Concerning Electronegativity as a Basic Elemental Property and Why The Periodic Table is Usually Represented In Its Medium Form

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Abstract

Electronegativity, described by Linus Pauling described as "*The power of an atom in a molecule to attract electrons to itself*" (Pauling 1960), is used to predict bond polarity. There are dozens of methods for empirically quantifying electronegativity including: the original thermochemical technique (Pauling 1932), numerical averaging of the ionisation potential & electron affinity (Mulliken 1934), effective nuclear charge & covalent radius analysis (Sanderson 1955) and the averaged successive ionisation energies of an element's valence electrons (Martynov & Batsanov 1980), etc. Indeed, there are such strong correlations between numerous atomic parameters – physical and chemical – that the term "electronegativity" integrates them into a single dimensionless number between 0.78 and 4.00 that can be used to predict/describe/model much of an element's physical character and chemical behaviour.

The design of the common and popular medium form of the periodic table is in large part determined by four quantum numbers and four associated rules. However, adding electronegativity completes the construction so that it displays the multi-parameter periodic law operating in two dimensions, down the groups and across the periods, with minimal ambiguity.

Key Words

Electronegativity, Periodic Table, Element, Substance, Periodicity

Basic Elemental Substance, Simple Elemental Substance

Scerri has reintroduced the idea that philosophers of chemistry consider the chemical elements in two distinct ways (Scerri 2005; Scerri 2009). First, there is the element as the **basic substance**, that is the *abstract or transcendental element*, the *essence of the element*, *the element as a bearer of properties but not having any actual properties, except for atomic number*, Z. Chemical symbols and names (H, hydrogen, Au, gold, etc.) are assigned to the basic element. Secondly, there is the notion of the element as the **simple substance**: a *real* piece of sodium metal placed on a table has numerous, measurable, intrinsic properties such as: density, conductivity, ductility, melting point, molar volume, chemical reactivity, etc. Crucially, only the ***basic elemental substance*** survives in a compound: Sodium's metallic properties and 'chlorine, the green gas' do not exist in the ionic material, sodium chloride, NaCl (Scerri, Personal Communication 2005).

- The metaphysical view about the nature of the elements as ***basic substances*** and ***bearers of properties*** goes back to the ancient Greeks, long before the discovery of atoms.

- Paneth considered *grundstoff* or basic substance as "the indestructible stuff present in compounds and simple substances" and *einfacher stoff* or simple substance as "that form of occurrence in which an isolated basic substance uncombined with any other appears to our senses". The in light of knowledge about atomic structure, the basic/transcendental/abstract property of an element changed from atomic weight/mass to atomic number, Z (Paneth 1962; Brakel 2012). Other authors prefer the terms "*element*" for the basic elemental substance and "*free element*" for the simple elemental substance (Hendry 2012).

- Considering the chemical elements as basic substances represents a set of ***natural kinds***, a well-understood philosophical position concerning the nature of classification. Elements as simple substances fail the *natural kinds* test, due to the existence of isotopes, allotropes, issues of purity, etc.

There is a problem with the above logic with respect to the periodic table of the elements. If atomic number, Z, is the only property of *the element as the basic substance*, then the periodic table of basic elemental substances should consist of a simple list: Z = 1, 2, 3… (H, He, Li…). There is little doubt that the periodic table shows the elements as their *natural kinds* and is therefore showing the basic elemental substance. Yet, as its name states, the periodic *table* is an ordered two-dimensional schema, and there are many rational three-dimensional formulations.

Thus – *and this is the thesis presented in this paper* – the ordered structure of the periodic table must be due to the chemical elements having some basic elemental property in addition to the atomic number, Z, that explains why the periodic table is so commonly formulated as it is.

Four Quantum Numbers and Four Rules

Experimentally, the closest that we can get to the element as the transcendental, basic substance is by studying the gas phase, mono-atomic species, M(g), the simplest of simple elemental substances. Spectroscopic, ionisation and electron affinity methods explore the behaviour of the electrons surrounding the positively charges nucleus of the gas phase atom. The electrons are found to associate *via* four quantum numbers and four rules.

The four quantum numbers, the Principle, Azimuthal, Magnetic & Spin, describe the topology and geometry of the various atomic orbitals:

Name	Symbol	Orbital Meaning	Range of Values	Value Example
Principal Quantum Number	n	Shell	$1 \leq n$	$n = 1, 2, 3, \ldots$
Azimuthal Quantum Number (angular momentum)	ℓ	Sub-shell (s orbital is listed as 0, p orbital as 1 etc.)	$0 \leq \ell \leq n - 1$	for $n = 3$: $\ell = 0, 1, 2$ (s, p, d)
Magnetic Quantum Number, (projection of angular momentum)	m_ℓ	Energy shift (orientation of the sub-shell's shape)	$-\ell \leq m_\ell \leq \ell$	for $\ell = 2$: $m_\ell = -2, -1, 0, 1, 2$
Spin Projection Quantum Number	m_s	Spin of the electron (−½ = counter-clockwise, ½ = clockwise)	−½, ½	for an electron, either: −½, ½

Electrons add to the atomic orbitals described by the quantum numbers, according to four rules: the Pauli exclusion principle, the Aufbau principle, Hund's rule and Madelung's rule:

Pauli Exclusion Principal	Electrons, which are fermions, cannot occupy the same quantum state simultaneously. Thus, orbitals are able to contain a maximum of two electrons but they must be of opposite spin.
Aufbau or **Build-up Principle**	Electrons enter and fill lower energy orbitals before higher energy orbitals.
Hund's Rule or the Rule of Maximum Multiplicity	If degenerate (equal energy) p or d-orbitals are available, electrons will enter the orbitals one-at-a-time so as to maximise degeneracy and spin, and only when all the orbitals are half filled will pairing-up occur.
Madelung's Rule	Orbitals fill with electrons as $n + \ell$, where n is the principal quantum number and ℓ is the subsidiary quantum number. This experimentally discovered relationship illustrates how, but does not explain why, the 4s orbital has a lower energy than the 3d orbital. $(n = 1) + (\ell = 0) = 1$ **1*s*** $(n = 2) + (\ell = 0) = 2$ **2*s*** $(n = 2) + (\ell = 1) = 3$ **2*p*** $(n = 3) + (\ell = 0) = 3$ **3*s*** $(n = 3) + (\ell = 1) = 4$ **3*p*** $(n = 4) + (\ell = 0) = 4$ **4*s*** $(n = 3) + (\ell = 2) = 5$ **3*d*** $(n = 4) + (\ell = 1) = 5$ **4*p***

	$(n = 5) + (\ell = 0) = 5$ **5*s*** Giving the order with which the orbitals fill with electrons as: **1*s* 2*s* 2*p* 3*s* 3*p* 4*s* 3*d* 4*p* 5*s*…**

This paper is not about the epistemology of quantum mechanics. Indeed, the four quantum numbers and the associated four rules are held to be *a priori*. As Richard Feynman was quoted as saying on many occasions (Feynman 1965): "Nobody understands quantum mechanics", in the sense that while we can observe, tabulate and make predictions from the quantum patterns that do arise, we cannot explain *why* they arise as they do because there is no deeper theory that lies behind quantum mechanics. Thus, it is our position that the four quantum numbers and the four rules by which electrons add to orbitals are an inevitable consequence of the atomic number, Z. They are an atom's "quantum signature" and so are basic and transcendental properties of Z. An illustration:

> The element Z = 3 is called lithium and it has the symbol Li.
>
> Element Z = 3 has a nucleus with three protons, so it has a charge of +3 and so attracts three electrons to achieve electrical neutrality. These three electrons adopt the ground state configuration: $1s^2\ 2s^1$ around the Li^{3+} nucleus. The $1s^2\ 2s^1$ configuration is empirical in that it can be observed in the 1st, 2nd & 3rd ionisation energies of Li(g) *and* it is theoretical in that it can be modelled using the Schrödinger wave equation with its multi-particle extensions. Crucially, both the Li the basic/transcendental substance and Li(g) the simple gas phase substance have the $1s^2\ 2s^1$ electronic configuration.

Periodic Table Formulations

The Internet Database of Periodic Tables (Leach 2004) has numerous formulations with names such as: “Elements Ordered By Their Sub-Shell” and “The Quantum Table of The Elements”. Many of these tabular, circular, spiral & 3-dimensional helical formulations are excellent, inventive and are true periodic tables in that they are contiguous with respect to Z and usually show the elements grouped into blocks (Note 1).

Historically the first periodic table that is *properly ordered with respect to quantum mechanics* by showing the sequence 1*s* 2*s* 2*p* 3*s* 3*p* 4*s* 3*d* 4*p* 5*s*... is generally taken to be Janet’s elegant Left-Step formulation, Fig. 1.

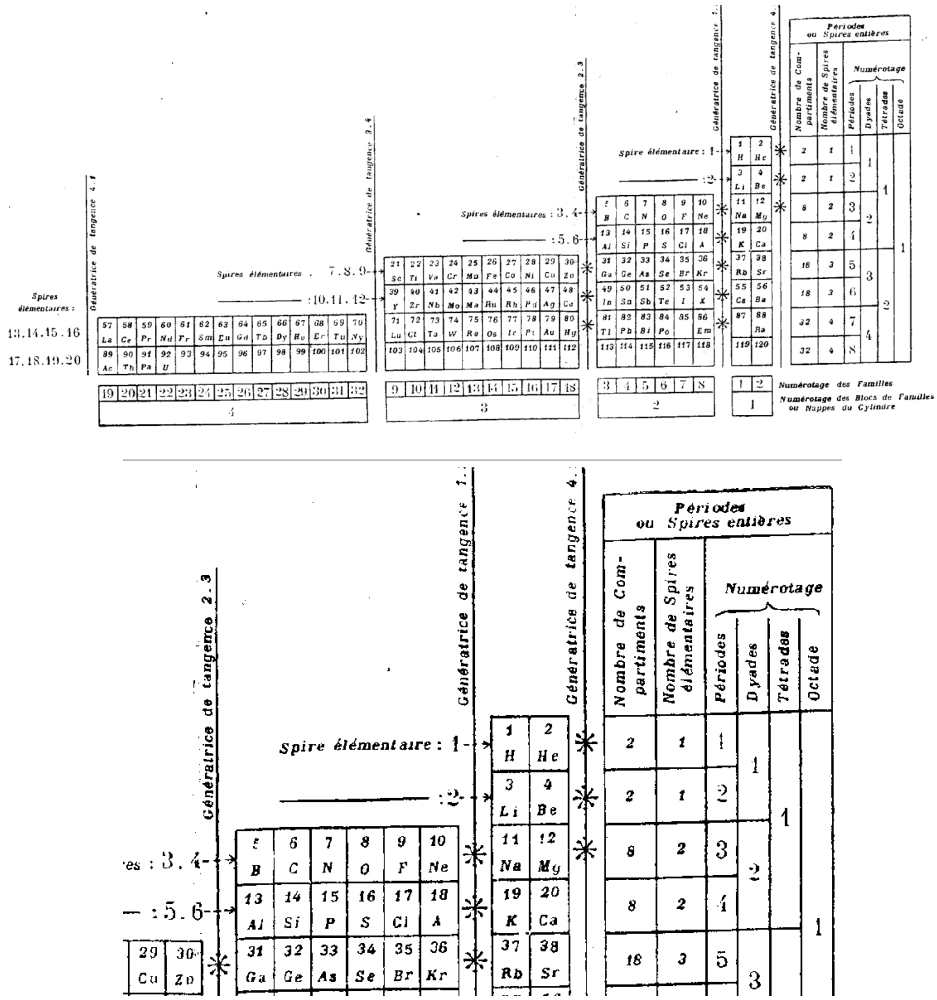


Fig. 1 Janet’s privately published Left-Step formulation of 1928 (Janet 1929)

Janet initially based his table on purely formal considerations but soon realised that it exactly corresponded with the newly developed quantum theory of electronic structure (Stewart 2010).

The Janet formulation has atomic number Z increasing contiguously in two dimensions, left-to-right and down, and the elements are arranged in blocks representing shells and sub-shells. But the Left-Step formulation is one for the purists, as it does not do a good job of showing across-the-period periodicity and the periodic law.

The Left-Step formulation can be transformed into the more common long and medium formulations. “The commonly used medium form of the periodic table involves a certain amount of ‘*hopping around*’ in terms of values of the *n* quantum number as one proceeds horizontally across periods” (Scerri 2009). The transformation sequence is shown in Fig. 2.

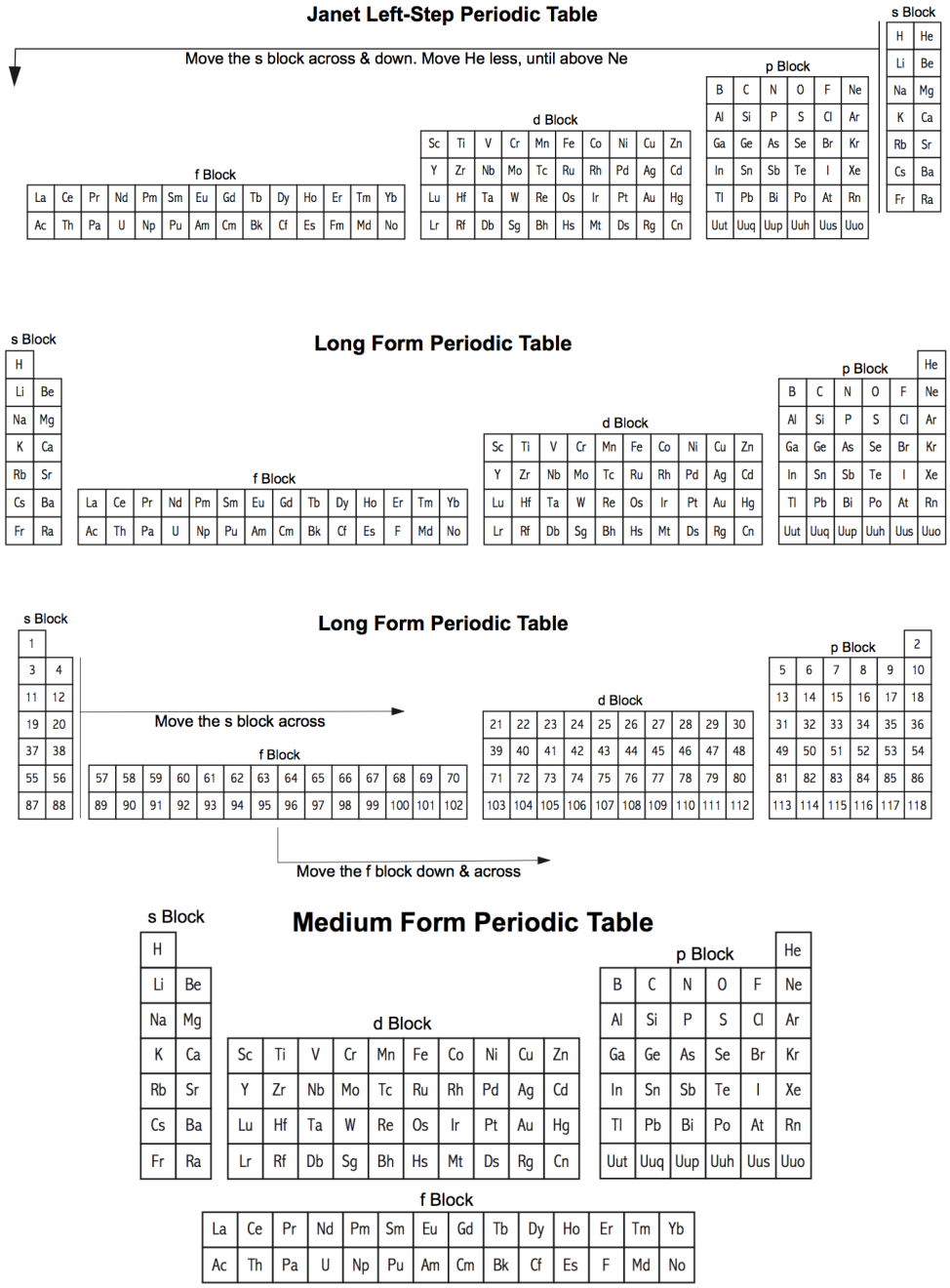


Fig. 2 The transformation of Janet’s Left-Step involves the *s*-block moving from the right-hand-side to the left of the *f* and *d*-blocks and down ‘one’ square. Helium, Z = 2 (He), is moved less than the rest of the *s*-block, and just one square down and across, until above Ne to give the long form of the periodic table. The conversion of the long form of the periodic table into the medium form is trivial. The *f*-block is moved down and to the right, and the *s*-block is moved to close the gap

There are aesthetic reasons to transpose from the long form periodic table to the medium form. The medium form is rectangular and naturally fits on A-sized paper. (ISO 216 defines

A-paper sizes as having a length-to-width ratio of 1.4142 = √2.) This makes the graphic design and printing of medium form periodic tables easy, whereas the useful long form periodic table just looks too wide. The *f*-block, with its increasingly important but chemically difficult rare earth lanthanide and radioactive actinide elements, is placed out of the way at the bottom of the chart.

An additional transformation converts the medium form of the periodic table into a short form that emphasizes the important *s* and *p*-block main group elements, Fig. 3.

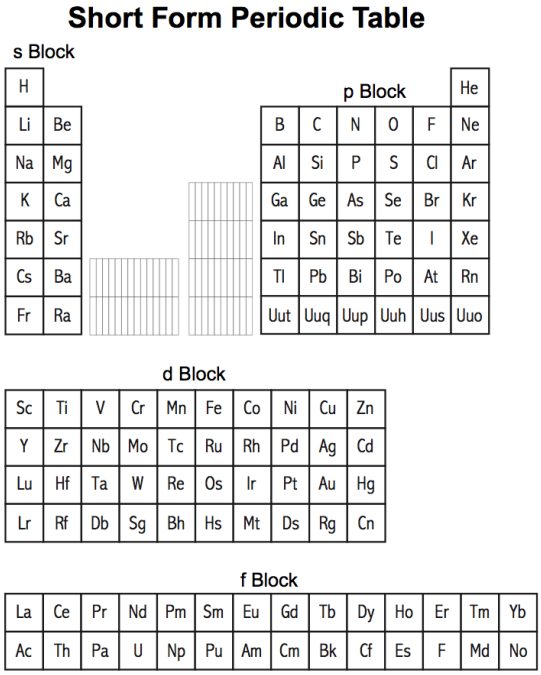


Fig. 3 The medium form of the periodic table can be further transformed into a short form that separates the main group elements form the *d* and *f*-block metals

While the above arguments may explain *how* the Janet Left-Step formulation is transformed into the long, medium and short forms of the periodic table, they do not explain *why* these transformations are deemed to be chemically necessary or appropriate.

The Periodic Law and Periodicity

The periodic law, as proposed by Mendeleev, states: *The properties of the elements are a periodic function of their atomic masses*. After Paneth, this has been modified to: *The properties of the elements are a periodic function of their atomic number, Z*. Periodicity manifests itself in two dimensions with respect to periodic tables: 'across-the-periods' and 'down-the-groups', however, these trends are not equally well displayed in all formulations.

Janet's Left-Step, Fig. 4., shows periodicity with respect to atomic number, Z, in two dimensions (across and down) and it shows general (physical & chemical) periodicity down the groups of the *s* and *p*-blocks. But the Left-Step formulation does not show general periodicity horizontally across the periods.

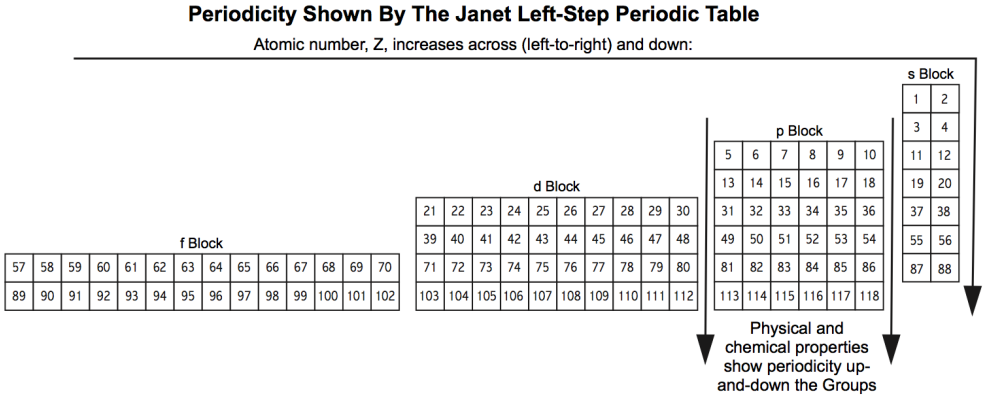


Fig. 4 Atomic number, Z, increases across (left-to-right) and down the Janet Left-Step formulation. Physical and chemical properties show periodicity down the Groups. There is no general left-to-right periodicity. Consider elements 9, 10, 11, 12 that correspond to the distinctly non-periodic: F, Ne, Na & Mg. The chemically unreactive element helium, Z = 2 He, is placed above the metal beryllium, Z = 4 Be

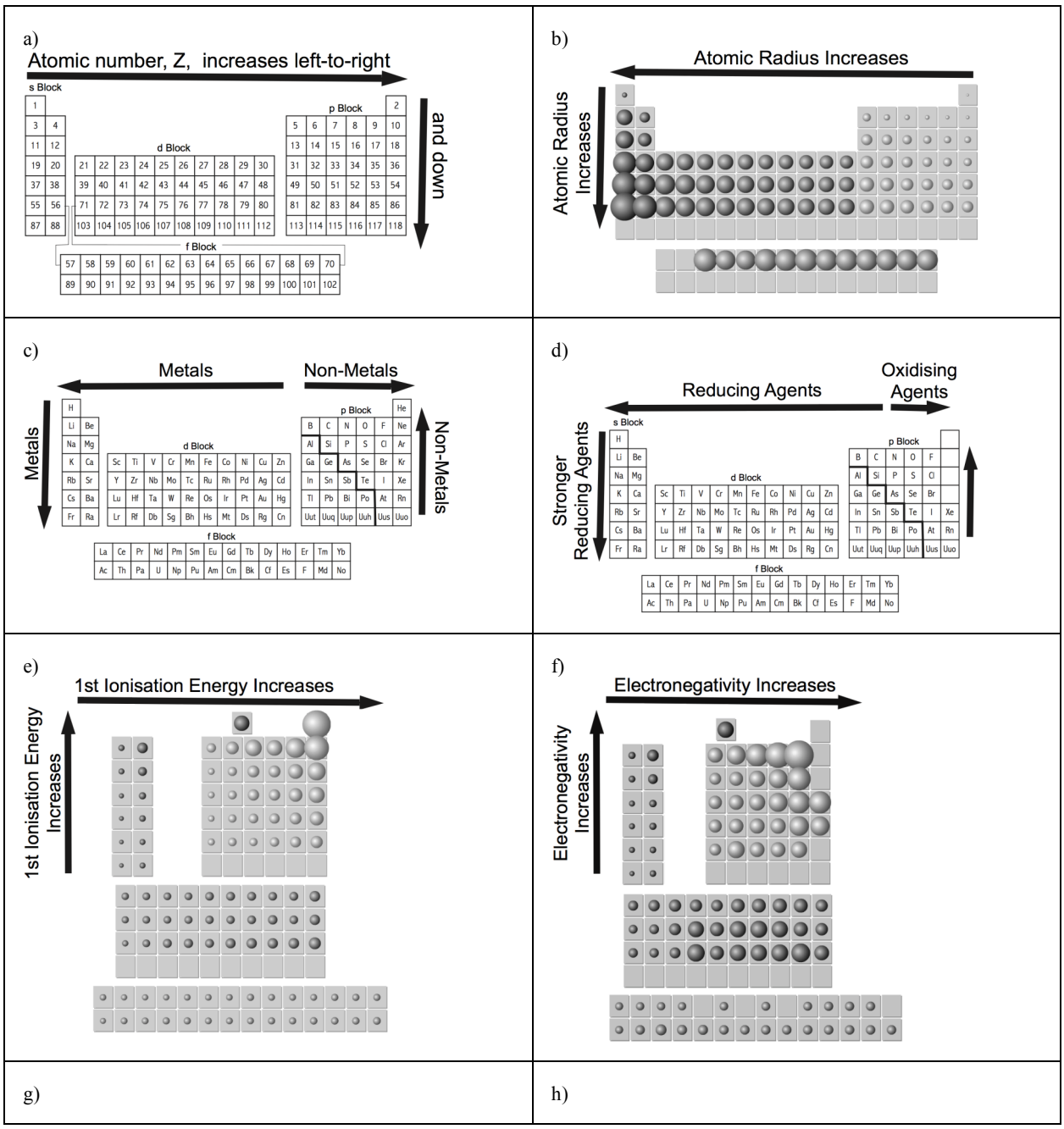
2-Dimensional 'across-the-period', as well as 'down-the-group' periodicity, is observed in the long, medium and short forms of the periodic table. As with the Left-Step, atomic number, Z, increases contiguously left-to-right and down but now atomic radius (Clementi 1963; Clementi 1967) increases in two dimensions as well: across (right-to-left) and down so that helium (radius 31pm, top right) is the smallest atom and cesium (298pm, bottom left) is the largest. Metals (elemental reducing agents) are found to the left and down the periodic table while non-metals (elemental oxidising agents, F_2, O_2) are found to the top right.

First ionization energy is more problematical; indeed it is a sensitive measure of a gas phase atom's quantum state. The short form of the periodic table shows a *general* trend of increasing 1st ionization energies across (left-to-right) and up the main group elements: Cs, 375.7 kJ mol^{-1}, to He, 2372.3 kJ mol^{-1}. However, a detailed examination shows that boron (Z = 5, IE = 800.6 kJ mol^{-1}) has a lower first ionization energy than Be (Z = 4, IE = 899.5 kJ mol^{-1}). Likewise with: O & N, Mg & Al, P & S, etc. This data can be explained in terms of the *s*, *p*, *d*, *f* sub-shell atomic structure.

The main group elements exhibit their most remarkable periodicity with respect to chemical valency and oxidation state. This is seen most clearly with the elemental hydrides, where

valency proceeds 1, 2, 3, 4, 3, 2, 1, 0 (and corresponding oxidation state: +1, +2, +3, ±4, –3, –2, –1, 0) across-the-period and is constant down-the-group.

Furthermore, there is periodicity with respect to structure and chemical reactivity. The *p*-block elemental hydrides show periodicity when plotting the bond-length of the hydride *vs*. the pK_a of the hydride (reacting as a Brønsted acid).



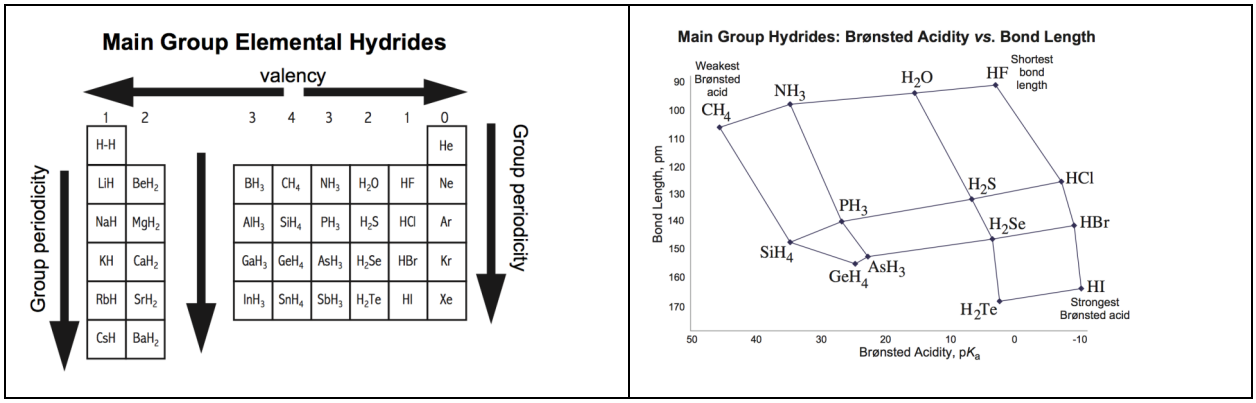


Fig. 5 Periodicity is seen down-the-groups and across-the-periods of the medium form periodic table. (a) Atomic number, Z, shows perfect periodicity. (b) Atomic radius is perfect across the *s*, *p* and *d*-blocks, but minor anomalies occur in the lanthanide *f*-block sequence. (c) There is broad sweep of metals to non-metals from bottom left to top right, matched by (d) the reducing and oxidising reaction chemistry. (e) The main group elements show periodicity with respect to the general trend in 1st ionization energy and (f) electronegativity. (g) The main group elemental hydrides show periodicity with respect to lower oxidation state valency. (h) When the *p*-block hydrides have their Brønsted acid pK_a plotted against their atom to hydrogen bond length, periodicity and a fragment of the periodic table emerges

Other periodicities map to the long and/or medium forms of the periodic table. There are diagonal relationships: For example, only lithium and magnesium metals react directly with atmospheric nitrogen to form the corresponding nitrides. Similar diagonal reactivity relationships are seen with: Be–Al, N–S, C–P, etc. (Rayner-Canham in press). Many triads are known, such as: He-Ne-Ar, P-As-Sb and Y-Lu-Lr (Scerri 2008). Knight's move relationships (Laing 1991) and group (n) and (n+10) linkage periodicities are seen (Rayner-Canham in press).

Electronegativity

Jensen discussed the origins and early history of electronegativity in two papers (Jensen 1996; Jensen 2003). Briefly, electronegativity grew out of the chemical concepts of affinity and dissimilarity that developed into Avogadro's oxygenicity scale of 1809 and then to Berzelius' Electrochemische Theorie table of 1836, which arranges 54 elements by their electronegativity. Baker's volume, *A Text-Book of Elementary Chemistry* (Baker 1870), introduced three atomic properties: weight, valency and electronegativity that respectively measured the "quantity of matter", "quantity of an atom's combining power" and the "quality of an atom's combining power". A late nineteenth century periodic table formulation by Thomsen clearly shows *elektropositive* metals and *elektronegative* non-metals, Fig. 6 (Thomsen 1895).

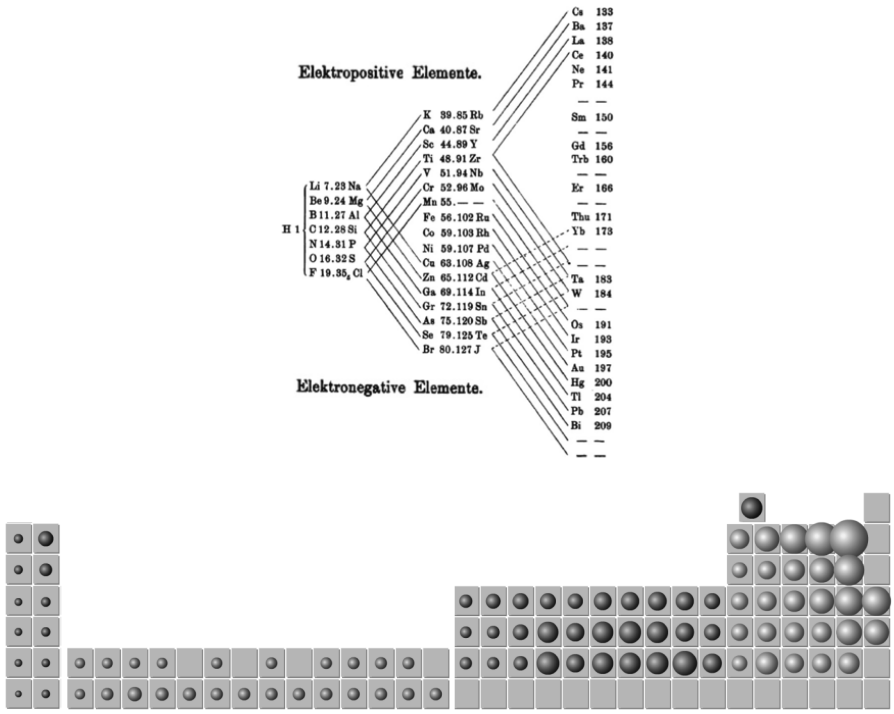


Fig. 6 The metals are electropositive and the non-metals are electronegative, such that there is a broad sweep from the most electropositive metal at the bottom left (cesium, Cs, $\chi = 0.79$) to the most electronegative non-metal to be found top right (fluorine, F, $\chi = 3.98$) of the long form of the periodic table. This trend can be seen in both Thomsen's 1895 formulation and in a modern 'ball' representation adapted from Mark Winter's Webelements (1993)

In 1932 Pauling introduced (Note 3) a quantitative electronegativity that he later described as "*the power of an atom in a molecule to attract electrons to itself*" and assigned the symbol χ. (Pauling 1932; Pauling 1960). Other synonymous definitions include: "the ability of an atom to withdraw electron density from a covalent bond" and "a chemical property that describes the ability of an atom (or, more rarely, a functional group) to attract electrons (or electron density) towards itself."

Beginning chemistry students the world over learn that electronegativity can be used to predict bond polarity. For example, chlorine ($\chi = 3.16$) is more electronegative than hydrogen ($\chi = 2.20$) so the HCl covalent bond is polarised $H^{\partial+}$– $Cl^{\partial-}$. From this, it is predicted that when HCl reacts with water it will ionise to H^+ and Cl^- (rather than H^- and Cl^+). Indeed,

hydrogen chloride dissolves in water to give hydrochloric acid, a solution rich in H^+(aq) ions and Cl^-(aq) ions. *Contra wise*, the covalent bond in molecular chlorine (dichlorine), Cl_2, is non-polar because there is no electronegativity difference and on heating chlorine undergoes homolytic bond fission to give a pair of chlorine radicals: $Cl_2 \rightarrow 2Cl^{\bullet}$.

Electronegativity is used to explain many aspects of the reaction mechanisms of organic chemistry. For example, the carbon–halogen bond of methyl iodide, CH_3I, is polarised $C^{\partial+}$–$I^{\partial-}$. An electron rich nucleophile [literally, a "positive charge seeking entity"], such as an aromatic sulfide ion, C_6H_5–S^-, is deemed to attack the $C^{\partial+}$ carbon centre of CH_3I, so initiating an S_N2 nucleophilic substitution reaction:

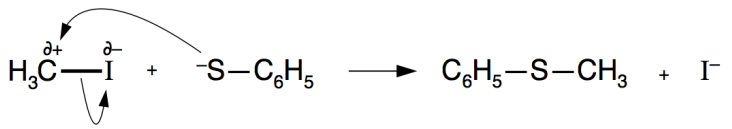


Fig. 7. Nucleophilic substitution. The carbon atom is rendered ∂+ by the electronegative iodine atom and so susceptible to attack by the electron rich, nucleophilic sulfur anion.

Trichloroacetic acid, CCl_3COOH, is a strong (fully dissociating) Brønsted acid while acetic acid, CH_3COOH, is a weak (slightly dissociating) acid. This difference is deemed to be due to the electron withdrawing nature of the three electronegative chlorine atoms that stabilise the negative charge of the CCl_3COO^- anion. Likewise, the nitro group, $–NO_2$, is deemed to deactivate the benzene ring of nitrobenzene, $C_6H_5NO_2$, towards electrophilic aromatic substitution, S_EAr. This is explained in terms of three electronegative atoms, one nitrogen and two oxygens, withdrawing electron density from the aromatic ring's π-system.

In main group chemistry, the electropositive metals react with the electronegative non-metals to give ionic salts: sodium chloride, NaCl, magnesium bromide, $MgBr_2$, etc. Non-metals react with each other to give non-polar (or 'homopolar') covalent bonds, Cl_2, or polarised covalent bonds depending upon the electronegativity difference.

In the nineteen nineties Allen and Jensen independently used electronegativity average, $\Sigma\chi = (\chi_a + \chi_b)/2$, and electronegativity difference, $\Delta\chi = |\chi_a - \chi_b|$, to construct semi-quantitative van Arkle-Ketelaar triangles of bonding (Allen 1992; Jensen 1995), Fig. 8.

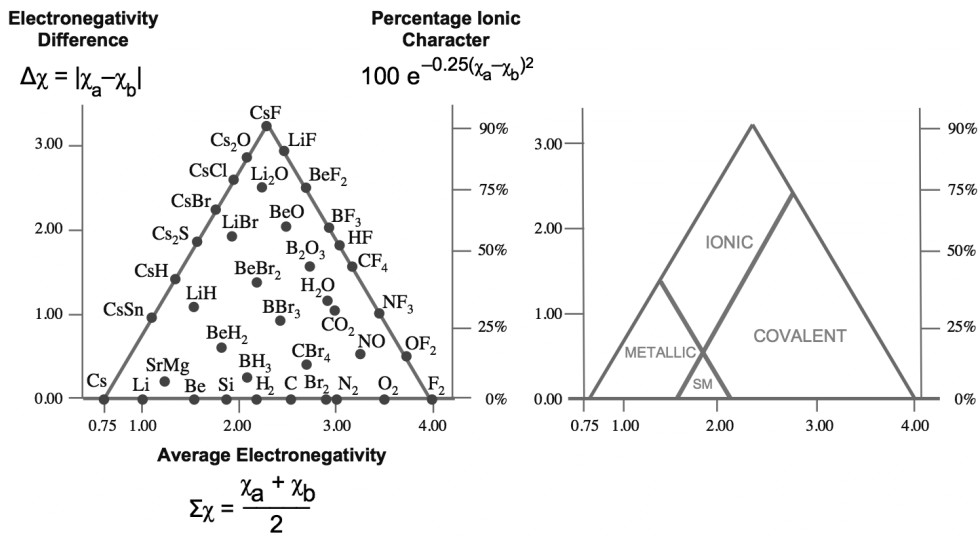


Fig. 8 Electronegativity average, $\Sigma\chi$ and difference, $\Delta\chi$ can be used to construct semi-quantitative van Arkle-Ketelaar triangles of bonding that allow the mapping of chemical elements, binary compounds and regions of structural similarity (Note 4). Areas of metallic, ionic and covalent bonding can be observed. SM equates with semi-metallic (semiconductor) materials such as Si and GaAs. Electronegativity difference, $\Delta\chi$, directly equates with Pauling's notion of percent ionic/covalent bonding (Pauling 1960)

In the nineteen twenties a tetrahedron of material types was constructed (Grimm 1928; Jensen 1998), with the four corners labelled: metallisch (metallic), van der Waals (molecular), heteropolar (ionic) and homöopolar (network covalent). The idea was lost, and then reintroduced by Laing (1994) who split the covalent bonding of the van Arkle-Ketelaar triangle into van der Waals (molecular) and covalent (network) material types. Using the logic of Allen and Jensen, it is possible to semi-quantify the Grimm-Laing object into a truncated tetrahedron of structure, bonding and material type (Leach 2009) with the four corners as: metallic, ionic, molecular and network-covalent, Fig. 9. The third dimension of the tetrahedron involves the periodic transition from molecular to network structure, as can be seen with the carbon allotropes:

- Buckminsterfullerene, C_{60}, a molecular van der Waals material.
- Single walled carbon nanotubes (SWCN) consist of linear tubes of carbon atoms.
- Graphene/graphite is a carbon allotrope consisting of flat plates of carbon atoms.
- Diamond has three is dimensional network of covalently bonded carbon atoms.

Likewise, the period 3 elements, Si, P, S and Cl have allotropes are 0, 1, 2 and 3-dimentionally bonded structures:

- Elemental chlorine, Cl_2, is molecular.
- Amorphous, or plastic, sulfur consists of 1-dimensional linear chains of sulfur atoms, $[–S–S–S–]_n$, in a helical structure with eight atoms per turn.
- Black, or β-metallic, phosphorus, has a 2-dimensional flat plate structure.
- Crystalline silicon has a 3-dimensional network of tetrahedral Si atoms in a diamond cubic crystal structure.

The ideal molecular-to-network transition sequence would be: F_2, $[–O–O–O–]_n$, flat plate $[N]_n$, and diamond, but unfortunately the oxygen and nitrogen allotropes are not known.

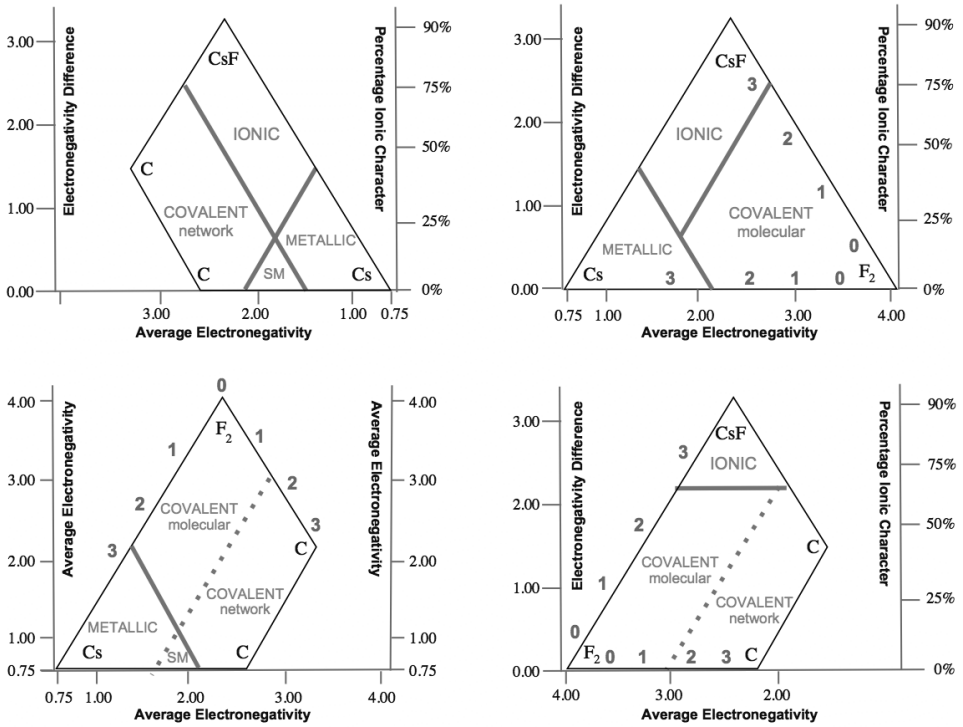


Fig. 9 The four sides of the truncated tetrahedron of structure, bonding and material type quantified with respect to electronegativity average, $\Sigma\chi$, electronegativity difference, $\Delta\chi$, and 0, 1, 2 & 3-dimensional connectivity. Thus, broad predictions of physical character and chemical behaviour can be predicted from electronegativity and valency data only. The tetrahedron is truncated because carbon (χ = 2.55) the most electronegative element that forms a network covalent structure, diamond

So What *Is* Electronegativity?

There are many methods of determining electronegativity, including:

Electronegativity Scale	**Methodology**
Pauling Scale (1932)	Thermochemical bond dissociation energies, expressed (originally) in electron volts: $\chi_r(A) - \chi_r(B) = (eV)^{-1/2}\sqrt{E_d(AB) - \frac{1}{2}\left[E_d(AA) + E_d(BB)\right]}$
Mulliken Relation (1934)	Defines a relation that depends upon the orbital characteristics of an atom in a molecule. Mulliken electronegativity is the numerical average of the ionisation potential and electron affinity.
Gordy Scale (1946)	Defines electronegativity in terms of the effective nuclear charge and the covalent radius. $(Z_{eff})e/r$. Gordy developed several scales.
Walsh Scale (1951)	Relates electronegativity to stretching force constants of the bonds of an atom to a hydrogen atom.
Huggins Scale (1953)	An alternative thermochemical procedure.
Sanderson Scale (1955)	The ratio of the average electron density of an atom to that of a hypothetical "inert" atom having the same number of electrons. This ratio is a measure of the relative compactness of the atom.
Allred-Rochow Scale (1958)	Defines electronegativity in terms of the effective nuclear charge and covalent radius. Like the Gordy scale but uses $(Z_{eff})e/r^2$.
Revised Pauling Scale (Allred 1961)	Electronegativity values from thermochemical data. An updating of the original Pauling methodology.
Jaffe Scale (Hinze & Jaffe 1962)	Uses the electronegativity of orbitals rather than atoms to develop group electronegativities for molecular fragments (e.g. CH_3 *vs*. CF_3) that take into account the charge of a group, the effects of substituents, and the hybridization of the bonding orbital.
Phillips Scale (1968)	Defines electronegativity in terms of the dielectric properties of atoms in a given valence state.
Michaelson Scale (1978)	The relationship between an atomic electronegativity scale and the work function.
Martynov & Batsanov Scale (1980)	Obtained by averaging the successive ionisation energies of an element's valence electrons.
Allen Scale (1992)	Configuration energy (CE), the average one-electron valence shell energy of the ground-state free atom, is used to quantify metal-covalent-ionic bonding.

Indeed, dozens of quantitative electronegativity scales have been suggested, using physical parameters including: enthalpy data, ionisation energy & electron affinity, effective nuclear charge & covalent radius, stretching force constants, average electron density, dielectric properties, the work function, relative compactness, configuration energy, polarizability, number of valence electrons, pseudopotentials, NMR chemical shifts and isomer shifts in Mössbauer spectroscopy.

Due to the importance of Pauling's scale, as published in The Nature of The Chemical Bond (Pauling 1960), where electronegativity ranges from Cs, $\chi = 0.7$ to F, $\chi = 4.0$, all the other electronegativity scales are routinely normalised with respect to Pauling's range, Fig. 10.

There are such strong correlations between numerous atomic parameters, physical and chemical, that the term "electronegativity" has the effect of integrating them into a single dimensionless number between 0.78 and 4.00. Consequently, the electronegativity of an element can be used to predict/describe/model much of its empirical physical character and chemical behaviour.

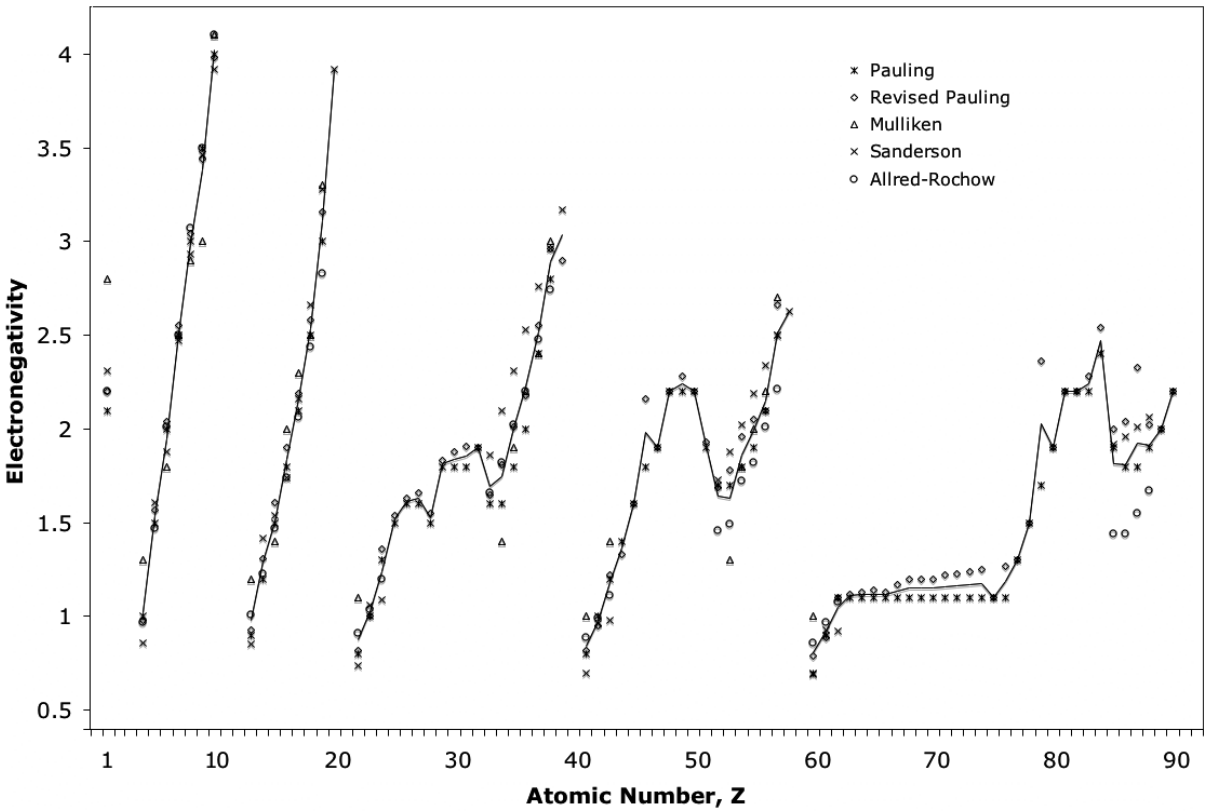


Fig. 10 When the Pauling, Revised Pauling, Mulliken, Sanderson and Allred-Rochow electronegativity scales are plotted together against atomic number, Z, the similarity of the data can be observed. The solid line shows the averaged data.

Electronegativity: The Missing Transcendental Property?

Many parameters correlate with electronegativity and, thus, electronegativity has the effect of correlating each of these parameters with each other. With the knowledge *only* of an element's electronegativity we can make predictions about the atomic radius and ionisation energy of the gas phase atom or whether the bulk substance will present as a metal, non-metal or metalloid. We know whether the simple elemental substance will be a reducing agent or whether it will be oxidising. With pairs of elements we can make predictions about the structure, bonding and material type of both the chemical element in its standard state and the binary compound. We can estimate the degree of bond polarisation, mode of bond fission, aqueous ionisation, susceptibility to nucleophilic substitution, aspects of Brønsted acidity, etc.

Electronegativity is clearly synthesized from empirical data, but is it telling us something rather profound about the nature of the element itself? Should electronegativity be considered to be a property of the basic element? Is electronegativity transcendental?

> "Only the *basic element* survives in a compound: sodium's metallic properties and 'chlorine, the green gas' do not exist in the ionic salt, sodium chloride (NaCl)".

We completely agree with this statement, but feel that it is made fully rational if the basic element also possesses the property of electronegativity. Now, the empirical facts that sodium ($\chi = 0.93$) is a metal with a low 1st ionisation energy, a large atomic radius and is a reducing agent, chlorine ($\chi = 3.16$), Cl_2, is a non-metal and is oxidising and sodium chloride ($\Delta\chi = \chi_{Cl} - \chi_{Na}$, $3.16 - 0.93 = 2.33$), NaCl, is an ionic substance are inevitable consequences of the properties of the *basic* element.

We propose a modification of the Paneth notion that the basic/transcendental element has only one property, Z. We propose that the basic element has two properties, atomic number, Z, and electronegativity, χ. We propose that a basic element's:

- Name and symbol are assigned with respect to the atomic number, Z.
- The four quantum numbers and four associated rules are an *a priori* consequence of the atomic number, Z, and so are basic properties by proxy.
- Electronegativity integrates the physical and chemical data associated with simple elemental substances and *back-maps* from the empirical world to the transcendental, basic substance. Thus, electronegativity is a property of the basic element that describes the physical and chemical properties with a single dimensionless number between 0.79 and 4.00.

Using this updated definition, the design and extensive periodicity of the medium formulation of the periodic table of basic elemental substances arises quite naturally and no *ad hoc* explanation is required.

Conclusion

The summary of second part of Jensen's three-part historical review of electronegativity (Jensen 2003) reads:

> "Nowhere in his 1932 paper on electronegativity did Linus Pauling bother to give an explicit definition of the concept [because] by the 1930s [the idea] was more than 120 years old and in its most recent reincarnation, in terms of an atom's ability to attract and retain its valence electrons, was almost 30 years old. Consequently, Pauling could be certain his readers knew exactly what he meant by the term."

Later, Pauling defined electronegativity as: "*the power of an atom in a molecule to attract electrons to itself"* (Pauling 1960). However, when considered in the context of semi-quantitative tetrahedra of structure of bonding and material type, this statement is literally too narrow because bulk binary compounds can be metallic, ionic or network covalent as well as molecular. Any definition of electronegativity must not be self-limiting.

An updated definition is: *"Electronegativity is measure, integrated over numerous physical parameters, of the power of a gas phase or bonded atom to attract electrons to itself."*

It is our thesis that the concept of electronegativity is so general and far-reaching that it should be considered to be a transcendental property of the basic elemental substance and, thus, a component of Paneth's *grundstoff* "the indestructible stuff present in compounds and simple substances".

Philosophically, electronegativity is an idea that exists in chemistry space. It is formulated by aggregating physical data into chemical information.

Notes

(1) There are many possible periodic tables, but to be 'a true periodic table' a formulation:

- Must be contiguous with respect to atomic number, Z.
- Must be at least two-dimensional: a simple list is not a periodic table.
- Should display *s*, *p*, *d* & *f*-blocks and hence be able to exhibit group periodicity.
- Ideally – and to be educationally useful – the formulation should be able to show how physical and chemical properties change in a regular manner across the periods as well as down the groups.

(2) The group 18 elements He and Ne do not have electronegativities on the Pauling, Revised Pauling, Mulliken, Sanderson and Allred-Rochow scales. Extrapolation from these data sets, and comparing with 1st ionisation energies and atomic radii data, gives approximate values of He $\chi = 5.8$ and Ne $\chi = 4.8$.

(3) Pauling says nothing about the etymology of the term electronegativity in his 1932 paper, and in later publications cites only this reference. Jensen explains this omission in the conclusion of his review (Jensen 2003).

(4) Allen and Jensen use different measures of electronegativity when constructing their semi-quantitative van Arkle-Ketelaar triangles of bond type. Jensen uses Martynov & Batsanov electronegativity and Allen uses configuration energy.

(5) The periodic table transformation sequence from Left-Step to the medium form outlined in Fig. 2 generates a periodic table with the four group 3 elements as: Sc, Y, Lu & Ac. Most published medium formulations of the periodic table have a group 3 consisting of: Sc, Y, La & Ac, a sequence that is both logically and chemically incorrect (Thyssen 2011).

(6) The atomic radius of a chemical element is not a well-defined physical entity as there are various non-equivalent definitions of atomic radius. Most authors take atomic radii data computed from theoretical models, as published by Enrico Clementi and others in 1967 as the definitive reference.

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