**Zintl-phases**

1. **Zintl-concept, principle, definition:**
   - Eduard Zintl (1898-1941, German chemist, research: intermetallic phases)
   - E. Zintl discovered discrete charges at some intermetallic phases: compounds with an electropositive part (alkali or alkaline earth metal) and an electronegative part (element of the 13th-15th group of the periodic table of the elements)
   - Zintl-(Klemm-Busmann-)concepts: Atoms/ions/molecules with the same number of valence electrons may build the same structure! \( \rightarrow \) NaTl: Tl\(^{-}\) has diamond structure (Tl has 4 valence electrons like C)

2. **Properties of Zintl-phases**
   - deeply coloured
   - some Zintl-phases are soluble in liquid ammonia (cluster anions)
   - compounds with fixed compositions (fixed stoichiometry)
   - brittle (like salts)
   - higher melting points than the pure metals they are built of
   - semiconductors (the higher the atomic number of the electronegative part, the smaller is the bandgap of the semiconductor)

3. **Syntheses of Zintl-phases**
   a) reduction in liquid ammonia:
      Metal salts of the electronegative part are in situ reduced by the electropositive metal:
      \[
      22\text{Na} + 9\text{PbI}_2 + n \text{NH}_3 (l) \rightarrow \text{Na}_4\text{Pb}_9 \times n \text{NH}_3 + 18\text{NaI}
      \]
      problem in the beginning of the research: decomposition when NH\(_3\) is removed
   b) direct solid state reaction:
      \[
      \text{Ca} + \text{Si} \rightarrow \text{CaSi}
      \]
      \(\text{Si}^2^-\) behaves like Se or Te)
   c) cathodic decomposition \(\rightarrow\) binary compound is decomposed at the cathode and polyanions go into solution

4. **Examples, structure, \((8 - N)\)-rule**
   \((8 - N)\)-rule: simplified \((8 - N)\)-rule makes a conclusion about the number of bonds in a compound \((N = \text{number of valence electrons of the element which builds the compound})
   Example: P \(\rightarrow\) N = 5 \(\rightarrow\) \((8 - N) = 8 - 5 = 3 \rightarrow\) Phosphorus has 3 bonds, i.e. white modification: P-tetraeder
   The \((8 - N)\)-rule has to be expanded in case of polyanions: \((8 - \text{VEC}) = \text{number of bonds}\)
   \(\rightarrow\) VEC = valence electron concentration = \([m \times e(M) + x \times e(X)]/x\) for the compound \(M_mX_x\)
   \(\rightarrow\) e(M) and e(X) are the number of valence electrons of the elements M and X, respectively
   Example 1: NaTl
   VEC = \([1 \times 1 + 1 \times 3]/1 = 4 \rightarrow\) electronegative part behaves like an element of the 4th main group \(\rightarrow\) X-ray diffraction shows diamond structure of Tl \(\rightarrow\) \((8 - \text{VEC}) = 8 - 4 = 4 \rightarrow\) 4 bonds are build
   Example 2: K\(_4\)Ge\(_4\)
   VEC = \([4 \times 1 + 4 \times 4]/4 = (4 + 16)/4 = 5 \rightarrow Ge_4^{4-}\) behaves like an element of the 5th main group \(\rightarrow\) X-ray diffraction shows a structure like white phosphorus \(\rightarrow\) \((8 - \text{VEC}) = 3 \rightarrow\) 3 bonds are build
   Example 3: Ba\(_3\)Si\(_4\)
   VEC = \([3 \times 2 + 4 \times 4]/4 = 5.5 \rightarrow Si_4^{6-}\) behaves partially like an element of the 5th and partially of the 6th main group \(\rightarrow\) 8 - VEC = 2.5 \(\rightarrow\) average of bonds of the polyanion is 2.5 \(\rightarrow\) Ba\(^{2+}\) + 2Si\(^{-}\) + 2Si\(^{2-}\) \(\rightarrow\) Si\(^-\) build 3 bonds, Si\(^{2-}\) build 2 bonds \(\rightarrow\) Butterfly-ion