

Zintl Phases

Zintl-concept, definition and principle;

Zintl Phases were named for the German Chemist Eduard Zintl who investigated them in the 1930's. These compounds consist of an electropositive cationic component (alkali metal, alkali earth metal) and anionic part (element of 13th - 15th group in periodic table of the elements) that is a metal, semimetal or small gap semiconductor.

The *Zintl concept* shows that atoms/ions/molecules with the same number of valence electrons can build the same structure.

A typical Zintl phases is NaTl. The anionic partial structure has diamond structure, because Tl has 4 valence electrons like Carbon.

Properties of Zintl phases :

- higher melting points than the pure metals they are build of
- fixed stoichiometry/composition
- brittle (like salts), deeply coloured
- semiconductors or poor conductors (the higher the atomic number of the anionic component, the smaller is the bandgap)

Syntheses of Zintl phases :

- reduction in liquid ammonia
- solid state reactions
- cathodic decomposition

(8-N) - Rule, examples :

The simplified (8-N) rule gives information about the number of bonds in a compound by considering the number of valence electrons of the anionic component (N). For polyions the number of bonds is given by (8-Valence Electron Concentration [VEC]), which can be calculated from

$VEC = [m \cdot e(M) + x \cdot e(X)] / x$ for Zintl Phases with the general composition M_mX_x and the number of valence electrons of the components $e(M)$ and $e(X)$. By considering the VEC, one can decide whether the compound is polyanionic or polycationic : $VEC < 8$ polyanionic compound, $VEC > 8$ polycationic compound, $VEC = 8$ simple ionic compound.

Example	VEC	no. of bonds	estimated bonding	structure of anionic part
NaTl	4	4	Polyanionic	Diamond
K ₄ Ge ₄	5	3	Polyanionic	White Phosphorus
Ba ₃ Si ₄	5.5	2.5	Polyanionic	behaviour of anion is a mixture of group 5 and group 6 elements; Si ⁻ has three bonds, Si ²⁻ has two bonds to neighboring atoms

Literature : *Ulrich Müller, Inorganic Structural Chemistry*

Tasks:

- 1- Describe a typical Zintl Phase!
- 2- By giving examples classify compounds according to the value of VEC!