



Bonding and Electronegativity: Van Arkel Triangles

Van Arkel triangles are used to show different compounds in varying degrees of ionic, metallic and covalent bonding. The triangle shows that ionic, metallic and covalent bonds are not just particular bonds of a specific type. Rather, bond types are interconnected and different compounds have varying degrees of different bonding character (for example, covalent bonds with significant ionic character are called polar covalent bonds).

The aim of the van Arkel triangle is to allow the three principal models of chemical bonding to be seen as part of a single scheme in which they are all related. It gives a quantitative appreciation of **intermediate** bonding and also demonstrates that intermediate bonding is not limited to polar-covalent /polarised ionic. Furthermore, it is based on the already-familiar topic of electronegativity.

Bonding Theories

The first of the idealised bonding theories to be developed was ionic bonding, inspired by Faraday's laws of electrolysis. Following a lot of important work in the first three decades of the twentieth century the Dutch chemists van Arkel and de Boer published a description of ionic bonding in 1929.

The theory of covalent bonding began its development later, in the first decade of the twentieth century, but the work came to fruition sooner with the publication of the seminal paper on covalent bonding by Lewis in 1916. He was also the first to recognise metallic bonding as a separate model to sit alongside the ionic and covalent models in a paper published in 1913.

Once the electronegativity scale was introduced by Pauling, the van Arkel triangle was first published in 1941. Van Arkel's triangle only considered intermediate bonding along the edges. In 1947 his colleague Ketelaar went on to consider compounds placed in the body of the triangle.

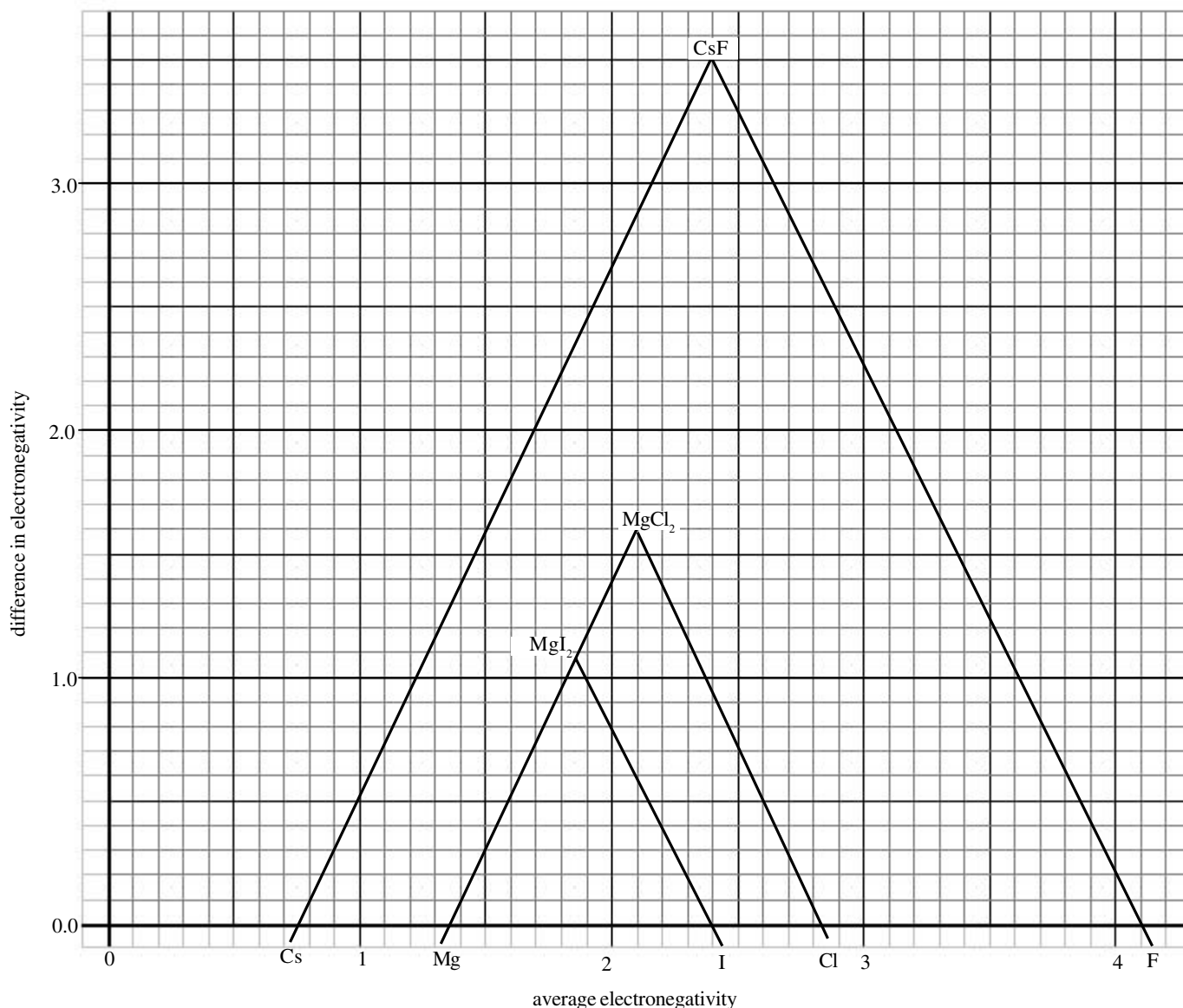
The van Arkel triangle only applies to binary compounds and elements whose atoms can bond together. It consists of a plot of the **difference** of the electronegativity values of the two elements in the compound (y axis) against the **average** of the electronegativity values (x axis). The electronegativity values are used without any regard for the stoichiometry (formula) of the binary compound.

Therefore, at the left hand extreme of the x axis (which corresponds to total delocalisation of the electrons), is the least electronegative element, caesium, whilst the most electronegative element, fluorine, is at the right hand extreme. At this covalent extreme the valence electrons are completely localised and evenly shared within the F-F bond.

In the van Arkel triangle the y axis therefore describes the extent to which the bonding electrons are unevenly shared between the two bonding atoms. At the bottom of the triangle, where $y = 0$, which is where the elements are found, there is no uneven electron distribution across the bond. At the top of the triangle, where there is the greatest asymmetry of the electron distribution in the bond, there is the extreme of ionic bonding. The compound at this apex is therefore caesium fluoride, which has the greatest difference in the electronegativity values between its component elements.

When plotting the point corresponding to any compound, one plots the intersection of two lines – each starting with a constituent element, positioned on the x axis in accordance with its electronegativity. The line from the left-hand element is drawn parallel to the left-hand edge of the triangle and the line from the right-hand element parallel to the right-hand edge. It follows then that all the compounds of an element lie on one of two lines, running parallel with the edges of the triangle, that intersect at the element on the x axis. On the left hand branch there are the compounds of which the element in question is the more electronegative while. on the right-hand branch, the element is the less electronegative of the pair.

On the example triangle below the positions of caesium, fluorine and caesium fluoride have been marked together with example lines giving the positions of the binary compounds magnesium chloride and magnesium iodide.



The chief conclusion to be drawn from the plots in the example above is that MgI_2 , being lower down in the body of the triangle, will have greater covalent character than the more truly ionic MgCl_2 , although the fact that MgCl_2 is well below the apex of the triangle suggests that its bonding has some covalent character as well.

The simplest application of the van Arkel triangle is to anticipate – based on electronegativity values – the nature of the bonding in an unfamiliar compound. This is straightforward in cases where a plot places a compound near to one of the bonding extremes. However, in more borderline cases, the assignment of bonding type is less straightforward. The main point about the van Arkel triangle is that it provides a clear picture of the fact that bonding is not black and white, but rather a continuous scale between idealised extremes.

One important point about the van Arkel triangle is that its reflection of bonding does not provide reliable information about structure. This is because structure depends on other factors besides electronegativity values. A similar problem is apparent with elements such as carbon, tin and phosphorus, which have allotropes of very different structures, yet of course the allotropes of an element will all have the same electronegativity value. A further shortcoming of the triangle is observed when multiple oxidation states are possible in a binary compound, for example the chlorides of lead. In this case lead(IV) chloride has appreciable covalent character but lead(II) chloride is essentially ionic – and this difference is not predicted by use of the van Arkel triangle.

The van Arkel triangle has the principal purposes of illuminating the idea of intermediate bonding, and being able to see the connection between ionic, covalent and metallic bonding.

Sample questions about the van Arkel triangle.

The type of bonding between two elements can be predicted using a van Arkel triangle. The triangle is based on electronegativity values.

(a) What is meant by the term electronegativity? [2]

(b) State and explain the trend in electronegativity

(i) across a period from left to right, [2]

(ii) down a group. [2]

(c) Considering only elements in period 2 (Li to Ne), write down

(i) the formula of the compound that has the greatest ionic character, [1]

(ii) the formula of a simple molecule that has pure covalent bonding [1]

(iii) the element that has the greatest metallic character. [1]

(d) Use the electronegativity values quoted to plot each of the following compounds on the template below. Label your points with the formulae.

(i) titanium boride, TiB₂

(ii) silicon carbide, SiC

(iii) gallium antimonide, GaSb [2]

Element	Electronegativity
B	2.05
C	2.54
Si	1.92
Ti	1.38
Sb	1.98
Ga	1.76

(e) What is the type of bonding present at each of these bonding extremes, labelled A, B and C on the triangle? [1]

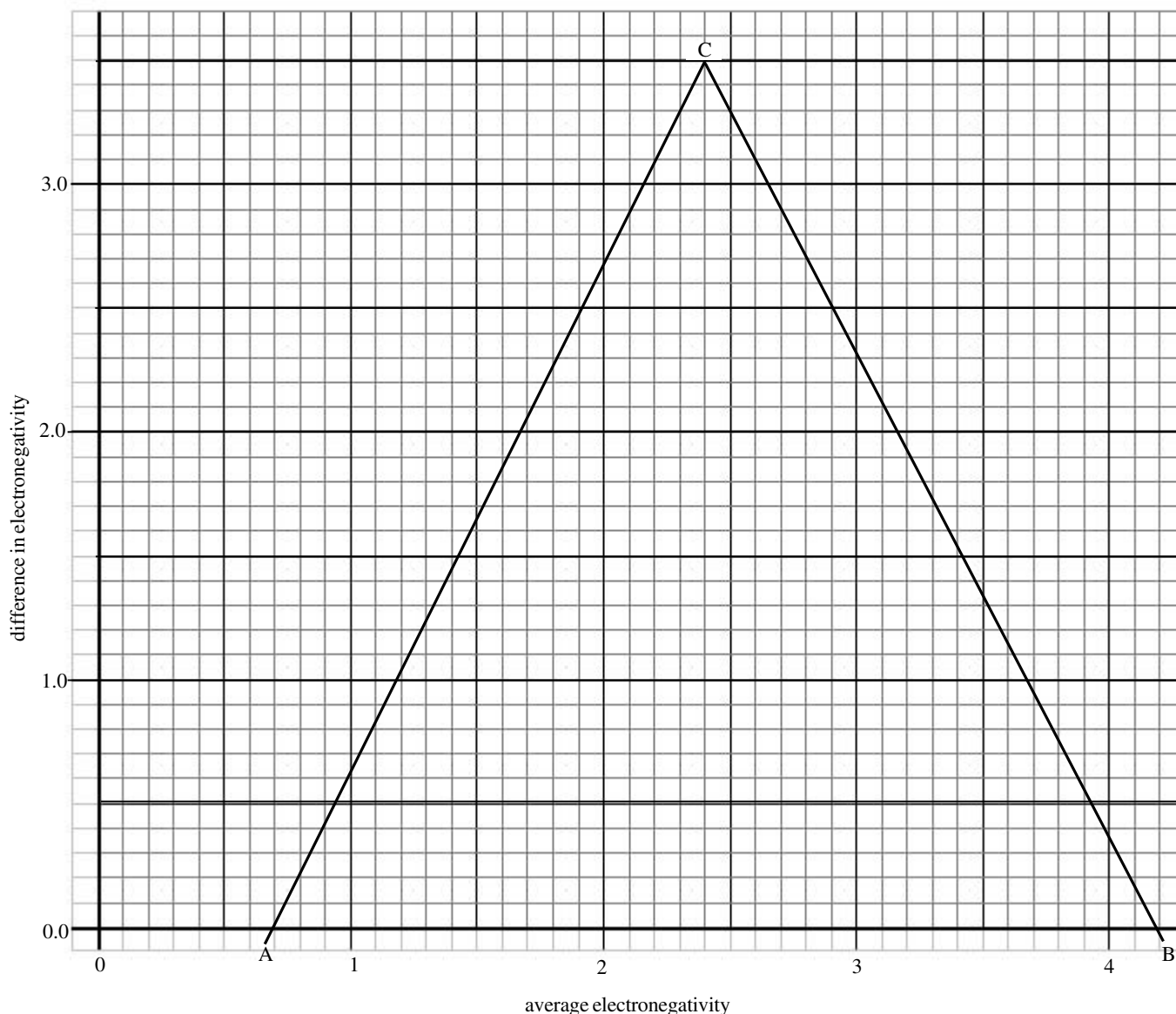
(f) The electrical properties of the materials in part (d) are all very different. Suggest which of the compounds in part (d) would be expected to be

(i) a good conductor, [1]

(ii) a semiconductor, [1]

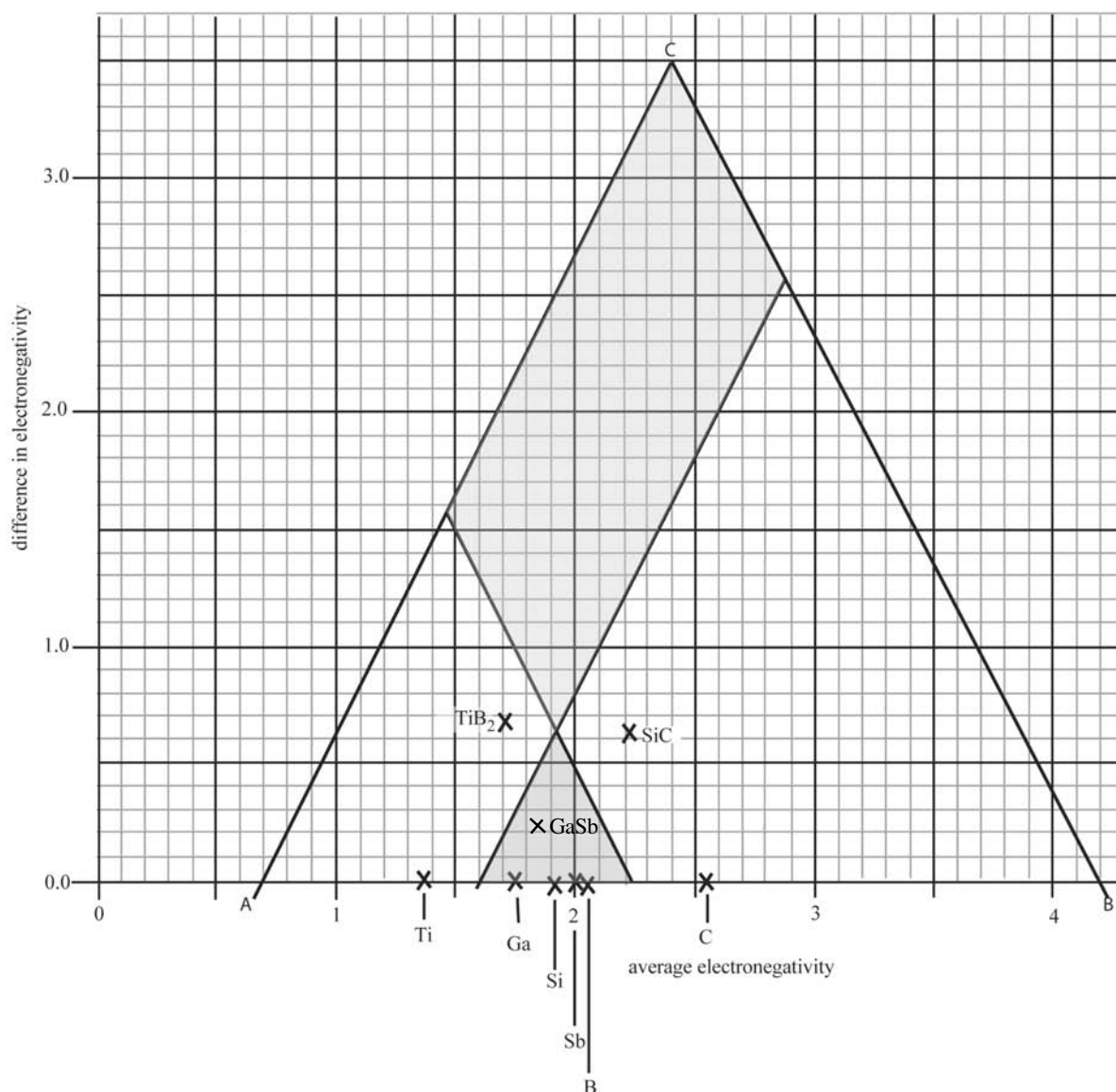
(iii) an insulator. [1]

[Total: 15]



Answers

- (a) must include reference to bonding electrons and their attraction to the nucleus e.g. the ability of an atom to attract (1)
bonding electrons (1) [2]
- (b) (i) increases (1) with increasing nuclear charge but same shielding (1) [2]
(ii) decreases (1) as electrons further from the nucleus / more shielding from the nucleus (1) [2]
- (c) (i) LiF [1]
(ii) F₂, O₂ or N₂ [1]
(iii) Li [1]
- (d) 2 marks for all points correctly plotted
1 mark for two points correctly plotted [2]



- (e) A metallic B covalent C ionic [1]
- (f) (i) TiB₂ not TiB [1]
(ii) GaSb [1]
(iii) SiC [1]

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