

## 1: Atomic Orbitals and Magnetism - Chemistry LibreTexts

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Contributors The Molecular Orbital picture we developed in Section 6. The two valence electrons are spin-paired in atomic Mg, as they are in the helium atom  $1s^2$ . When the 3s orbitals of Mg combine to form a band, we would expect the band to be completely filled, since Mg has two electrons per orbital. By this reasoning, solid Mg should be an insulator. But Mg has all the properties of a metal: In this case the 3s and 3p bands are sufficiently broad because of strong orbital overlap between Mg atoms that they form a continuous band. This band, which contains a total of four orbitals one 3s and three 3p per atom, is only partially filled by the two valence electrons. The cohesive energy of Mg metal is the difference between the bonding and promotion energies. The heat of vaporization, or the cohesive energy of a metal, is the difference between the bonding energy and the promotion energy. The concepts of promotion energy and bonding energy are very useful in rationalizing periodic trends in the bond strengths and magnetic properties of metals, which are described below. Schematic representation of the sizes of different orbitals of Cr and W. In the first transition series, shielding of the 3d orbitals is poor. Therefore the 4s and 4p orbitals are more effective in bonding than the 3d. In the third transition series, the situation is reversed. The increased nuclear charge is felt most strongly by the 6s, which takes on the character of an inert electron pair. Periodic trends in d-electron bonding While electrons in s and p orbitals tend to form strong bonds, d-electron bonds can be strong or weak. There are two important periodic trends that are related to orbital size and orbital overlap. These trends explain the distinct behavior of the 3d elements relative to those in the 4d and 5d series. In the 3d series, the contraction of orbitals affects the ability of the d electrons to contribute to bonding. Past V in the first row of the transition metals, the 3d electrons become much less effective in bonding because they overlap weakly with their neighbors. Weak overlap of 3d orbitals gives narrow d-bands and results in the emergence of magnetic properties as discussed below. The heat of vaporization the cohesive energy of metals in the 3d and 5d series, measured at the melting point of the metal. The number of bonding electrons, and therefore the bonding energy, increases steadily going from Rb to Mo in the 4d series, and from Cs to W in the 5d series. Mo and W have the most bonding energy because they can use all six of their valence electrons in bonding without promotion. Elements past Mo and W have more d electrons, but some of them are spin paired and so some promotion energy is needed to prepare these electrons for bonding. Because of their strong bonding energy, elements in the middle of the 4d and 5d series have very high melting points. We do not see magnetism in the 4d or 5d metals or their alloys because orbital overlap is strong and the bonding energy exceeds the electron pairing energy. With strong overlap between orbitals, the bonding energy exceeds the pairing energy and electrons spin-pair. With weaker overlap, bonding is weak and spins unpair, resulting in magnetic behavior. In the 3d series, we see the expected increase in cohesive energy going from Ca  $4s^2$  to Sc  $4s^2 3d^1$  to Ti  $4s^2 3d^2$  to V  $4s^2 3d^3$ , but then something very odd happens. The 3d series has a "crater" in the cohesive energy plot where there was a peak in the 5d series. We can explain this effect by remembering that the 3d orbitals are progressively contracting as more protons are added to the nucleus. For elements beyond V, the orbital overlap is so poor that the 3d electrons are no longer effective in bonding, and the valence electrons begin to unpair. Depending on the way the spins order, metals and alloys in this part of the periodic table can be ferromagnetic spins on neighboring atoms aligned parallel, as in the case of Fe or Ni or antiferromagnetic spins on neighboring atoms antiparallel, as in the case of Mn. We have seen the trade-off between orbital overlap and magnetism before in Chapter 5 in the context of paramagnetic transition metal complexes. It is worth recalling that this behavior is predicted in the energy vs. At short interatomic distances or with strong overlap between atomic orbitals, the spins of the electrons pair and a bond is formed. Unpairing the electrons becomes favorable at larger interatomic distances where the overlap between orbitals is poor. Strong permanent magnets often contain alloys of Nd, Sm, or Y, usually with magnetic 3d elements such as Fe and Co. Because the 4f orbitals are contracted and not very effective in bonding, other physical properties of the lanthanides are also affected. For example, oxides of the 4f elements have rather weak surface interactions with polar molecules such as water. Late transition metal

alloys Although the bonding in the 5d series follows a "normal" volcano plot, the situation is a bit more complex for alloys of Re, Os, Ir, Pt, and Au. There is strong overlap between the 5d orbitals, but because these elements contain more than five d-electrons per atom, they cannot make as many bonds as 4d or 5d elements with half-filled d-shells such as Mo or W. This progressive filling of the d-band explains the steady decrease in bonding energy going from Os to Au. Pt and Au are both soft metals with relatively low heats of vaporization. However, these metals especially Ir, Pt, and Au can combine with early transition metals to form stable alloys with very negative heats of formation and high melting points. This reactivity is unusual because we normally think of Pt as a "noble" i. The favorable combination of early and late transition metals has been interpreted as arising from a d-electron "acid-base" interaction. For example, in HfPt<sub>3</sub>, Hf is the "acid" with an electron configuration of 6s<sup>2</sup>5d<sup>2</sup>, while Pt is the "base" with the electron configuration of 6s<sup>1</sup>5d<sup>9</sup>. They combine to create a stable "salt" product with a filled 5d electron configuration without promoting any electrons to higher orbitals. The implication is that Pt donates d-electrons to the "d-acid," Zr or Hf. Regardless of the source of their stability, some early-late transition metal alloys are of particular interest for use in catalysis. Even though Sc is an active metal that is, it is stabilized in the aqueous acid environment of the fuel cell by its strong interaction with Pt. Progressive filling of the 3d and 4s,4p bands going across the periodic table from Sc to Ge. Filling of the 3d and 4s, 4p bands In the 3d series, we see magnetic behavior for elements and alloys between Cr and Ni. Past Ni, the elements Cu, Zn, Ga, We can understand this behavior by considering the overlap of 4s, 4p, and 3d orbitals, all of which are close in energy. The 4s and 4p have strong overlap and form a broad, continuous band. On the other hand, the 3d electrons are contracted and form a relatively narrow band. Progressing from the early 3d elements Sc, Ti, V, we begin to fill the 3d orbitals, which are not yet so contracted that they cannot contribute to bonding. Thus, the valence electrons in Sc, Ti, and V are all spin-paired, except for a small number near the Fermi level that give rise to a weak Pauli paramagnetism. Moving across the 3d series to the magnetic elements Fe, Co, Ni, the d-orbitals are now so contracted that their electrons unpair and we see cooperative ordering of spins ferromagnetism and antiferromagnetism. Referring to the band diagram at the right, the 3d band is only partially filled and the Fermi level cuts through it. For Cu, Zn, and Ga, the 3d orbitals are even more contracted and the 3d band is thus more narrow, but now it is completely filled and the Fermi level is in the 4s,4p band. The strong orbital overlap in these bands results in spin pairing and a high degree of electron delocalization. Consequently, metals in this part of the periodic table Cu, Ag are diamagnetic and are among the best electrical conductors at room temperature. Finally, at Ge, the 4s,4p band is completely filled and the solid is a semiconductor. Materials are classified as diamagnetic if they contain no unpaired electrons. Diamagnetic substances are very weakly repelled from an inhomogeneous magnetic field. As we learned in Chapter 5, molecules or ions that have unpaired spins are paramagnetic and are attracted to a magnet, i. This attractive force results from the alignment of spins with the field, but in the case of paramagnetism each molecule acts independently. In metals, alloys, oxides, and other solid state compounds, the unpaired spins interact strongly with each other and can order spontaneously, resulting in the cooperative magnetic phenomena described below.

### 2: Encyclopedia of the Alkaline Earth Compounds - Richard C. Ropp - Google Books

$V - nb = V(\text{obs})$  self-explanatory. the number of pairs of particles interacting is the square of particles, or the square of the concentration  $(n/V)^2$ . therefore  $P(\text{observed}) = P' - a(n/V)^2$  where  $a$  is a proportionality constant.

Why does a gas expand when we heat it? In the 19th century, a number of physicists, mainly Ludwig Boltzmann and James Clerk Maxwell, found that the physical properties of gases can be explained in terms of the motion of individual molecules. This motion is a form of energy, which we define as the capacity to do work or to produce change. The molecular nature of the gases gives rise to their macroscopic properties. Kinetic molecular theory of gases: The following assumptions are central to this theory: Think of the molecules as very small points that have mass but negligible volume. These collisions are perfectly elastic no loss of energy. Any two gases at the same temperature will have the same average kinetic energy, which is given by:  $\frac{1}{2}mv^2$ . The horizontal bars denotes average values. Therefore, we may write: It depends on the frequency of collisions per unit area and how hard the molecules strike the wall. The theory also provides a molecular interpretation of temperature. The absolute  $T$  of a gas is a measure of the average KE of the molecules. Or,  $K$  is a measure of the random motion of the molecules: Application to the Gas Laws We can use kinetic molecular theory of gases to account for many properties of these gases: Think of the very large empty spaces between the molecules. The pressure exerted by gas molecules results from the impact of the molecules on the walls of the container. The collision rate of collisions with the walls per second is proportional to the number density  $i$ . As we raise the  $T$  of a gas, this raises the average KE of the molecules. Therefore, the molecules will collide with the walls more frequently and the  $P$  will increase. The volume of the gas will expand until the  $P$  is balanced by the constant external pressure. If molecules do not attract or repel one another, then the  $P$  exerted by one type of molecule is unaffected by the presence of another gas. Therefore, the total  $P$  is given by the sum of individual gas pressure. As long as we hold  $T$  constant, then the average KE and mean-square speed of the molecules stay the same as time passes. At any given time, how many molecules are moving at a particular speed? Maxwell analyzed this and gave speed distribution curves as a function of  $T$ . The peak gives the most probable speed largest of molecules have this speed. Note that the most probable speed increases as  $T$  increases the peak shifts toward the right. Also, the curve begins to flatten out with increasing  $T$ , showing that larger numbers of molecules are moving at greater speed. Also, note that at the same  $T$ , lighter gas molecules move faster than heavier ones: How fast does a gas molecule move, on average, at any given  $T$ ? We can calculate the root-mean-square speed  $rms$  [this is an average molecular speed]. Also, because  $MW$  is in the denominator, the heavier the gas, the more slowly the molecules move. Calculate the  $u_{rms}$  of oxygen molecules at  $25^\circ\text{C}$ . Diffusion takes a relatively long time to complete. If you take a bottle of concentrated ammonia at one end of a large room and a 2nd bottle of concentrated  $\text{HCl}$  at the other end of the room, the following reaction will take place: Also, a lighter gas will diffuse through a space faster than a heavier gas. An unknown gas diffuses at a rate that is 0. Find the ratio of diffusion rates of hydrogen gas and krypton gas. Diffusion is when 2 or more gases gradually mix with one another; effusion is the process by which a gas under pressure escapes from one compartment to another by passing through a small opening or hole. A He-filled balloon deflates faster than an air-filled one because the rate of effusion through the pores of the rubber is faster for He than it is for oxygen and nitrogen larger  $MW$  molecules.

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View Notes - Chapter 5 from CHEM at University of Southern California.  $P(\text{observed}) = \frac{nRT}{(V-nb)} - a(n/v)^2$   $a$ : interactions  $b$ : volume Example Problem: use van der Waals equation and ideal.

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