

4 The van Arkel Triangle

A Background information

History

The van Arkel triangle has not had a prominent place in British chemical education. It has, however, been more popular in continental Europe and the United States.

Being a scheme in which the three idealised forms of chemical bonding – covalent, ionic and metallic – are related to one another, its development had to wait until all three modes of chemical bonding were established.

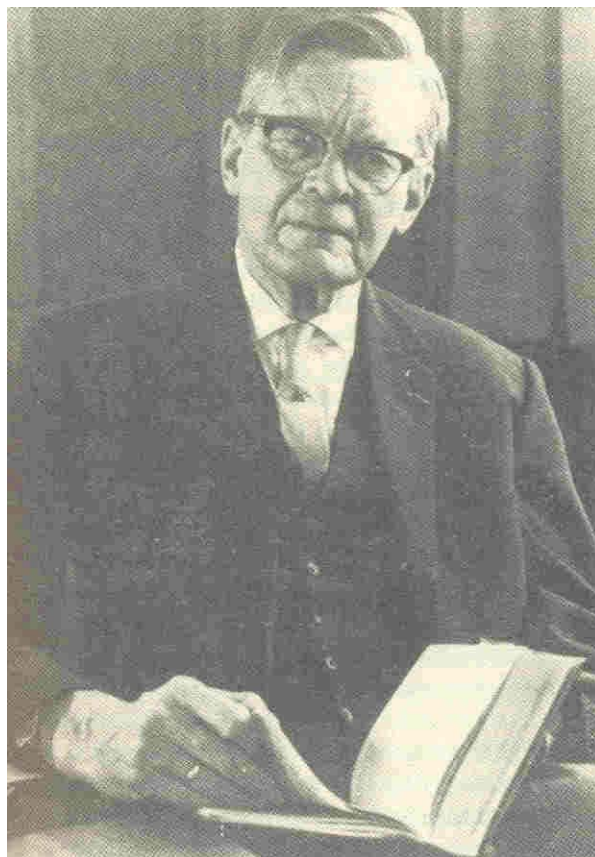
The first of these bonding theories to be developed was ionic bonding, which was first pioneered by the German, Helmholtz in 1881, who was inspired by Faraday's laws of electrolysis. Following much important work in the first three decades of the twentieth century by J J Thompson, Lewis, Born, Landé, Fajans and many others, the Dutch chemists van Arkel and de Boer published a definite description of ionic bonding in *Chemical Bonding as an Electrostatic Phenomenon* in 1929.

The theory of covalent bonding began its development in the first decade of the twentieth century with the work of the Germans Stark and Kauffmann, as well as J J Thompson, William Ramsay and others. The seminal paper on covalent bonding came from Lewis in 1916.

Metallic bonding has a much less glorious history in the chemical literature. Chemists have long been put off by the non-stoichiometric intermetallic compounds and alloys, which often defy simple electron-counting rules. It has mainly therefore been solid-state physicists and metallurgists who have made the most impressive advances in metallic bonding theory. Lewis, in 1913, was the first chemist to recognise metallic bonding as a model to sit alongside the ionic and covalent models in chemical bonding theory.

The use of a triangle to describe the relationship between the three main types of bonding did not strictly begin with van Arkel. The German, Grimm produced the first in 1928, before the concept of electronegativity was even developed. The electronegativity scale was first introduced by Pauling in 1932. The triangle, with the appearance that we associate with it today, was first published by van Arkel in his text book *Molecules and Crystals* 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.

Van Arkel's and Ketelaar's triangles were only made strictly quantitative in 1980 by Bill Jensen of the University of Cincinnati. He has investigated the appearance of the triangle using other types of electronegativity scale than Pauling's and considered the limitations of the triangle in predicting the structure and properties of compounds.



Anton Eduard van Arkel

Picture taken from W B Jensen. *Bulletin Hist. Chem.* 13-14, 47 ('92-'93)

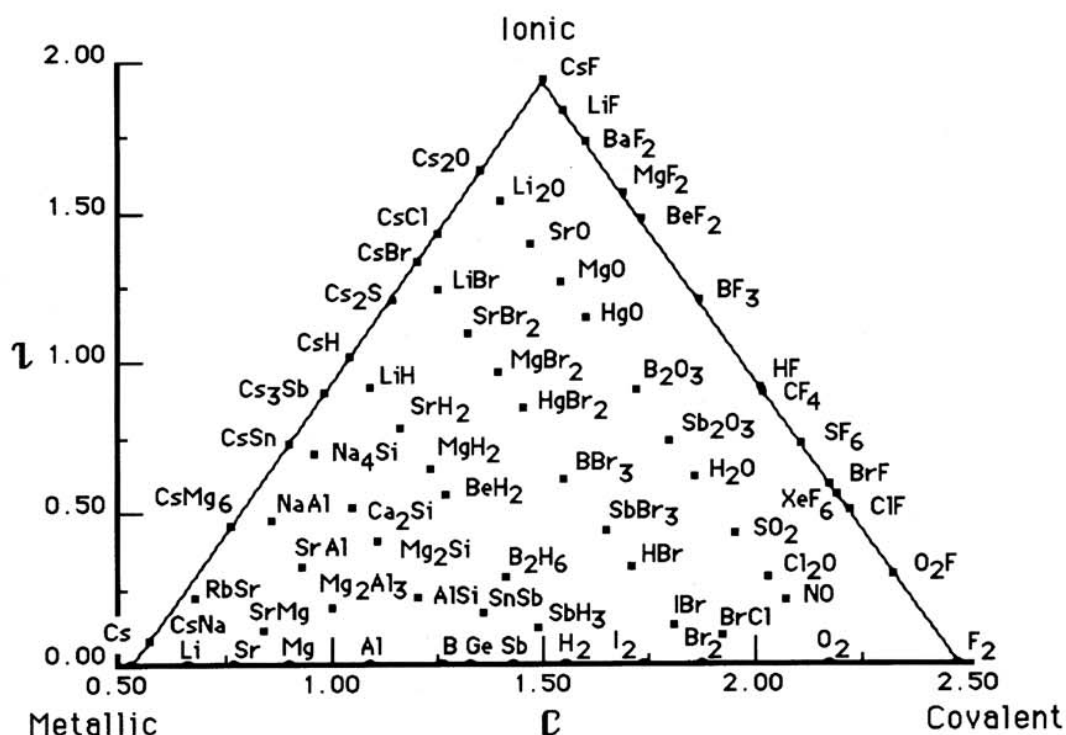
Theory

The van Arkel triangle pertains only to binary compounds and elements whose atoms can bond together. It arises from 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 of the binary compound.

In the van Arkel triangle the x axis therefore describes the degree of localisation of the bonding electrons. At the left hand extreme of the x axis lies the most electropositive element, caesium. [Francium is probably not more electropositive than caesium as it has been shown to have a higher first ionisation energy than caesium – due to relativistic effects.] At this metallic extreme the valence electrons are delocalised. At the right hand extreme of the x axis lies the most electronegative element, fluorine. [The light noble gases are not at this extreme as they do not bond with themselves, or indeed anything else.] At this covalent extreme, the valence electrons are absolutely localised within the F–F bond.

In the van Arkel triangle the y axis therefore describes the degree of asymmetry of the bonding electrons between the two bonding atoms. At the bottom of the triangle, where y

= 0, which is where the elements are found there can be no asymmetry in the 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 of its constituent elements.



In the figure above, the label *I* on the y axis is used by Jensen to denote the ionicity parameter (the difference in electronegativity values); the label *C* on the x axis stands for the covalency parameter (the average electronegativity value). The figure is taken from W B Jensen. *J. Chem. Ed.* 72, 395 ('95).

When plotting the point corresponding to some compound, one can simply plot the intersection of two lines – each starting with a constituent element on the x axis. The line from the left-hand element runs parallel to the left-hand edge pointing towards the ionic vertex, 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 that intersect at the element on the x axis. These lines run parallel with the two edges leading to the ionic vertex. On the left hand branch there are the compounds of which the element in question is the more electronegative; on the right-hand branch the element is the less electronegative of the pair. The compounds of caesium and of fluorine are exceptional in this regard, lying at the extremes of the base of the triangle: their compounds only lie the line connecting them to the ionic vertex.

The great advantage of the van Arkel triangle is that the three principal models of chemical bonding are seen to be part of a single scheme in which they are all related and indeed have equal weighting. It offers a quantitative appreciation of intermediate bonding, and also demonstrates that intermediate bonding is not limited to polar-

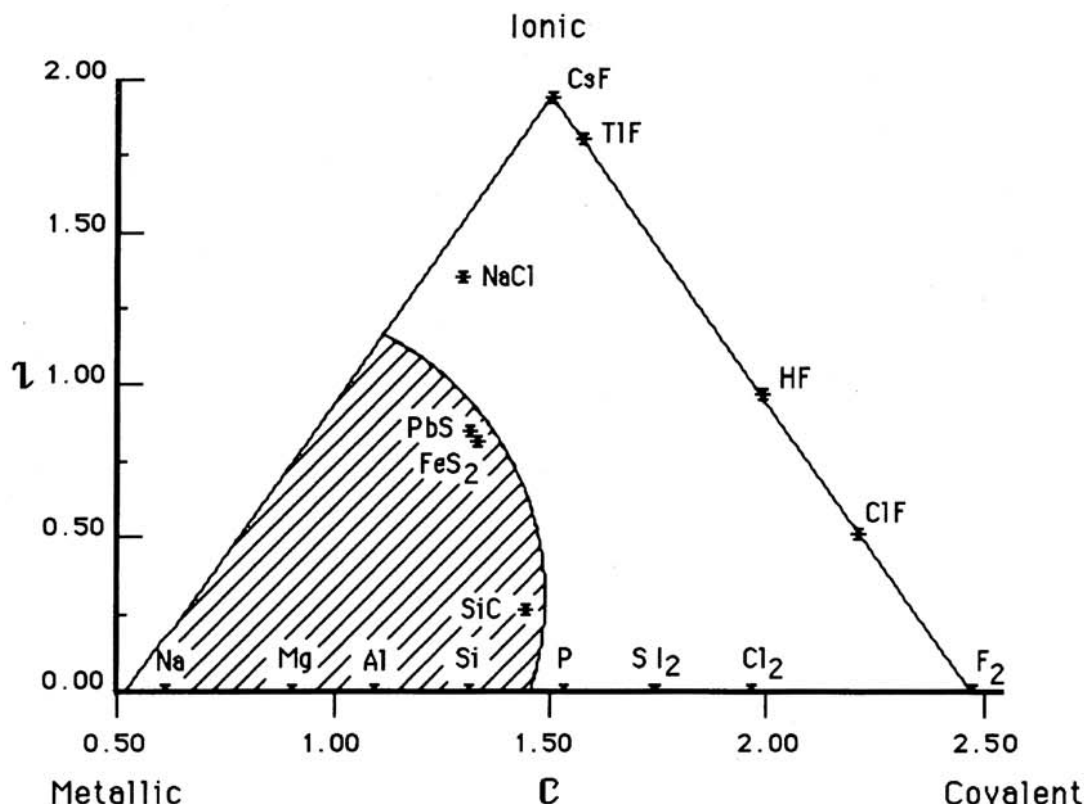
covalent / polarised ionic. Furthermore, it is based on the already-familiar topic of electronegativity.

The most simple application of the van Arkel triangle is to anticipate – based on electronegativity values – the type of bonding in some 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 there is a danger of the assignment of bonding type being the result of a circular process, where bonding type is arbitrarily defined by electronegativity values. The main point about the van Arkel triangle should lead be that it provides a clear picture of the fact that bonding type is not black and white, but rather a continuous scale between idealised extremes.

One subtle but important point about the van Arkel triangle is that its reflection of bonding type cannot be assumed to provide reliable information about structure. This is because structure depends on other factors besides electronegativity values – principally stoichiometry and electronic configuration. A similar problem is apparent when considering elements such as carbon, tin and phosphorus. These elements have allotropes of very different structures and electrical properties, 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 lead chloride. In this case the 4-valent compound has appreciable covalent character while the 2-valent analogue is essentially ionic.

It is however possible to find systematic predictors of structure in the van Arkel triangle if the compounds being considered are limited to those with a fixed stoichiometry and electronic configuration. This has been demonstrated by Bill Jensen.

There has been some discussion in the literature about semiconductor regions in the van Arkel triangle. Some authors have proposed a small triangle sitting on the base line of the main triangle. However semiconductivity is also seen along the metallic–ionic edge of the triangle. Owing to the problems of definition as to what constitutes a semiconductor, Bill Jensen performed a simple probe–buzzer–battery conductivity detector on a range of compounds and found a region within a distance of the metallic corner that showed appreciable conductivity (see figure on next page). It can be assumed that a semiconducting region will be found around the edge of this conductivity region.



The shaded in area in the figure above contains compounds that showed detectable conductivity in the simple test referred to above. Compounds outside this region did not show detectable conductivity in this test. The axes are the same as in the previous figure. The figure is taken from W B Jensen. *J. Chem. Ed.* 72, 395 ('95).

A range of electronegativity scales has been applied to the constructing of van Arkel triangles. Allen has proposed that his scale produces the most realistic placement of compounds according to their properties. Jensen has found that the variation between the different electronegativity scales is not significant. He used the little-known Martynov Batsanov scale which uses the average of the successive ionisation energies of the valence electrons of an atom. Allen's scale uses the average orbital energy of the valence electron orbitals, which he calls the configuration energy.

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B Possible teaching strategy

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.

One possible place to put it in the curriculum would be after teaching electronegativity. The electronegativity concept is only commonly used to explain the existence of dipoles, which indicate a form of intermediate bonding, though this angle may not always be pursued at the time. Therefore the van Arkel triangle should make for a substantial and meaningful application of the electronegativity concept and relate it to the dipoles seen in heteronuclear covalent bonds. The three basic bonding models will have been met by students in their pre-16 chemistry course. This strategy will serve to revise and re-inforce their understanding of the basic modes of bonding within a different framework.

Given the template van Arkel triangle provided, teachers can easily set straightforward exercises to plot binary compounds and to make predictions about bonding type and electrical properties. Piloting this topic showed that students do require some practice of this plotting. We also found that teachers will need to emphasise that the electronegativity values used must not be modified to take into account stoichiometry.

This topic also lends itself well to extension work. Groups could consider the more subtle points discussed in the theory section, and investigate the basis of the different types of electronegativity scale (which ties in with thermodynamics [Pauling], effective nuclear charge [Allred-Rochow], ionisation energy [Mulliken, Allen and Martynov Batsanov] and atomic radius [Sanderson]).

C Classroom materials

Summary notes

The van Arkel triangle

- It is only for binary compounds (between only two elements) and elements.
- The x axis gives a measure of how localised the electrons are on their atoms. On the left hand side the electrons are delocalised and the element is a metal. On the right hand side the electrons are localised and element is a covalently bonded non-metal.
- The y axis gives a measure of how equally the electrons are shared between the two elements. When $y = 0$ (ie on the x axis) the two atoms bonded are the same and so the electron in the bond are equally shared between them. At high values of y , towards the top of the triangle, there is a big difference in electronegativity and so the electrons are very unequally shared: the electrons are pulled towards the most electronegative element. This is what leads to ionic bonding.

- The three types of bonding can all be rationalised in terms of electronegativity values:
 - Small similar values = metallic
 - Large similar values = covalent
 - Very different values = ionic

How to plot a compound on a van Arkel triangle

Method One

- Take the average of the electronegativity values of the two elements. This is the x value.
- Work out the difference between the two electronegativity values. This is the y value.
- Ignore the stoichiometry of the compound, *ie* the numbers in the formula.

Method Two

- Find the two elements that constitute the compound on the x axis.
- Draw lines from these elements that are parallel to the sides of the triangle. The line from the left hand element is parallel to the left hand side; the line from the right hand is parallel to the right hand side.
- Where these lines intersect is the place to plot the compound in the triangle.

Intermediate bonding

- At the corners of the van Arkel triangle are the idealised cases of bonding. We can consider caesium to be pure metallic, fluorine as pure covalent, and caesium fluoride as pure ionic. However, most compounds are not right at the corners.
- The van Arkel triangle shows that many combinations of elements produce a type of bonding that is intermediate between the three idealised models. Silicon lies between metallic and covalent. Hydrogen fluoride lies between covalent and ionic. Caesium hydride lies between ionic and metallic. Mercury(II) bromide is near the centre of the triangle and so is intermediate between all three types of bonding.

Electrical properties

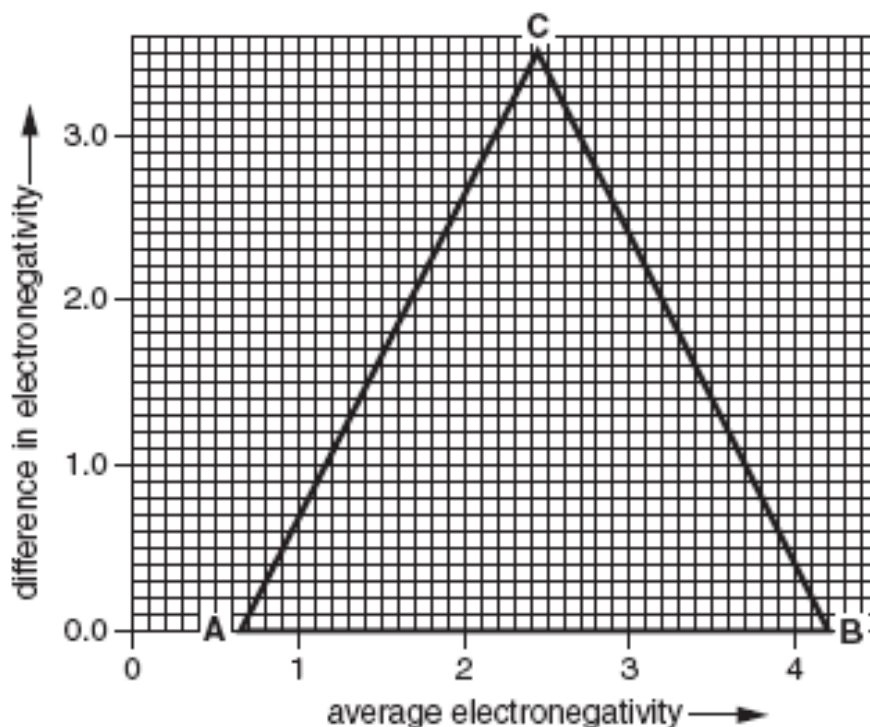
- Metallic compounds conduct electricity. Covalent and ionic compounds do not. We can therefore predict whether or not a compound will conduct electricity or not if it is near one of the corners of the van Arkel triangle.
- Compounds which conduct electricity can be found in a segment of the triangle around the metallic corner. Compounds near to the borderline of this segment are likely to be semiconductors.

1. Example question

This question is about electronegativity and bonding

- (a) Define electronegativity.
- (b) Explain why elements with low electronegativities can conduct electricity.
- (c) Ionic bonding results from the transfer of one or more electrons from one atom to another. Explain in terms of electronegativities why this transfer takes place.
- (d) Where might a compound that is described as polar covalent be found in the van Arkel triangle?
- (e) Plot the following compounds on the van Arkel template using the electronegativity values provided.
- Li_2O
 - NO
 - AlN
 - AlLi

Element	Electronegativity
Li	0.91
N	3.07
O	3.61
Al	1.61



(f) For the four compounds in the previous part, decide which of the following words best describes the bonding. Write the name of the compound beneath the word describing its bonding.

Ionic Covalent Metallic Intermediate

(g) Suggest for each of the four compounds which of the following words is most likely to describe its electrical conductivity. Write the name of the compound beneath the word describing the conductivity.

Conductor Semiconductor Insulator