

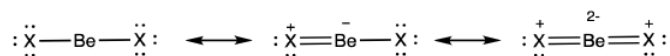
2.2.5: Limitation of Lewis Theory

Two notable cases where Lewis theory fails to predict structure is in the cases of beryllium (Be) and boron (B). These two atoms are in period 2 ($n = 2$) of the periodic table and their atoms have the valence electron configurations of $2s^2$ and $2s^2 2p^1$, respectively.

Beryllium

Prediction based on Lewis structure:

The Lewis electron dot structures are shown below for BeX_2 , where X is one of the halogens, F or Cl.



Each of the structures above would predict a linear geometry for the BeX_2 molecule. Together the three resonance structures suggest partial double-bond character in the Be-X bond, which results in an intermediate bond length between a single and double bond.

There are issues with each of these resonance structures. The structure on the left would predict only four electrons around Be; thus, the atom does not fulfill the octet rule. The structure on the right suggests multiple bonds for the halogen (X) and high separation of charge with formal charge on each atom. The structure in the middle is a mix of these problems. None of these situations is ideal according to Lewis theory. Further, experimental data is not consistent with any of these structures or their resonance hybrid (except in the case of BeCl_2 at very high temperatures).

It turns out that the monomer of BeX_2 (shown above) does exist, but only at very high temperatures and low pressures. Even under extreme conditions, the monomer is not particularly stable due to the electron deficiency around Be.

BeF_2

At ambient temperature and pressure, BeF_2 is a solid that looks similar to quartz (Figure 2.2.5.1). The Be is four-coordinate with tetrahedral geometry; each F is two-coordinate and the Be-F bond length is 1.54 Å. This structure is possible due to an extended 3-dimensional network in the solid where adjacent BeF_2 units are bonded to one another, as shown in Figure 2.2.5.1.

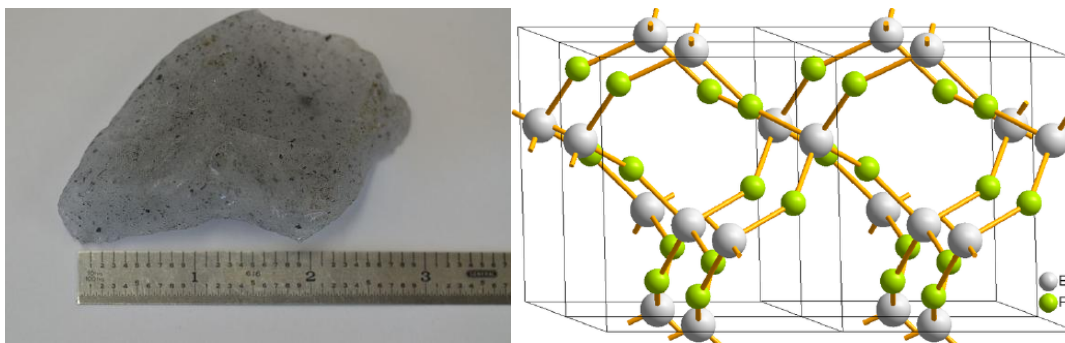


Figure 2.2.5.1: (left) A nugget of beryllium fluoride obtained from Materion. Black spots are carbon (CC BY-SA 3.0; Bckelleher via Wikipedia). (right) BeF_2 structure (CC BY-SA 3.0 Unported; MaterialsScientist via Wikipedia)

In the liquid phase, BeF_2 has a fluctuating tetrahedral structure where Be and F ions exchange. The vapor phase is reached at temperatures higher than 1000 °C (at ~ 1 atm). In the vapor phase, BeF_2 exists as a monomer with linear geometry and a bond length of 1.43 Å, consistent with a double bond between Be and F.

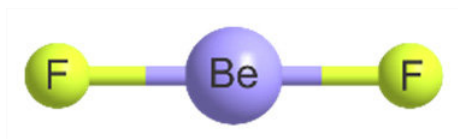


Figure 2.2.5.2: Geometries of BeF_2 . (CC BY; Ibon Alkorta and Anthony C. Legoe via Inorganics)

BeCl₂

At ambient temperature and pressure, BeCl₂ is a solid. As in BeF₂ described above, BeCl₂ has four-coordinate, tetrahedral Be and two-coordinate F. In contrast to BeF₂, solid BeCl₂ is a 1-dimensional polymer consisting of edge-shared tetrahedral.

In the gas phase, BeCl₂ exists as a dimer with two chlorine atoms bridging two Be atoms. In the dimer, the Be atoms are 3-coordinate. Bridging Cl atoms are two-coordinate, while terminal Cl atoms are one-coordinate. At higher temperatures in the vapor phase, the linear monomer also exists.

Boron (2s²2p¹)

Prediction based on Lewis structures:

Lewis structures of BH₃ and BF₃ were described in [Exercise 3.1.2](#), and are drawn again below for convenience.

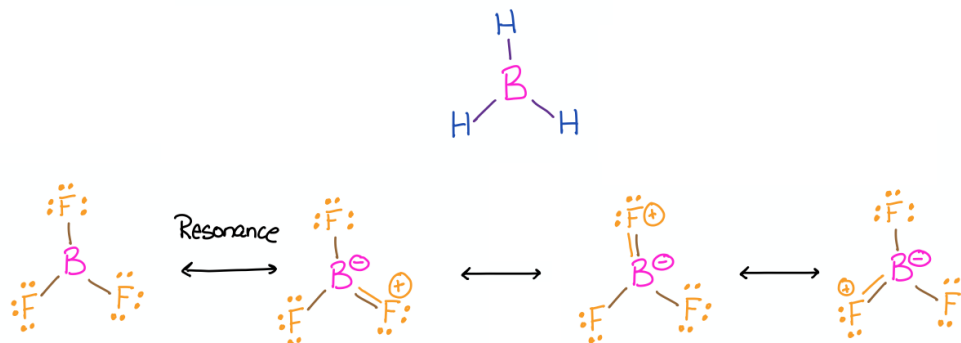


Figure 2.2.5.3:
Lewis structures of BH_3 and BF_3

Boron trihalides (ex. BF₃)

Boron trihalides, like BF₃, have properties that are largely predicted by Lewis structures and VSEPR theory. The Lewis structure for BF₃ includes several resonance structures. The structure with only single bonds is the most common representation for this molecule because the charge separation shown in the other structures is considered to be unfavorable. The highly polarized B-F bond has a dipole moment that lies opposite of the indicated formal charges shown in the resonance structures with double bonds between boron and fluorine.

The resonance hybrid of BF₃ predicts partial double bond character between boron and fluorine, thus a bond length shorter than a single bond. Using the Lewis structures and VSEPR theory, we would predict a trigonal planar geometry around boron. In fact, the actual structure of BF₃ is a monomer with trigonal planar geometry and with bond length that is shorter than a single bond. The case is similar to structures of other boron trihalides as well.

Boron trihalides are electron deficient at the boron center and react readily with Lewis bases. In other words they are strong Lewis acids (electrophiles).

Boron trihydride (BH₃ is really B₂H₆)

The properties of boron trihydride (BH₃) are not predicted by the simple predictions made through Lewis structures and VSEPR. The monomer, BH₃, is not stable, but when dissolved in the presence of a Lewis base, BH₃ can form a stable acid-base adduct. In its pure form, the compound actually exists as a dimeric gas with a molecular unit of B₂H₆ (try drawing a valid Lewis structure for that!). Its unexpected structure includes two H's that bridge the two boron atoms in 3-center-2-electron bonds. You can read more about B₂H₆ on the Wikipedia page for Diborane.

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