

Title: Speed of Sound Lab

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Abstract

In this experiment, the magnetic susceptibility of metals in complexes were found. To be diamagnetic, the compound gave a low and negative response reading on the magnetic susceptibility balance. To be paramagnetic, the compound gave a high and positive response reading. The samples that are paramagnetic are $\text{HgCo}(\text{SCN})_4$, $\text{MnSO}_4 \cdot 2\text{H}_2\text{O}$, MnO_2 , $\text{Cu}(\text{HCOO})_2 \cdot \text{H}_2\text{O}$, Mn_2O_3 , $\text{Ni}(\text{en})_3\text{S}_2\text{O}_3$, $\text{Co}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$. The samples that are diamagnetic are KMnO_4 , $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$, $\text{K}_2\text{Cr}_2\text{O}_7$. Using the responses that were given, the estimated number of free electrons could be calculated for that metal and was compared to the number of free electrons in its electron configuration. Both values matched with minimal error so both methods are considered correct in respect to one another.

Keywords: paramagnetic, diamagnetic, weak field ligand, strong field ligand, response, electron configuration, complex, estimated number of free electrons.

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Introduction

The purpose of this experiment was to determine if a metal within its complex was paramagnetic or diamagnetic with the help of a magnetic susceptibility balance. Paramagnetic substances yield a high and positive response from the balance while diamagnetic substances yield a low and negative response. In depth, for something to be diamagnetic, there must be no unpaired electrons in any subshell, specifically in the orbitals within the subshell. To paramagnetic, the opposite occurs where there is at least one unpaired electron. All compounds studied in the experiment are first period d-block metals so only the 3d orbitals would be considered. Some complexes, such as $K_4Fe(CN)_6 \cdot 3H_2O$ are influenced by the ligands that are attached to the compound. There is a spectrochemical series of ligands where on one end the ligand is a weak field ligand, but produces high spin complexes. The other side contains strong field ligands but produces low spin complexes. The ligands to look at in this experiment would be CN^- and H_2O . These two would be considered strong ligands where d orbital splitting would occur. Splitting occurs displayed in Figure 1.

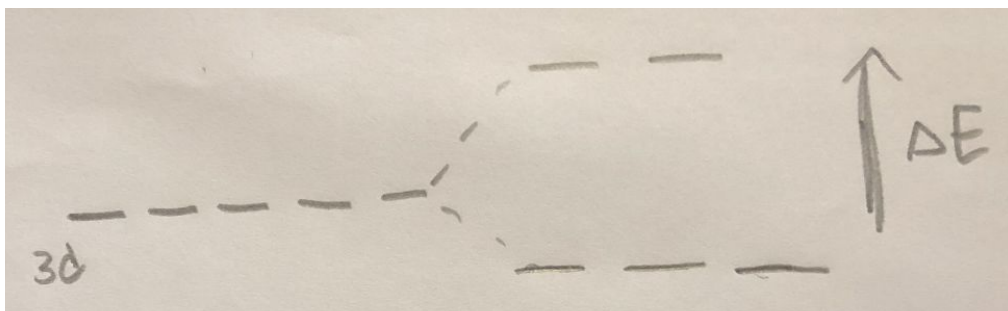


Figure 1. Octahedral complex splitting d-orbitals

This split allows for Hund's rule and Pauling's rule to take place with electrons occupying one electron each before doubly occupying with opposite spins. This helps explain how some compounds with strong ligands can be diamagnetic and the same compound with the same oxidation state can also be paramagnetic. For the calculations, mass susceptibility, χ_g , is calculated by:

$$\chi_g = \frac{LC_{bal}(R-R_o)}{(m \cdot 10^9)} \quad (1)$$

where L is the length of the sample in cm, R is the response given by the compound, R_o is the response given by the empty tube, C_{bal} is the calibration constant of the balance being 1.19, and m is the mass of the sample in the tube. After finding the mass susceptibility, molar magnetic susceptibility, χ_m , could be calculated by:

$$\chi_m = \chi_g * \frac{MW}{Z} \quad (2)$$

where MW is the molecular weight including the waters of hydration, and Z is the number of magnetic ions per formula unit of the compound. Using χ_m , μ_{eff} can be calculated by:

$$\mu_{eff} = 2.828[\chi_m(T - \theta)]^{\frac{1}{2}} \quad (3)$$

where T is the temperature at the time of the experiment in Kelvin, and θ is the paramagnetic Curie temperature or Weiss constant.¹ The final equation to be used is to calculate the estimated number of free electrons in the compound:

$$\# \text{ free electrons} = \sqrt{1 + \mu_{eff}^2} - 1 \quad (4)$$

Methods

In this experiment, twelve compounds were tested in the magnetic susceptibility balance. These twelve compounds were already prepared by the professor with 11 of them being the ones known to us and 1 being the ionic compound. The tube containing the compound was carefully taken out of the tray and placed into the magnetic susceptibility balance and a response reading was noted. If the response reading was too large, the knob was turned from the x1 setting to x10 setting to get a reading that would be multiplied by 10 in the final acquisition of the data. After reading the data, the tube was carefully taken out of the balance and placed back onto the tray. After all readings were done, the machine was turned off and the lab notebooks were signed.

Results

Table I: Experimental Conditions

Compound	m_o (g)	m (g)	L (cm)	R (cm ²)	R_o (cm ²)
HgCo(SCN) ₄	0.830	1.279	3.8	1371	-2
MnSO ₄ * 2H ₂ O	0.875	1.266	3.1	8780	-2
MnO ₂	0.834	1.112	3.3	2340	-2
Cu(HCOO) ₂ * H ₂ O	0.890	1.221	3.8	287	-2
Mn ₂ O ₃	0.872	1.355	3.0	11500	-2
Ni(en) ₃ S ₂ O ₃	0.876	1.144	3.4	644	-2
KMnO ₄	0.825	1.309	3.5	-2	-2
K ₄ Fe(CN) ₆ * 3H ₂ O	0.859	1.209	3.7	-55	-2
Co(NH ₄) ₂ (SO ₄) ₂ * 6H ₂ O	0.801	1.266	4.2	1090	-2
Fe(NH ₄) ₂ (SO ₄) ₂ * 6H ₂ O	0.809	1.114	4.1	1513	-2
K ₂ Cr ₂ O ₇	0.887	1.459	4.5	-19	-2

m_o is the mass of the empty tube, m is the mass of the sample + tube.

Table II: Calculated Values

Compound	$\theta(K)$	$u_{eff}(BM)$	$\sqrt{1 + u_{eff}^2} - 1$	d^m	n
HgCo(SCN) ₄	-10	4.09	3.21	7	3
MnSO ₄ * 2H ₂ O	-2	6.10	5.18	5	5
MnO ₂	-500	4.28	3.40	3	3
Cu(HCOO) ₂ * H ₂ O	-175	1.60	0.89	9	1
Mn ₂ O ₃	-192	5.13	4.23	4	4
Ni(en) ₃ S ₂ O ₃	43	2.64	1.83	8	2
KMnO ₄	0	0	0	0	0
K ₄ Fe(CN) ₆ * 3H ₂ O	0	0	0	6	0
Co(NH ₄) ₂ (SO ₄) ₂ * 6H ₂ O	40	3.09	2.25	7	3
Fe(NH ₄) ₂ (SO ₄) ₂ * 6H ₂ O	-3	4.78	3.89	6	4
K ₂ Cr ₂ O ₇	0	0	0	0	0

$\sqrt{1 + u_{eff}^2} - 1$ is the estimated number of free electrons.

Sample Calculations for MnO₂: (same for the other compounds)

Using equation 1 from the introduction:

$$\chi_g = \frac{LC_{bal}(R-R_o)}{(m*10^9)} = \frac{3.3cm * 1.19 * (2340cm^2 + 2cm^2)}{(1.112g - 0.834g)*10^9} = 0.000014 \frac{cm^3}{g}$$

After calculating χ_g , χ_m can be calculated from equation 2:

$$\chi_m = \chi_g * \frac{MW}{Z} = 0.000014 \frac{cm^3}{g} * \frac{86.9368 \frac{g}{mol}}{1} = 0.0029cm^3$$

Using this value of χ_m , we can find μ_{eff} :

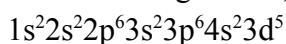
$$\mu_{eff} = 2.828[\chi_m(T - \theta)]^{\frac{1}{2}} = 2.828[0.0029cm^3(298.15K + 500K)]^{\frac{1}{2}} = 4.28$$

Finding this value for μ_{eff} , equation 4 let's us calculate the estimated number of free electrons:

$$\# free electrons = \sqrt{1 + \mu_{eff}^2} - 1 = 3.40$$

Determining d^m :

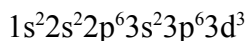
For species, write out the metal spdf electron configuration, so for MnO₂:



Figuring out the oxidation state of the metal:

From 2 oxygens contribute 4- total charge so Mn has to be an oxidation state of Mn(IV).

This yields an electron configuration of:



which has 3 unpaired electrons causing this compound to be paramagnetic as well as this value being close to the calculated estimated number of free electrons being 3.40 which is 3 rounded down.

Conclusion

In the experiment, compounds were found to exhibit paramagnetic and diamagnetic properties based on the ligands, oxidation state, and the response from the balance. The samples that are paramagnetic are HgCo(SCN)_4 , $\text{MnSO}_4 \cdot 2\text{H}_2\text{O}$, MnO_2 , $\text{Cu(HCOO)}_2 \cdot \text{H}_2\text{O}$, Mn_2O_3 , $\text{Ni(en)}_3\text{S}_2\text{O}_3$, $\text{Co(NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Fe(NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$. The samples that are diamagnetic are KMnO_4 , $\text{K}_4\text{Fe(CN)}_6 \cdot 3\text{H}_2\text{O}$, $\text{K}_2\text{Cr}_2\text{O}_7$. From calculating the estimated number of free electrons and comparing it to the electron configuration method, it was shown that both methods are accurate to one another and explain why the compound was either diamagnetic or paramagnetic.

Acknowledgements

I used the lecture notes, lab manual, and the provided document on Sakai.

Discussion Questions

1. Complete Table I. Which samples are paramagnetic and which are diamagnetic?

From class, paramagnetic substances have large responses from the instrument and diamagnetic substances have small and negative responses from the instrument. The samples that are paramagnetic are HgCo(SCN)_4 , $\text{MnSO}_4 \cdot 2\text{H}_2\text{O}$, MnO_2 , $\text{Cu(HCOO)}_2 \cdot \text{H}_2\text{O}$, Mn_2O_3 , $\text{Ni(en)}_3\text{S}_2\text{O}_3$, $\text{Co(NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Fe(NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$. The samples that are diamagnetic are KMnO_4 , $\text{K}_4\text{Fe(CN)}_6 \cdot 3\text{H}_2\text{O}$, $\text{K}_2\text{Cr}_2\text{O}_7$.

2. Choose one of the transition metal compounds from the table, and be sure that your lab partner chooses a different one. Determine the number of unpaired electrons, showing all calculations, and using both calculation schemes: the first being the number of unpaired electrons based on the charge on the ligands; the second method being described in the lab instructions. Now complete table II, where μ_{eff} is the effective magnetic moment, d^m is the number of d electrons for the valency of the transition metal, and n is the number of unpaired d electrons.

The compound that was selected was MnO_2 . Calculations under the results, but for the first method based on ligands, the number of unpaired electrons were 3. For the second method using the effective magnetic moment, the value was calculated to be 3.40.

3. In $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ and $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ the iron is a d^6 ion configuration. However, significantly different responses are observed for the two different iron compounds. Explain.

Since in both compounds the iron exhibits a d^6 ion configuration, this tells us that there are 6 electrons left in the d subshell. Looking at the ligands, the first compound has a strong field ligand, while the second compound has a very weak field ligand. The strong field ligand splits the d orbitals better than the weak field ligand thus having a difference in energy between the orbitals in the d subshell. Filling the orbitals from lowest energy to highest energy, the first compound results in no unpaired electrons, which yields a diamagnetic response. For the second compound, filling again from lowest to highest yields a paramagnetic response due to the 4 unpaired electrons in the subshell.

4. The 12th compound is ferrocene dissolved in an ionic liquid: 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide. What is an ionic liquid? Did your experiment show this to be diamagnetic or paramagnetic? Discuss why ferrocene shows this type of magnetism.

An ionic liquid is a salt that contains two differently sized ions that doesn't allow very good coordination of the salt. This results in the salt to become an ionic liquid. From our experiment, the response of the 12th compound was -65. This followed the trend of diamagnetic compounds having small and negative responses. Ferrocene shows this type of magnetism because of the 18 electron rule. The two cyclopentadienyl rings contribute 12 electrons to the 6 electrons that Fe(II) already has. This creates a full 18 electrons that completely occupy the d subshell that Fe(II) has. Because of the full 18 electrons occupying the Fe(II) orbitals, there is no space for electrons to be added, but can be removed if enough energy is given. This yields a diamagnetic response and the experiment shows it as well.

5. Chromium, Cr, has 24 electrons. Write out the electron configuration for chromium using spdf notation. How many unpaired electrons would you expect for chromium in ammonium chromate, $(\text{NH}_4)_2\text{CrO}_4$? Is this a paramagnetic or diamagnetic material?

For chromium, the electron configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^4$. In the compound, chromium has an oxidation state of Cr(VI). This means that there are 6 electrons loss which means both the 4s orbital and 3d subshell are empty and yields an electron configuration of $1s^2 2s^2 2p^6 3s^2 3p^6$. This has no unpaired electrons which means that this substance is a diamagnetic substance.

6. How many unpaired electrons would you expect for the chromium in the complex $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$? Is this a paramagnetic or diamagnetic material?

Since the ligand is H_2O , this is considered a semi-strong field ligand. Since this is a strong field ligand, it can split the orbitals in this octahedral complex. Water has a neutral charge to it so the oxidation state of chromium in this compound is Cr(III). This means that there are 3 electrons

taken away from its total electrons of 24. This yields an electron configuration of $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$. Splitting here doesn't matter as much because of the minimal amount of d electrons there are but when filling up the orbitals, one electron of the 3 go to each orbital on the bottom splitting levels which makes this compound have 3 unpaired electrons and making it a paramagnetic metal.

7. Consider the two compounds: $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ and $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$. One is yellow, the other is violet. Which is what color? Explain how you determined this.

Since both chromium oxidation states are the same being Cr(III). Since NH_3 is a stronger field ligand than that of water, the splitting of the d orbitals in the second compound is greater than that of the first compound. Both chromiums in each compound only have singly filled lower d orbitals in the split, but since the splitting in the second compound is greater than the first, more energy is required to excite that electron up to the higher d orbitals. Since energy is inversely proportional to the wavelength emitted when the electron goes back to rest from excited state, the first compound, which required less energy to excite the electron, the first compound is violet in color. The second compound that required more energy to excite an electron would yield a yellow color.

References

1. Teweldemedhin, Z. S.; Fuller, R. L.; Greenblatt, M. Magnetic Susceptibility Measurements of Solid Manganese Compounds with Evan's Balance. *Journal of Chemical Education* **1996**, 73 (9), 906–909.