**Fajans’ Rules and Polarizability**

In Section 4.5 in Chapter 4, we introduced the van Arkel-Ketelaar or element triangle as a means of understanding the varied properties of s- and p-block element compounds based on electronegativity differences, Dc. Thus, compounds where Dc is large exhibit ionic bonding (e.g. NaF) whereas for those compounds where Dc is zero or small, we are in the realm of covalent bonding, specifically metallic bonding where the absolute value of c is low (e.g. Na) and more directional covalent bonding where c is large (e.g. F2). For compounds with a medium Dc, polar covalent bonding is observed which often results in polymeric structures such as in GeF2. Numerous examples were presented and described for element halides, oxides and hydrides in Chapter 5.

Covalent and ionic bonding represent extremes on a bonding continuum, equal or largely equal sharing in the former and a transfer of electrons from one atom to another to form cations and anions in the latter. In a polar covalent bond, electrons are shared but not equally; the more electronegative element has the larger share of the bonding electron density.

This approach to bonding based on electronegativity differences owes much to Linus Pauling and is the approach we have adopted to rationalise the properties of the classes of compound we examined in Chapter 5, principally structure but including reactivity and certain physical characteristics. Thus, we can think of starting with a covalent bond A–B which is increasingly polarized as Dc between A and B increases until the situation is best described as ionic with polar covalent bonding in between. However, we may also start by considering a compound AB to be ionic, i.e. A+B– in the simplest case, and then examine the extent to which any covalency is present according to how much electron density is attracted from the B– anion to the A+ cation, that is, the extent to which the cation polarizes the anion. Polarization and polarizability are briefly mentioned in the marginal note on page 84, but we’ll consider what they mean in more detail here.

The approach where we start from an ionic bond and consider to what extent a cation polarizes an anion was described in some detail by Kasimir Fajans who, in the early 20th century, developed a set of rules which now bear his name. Specifically, Fajans considered the effect a small, highly charged cation would have on an anion, particularly a large highly charged anion and the eponymous rules can be stated as set out below.

1. Small, highly charged cations will exert a greater polarizing effect on anions than large, singly charged cations.
2. Large, highly charged anions will be more easily polarized than small, singly charged anions.

There is a third rule which relates to the electronic structure of the cation. For example, Hg2+ is more polarizing than Ca2+ even though both ions have the same charge and very similar ionic radii. This difference is a consequence of the incomplete shielding of the d electrons in the Hg2+ cation but since this is a text on s- and p-block element chemistry, we’ll not consider this third rule any further.

The effect of this polarization (or distortion) of electron density from the anion towards the cation is therefore to transition from an ionic interaction to a more covalent one where electrons are increasingly shared the more the cation polarizes the anion. Accordingly, Fajans’ Rules can also be stated as follows:

1. For a given anion, covalent character increases with decreasing size of the cation.
2. For a given cation, covalent character increases with the size of the anion.
3. Covalent character increases with increasing charge on either cation or anion or both.
4. For cations of like charge and similar size or ionic radius, a cation which does not have a noble gas configuration is more polarizing than one which does: this is the third rule noted above.

As an illustration which exemplifies the first two rules above, we might consider CsF *vs* LiI, the former being essentially purely ionic whereas the latter has a considerable degree of covalency. More generally, we can often account for trends in the properties of compounds in terms of the extent of polarization (and hence covalency) based on Fajans’ Rules in much the same way as we did with electronegativity differences in Chapter 5 although it is probably fair to say that electronegativity arguments are more commonly encountered in modern texts.

We should note that it is also possible to quantify Fajans’ Rules in terms of the polarizing ability of cations, for example, by considering the charge (*q*) to size (ionic radius, *r*) ratio *q*/*r*, the larger the number, the more polarizing the cation. This can be useful when comparing different cations and the properties of their compounds.

Finally, we should recognise the relationship between polarizability and hard and soft acids and bases (HSAB) which were considered in Section 6.4 in Chapter 6. Thus, hard acids are strongly polarizing and hard bases are strongly resistant to being polarized whilst soft acids are weakly polarizing and soft bases are easily polarized. Despite the polarizing power of a hard acid, hard plus hard favours an ionic interaction since the hard anion is not easily polarized and the strength of the ionic interaction (or lattice energy) is large for this arrangement. Conversely, soft plus soft favours a purely covalent interaction. Although something of an over-simplification which ignores any detail of orbital energies, these statements account, at least in part, for the observed preference of hard acids for hard bases and soft acids for soft bases.

A useful introduction to Fajans’ Rules in provided in Huheey, Keiter and Keiter (which also provides some quantitative data)1 and a more in-depth discussion both of Fajans’ Rules and HSAB together with some other related quantitative measures in provided in Miessler and Tarr.2 Other texts which deal more briefly with Fajans’ Rules are listed below in refs. 3-5.

***References***

1. Huheey, J. E., Keiter, E. A., Keiter, R. L. (1993). *Inorganic Chemistry: Principles of Structure and Reactivity* (4th edn), Harper and Row. See pages 129-131.
2. Miessler, G. L., Tarr, D. A. (2004). *Inorganic Chemistry* (3rd edn), Pearson. See pages 181-192.
3. Weller, M. T., Overton, T. L., Rourke, J. P., Armstrong, F. A. (2018). *Inorganic Chemistry* (7th edn), Oxford University Press. See pages 32-33.
4. Douglas, B. E., McDaniel, D. H., Alexander, J. J. (1994). *Concepts and Models of Inorganic Chemistry* (3rd edn), Wiley. See pages 200-203.
5. Lee. J. D. (1996). *Concise Inorganic Chemistry* (5th edn), Blackwell. See pages 156-157.