ISOMORPHISM AND BOND TYPE

W. S. Fyfe, *University of Otago, New Zealand.*

Since the classical work of V. M. Goldschmidt on ionic radii and crystal structure, mineralogists have considered that a necessary and almost sufficient condition for two atoms to show mutual replacement, is that they should have similar ionic radii. In a recent paper on the geochemistry of zinc, Dr. H. Neumann (1) has drawn attention to the fact that magnesium and iron enter only to a limited extent minerals of zinc. As these three atoms have similar ionic radii and identical charge they would be expected to permit a large amount of mutual solid solution.

During the past few years studies on bond lengths, bond energies, etc., have indicated that, in general, a bond between unlike atoms cannot be described as being purely ionic or covalent, but will be some combination of the two extreme types, or will be a hybrid bond, resonating between the two extreme forms. It has also been recognized that even where ionic bonding predominates the partial covalent character of the bond may lead to a considerable shortening of interatomic distance and ionic radii have not been entirely additive. For this reason it has been necessary to construct tables of covalent as well as ionic radii. One of the classical differences between ionic and covalent bonding is that where ionic bonding predominates there are no special restrictions on the bonds and the radius ratio rule will apply; i.e. the structure will depend on the relative sizes of the cations and anions, while in structures where covalent bonding predominates the structure is largely determined by the directional properties of the bonds; e.g. the bonds in carbon compounds where the carbon atom always forms four bonds directed to the corners of a regular tetrahedron. It is thus of considerable interest to the mineralogist to know approximately what type of bond exists in particular minerals so that some idea of whether these restrictions of configuration will be present or not.

The extent to which atoms form ionic or covalent bonds depends largely on two factors. If the ionization potential is low it will require little energy to remove electrons and thus an atom with a low ionization potential will tend to form ionic bonds. Conversely if the ionization potential is high there will be little tendency to lose electrons. Again, if the electron affinity is high an atom will have a tendency to acquire electrons and form an ionic bond. The balance of these two factors, ionization potential and electron affinity, largely determines the character of a bond. Thus, cesium fluoride is one of the most ionic compounds known because cesium has the lowest ionization potential of any element and a negligible electron affinity, while fluorine has a very high electron affinity and ionization potential. These two factors have been combined in what is known as the electronegativity of an atom. L. Pauling (2) from work on the dipole moments of the halogen hydrides has related the difference in electronegativity of atoms to the type of bond that will form between them (Fig. 1). It is thus possible to estimate approximately from the electronegativities of atoms the extent of covalent and ionic bonding. Probably the most reliable electronegativity values are those of Haissinsky (3).

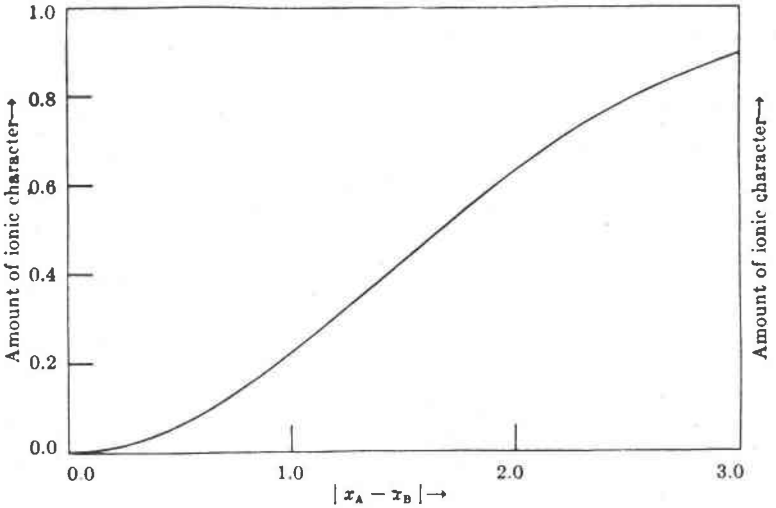

FIG. 1. Curve relating amount of ionic character of a bond A—B to the difference in electronegativity $x_A - x_B$ of the atoms. (Reproduced by courtesy of L. Pauling.)

If covalent bonding predominates the configuration and coordination number of an atom will depend on the type of covalent bond formed, which in turn depends on the number and type of orbitals available for covalent bond formation. Thus, if a combination of one "s" and three "p" orbitals are available, four tetrahedrally directed bonds will occur. Again if two "d" one "s" and three "p" electrons are available an octahedral configuration will be assumed. The major types of possible hybridizations are summarized by Syrkin and Dyatkina (4). The situation is complicated further by the fact that when the covalent bonding is weak, resonance may occur leading to a larger number of bonds than there are available orbitals e.g. four tetrahedral bonds may resonate among six positions leading to an octahedral configuration (5).

It will now be of interest to consider the case of isomorphism in zinc,

TABLE 1. ELECTRONEGATIVITIES OF ELEMENTS

Element	Electronegativity	Element	Electronegativity
Hydrogen	2.1	Niobium	(1.6)
Lithium	1.0	Molybdenum^{4}	(1.6)
Beryllium	1.5	Molybdenum^{5}	(2.1)
Boron	2.0	Ruthenium	2.05
Carbon	2.5	Rhodium	2.1
Nitrogen	3.0	Palladium	2.0
Oxygen	3.5	Silver	1.8
Fluorine	4.0	Cadmium	1.5
Sodium	0.9	Indium	1.6
Magnesium	1.2	Tin^{2}	1.65
Aluminium	1.5	Tin^{4}	1.8
Silicon	1.8	Antimony^{3}	1.8
Phosphorus	2.1	Antimony^{5}	2.1
Sulfur	2.5	Tellurium	2.1
Chlorine	3.0	Iodine	2.6
Potassium	0.8	Cesium	0.7
Calcium	1.0	Barium	0.85
Scandium	1.3	Lanthanum	0.85
Titanium^{4}	1.6	Cerium	1.05
Vanadium^{3}	1.35	Praseodymium	1.1
Vanadium^{4}	1.6	Hafnium	(1.3)
Vanadium^{5}	1.8	Tantalum	(1.4)
Chromium^{2}	1.5	Tungsten^{4}	(1.6)
Chromium^{3}	1.6	Tungsten^{6}	2.1
Chromium^{6}	(2.1)	Osmium	(2.1)
Magnanese^{2}	1.4	Iridium	2.1
Manganese^{3}	(1.5)	Platinum	2.1
Manganese^{7}	(2.3)	Gold	2.3
Iron^{2}	1.65	Mercury^{1}	1.8
Iron^{3}	1.8	Mercury^{2}	1.9
Cobalt	1.7	Thallium^{1}	1.5
Nickel	1.7	Thallium^{3}	1.9
Copper^{1}	1.8	Lead^{2}	1.6
Copper^{2}	2.0	Lead^{4}	1.8
Zinc	1.5	Bismuth	1.8
Gallium	1.6	Polonium	(2.0)
Germanium	1.7	85	(2.4)
Arsenic	2.0	87	0.7
Selenium	2.3	Radium	0.8
Bromine	2.8	Actinium	(1.0)
Rubidium	0.8	Thorium	1.1
Strontium	1.0	Proto Actinium	(1.4)
Yttrium	1.2	Uranium	1.3
Zirconium	1.4		

Values are taken from Haissinsky and Pauling.
Those in parentheses are only approximate.

manganese and iron minerals. Some of the binary compounds of these minerals are listed in Table 2 with the co-ordination numbers and approximate covalent character of the bonds.

TABLE 2. APPROXIMATE TYPE OF BOND IN BINARY COMPOUNDS OF ZINC, MAGNESIUM AND IRON

Non-Metal	Zinc		Magnesium		Iron	
	% Cov.	C.N.	% Cov.	C.N.	% Cov.	C.N.
Fluorine	23	6	14	6	27	6
Chlorine	57	6	45	6	65	6
Bromine		?	55	6	75	6
Iodine		?	60	6	80	6
Oxygen	37	4	28	6	43	6
Sulfur	78	4	67	6	84	6
Selenium	85	4	74	6	90	6
Telurium	92	4	82	4	95	6
Silicon			90	4		
Germanium			90	4		
Tin			93	4		

On the basis of the electronic structures of these three elements it would be predicted that zinc and magnesium would most readily form tetrahedral hybrid bonds while iron would form octahedral bonds. In the compounds where covalent bonding predominates this is certainly the case. It will also be noticed that in compounds with more ionic character that zinc and magnesium are both octahedrally co-ordinated. This may be due to resonance of the four bonds among six positions. Zinc has a greater electronegativity than magnesium and hence zinc compounds are more covalent. Magnesium only assumes the co-ordination number four in extremely covalent structures. This may be due to the fact that magnesium has an eight electron shell inside its valence electrons while zinc has a shell of eighteen. In general metals with eight shells are reluctant to form covalent bonds unless they are of small size.

It would be expected that the fluorides and chlorides of these metals would be isomorphous, for in all these cases the configuration and size of the groups will be similar.

It is rather surprising that zinc in zinc oxide has a co-ordination number four in a compound of such ionic character. However, zinc and iron do enter into periclase to a marked extent, and zinc is also in six-co-ordination in its carbonate. It does appear in fact, that the zinc-oxygen bond is fairly near a transition point from tetrahedral to octahedral bonding. It is in this class of compound as Neumann points out that most of the isomorphous replacement of zinc by iron and magnesium occurs.

Consideration of these conceptions suggests that the rules predicting isomorphism may require some extension. It appears that two atoms will be mutually replaceable in ionic compounds if their sizes are similar, and will be replaceable in more covalent compounds only if the number, and directional properties of their bonds, are similar.

Atoms of similar electronic structure and size should be isomorphous for they will form similar hybrid bonds. The transition metals do show a large amount of isomorphism and this would be expected from their similar sizes and the fact that they would all form octahedral hybrid covalent bonds. The alkali and alkaline earths also form a group for these are the most electropositive elements and the bonding in most of their minerals will be ionic and thus ionic radius will be the major governing factor. Zinc, cadmium and mercury all show some mutual solubility as would be expected. It thus appears that groups of the periodic table with similar structures do show some mutual solubility where the sizes are not too different.

REFERENCES

1. NEUMANN, H., *Mineral. Magazine,* **XXVIII,** 575 (1949).
2. PAULING, L., "Nature of the Chemical Bond," *Cornell University Press* (**1940**), p. 69.
3. HAISSINSKY, M., *J. de Physique et Le Radium* (VII) (**Jan. 1946**).
4. SYRKIN & DYATKINA, "Structure of Molecules," *Butterworths Scientific Publications,* London (**1950**), p. 348.
5. PAULING, L., *J. Chem. Soc.*, 1461 (**1948**).

Manuscript received Nov. 11, 1950