Filtrates & Residues ━━━━━━━━━━━━━━━━━━

Demonstrations on Paramagnetism with an Electronic Balance

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A paramagnetic substance is attracted by a magnetic field with a force proportional to its magnetic susceptibility, which is related to the number of unpaired electrons of the atoms ([1]). Thus, magnetic data, together with spectroscopic measurements, are used to establish oxidation states and bonding properties ([2]). This important feature is a motive for designing experiments to observe and measure this phenomenon. The simple setup described below allows demonstrating the paramagnetism of common inorganic compounds, measuring the force with which they are attracted by a magnet over the plate of an electronic balance. The balance must have a sensitivity of 0.01 g or better. A powerful magnet[1] is needed with its magnetic field directed vertically. The magnet must be placed on a wooden block, which rests on the plate of the balance.[2]

A test tube containing the substance or its concentrated aqueous solution is held by a clamp, so that the bottom of the tube is just over the magnet. A small piece of paper is wrapped around the test tube and the clamp is adjusted so that the tube can be moved easily up or down (Fig. 1). The variation of weight is easily measured if the balance is tared before lowering the test tube over the magnet.

Paramagnetic substances (e.g., $CoCl_2 \cdot 6H_2O$, $FeCl_3 \cdot 6H_2O$, $FeSO_4 \cdot 7H_2O$, and especially $MnSO_4 \cdot H_2O$) attract the magnet with a force—perfectly measurable with the balance (Tables 1, 2)—equal and opposite to that which the magnet exerts on the substances.
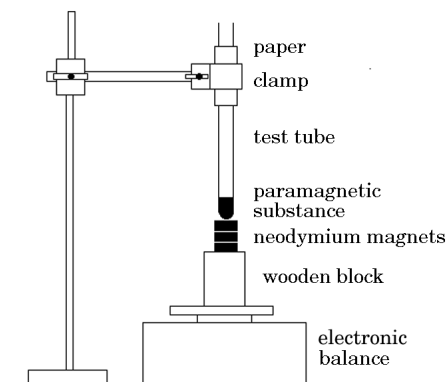

Figure 1. Three neodymium magnets provide a powerful magnetic field, suitable for measuring the attraction over paramagnetic substances with an electronic balance.

If magnets as powerful as neodymium magnets are not available,[3] a "force multiplier" can be built. This multiplier is simply a lever made with a rigid aluminium strip, a counterweight, and the magnet, whose pivot is a spatula held by a support and a nut, as shown in Figure 2. The short arm of the lever, with the counterweight, rests over the plate of the balance. Its pressure increases when the magnet, in the long arm, is attracted by the paramagnetic substance in the test tube. The multiplication factor of the force will be approximately the ratio of the lengths of the two arms of the lever. The use of this setup allows observing paramagnetism with Alnico magnets, but this assembly is

sensitive to vibrations and it is difficult to reproduce results.

The magnetic field of a magnet decreases with distance. Therefore the value of the force is very sensitive to the distance between the magnet and the bottom of the tube. To compare the paramagnetism of different substances it is convenient to measure the highest force of attraction, gradually lowering the tube (making it rotate inside the clamp) and taking readings of the balance. Just before contact with the magnet, the measured weight will be minimum and from this point on the weight will increase. The force of attraction also depends on the quantity of substance in the tube, so all the measures in Table 1 were done with the same amount of sample (3 g) in the tube.[4] The results with test tubes containing 3 g of aluminium, potassium, calcium, and zinc sulfate and silver nitrate (none of them is attracted) are not included. Because of the atomic nature of the force, the paramagnetism of the different samples must be compared on the basis of $\Delta m/n$, the decrease of weight per mole of the substance.

From the data it can be deduced that:

1. Paramagnetism is associated with the unpaired electrons. The salts whose ions have complete electronic subshells (Al^{3+}, Zn^{2+}, Ca^{2+}, Cu^+, Ag^+) are not paramagnetic. The comparison between Cu^{2+} (d^9) with one unpaired electron and Cu^+, with complete subshell d^{10}, confirms this fact.

2. The different paramagnetism of the compounds of the same metal can be associated with a different number of unpaired electrons. Thus, the comparison of the attraction over the ammonium dichromate and chromium(III) sulfate samples or between potassium ferrocyanide and ferricyanide shows the relationship between the magnetic properties and the oxidation state of the metallic ion.

3. In a free atom the five d orbitals are equivalent, but in a coordination compound there is a splitting of those orbitals according to the crystal field theory (2). The different behavior of the listed iron compounds (as in ferrocyanide and iron(II) sulfate or in ferricyanide and iron(III) chloride) arises from the different energy gap between the two groups of d orbitals in both compounds: the cyanide ligand has a strong field, whereas chloro, aqua, or oxo ligands do not have such a strong field. As a result, the 6 d electrons in ferrocyanide are paired in the lower 3 orbitals, whereas in the ferrous sulfate there are 4 electrons in the 3 lower orbitals and 2 electrons in the higher ones, with 4 unpaired electrons. The different attraction of potassium ferricyanide and iron(III) chloride can be understood in a similar way (Fig. 3). The similar attraction over potassium ferricyanide (d^5) and copper(II) compounds (d^9) suggests the presence of one unpaired electron in this iron compound.

4. There is a correlation between the force of attraction and the number of unpaired electrons. This number is easily established for ions such as Cu^{2+}, Ni^{2+}, and Cr^{3+}, whose electronic configurations d^9, d^8, and d^3, respectively, are associated with 1, 2, and 3 unpaired electrons. In the d^4–d^7 ions this number depends on the ligands attached to them and its coordination, as discussed above for the iron compounds. The theory of magnetochemistry (1) indicates that the force of attraction is proportional to $N(N+2)$ (N is the number of unpaired electrons). Thus we can establish a scale of the

Table 1. Paramagnetic Behavior of Some Inorganic Solids

Salt	Δm (g)	MW	n (mmol)	$\Delta m/n$ g/mol	X_m[a] emu/mol	Unpaired spins
$FeCl_3 \cdot 6H_2O$	-0.95	270.3	11.1	85.6	15,250	5
$MnSO_4 \cdot H_2O$	-1.26	169.0	17.7	71.2	14,200	5
$FeSO_4 \cdot 7H_2O$	-0.51	278.1	10.8	47.2	11,200	4
$CoCl_2 \cdot 6H_2O$	-0.47	237.9	12.6	37.3	9,710	3
$KCr(SO_4)_2 \cdot 12H_2O$	-0.17	499.0	6.0	28.2	6,220	3
$NiSO_4 \cdot 7H_2O$	-0.22	280.9	10.5	20.9	4,300	2
$K_3[Fe(CN)_6]$	-0.08	329.3	9.0	8.9	2,290	1
$CuSO_4 \cdot 5H_2O$	-0.09	249.7	12.2	7.4	1,570	1
$K_4[Fe(CN)_6] \cdot 3H_2O$	0.00	422.4	7.1	0	-172	0
$(NH_4)_2Cr_2O_7$	0.00	252.0	12.0	0	38	0
$CuCl$	0.00	99.0	30.8	0	-40	0

[a]X_m = magnetic susceptibility.

Table 2. Paramagnetic Behavior of Some Inorganic Solutions

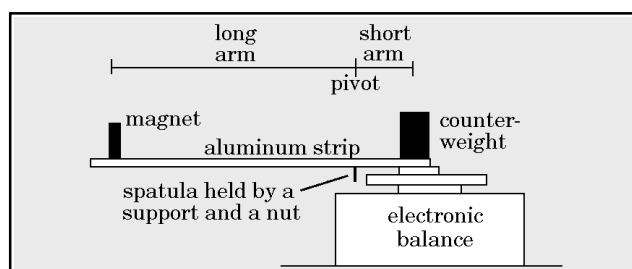| Solution	Δm (g)	$\Delta m/n$ (g/mol)
$FeCl_3 \cdot 6H_2O$ (2.0 g in 5 mL of water)	-0.22	29.7
$FeCl_3 \cdot 6H_2O$ (1.0 g in 5 mL of water)	-0.11	29.7
$MnSO_4 \cdot H_2O$ (1.0 g in 5 mL of water)	-0.16	27.0

Figure 2. A lever made of aluminium and held by a spatula allows multiplying the small force that Alnico or ferrite magnets exert on paramagnetic substances.
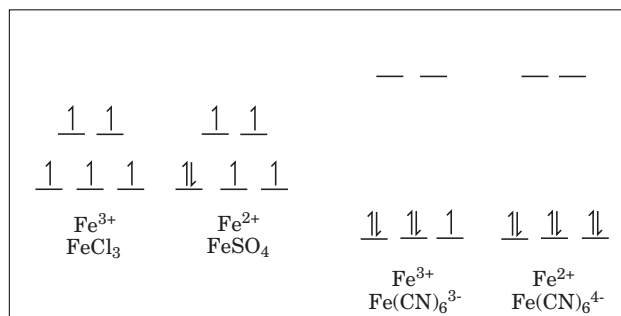

Figure 3. The different splitting of the d orbitals of Fe^{2+} and Fe^{3+} in strong and weak ligand fields accounts for the observed differences in the paramagnetism of these compounds.
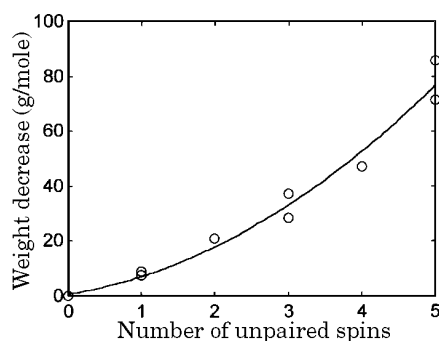
Figure 4. Plot of weight decrease per mole versus number of unpaired spins of compounds listed in Table 1. The data fit to a polynomial $2.2(N^2 + 1.9N + 0.3)$, (SD 1.3), close to the $k(N^2 + 2N)$ polynomial predicted by theory.
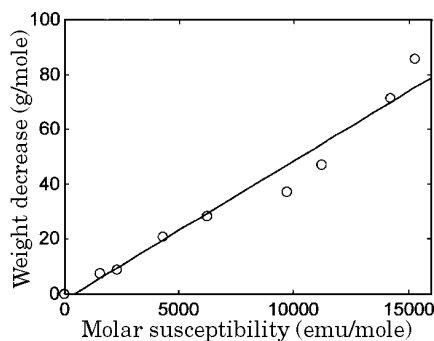

Figure 5. Linear correlation (standard deviation 1.7) between the weight decrease by mole and the molar susceptibility for compounds listed in Table 1.

force of attraction as shown in Table 3.

The values of $\Delta m/n$ in Table 1 show that the attraction for iron(III) chloride is about 12 times greater than for copper sulfate, as the scale of force in Table 3 suggests. The scale also predicts that in $MnSO_4 \cdot H_2O(s)$, Mn^{2+} has 5 unpaired electrons, owing to its d^5 electronic configuration in a weak field. If we plot the force of attraction per mole versus the number N of unpaired electrons of the compounds listed in Table 1, where N has been established as discussed above, the fit to a polynomial of second degree by the least squares method gives $2.2(N^2 + 1.9N + 0.3)$, with a standard deviation of 1.3, very close to the $k(N^2+2N)$ polynomial predicted by the theory (Fig. 4). The linear correlation between $\Delta m/n$ and the known values of molar magnetic susceptibility (3), with a standard deviation of 1.7, is shown in Figure 5.

Unlike paramagnetism, diamagnetism is a general property of all substances. The force of repulsion by a diamagnetic sample introduced in a magnetic field is much weaker, but this setup also allows demonstrating the diamagnetism of solid bismuth, the most diamagnetic element. If a sample of bismuth is brought over the magnet, an increase of weight is observed because of the repulsion force. For example, with a 300-g sample of bismuth, an increase of weight of nearly 1 g has been measured; but with a test tube filled with 10 g of ground bismuth, the increase is only 0.08 g. The diamagnetism of aluminium could not been observed.

Acknowledgments

Notes

1. I have used a set of three cylindrical neodymium magnets of 22 mm diameter and 10 mm height. The magnetic field of a single magnet is 0.29 T, but by putting 3 magnets together it increases to 0.43 T. CAUTION: these magnets are very powerful and must be handled far from any sensitive material such as computer hardware or software. (I demagnetized my credit cards by handling the magnets too close to my pocket!). When they are pulled apart, the force is so strong that they can easily pinch your fingers. In previous experiments I used smaller neodymium magnets with a similar magnetic field (12 mm diameter and 7 mm height), but since the diameter of the test tubes is 15 mm, the use of bigger magnets allows all the sample to be kept inside the magnetic field and the force is almost twice the force of the small magnets. Furthermore, with bigger magnets the accurate centering of the test tube over the magnet is not a noticeable factor. As the magnetic field decreases quickly with distance, the force must be bigger if the substance is well packed in the tube; but some experiments with different ground samples have shown that this effect is not noticeable if the substances already have a small grain size (as most commercial reagents do). The use of test tubes is recommended over Petri dishes or watch glasses because it permits a bigger distance between the metallic pieces of the clamp that holds them and the magnet.

2. With our balance there is an interaction between the magnetic field of the magnet and the mechanism of the balance. Therefore it is necessary to put a wooden or plastic block between the magnet and the balance plate.

3. The Alnico and ferrite magnets in our laboratory have much smaller magnetic fields than the neodymium ones. An Alnico magnet (cylindrical, 12-mm diameter and 50-mm length) has a magnetic field of 0.11 T; a ferrite one (prismatic, $39 \times 10 \times 20$ mm) has a magnetic field of 0.08 T.

4. The samples are stored in stoppered test tubes. The results are very reproducible (within 0.02 g) along successive months using the same magnets, except for hygroscopic salts such as iron(III) chloride.

Table 3. Relationship between Number of Unpaired Electrons (N) and Force of Attraction (F)

N	N(N + 2)	F[a]
0	0	0
1	3	1
2	8	2.7
3	15	5
4	24	8
5	35	11.7

[a]Measured in arbitrary units.

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