	He			
Li	Be	...	F	Ne

(D)

1	2	0	17	18
		H		He
Li	Be	...	F	Ne

Fig. 5 Four possible positions of He in the Periodic Table of Chemical Elements: **a** classical version placing H in Group 1 and He in Group 18; **b** alternative version, which emphasizes similarity of H to halogens; Scerri's proposal differs but preserves the placement of H, F, He and Ne (Scerri 2009); **c** version placing He out of the noble gas group, close to H and simultaneously above Be (and not above Ne); **d** IUPAC-supported version placing H in a distinct group No. 0, while He stays in Group 18. The theoretical (computational) results described here support version (c) (reproduced with permission from Grochala 2009a)

for the former it is the s shell which is ionized, while for the latter it is the p shell. Precisely this argument has been used by Bent (Bent 2006) who was fierce advocate of situation C) in Fig. 5.

If, however, we accept that H should be placed together with halogens while helium should join other noble gases, the picture of normalized I_p changes substantially. Although the normalized I_p values fall as before with the increase of the Period number, yet there appear marked (quantitative) differences between the first two groups of elements (Groups 1 and 2), as well as between the latter two (Groups 17 and 18).

Fig. 6 The normalized I_P (top) and E_A (bottom) values for atoms representing the chemical elements from Groups 1, 2, 17 and 18 (*cf.* text for details of normalization). Since the E_A values are predominantly null for the elements of Groups 2 and 18, and the normalization to the value shown by the first member is not possible, we have not plotted these values here. The **c**, **b** and **a** variants from Fig. 5, are explicitly showed

Table 1 Some Pros (Y) and Cons (N) of placing He above Be, or above Ne, in the Periodic Table

Feature	He in Group 2	He in Group 18
Clear separation of s and p blocks (Lewis doublet vs. octet)	Y	N
Clear separation of Period 1 and 2 elements	Y	Y
Consistently large gap between properties of Period 1 and 2 elements	Y	N
Trends of absolute I_p preserved	Y	Y
Trends of normalized I_p preserved	Y	N
Highest- I_p gas opens the Group 18	N	Y
Most inert* gas opens the Group 18	Y	N
All historical noble gases are in one Group	N	Y

* In terms of the discussed propensity of He and Ne for chemical bond formation, as discussed above in this work based on theoretical results

Finally, if we decide to follow the traditional placement with H in Group 1 and He in Group 18, the discrepancies between the trends seen for Group and Group 2 are even larger than in the previously discussed case. And the (natural) large drop of the normalized I_p between H and Li is not seen for Group 2, since He is no longer in this Group.

The supplemental analysis of the normalized E_A concerns two major situations: H is placed in Group or in Group 17. The placement of He does not matter here since its E_A is null, and therefore it fits either Group 2 (with Be showing the same value) or Group 18 (Ne having the same feature). Among the two situations the one with H placed in Group 1 seems more natural, as the normalized E_A value drops slowly for Group 1 elements (again, except the reversed trend from Period 6 to Period 7 due to relativistic effects). However, if H is placed in Group 17, as advocated by some, the normalized E_A skyrockets up to nearly 5, since the values for F and Cl are much larger than that for H. Thus, the traditional placement of H in Group 1 does indeed have more pros than cons, and more supporters.

Taking this altogether, it seems that placement of H over Li and He over Be leads to the most balanced picture, with natural trends for both the normalized I_p and the normalized E_A as one goes down the four respective Groups of the Periodic Chart.

So, what do we have to lose by placing He over Be? Some Pros and Cons are displayed in Table 1.

As it may be seen in Table 1, there are a few Pros as well as some Cons against the placement of He in Group 2. One particular Con is that with placement of He above Be, the first (historically) gaseous noble element, helium, discovered 150 years ago, would be absent from the group colloquially called “noble gases”. Simultaneously, in the traditional constructions of the periodic Chart (Fig. 1), the elements with the largest I_p values are expected to appear in the upper right corner; while in this case the highest- I_p element, helium, would be elsewhere (this is irrelevant, though, to the left-step forms, where each block has its right top corner).

However, among numerous Pros for placing He above Be, one notices that such placement reproduces consistently the large gap between properties of Period 1 and 2 elements. In other words, nonmetals open Groups 1 and 2 (where mostly metals reside). Hydrogen is as much an alkali metal as helium is an alkali earth metal (as Fig. 6, top left part clearly shows).

As Schwarz has insightfully put it in his e-mail exchange with this author (2016), there are as many versions of the Table as many features you expected to be assembled, rationalized, and taught to students. This is definitely true. There is no single way to solve

this puzzle. So I am following personal idiosyncrasies here.² What an experimentalist in me expects from the Periodic Table when I teach students, is that—aside from its key feature, periodicity—I may easily follow the trends of element properties as I go down the Group. And that they will make qualitative and semi-quantitative sense (while relativistic effects may be blamed for small deviations seen for the heaviest elements). And as a computational chemist, I value clear separation of elements with s, and p shells being systematically occupied by electrons. In this way also the Lewis's doublet (for H^- , He,

² A dispute between the Reviewer (R) and the Author (A).

The presented manuscript received valuable comments during the peer-review process. They represent interesting and critical point of view. Some of them are given below, together with the responses from the author. The purpose of presenting this debate is to illustrate the complexity of argumentation which may arise when one faces the choice of the “best” place of helium in the Periodic Table.

R: There is some feeling of unreality about the debate where to put He, both in this paper and in general discussions in the literature. The viability of the Periodic Table lies in its being an organizational paper tool for similarities that accepts differences. So no inorganic chemist is put off by Si going 5- and 6-coordinate, which C remains quadrivalent, or that PbO does not dissociate into $Pb + PbO_2$.

A: This is certainly true that the construction of the Table began as organizational paper tool (the mature form of the Table was about to serve to Mendeleyev's students). However, the major effort beyond creation of the Table was driven by quest for similarities and not for differences. Only after the similarities helped to build the Table, one could dwell into differences. I do not share the reviewer's feeling of unreality about the debate where to put He is such sense that this debate may be simplified to a question: which organizational paper tool is more practical and helps us to more emphasize similarities? This author claims simply that more essential similarities are better revealed by placement of He in Group 2. But there are certain, rare but important, properties, such as the very notion of inertness, which are better reflected by traditional placement of He.

R: Difference is accepted as one goes down the Table, why not accept it as one goes up, as is the case with He?

A: This is important argument. However, the departure from trends in chemical properties for heavy elements (as one goes down the Group) are well understood based on the impact of relativistic effects. However, important trends do not change for the lightest Group members, hence if we start accepting that for He, we may rebuild the entire Periodic Table to accept even more. Personally, I dislike such post-modernistic possibility.

R: I do not like the identification in italics of “chemical compounds” with neutral molecules. Charged molecules (or bonded ions from carbonate to borohydride) have a right to be called compounds. Perhaps some effort in fact might be directed to making salts of the stable noble gas ion molecular units.

A: The referee is right about the effort of making salts of the stable noble gas ion molecular units – this was discussed extensively by Christe (and it is cited here). Also, $HArF$ may be viewed as a salt of ArH^+ , as this is the most important resonance structure of this molecule. But this does not change the attitude of most chemists towards ions – since you cannot isolate 1 mol of them in the bottle, they are not compounds. They are molecules, but not compounds. The ArH^+ cation has been flying around for 100 years in the chambers of the mass spectrometers, as it is very stable. Yet this is neutral $HArF$ which is considered by the community to be the first isolable compound of Ar. Otherwise, no one would pay attention to this discovery.

I understand the reviewer's hesitance to discard ions as “compounds”; but I think this is a matter of nomenclature. I agree with those who restrictively claim that only neutral species may be called compounds. And also with those who agree that ions have chemistry (obviously!), and mass spectroscopists do genuine chemistry. But there is no contradiction between these two claims!

R: There might be some chemistry of He anion, which is not bound in its ground state, but one excited state has a reasonable lifetime.

A: I agree but I would not like to dwell into excited states. Excited states always have rich chemistry, so if one examines neutral He atom (with its unreactive doublet) and excites it to the $1s12s1$ configuration, it may even form a doubly bonded He_2 molecule! Indeed, the diagram of electronic states of He_2 reveals many bonded excited states. But this is usually not discussed while thinking of the element's position in the Table, since any element shows rich chemistry in its excited states. Excited He and Ne are not inert at all. While the Table reveals mostly the ground state properties.

Li^+ , etc.) (Lewis 1916, 1923) is clearly separated from the octet (for F^- , Ne, etc.). Thus, to my personal taste, Periodic chart should look like in Fig. 5c, revealing both the Periodic law and the more subtle tendencies associated with element properties (cf. Wang and Schwarz 2009; Schwarz 2013; Pyykkö 2011, 2012).

Acknowledgements When this manuscript was in review, the author became conscious of the important contribution (Novaro 2008) where the author advocates the placement of helium in Group 2 based on subtle nevertheless sound arguments related to many-body contributions to interatomic interactions. This paper also contains mentions to a valuable philosophical work by Scerri (Scerri 2005b) which also escaped my attention. Simultaneously, two important references (Bartlett 1998; Vos et al. 1992) discussing weakly interacting He atoms (dispersive interactions in HeBeO , and van der Waals compound of He and N_2) were also brought to my attention. The author would like to acknowledge Roald Hoffmann for recommending the Bent's book, and he appreciates the discussions with W. H. Eugen Schwarz. This research has been funded from the statutory funds of the CeNT, University of Warsaw. Prof. Davide Prosepio kindly brought to my attention the above-mentioned works by Novaro (2008) and Furtado et al. (2015), while Dr. Zoran Mazej reminded me of comment from Bartlett (1998) and contribution from Vos et al. (1992).

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