Measurement of magnetic susceptibility of transition metal ions

Experiment 32 in the 7th edition of Garland-Nibler-Shoemaker

As an introduction, **READ** the description of the experiment and a bit of the underlying theory (pp. 361-370). An alternative, and perhaps simpler description is presented here.

I. INTRODUCTION

The presence or absence of unpaired electrons is a fundamental and important property of molecules. It is particularly important in transitional metal chemistry. The purpose of this experiment is to determine the number of unpaired electrons in some transition metal compounds. This is best accomplished by measuring the magnetic effect of unpaired electrons. The spin of the electrons, like all motion of charged bodies, generates a magnetic moment: the electron behaves like a miniature bar magnet, with a north and south pole. If orbitals are doubly occupied, the magnetic moments of the two electrons cancel out but if there are unpaired electrons, there is a net residual magnetic moment.

Magnetism is always produced by moving electric charges. As all substances contain moving charged particles (mainly electrons), all materials exhibit magnetism. There are three main classes of materials as far as magnetism is concerned:

1. Diamagnetic. These materials have a higher energy in magnetic field than without the field. Therefore, the magnetic field tends to expel diamagnetic substances. An equivalent, alternative statement is that a magnetic field induces a magnetic moment that is opposite to the field, and thus weakens it. Essentially all closed-shell molecules are diamagnetic because the effect of two opposite spins cancel; for reasons that I cannot explain here, a small diamagnetic term remains. Diamagnetism is a weak effect; it can be measured but a diamagnetic substance like water is not visibly affected by magnetic fields.

2. Paramagnetic. In paramagnetic substances, the magnetic field aligns moving charge, most often the spins of the electrons, so that the intrinsic magnetic moment of the electrons line up parallel to the existing field, and add to it. Without a

magnetic field, the magnetic moments of the molecules are randomly oriented and the magnetic fields of the individual molecules largely cancel (Fig. 1). In the field, there is a slight tendency of the magnetic moments to align with the external field. This is opposed by the thermal motion, as one would expect on account of entropy. The energy of a paramagnetic substance is lower in the field than outside the field; the magnetic field sucks a paramagnetic material in the field. In general, only molecules that contain unpaired electrons are paramagnetic. Dioxygen, O_2, is paramagnetic because its ground state is triplet, i.e. contains two parallel spin electrons and no canceling opposite spins. This behavior is very rare among main group compounds, although there are some small, stable main group molecules that contain unpaired electrons. Can you come up with some? (Hint: oxides of nitrogen and chlorine). However, paramagnetism is common among transition metals that have partially filled d and f shells. Paramagnetism is stronger than diamagnetism but still weak because the magnetic moments are only weakly oriented at room temperature.

Fig. 1. Random orientation of magnetic moments in a paramagnetic material

3. In some cases, the electronic structure causes the magnetic moments of molecules (or atoms) in a solid (crystal) align spontaneously. This leads to a phenomenon called ferromagnetism. Only a few substances (iron, nickel, and some alloys and oxides, like Fe_3O_4 and CrO_2) exhibit ferromagnetism. The magnetic effect is MUCH stronger because the magnetic moments of all atoms or molecules are 100 % aligned; in paramagnetic materials, even a strong magnetic field has trouble orienting more than a tiny fraction of the moments. Ordinary soft iron is seemingly not magnetic. However, if coated with a fine magnetic powder and observed under the microscope, it becomes clear that it contains strongly magnetized small areas (domains). The magnetism of the domains is random, so the net effect is very small. However, even a weak magnetic field can orient the domains (unlike individual molecules) because the magnetism of the domains is much stronger. This is the principle of the electromagnet, and all electric motors rely on electromagnets. In soft iron, the domains revert to randomness when the external magnetic field is removed. In hardened iron, or some alloys and oxides, the magnetism persists because the domains cannot easily move (this is why hardened steel is mechanically hard).

II. MAGNETIC SUSCEPTIBILITY AND UNPAIRED ELECTRONS

The magnetic behavior of diamagnetic and paramagnetic substances can be characterized by the (volume) magnetic susceptibility χ. This **dimensionless** quantity is positive for paramagnetic materials and negative for diamagnetic ones. Its simplest definition relates the energy of a volume v of a material in the presence of a magnetic induction or flux density B (closely related to the magnetic field), relative to the field-free situation, as

$$\Delta E = -\tfrac{1}{2}\, \chi\, B^2\, v/\mu_0. \qquad (1)$$

Here μ_0 is a defined constant; in SI units, $\mu_0 = 4\pi\times10^{-7}$ N A^{-2}. The unit of B is the Tesla; 1 T = 1 kg s^{-2} A^{-1}. In a 1 T field, a 1 m long wire carrying 1 A (ampere) current perpendicular to the field experiences 1 N force. (The dimension kg s^{-2} A^{-1} follows

from the formula force=current×length×B; from this, B=force/(current×length); substituting SI units we get 1 T=1N/(1 A×1 m) = 1 kg m s^{-2}/(A m) = 1 kg s^{-2} A^{-1}). **Exercise:** Prove that ΔE has indeed the correct dimension (energy). Include this proof in your lab report.

Unfortunately, several different systems of units are in use for magnetic properties. Part of the reason is that the units can be derived both from electrical and magnetic measurements, and there is a factor of 4π (among others) between them. The old cgs (centimeter-gram-second) system uses units derived from electrostatics. It is still widely used, although the SI system, which uses units derived from magnetism, is slowly winning. The volume magnetic susceptibility in SI units is 4π times that of the cgs units. The manual of the instrument we use is based on the cgs units while the book uses the SI system. If you want to follow the calculation described in the book, the values of the instrument have to be converted to SI units.

Magnetic susceptibility can also be specified per unit mass and per mole, instead of per unit volume. Dividing the (dimensionless) volume susceptibility by the density we get the mass susceptibility χ_g which obviously has the dimension volume/mass. Its (unwieldy) SI unit is m^3 kg^{-1}. For our purposes, the *molar* susceptibility is more important. This is obtained from the mass susceptibility by multiplying it with the molar mass. Its unit is m^3/mol. To illustrate the above, the volume susceptibility of pure water (air and iron free - both oxygen and Fe^{2+} or Fe^{3+} are paramagnetic!) is -0.72×10^{-6} in cgs units. Its susceptibility in SI units is -9.42×10^{-6}, its mass susceptibility in SI units is -9.42×10^{-9} m^3/kg (taking the density of water exactly 1000 kg/m^3), or -9.42×10^{-6} cm^3/g. Its molar susceptibility is -9.42×10^{-6} cm^3 g^{-1} × 18.0 g mol^{-1} = -170×10^{-6} cm^3 mol^{-1} or, in SI units, -170×10^{-12} = 1.70×10^{-10} m^3/mol. The negative sign shows that water is diamagnetic.

III. MEASURING THE VOLUME MAGNETIC SUSCEPTIBILITY USING THE JOHNSON-MATTHEY SUSCEPTIBILITY BALANCE

The traditional method for measuring susceptibility is with the Guoy balance. This is described in detail in the book. The Guoy balance is a big instrument; the electromagnet of ours weighs more than 200 pounds, and has to be water cooled when energized. The development of new, very strong permanent magnets allowed the development of a small desktop instrument that is superior to the behemoth Guoy balance. The most generally used such instrument is the Johnson-Matthey susceptibility balance. Its operating principle is the same as that of the Guoy balance. The sample is immersed halfway vertically in a strong magnetic field that either tends to suck it in further or tends to expel it. The force generated (based on the formula force = $-dE/dz$ where E is the potential energy, see Eq. 1, and z is the vertical position of the sample tube) is measured. The change in the volume of the sample inside the magnetic field is $dv = -A \times dz$ if the sample tube moves up by an infinitesimal distance dz, and the inner cross section area of the sample tube is A. According to Eq. (1), the infinitesimal energy change dE is $dE = \frac{1}{2}\, \chi\, B^2 \times A \times dz/\mu_0$ and the force is $-dE/dz = -\frac{1}{2}\, \chi\, B^2 \times A/\mu_0$. The force is proportional to the cross section of the sample tube and the volume susceptibility of the sample; it is downward if the sample is paramagnetic.

The permanent magnet solution has several important advantages. First, no electricity is needed to generate the magnetic field, and no cooling is needed. Unlike in the Guoy balance, the Johnson-Matthey susceptibility balance measures not the force on the sample but the equal and opposite force on the magnet. This is obviously not practical with the Gouy balance, since a few milligram force is difficult to measure along the hundreds of pounds of the weight of the magnet. Measuring the force on the magnet has important advantages: the balance beam does not have to be touched at all, and the load on it is always constant, eliminating problems with flexing the beam etc. The balance mechanism is similar to a standard modern electronic balance.

IMPORTANT. The sample tubes are expensive and there are only 2 of them. Please be extra careful. They are made of a special grade of quartz (iron-free).

The operation of the instrument is described in the enclosed manual from Johnson-Matthey. This also has some data and a brief background on the theory of magnetic phenomena. The operation is summarized below:

Switch on the instrument (turn it to scale 1x) and wait 10 min. This time can be used to generate some boiled water. Boiling for a few minutes drives the dissolved oxygen out of the water. The deoxygenated water should be kept in an Erlenmeyer flask, well stoppered. After 10 minutes, zero the instrument and wait a few minutes to see if it is stable. **Do not sit on or lean on the table on which the instrument is. This changes the zero.** Now **gently** insert the calibration tube provided. The liquid in it should be at the bottom of the tube, **with no bubbles**. Check the calibration of the instrument. The number shown ought to be the sample susceptibility plus the correction for the test tube; the latter is negative. Both are marked on the calibration tube. Normally, the calibrations is OK. If it is a bit off, you need to scale your results up or down a bit.

Now determine the reading of the empty, **dry** sample tube, and **record it.** Make sure to use the same tube for your measurements. Insert the tube gently and vertically. The reading will be negative, indicating that the tube is diamagnetic.

The susceptibility can be measured either for a solution, or for a finely ground powder. We will use the solution method.

Prepare the following solutions using deoxygenated water **in 10 mL volumetric flasks.** (Disregard what the book says about 50 or 100 mL scale. It is a waste of time and material, and generates lots of waste). We will need to determine the density of our solution, so first weigh the dry volumetric flask **on a moderately sensitive (cg) balance. No need for 0.0001 g accuracy here.** Weigh out approximately 0.004 mol of the following transition metal salt with mg accuracy. This will make the concentration of the solution about 0.4 M. We may vary the salts that are used in the experiment. In the first run, the following will be used:

Water (deoxygenated)

$(NH_4)_2Fe(SO_4)$. $6H_2O$ (Mohr's salt; this is basically $FeSO_4$ but is more stoichiometric and resists oxidation to Fe(III) better).

$MnSO_4.H_2O$ (Other hydrated forms such as $MnSO_4.4H_2O$ are equally suitable but we have to know the formula)

$CuSO_4.5H_2O$

$K_4Fe(CN)_6$

$K_3Fe(CN)_6$ (Caution – toxic)

Other transition metal compounds can be tried – e.g. $NiCl_2.6H_2O$, $KCr(SO_4)_2.6H_2O$, even cerium salts.

First weigh the empty volumetric flask on a moderate-accuracy (cg) balance. Put the weighed amount of your salt in a small beaker, add a little deoxygenated water, pour the mixture in the volumetric flask, rinse the beaker with water and empty it into the flask until you have quantitatively transferred all your salt to the flask. The flask should be only 2/3 full at this point. Shake it until the salt has dissolved, and fill it up to the mark with water, using a pipette fashioned from a glass capillary. Weigh the volumetric flask with the solution on a moderately accurate balance. This will be used to calculate the density of the solution. Stopper the flask or cover with parafilm and shake it to make sure that the solution is thoroughly mixed. Calculate the molar concentration of the solution in mol/L.

Fill the liquid about 1 ¼ - 1 ½ inch high into the dry test tube of the balance, using a **dry** capillary pipette. **Do not pipette by mouth. Use a rubber finger.** If the test tube is not dry and you do not want to dry it, you may suck out the previous liquid with a pipette, fill it with your new solution, shake it gently, suck it out again (using a different pipette for this), and repeat this 3 times.

The first determination will be done on deoxygenated water, then on the metal salt solutions. Check your zero (with the sample tube removed) before and after each run.

Insert the tube in the instrument **gently** and record your reading. If it is over the maximum, use the 10X scale. The volume susceptibility reading of your solution, in the cgs units used by the firm, is $R=R_{sample} - R_{tube}$. As the empty tube reading is negative, this will be bigger (more positive) than the reading of the sample.

The volume susceptibility (in SI units) of your sample is given by

$$\chi_{Vol} = 4\pi \times 12.13 \times 10^{-9} \times R = 152.43 \times 10^{-9} R + 0.029 \times 10^{-6} \quad (2)$$

Here 4π is the conversion factor between cgs and SI, 12.13 is the inverse internal area of the sample tube in cm^{-2} =1/0.08245 cm^2, and R is the reading, and the last term is a correction for the paramagnetism of air (Why is air paramagnetic?). The air susceptibility correction can be neglected for paramagnetic samples but is needed for water.

IV. CALCULATIONS

The molar susceptibility of the dissolved substance can be calculated from the volume susceptibility of the solution by

$$\chi_{Molar} = \chi_{Vol}/c + 9.048 \times 10^{-9}(\rho/c - M) \quad (3)$$

Here all units have to be SI units: c is the molarity (in mol/m^3), ρ is the density of the solution (in kg/m^3; note that it should be 1000 kg/m^3 for water and somewhat larger for the solutions), and M is the molecular mass (in kg/mol). Obviously, the concentration in mol/m^3 is 1000 times the concentration in mol/L, and the molecular mass in kg/mol is 0.001 times the molecular mass in g/mol. See the book. The second term is a correction for the diamagnetic effect of water, itself corrected by the fact that the water is the solution is not pure water but "diluted" by the salt we measure. The total correction term should be **positive**, since we correct for the diamagnetic effect of the water which decreases the reading (makes it less positive). χ_{Molar} is obtained in m^3/mol.

The magnetic susceptibility of paramagnetic substances is inversely proportional to the absolute temperature, assuming that no significant magnetic interaction occurs between the molecules. This is usually true in solution, and often also in crystals if the unpaired electrons are localized. (More accurately, there is a small constant diamagnetic contribution, arising from the presence of closed shells in the molecule but this can usually be neglected). The reason for this is that thermal motion tries to randomize the directions of the magnetic moments (see Fig. 1), while the magnetic field tries to align

them. At not too low temperatures, the thermal motion wins hands down, and the molecules are only slightly aligned. This is true even in the solid state where the positions of the atoms are not random: the direction of the magnetic moments (with the exception of ferromagnetic materials) is random due to thermal motion.

The molar susceptibility of a paramagnetic substance is described by the formula

$$\chi_{molar} = (\text{diamagnetic term}) + C/T \qquad (4)$$

where the diamagnetic term is often neglected since it is small compared to the paramagnetic term. *C* is called the Curie constant (Prof. Pierre Curie was the husband of the more famous Madame Curie, nee Maria Sklodowska. They discovered radium together but she was the driving force in this enterprise, and she got the Nobel prize for it). C (in SI units, i.e. m^3 mol^{-1} K) can be obtained by multiplying the molar susceptibility (also in SI units) with the *absolute* temperature T. *C* is related to the magnetic moment of a molecule (or unit cell in a crystal) as

$$\mu = 798\ C^{1/2} \qquad (5)$$

if *C* is in SI units and μ is expressed in Bohr magnetons, $\mu_B = (eh/4\pi m_e)$, the natural unit of the magnetic moment for an electron. This equation can be used to determine μ in units of μ_B.

The magnetic moment (in Bohr magnetons) is further related to the number of unpaired spins by

$$\mu = [n(n+2)]^{1/2} \qquad (6)$$

This equation can be solved for *n* (see below).

The whole calculational procedure is described only indirectly in the book, causing difficulties even for the better students. It is summarized below.

1. The magnetic susceptibility balance used here (Johnson-Matthey) gives values in the obsolete cgs units. (More accurately in units of 10^{-6} cgs). These values

must be converted to SI units if we want to follow the treatment in Garland-Nibler-Shoemaker according to Eq. (2). This give the volume susceptibility of the solution.

2. Calculate the molar susceptibility, use Eq. (3). Make sure that you use kg and m^3 everywhere, not g and L.
3. Multiply this by the absolute temperature of the measurement to get the Curie constant C in SI units: $m^3\ mol^{-1}\ K$ (Eq. 4).
4. Calculate the square root of C (expressed in SI units) and multiply it by 798 (Eq. 5). This gives the magnetic moment of a molecule, in Bohr magneton units.
5. To determine the number of unpaired electrons, solve Eq. (6) for *n*. You do it first by squaring it and collecting all terms on the right-hand side, and solve it like a usual quadratic equation in *n*.
6. Check your number for the right order of magnitude. It should be a reasonable number, say between 0 and 6 or 7. Ideally, it ought to be an integer but there are some effects (besides experimental errors) that cause it to deviate from a strict integer. If you get an impossible number (say -12 or 9766) check everything and find your error.

For instance: the molar concentration is 0.47 mol/L = 470 mol/m^3, and the density of the solution is 1.05 g/mL = 1050 kg/m^3. The reading of the solution is 388, the empty tube gives -34. From this, the volume susceptibility of the solution is 6.43_3E-5. The formula weight is 169.0 g/mol = 0.169 kg/mol. The molar susceptibility of the *solute* is, from Eq. (3), 1.55_6E-7 m^3/mol. The temperature was 24.5 ^oC; this gives a Curie constant of 4.63_1E-5 $m^3\ mol^{-1}$ K, corresponding to a magnetic moment per molecule of $5.43_1\ \mu_B$. Solving for *n*, the number of unpaired spins gives 4.52. Therefore the number of unpaired spins is either 4 or 5. As a check, we calculate μ from *n*: $\mu=[4.52 \times 6.52]^{1/2} = 5.43\ \mu_B$ ✓.

The theoretical background of this treatment has some smaller terms neglected. These are (a) The diamagnetic contribution of the closed shells in the magnetic atom itsef and in the counterions and the crystal water in Eq. (2). This can be approximately corrected

for but if the goal is to determine *n*, the number of unpaired electrons, it is often not important

(b) The magnetic effect of the orbital motion. For reasons that are too involved to detail here, the *orbital* motion of the electrons does not appreciably contribute to the observed magnetic moment (in the jargon of physical chemists, it is quenched). However, they are not zero, particularly in heavier transition metals.

(c) The effect of the effective *g* value of the electron. To consider this, we have to give the theoretical basis of Eq. (5). The original equation is (see the book)

$$\mu = g_e\,[S(S+1)]^{1/2}\,\mu_B. \qquad (6)$$

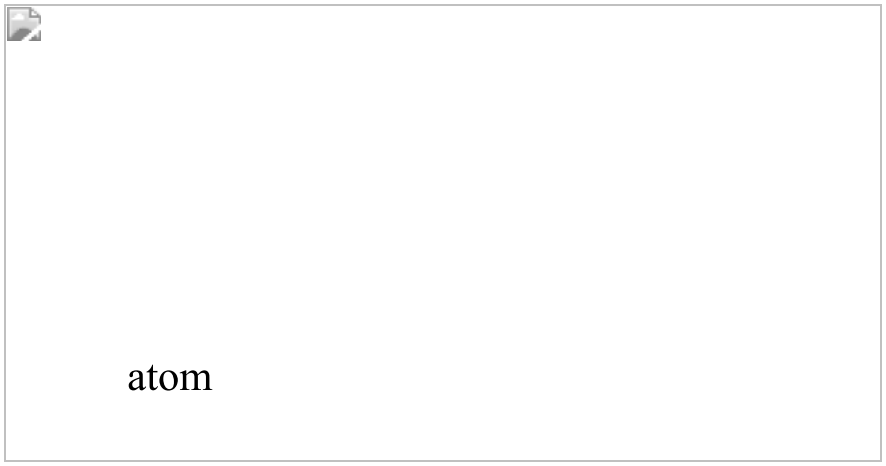
Here g_e characterizes the relation between the angular momentum of the rotating motion and the magnetic moment it generates. For orbital motion, g_e=1. For the spin, *g* is approximately 2, i.e. spin generates twice as much magnetism per unit angular momentum than orbital motion. S is the total spin angular momentum (and recall that 2S+1 is the *multiplicity*: singlet, double, triplet etc.). If the spins are aligned then S=*n*/2 since the spin quantum number of an electron is ½. Eq. (5) is obtained if g_e in Eq. (6) is taken as 2 (the accurate value for a free electron is 2.002319..) and S is replaced by *n*/2. **Exercise:** Derive Eq. (5) from Eq. (6). We made a small error by using g_e=2. For heavier elements, g_e deviates more strongly from 2 because of spin-orbit mixing.

V. ELECTRONIC STRUCTURE OF TRANSITION METAL COMPLEXES

Transition metal complexes (the classical Werner complexes) have a positively charged transition metal ion (usually +2 or +3), surrounded by either negative ions, or dipole molecules with lone pairs that turn their negative (lone electron pair) end toward the positive central ion. The bonding in these complexes is largely ionic. We will consider here only first-row transition metals, the elements from Sc to Cu (some people include Zn but it has a fully filled 3d shell). There are also largely covalently bound complexes, often with organometallic ligands but we do not consider them. The most common coordination pattern is octahedral coordination with 6 ligands, e.g. in $Fe^{2+}(H_2O)_6$.

Transition metals have partially filled *d* of *f* shells. The presence of these open shells is responsible to a large degree for the properties of transition metals. Their compounds are often colored (because low-energy transitions are possible in the open shells), they exhibit variable valences, and are often effective catalysts. The orbital occupancy in first-row transition metal atoms is in general (Ar) $3d^n$ $4s^m$ where n=1-10 and m=0-2. All 5 *d* orbitals (10 spin-orbitals) are degenerate (have the same energy) in the atom. However, in a complex, even in a high-symmetry complex like FeF_6^{3-}, the equivalence of the 5 *d* orbitals is destroyed by the ligands. The simplest case is octahedral symmetry. In this case, the electrostatic effect of the ligands separates the 5 *d* orbitals in two groups: a group of 3 degenerate orbitals denoted as t_{2g} in group theory, and a group of 2 degenerate orbitals, $e_{g,}$ at somewhat higher energy (Fig. 2). The energy separation between the t_{2g} and e_g orbitals depends mainly on two factors: the charge of the central ion, and the nature of the ligand. Higher charge on the metal (say +3 instead of +2) draws the ligand closer, and disturbs the *d* orbitals more, increasing the energy gap between the t_{2g} and e_g orbitals. The second factor is the nature of the coordinating atom. This increases in the order F<O<N<C for first-row ligand atoms. (There are only a few molecules with a lone pair on the carbon, like CN^- and CO but these coordinate very strongly). The effect of the ligands is sometimes called “crystal field” because it was first explored in crystals, for instance the Cr^3 ion incorporated in the Al_2O_3 (corundum) base in rubies.

Figure 2. Splitting of *d* orbitals of a transition metal ion in octahedral crystal field
Note that the degenerate orbitals are plotted as close in energy but not exactly the same in order to show the degree of degeneracy.



A central question in transition metal chemistry is how the electrons occupy the *d* orbitals, and whether their spins are parallel or opposite. People often wrongly assume that opposite spin electrons somehow attract each other, or that double occupancy of an orbital is energetically lower than occupying 2 orbitals singly. You will hopefully know that the exact opposite is true. If the orbital energies are the same, the electrons prefer to occupy different orbitals *with the same (parallel) spin*. This minimizes the electrostatic repulsion. The catch is that orbital energies are seldom the same. If, as usual, the orbital energy differences are large compared to the savings from reduced electron-electron repulsion, the electrons will occupy the lower orbital doubly, and of course the can do that only with opposite spins because of the Pauli principle. In some cases symmetry causes orbitals to have the exact same energy (degeneracy). If, for instance, there are 2 electrons and 2 degenerate orbitals at the HOMO level, the electrons will occupy both singly, *and the ground state is the state with parallel spins.* This situation is very common in atoms where the high symmetry causes much degeneracy. Among molecules, the most famous example is O_2 which is a triplet (S=1) in the ground state. The reason is that the HOMO is doubly degenerate but there are only 2 electrons to occupy it.

An interesting case arises if two orbitals that are close in energy but not quite degenerate are occupied by two electrons. In this case, the electrons can either occupy the lower orbital with opposite spins (giving a singlet state), or both with parallel spins, yielding a triplet. Which is the ground state depends on the relative magnitude of the orbital energy difference compared with the electrostatic energy penalty. If the orbital splitting is small, the electrons occupy both orbitals with parallel spins. As the splitting increases, at one point it becomes energetically more advantageous to occupy only the lower orbital with two electrons and opposite spins. As we see, this can be generalized to more than two electrons.

Consider the fill-up of the *d* orbitals in an octahedral complex. As we add electrons, the first, second and third occupy the 3 levels of t_{2g} *with parallel spins*. However, the fourth electron can either be added to e_g with the same spin, or to t_{2g} with opposite spin. The same is true for the fifth electron. If the splitting of the t_{2g} and e_g levels is small, the spins stay parallel and the e_g level is filled up first. If the splitting is big, the electrons occupy first the t_{2g} level fully (with 6 electrons) before populating the e_g level. In the first case, there are many more parallel spins and the molecule is much more magnetic. This si called a *high-spin* complex. The opposite is *low-spin*. Note that the two cases differ only for 4,5,6 and 7 *d* electrons; for 1-3 and 8-10 *d* electrons, the occupation pattern is the same in both cases.

Exercise: work out the occupation numbers and the total spin quantum number S for (a) high-spin case, 6 *d* electrons (b) low-spin case, 7 *d* electrons. [Answer: (a) $t_{2g}^4\ e_g^2$, S=2; (b) $t_{2g}^6\ e_g^1$, S=1/2].

Low-spin complexes are more common for +3 central ion charge and for “strong” ligands (N and in particular C) than for +2 charge ions and “weak” ligands (O,F); the latter tend to have high spin forms. In some cases the two forms have almost the same energy and the spin state can change, e.g. on heating.