170 quiz 2

1. (40)

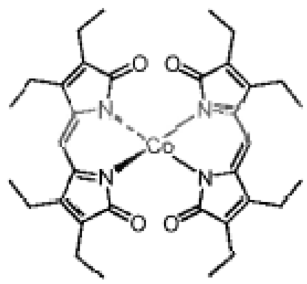
a. Paramagnetic 물질의 magnetic susceptibility가 절대온도에 반비례함을 보여라. (Curie law를 유도하여라.) S = 1/2로 생각하고 풀어라. 20

b. Ferromagnetic 과 antiferromagnetic 물질은 온도에 따라 magnetic susceptibility가 paramagnetic 물질과 어떻게 다른지 설명하여라. (Curie-Weiss law) 10

c. Magnetic susceptibility vs. T 의 그래프를 위의 각 물질에 대하여 그려라. (한 그래프 위에) 10

2. high-spin Fe^{3+}는 5개의 unpaired d-전자를 가지고 있다. (S=5/2) 우리가 Fe^{3+} 착물의 magnetic moment를 생각할 때 orbital angular momentum (L)을 생각할 필요가 없이 S값만 생각하면 된다. 그 이유는? (20)

3. 다음 Cobalt 착물의 gram subsceptibility (χ)를 298K에서 측정하였더니 $9.783 \times 10^{-6} cm^3 g^{-1}$ 였다. (70)



a. χ_{dia} 와 χ_{para} 에 대한 molar susceptibility는 각각 얼마인가? 40

b. μ_{eff}는? Bohr Magneton 단위로 표시하라. $(3k/N\beta^2)^{-1/2} = 2.828$ (298K) 20

c. 이 착물에는 몇 개의 unpaired electron이 있나? 10

4. Magnetic susceptibility를 측정하는 방법중 Gouy method와 Faraday method를 설명하여라. (40)

풀이

a. In a magnetic field strength, H, the energy level of a state with m_s is

$$E_n = m_s g\beta H$$

$\frac{1}{2}g\beta H$: $|\frac{1}{2}\rangle$

$\updownarrow g\beta H$

$-\frac{1}{2}g\beta H$: $|-\frac{1}{2}\rangle$

∴ Boltzman distribution

$$P_{(m_s=1/2)} = \frac{e^{-1/2 g\beta H/kT}}{e^{-\frac{1}{2}g\beta H/kT} + e^{+\frac{1}{2}g\beta H/kT}}$$

$$P_{(m_s=-1/2)} = \frac{e^{1/2 g\beta H/kT}}{e^{-1/2 g\beta H/kT} + e^{\frac{1}{2}g\beta H/kT}}$$

∴ molar magnetic moment

Avogadro's #

$$M = [\mu_{(m_s=1/2)} P_{m_s=1/2} + \mu_{(m_s=-1/2)} P_{(m_s=-1/2)}] N_A$$

$\mu_n = -m_s g\beta$

$$= \frac{-\frac{1}{2}g\beta e^{-1/2 g\beta H/kT} + \frac{1}{2}g\beta e^{1/2 g\beta H/kT}}{e^{-1/2 g\beta H/kT} + e^{1/2 g\beta H/kT}} \cdot N_A$$

$$= \frac{1}{2}g\beta \frac{e^{1/2 g\beta H/kT} - e^{-1/2 g\beta H/kT}}{e^{-1/2 g\beta H/kT} + e^{1/2 g\beta H/kT}} \cdot N_A$$

$$= \frac{1}{2}g\beta \frac{e^{g\beta H/2kT} - 1}{e^{g\beta H/kT} + 1} \cdot N_A$$

when $g\beta H >> 2kT$

$$\simeq \frac{1}{2}g\beta \times \frac{g\beta H}{2kT} \cdot N_A = \frac{N_A g^2\beta^2 H}{4kT}$$

∴ molar magnetic susceptibility, X

$$X = \frac{M}{H} = \frac{N_A g^2\beta^2}{4kT} \quad \therefore \boxed{X \propto \frac{1}{T}}$$

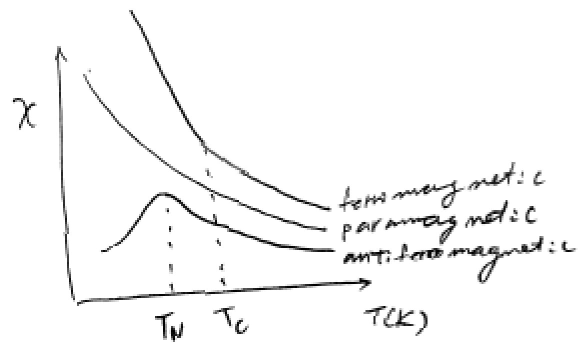
Curie law

1. cont'd

b Ferromagnetic material : 1. magnetic susceptibility (χ) depends on both applied field and temperature. 2. Above the Curie temperature (T_C), ferromagnetic material shows paramagnetic behavior 3. Below T_C, χ increases much faster than in paramagnetic materials

Antiferromagnetic material : 1. χ depends on both applied field and temperature. 2. Above the Neel temperature (T_N), antiferromagnetic material shows paramagnetic behavior. 3. Below T_N, χ decreases.

c.



2. When Fe^{3+} forms a complex, 5 d orbitals are no longer equivalent, that is, L is effectively quenched (L=0). Therefore magnetic moment is determined by S.

3.

a. $\chi^{molar}_{measured} = \chi^{gram}_{measured} \times \text{mol. mass}$

$= 6.132 \times 10^{-3}\ cm^3/mol = \chi^{molar}_{para} + \chi^{molar}_{dia}$

$\chi^{molar}_{dia} = -293\ 18 \times 10^{-6}\ cm^3/mol$ (from Pascal constants)

$\therefore \chi^{molar}_{para} = 6.425 \times 10^{-3}\ cm^3/mol$

b $\mu_{eff} = \left(\frac{3k}{N\beta^2}\right)^{1/2} \sqrt{\chi_{para} T}$

$= 2.828 \sqrt{6.425 \times 10^{-3}\ cm^3/mol \times 298K}$

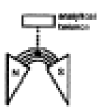
$= 3.91$ BM

c. $\mu_{eff} = g\sqrt{S(S+1)} = 2\sqrt{S(S+1)} = 3.91$

$\therefore S = \frac{3}{2}$

Faraday Method

This technique is very similar to the Gouy method. However it is not sensitive to the cross sectional area of the sample in the sample tube. The Faraday method uses a specially designed magnet to create an area of constant magnetic field. A schematic illustration of the magnetometer is shown on the right. The specially designed magnet produced a field such that a relatively large portion of it has a constant $H\frac{\partial H}{\partial z}$. If the sample is placed into this region then the force acting on the sample is independent of the density of the sample and only dependent upon the mass of the sample:



$$F = H\frac{\partial H}{\partial z} = \chi_m (Mass) H \frac{\partial H}{\partial z}$$

Although the field is constant, we still do not know its value. So, again, it is more practical to use a calibration standard.

The gram susceptibility in the Faraday method is given by:

$$\chi_g = \beta \frac{\Delta_{mass}^{sample} - \Delta_{mass}^{tube}}{mass\ sample}$$

again, β is the calibration constant calculated for the specific Faraday magnetometer using a standard. The sample tube is usually a small quartz boat, which is small enough that we can neglect the magnetic buoyancy caused by the air displaced.

The pros and cons of this method are:

pros
- stronger magnetic – increased sensitivity
- practical temperature range 80-400K
- sensitivity is 10^{-4} to 10^{-8} emu
- very small sample needed (few milligrams)
- uniform sample packing not needed
- direct measurement of χ_g lowers uncertainty to ~1%

cons
- need specially designed magnet

The biggest advantage of the Faraday method is the small amount of sample that is needed.

Gouy Method

The general layout of the Gouy magnetometer is shown to the left. The sample is placed in a cylindrical tube and suspended on a thread (or non-magnetic wire such as a silver chain) from an analytical balance. The sample tube is placed such that some of the material is in the region of homogeneous field and some of the sample is out of the field. This guarantees that there will be a force acting on the sample to draw it into the area of strongest magnetic field.

The force acting on this sample is:

$$F = M\frac{\partial H}{\partial z} = \chi_v V H \frac{\partial H}{\partial z}$$

where χ_v is the volume susceptibility of the sample, V is the volume of the sample, and H is the field strength of the magnet. If we integrate this equation along the entire length of the sample, we find:

$$F = \frac{1}{2}\chi_v H^2 A$$

where A is the cross-sectional area of the sample.

The force is measured with the magnetic field turned on and with the field off. In order to determine the volume susceptibility, we must know the exact cross sectional area (A) and the magnetic field strength (H). This is not very practical, however we can use a calibration standard. The use of a calibration standard eliminates the need to know the values for H and A.

The gram susceptibility (χ_g) for a sample is given by:

$$\chi_g = \beta \frac{\left(\Delta_{mass}^{sample} - \Delta_{mass}^{tube}\right) + \chi_v^{air} V}{mass\ sample}$$

where β is a calibration constant, Δ_{mass}^{sample} is the change in mass of the sample with the field on and the field off. The same is true for the empty sample tube, Δ_{mass}^{tube}. χ_v^{air} is the volume susceptibility for air, and V is the volume of the sample in the tube.

The term χ_v^{air} V compensates for the susceptibility of the air displaced from the sample tube by the sample. Since this measurement is performed in a room full of air, the displaced air leads to magnetic buoyancy. The value of χ_v^{air} can be obtained from the literature. The value Δ_{mass}^{tube} is included to compensate for the magnetic behavior of the empty sample tube. The calibration constant can be calculated for the specific magnetometer by using a sample with known gram susceptibility and solving for β.

As with any method, there are pros and cons with the Gouy method:

pros
- stronger magnetic – increased sensitivity
- practical temperature range 80-400K
- sensitivity is 10^{-6} to 10^{-8} emu

cons
- large amount of sample needed (100's mg)
- sample must be packed into tube very uniformly
- uncertainty of measurement is ~2-5%

The biggest disadvantage is the requirement of packing the sample tube as uniformly as possible. Small changes in the cross sectional area of sample in the tube is the leading contributor to the uncertainty of the measurement.