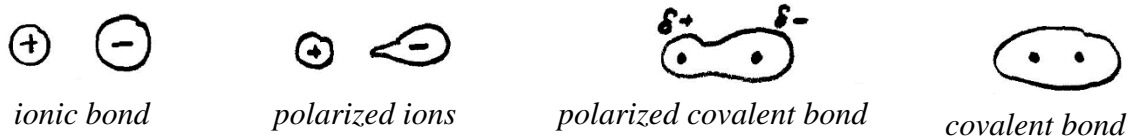


**POLARIZATION THEORY**

**POLARIZING POWER & POLARIZABILITY-FAJAN'S RULES-TRANSITION BETWEEN IONIC AND COVALENT BONDING**

Theoretically, when ions like  $A^+$  and  $B^-$  come together to form a new chemical bond, whether the bond is ionic or covalent is explained by polarization of those ions (polarization of electron cloud, changing shape). Positive ion attracts the electrons on the negative ion at the same time it repels the nucleus and it deforms the global structure of negative ion. In other words the positive ion polarizes the negative ion and changes its shape. The magnitude of polarization depends on the power of an ion to affect the other. The electron cloud of an anion involves the cation.



Generally, polarizing power is increased by the decreasing of positive ion radius and increasing the charge. In other words polarizing power is increased by the increasing of charge density (ionic potential= $q/r$ . Ionic potential is the ratio of electric charge to the Radius of an ion). Due to the difference in the effective nuclear charge, the valence electrons are kept weakly in the negative ion compared to the positive ion. Therefore, the polarization of negative ions is easier than the positive ions. The polarizability of negative ions increases with the increasing the charge and radius of ion. If the degree of polarization is small, the bond is substantially ionic. If the degree of polarization is large, the electrons of the negative ion are drawn towards the positive ion direction. Thus, the electron density between the two nucleus increases and the bond gains covalent character.

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According to the Fajans:

1. The positive ion which has a higher charge density increases the covalent character. The positive charge in these ions is concentrated in a small volume. This structure give a high degree of polarizing power to the ion.  $Si^{+4}$ ,  $P^{+5}$ ,  $Cl^{+7}$  cannot be present because their ionic potential is so high that they immediately attract oxygen from the water and show strong acidity and give strong covalent bonds. (Li is similar to Mg, B is similar to Si, Be is similar to Al; their ionic potentials are nearly the same). The polarization capacity of  $K^+$ ,  $Ca^{+2}$ ,  $Sc^{+2}$  (which have noble gas structure) are very low.
2. The negative ion with a large radius increases the covalent character. The shape of negative ions, whose radius is large, can be easily destroyed by positive ions. This is because the effective nuclear charge, which sees valence electrons in large negative ions, is reduced. The anions such as  $I^-$ ,  $Se^{2-}$  which have large radius and  $N^{3-}$ ,  $P^{3-}$ ,  $As^{3-}$  which have big charges form covalent bond.
3. The increase in the charges on the anion and cation increases the degree of polarization and thus increases the covalent character.
4. If the positive ion is not in the inert gas structure, the covalent character increases. Inert gas structure is a structure where the effective nuclear charge is effectively shielded (orbital shielding sequence is  $s > p > d > f$ ). Therefore, ions such as  $Tl^+$ ,  $Pb^+$ ,  $Bi^{+3}$ ,  $Ti^{+3}$ ,  $V^{+3}$ ,  $Cr^{+2}$ ,  $Mn^{+2}$ ,  $Cu^{+2}$ ,  $Ce^{+3}$ ,  $Eu^{+2}$ , which do not have an inert gas structure, have high polarizing power.  $K^+$ ,  $Ca^{+2}$ ,  $Sc^{+3}$  have noble gas (Ar) structure and their polarization degrees are small. Although  $Ti^{+4}$  is isoelectronic with Ar,  $TiCl_4$  is covalent because  $Ti^{+4}$  has the small radius and big charge. In the cations with d orbitals, the ionic potential is large, since the d orbital cannot shield as much as s and p orbitals. If one of the two ions with the same charge and radius is the transition element cation, it gives covalent bond by the polarizing the anion more.

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*The Aqueous Solubility of 2A Group Hydroxides, Sulfates and Carbonates*

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**$M(OH)_2$**

↓ *Hydration energy decreases*

*Lattice energy decreases*

*The solubility increases*

*The OH<sup>-</sup> ion is a small anion. OH<sup>-</sup> enters the hole formed by alkaline earth cations. The OH<sup>-</sup> ion is a small anion. OH<sup>-</sup> enters the cavity formed by alkaline earth cations. Lattice energy decreases, solubility increases.*

**$M(SO_4)_2$  or  $M(CO_3)_2$**

↓ *Hydration energy decreases*

*Lattice energy remains the same*

*The solubility decreases*

*CO<sub>3</sub><sup>2-</sup> and SO<sub>4</sub><sup>2-</sup> ions are large anions. Alkaline earth cations enter the holes formed by these ions. Therefore, the lattice energy remains approximately the same in all of them. What is effective in solubility is the hydration energy. The solubility decreases since hydration energy decreases. The lattice energy decreases, solubility increases.*

