Topic 0

Course Prep

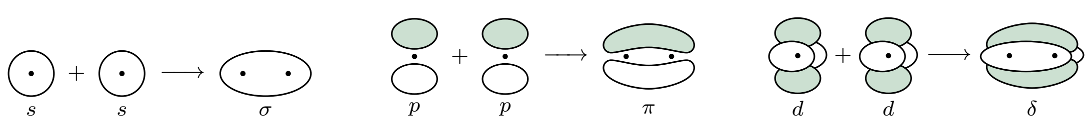
0.1 Chapter 1: Introduction to Inorganic Chemistry

From Miessler et al. (2014).

0.1.1 Notes

12/21:

- **Inorganic chemistry**: The chemistry of everything that is not organic chemistry (the chemistry of hydrocarbon compounds and their derivatives).
- **Organometallic chemistry**: The chemistry of compounds containing metal-carbon bonds and the catalysis of many organic reactions.
- There is also both **bioinorganic chemistry** and **environmental chemistry** (Miessler et al., 2014, p. 1), as well as **analytical chemistry**, **physical chemistry**, **petroleum chemistry**, **polymer chemistry** (Miessler et al., 2014, p. 4).
  - Note, though, that there are no strict dividing lines between subfields of chemistry nowadays, and most professionals work in multiple fields.
- Single, double, and triple bonds (both metal-metal and metal-carbon bonds) are found in organic and inorganic chemistry.
- Quadruple bonds exist between metal atoms in some compounds.



(a) Sigma (σ) bond. (b) Pi (π) bond. (c) Delta (δ) bond.

Figure 1: Examples of bonding interactions.

  - No such bonds exist between carbon atoms because two carbon atoms max out at a triple bond.
  - Quadruple bonds possess one sigma bond, two pi bonds, and one delta (δ) bond.
  - The delta bond is only possible with metal atoms because these atoms possess energetically accessible d orbitals.
- Quintuple bonds between transition metals have been reported, but scientists have not yet reached a consensus on to what extent these exist.

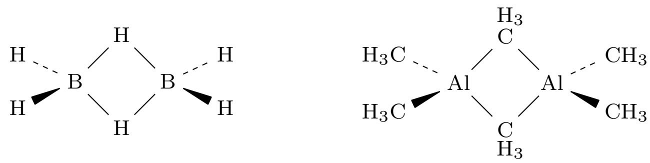


Figure 2: Inorganic compounds containing bridging hydrogens and alkyl groups.

- Hydrogen atoms and alkyl groups can act as bridges in inorganic chemistry, excessively disobeying the octet rule (see Figure 2).
- **Coordination number**: The number of other atoms, molecules, or ions to which an atom is bonded.
- "Numerous inorganic compounds have central atoms with coordination numbers of five, six, seven, and higher" (Miessler et al., 2014, p. 2).
  - The most common coordination geometry for transition metals is octahedral.
- 4-coordinate carbon is almost always tetrahedral. 4-coordinate metals and nonmetals can be either tetrahedral or square planar.
- **Coordination complex**: A compound with a metal as the central atom or ion and some number of **ligands** bonded to it.
- **Ligand**: An anion or neutral molecule bonded to a central atom (frequently through N, O, or S).
- **Organometallic complex**: A coordination complex where carbon (potentially bonded to other things) is one of the ligands.

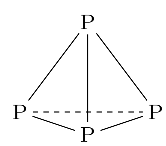


Figure 3: Tetrahedral geometry without a central atom.

- There are multiple kinds of tetrahedral structures. There is the standard arrangement seen in molecules such as methane, but there is also a form that lacks a central atom, as in elemental phosphorous P_4 (see Figure 3).
  - Other atoms such as boron and carbon also form units that surround a central cavity (e.g., icosahedral B_{12} and buckyballs C_{60}).
- Aromatic rings can bond to metals using all of their pi orbitals. This results in a metal suspended above the ring's center.
- **Cluster compound**: A compound where "a carbon atom is at the center of a polyhedron of metal atoms" (Miessler et al., 2014, p. 3).
  - There exist examples of carbon surrounded by five, six, or more metal atoms[1].
- Many new forms of elemental carbon have been discovered since the mid-1980s, notably including fullerenes (such as buckminsterfullerene, or buckyballs), carbon nanotubes, graphene, and polyyne wires.
- Miessler et al. (2014) give a brief history of inorganic chemistry for context.
  - Be aware of **crystal field theory** and **ligand field theory**.

[1]This provides a challenge to theoretical inorganic chemists.

0.2 Chapter 2: Atomic Structure

From Miessler et al. (2014).

0.2.1 Problems

9/13: **2.8** The details of several steps in the particle-in-a-box model in this chapter have been omitted. Work out the details of the following steps:

a. Show that if $\Psi = A\sin rx + B\cos sx$ (A, B, r, and s are constants) is a solution to the wave equation for the one-dimensional box, then

$$r = s = \sqrt{2mE}\left(\frac{2\pi}{h}\right)$$

Solution.

$$\begin{aligned}
\frac{-h^2}{8\pi^2 m}\cdot\frac{\partial^2\Psi(x)}{\partial x^2} &= E\Psi(x)\\
\frac{-h^2}{8\pi^2 m}\cdot\frac{\partial^2}{\partial x^2}(A\sin rx + B\cos sx) &= E(A\sin rx + B\cos sx)\\
\frac{-h^2}{8\pi^2 m}\cdot\frac{\partial}{\partial x}(Ar\cos rx - Bs\sin sx) &= E(A\sin rx + B\cos sx)\\
\frac{-h^2}{8\pi^2 m}\cdot\left(-Ar^2\sin rx - Bs^2\cos sx\right) &= E(A\sin rx + B\cos sx)\\
\frac{Ar^2h^2}{8\pi^2 m}\sin rx + \frac{Bs^2h^2}{8\pi^2 m}\cos sx &= AE\sin rx + BE\cos sx\\
0 &= \left(\frac{Ar^2h^2}{8\pi^2 m} - AE\right)\sin rx + \left(\frac{Bs^2h^2}{8\pi^2 m} - BE\right)\cos sx
\end{aligned}$$

Choose $x = 0$.

$$\begin{aligned}
&= \frac{Bs^2h^2}{8\pi^2 m} - BE\\
E &= \frac{s^2h^2}{8\pi^2 m}\\
\frac{8\pi^2 mE}{h^2} &= s^2\\
s &= \sqrt{\frac{8\pi^2 mE}{h^2}}\\
&\boxed{s = \sqrt{2mE}\frac{2\pi}{h}}
\end{aligned}$$

With this result ...

$$\begin{aligned}
0 &= \left(\frac{Ar^2h^2}{8\pi^2 m} - AE\right)\sin rx + \left(\frac{Bs^2h^2}{8\pi^2 m} - BE\right)\cos sx\\
&= \left(\frac{Ar^2h^2}{8\pi^2 m} - AE\right)\sin rx + \left(B\left(\frac{s^2h^2}{8\pi^2 m}\right) - BE\right)\cos sx\\
&= \left(\frac{Ar^2h^2}{8\pi^2 m} - AE\right)\sin rx + (BE - BE)\cos sx\\
&= \left(\frac{Ar^2h^2}{8\pi^2 m} - AE\right)\sin rx
\end{aligned}$$

Choose $x = \frac{\pi}{2r}$.

$$= \frac{Ar^2h^2}{8\pi^2 m} - AE$$

$$\boxed{r = \sqrt{2mE}\frac{2\pi}{h}}$$

$\square$

d. Show that substituting the value of r given in part c into $\Psi = A \sin rx$ and applying the normalizing requirement gives $A = \sqrt{2/a}$.

Solution.

$$\begin{aligned}
1 &= \int_{\text{all space}} \Psi\Psi^* \, \mathrm{d}\tau \\
&= \int_0^a \left(A \sin \frac{n\pi x}{a}\right)\left(A \sin \frac{n\pi x}{a}\right) \mathrm{d}x \\
&= \int_0^a A^2 \sin^2 \frac{n\pi x}{a} \, \mathrm{d}x
\end{aligned}$$

Use $\sin^2 u = \frac{1-\cos 2u}{2}$.

$$\begin{aligned}
&= A^2 \int_0^a \frac{1 - \cos \frac{2n\pi x}{a}}{2} \, \mathrm{d}x \\
&= \frac{A^2}{2}\left(\int_0^a \mathrm{d}x - \int_0^a \cos \frac{2n\pi x}{a} \, \mathrm{d}x\right) \\
&= \frac{A^2}{2}\left([x]_0^a - \left[\frac{a}{2n\pi} \sin \frac{2n\pi x}{a}\right]_0^a\right) \\
&= \frac{A^2}{2}\left((a-0) - \left(\frac{a}{2n\pi} \sin 2n\pi - \frac{a}{2n\pi} \sin 0\right)\right) \\
&= \frac{A^2}{2}\left(a - \left(\frac{a}{2n\pi} \sin 2n\pi\right)\right)
\end{aligned}$$

Since n is an integer, $\sin 2n\pi = 0$.

$$\begin{aligned}
&= \frac{aA^2}{2} \\
\frac{2}{a} &= A^2 \\
\Aboxed{A &= \sqrt{\frac{2}{a}}}
\end{aligned}$$

$\square$