

GENERAL READING

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EXPERIMENT 32

Magnetic Susceptibility

When an object is placed in a magnetic field, in general a magnetic moment is induced in it. This phenomenon is analogous to the induction of an electric moment in an object by an electric field (see Exps. 30 and 31) but differs from it in that an induced magnetic moment may have either direction in relation to the applied field. If the induced moment is parallel to the external field (as in the electric case), the material is called *paramagnetic* or *ferromagnetic*, depending on whether the field due to the induced moment is small or large in comparison with the external field. If the moment is antiparallel to the external field, the material is called *diamagnetic*; the moment in this case is always small. This experiment will deal only with paramagnetic and diamagnetic substances in solution.

THEORY

If \mathbf{M} is the magnetization (magnetic dipole moment per unit volume, analogous to the dielectric polarization \mathbf{P}) induced by the field \mathbf{H} , the volume magnetic susceptibility χ is defined by the equation

$$\mathbf{M} = \chi \mathbf{H} \quad (1)$$

For a paramagnetic substance, χ is positive; for a diamagnetic substance, it is negative. It is a dimensionless number, ordinarily very small in comparison with unity (except in the case of ferromagnetism) and essentially independent of \mathbf{H} for fields readily available in the laboratory.

Magnetic susceptibilities are usually given in the literature on a mass or molar basis. Thus, while the volume susceptibility χ is induced moment per unit volume per unit applied field and is dimensionless, the mass susceptibility

$$\chi_{\text{mass}} = \frac{\chi}{\rho} \quad (2)$$

(where ρ is the density) is induced moment per unit mass per unit applied field and has SI units of $\text{m}^3 \text{kg}^{-1}$. The molar susceptibility

$$\chi_M = M \chi_{\text{mass}} = \frac{M}{\rho} \chi = \tilde{V} \chi \quad (3)$$

(where M is the molar mass and \tilde{V} is the molar volume) is induced moment per mole per unit applied field and has SI units of $\text{m}^3 \text{mol}^{-1}$.†

Diamagnetism. Nearly all known substances are diamagnetic. Diamagnetism results from the precession of the electronic orbits in atoms that occurs when a magnetic field is present. Volume diamagnetic susceptibilities are generally very small in magnitude compared with volume paramagnetic susceptibilities for pure substances. In paramagnetic substances the observed susceptibility is the net result of a paramagnetic contribution and a very much smaller diamagnetic contribution. In an estimation of the paramagnetism this diamagnetic contribution is often neglected, but in the case of aqueous solutions a correction should be made for the diamagnetic susceptibility of the water owing to the relatively large amount of it present.

Paramagnetism. The most important source of paramagnetism is the magnetic moment associated with the spin of the electron. The electron has two spin states, having spin magnetic quantum numbers $-\frac{1}{2}$ and $+\frac{1}{2}$, with the principal component of magnetic moment, respectively, parallel and antiparallel to the magnetic field direction. Spin paramagnetism (or in some cases ferromagnetism) exists in a substance if the atoms, molecules, or ions in it contain unequal numbers of electrons in the two possible spin states. This condition obviously exists when the atom, molecule, or ion contains an odd number of electrons [as in Fe^{3+} , Cu^{2+} , $(\text{C}_6\text{H}_5)_3\text{C}\cdot$ and other free radicals, etc.]. It may also exist when the number of electrons is even, if a degenerate electronic level (such as a d or f atomic subshell) is only partially filled. For example, the free ferrous ion Fe^{2+} has six electrons outside the argon shell. The available orbitals of lowest energy are the five degenerate (i.e., equal-energy) $3d$ orbitals. Each of these may contain two electrons with their spins opposed (one with spin $+\frac{1}{2}$, the other with spin $-\frac{1}{2}$, in accord with the Pauli exclusion principle) or a single electron with either spin. No spin paramagnetism would occur if the six outer electrons of Fe^{2+} occupied three of the five $3d$ orbitals in pairs so that all spin magnetic moments cancelled. However, this would be contrary to a principle known as *Hund's first rule*, which states that when several electronic orbitals of equal or very nearly equal energy are incompletely filled, the electrons tend to occupy as many as possible of the orbitals singly rather than in pairs, the electrons in singly occupied orbitals all having the same spin. In Fe^{2+} this rule predicts that one $3d$ orbital will contain a pair of electrons with spins opposed and the other four orbitals will each contain a single electron, the four spins being the same. Thus the free ferrous ion is paramagnetic. In molecular oxygen O_2 , two molecular orbitals of equal energy each contain a single electron in accordance with Hund's first rule; consequently oxygen gas is paramagnetic.

An atom, molecule, or ion containing one or more unpaired electrons with the same spin has a permanent magnetic dipole moment μ . In the absence of orbital contributions to the moment (see below), the magnitude μ of this moment is completely determined by the number of unpaired electrons n :¹

$$\mu(\text{spin only}) = g_e \mu_B \sqrt{S(S+1)} = \sqrt{n(n+2)} \mu_B \quad (4)$$

†The use of $\text{cm}^3 \text{mol}^{-1}$ units for χ_M was standard practice in the past (cgs system) and still persists. Such values are almost always cgs values for $\chi_M(\text{ir})$, the irrational molar susceptibility given by $\chi_M(\text{ir, cgs}) = \chi_M(\text{cgs})/4\pi = 10^6 \chi_M(\text{SI})/4\pi$.

where S is the spin quantum number (equal to the sum of the individual electron spin quantum numbers s_i), the electron g -factor g_e has been taken as 2 for simplicity rather than 2.0023, and μ_B is the *Bohr magneton*, given by

$$\mu_B = \frac{eh}{4\pi m_e} = 9.274 \times 10^{-24} \text{ J T}^{-1} \quad (5)$$

where T denotes tesla (1 T = 10^4 gauss). Thus, for example, the "spin-only" magnetic moment of Fe^{2+} is

$$\mu = \sqrt{4 \times 6} \mu_B = 4.90 \text{ Bohr magneton}$$

Orbital magnetic moments may also contribute to paramagnetism. An electron in an orbital with one or more units of angular momentum behaves like an electric current in a circular loop of wire and produces a magnetic moment. When all orbitals in a subshell (e.g., all five $3d$ orbitals) are equally filled (with one electron each, as in Fe^{3+} , or two electrons each, as in Cu^-), the orbital moments cancel one another and there is no orbital contribution to the observed moment. In other cases (e.g., Fe^{2+}) an orbital contribution may arise, although usually it is "quenched" to a large extent by interactions with neighboring molecules or ions and does not contribute more than a few tenths of a Bohr magneton to the total moment. (Important exceptions are certain rare-earth ions, since quenching occurs to a much smaller extent for $4f$ orbitals than for $3d$ orbitals.) Atomic nuclei often possess spin magnetic moments, but these nuclear moments are so small as to have a negligible effect on magnetic susceptibility. They are important, however, in NMR spectroscopy.

In the absence of an applied field, the atomic moments in a paramagnetic substance orient themselves essentially at random owing to thermal motion and there is no net observable moment. In the presence of a magnetic field, the atomic moments tend to line up with the field, but the degree of net alignment is slight because of the disorienting effect of thermal motion. It is possible to show¹ that the paramagnetic contribution to the molar susceptibility is $N_0 \mu_0 \mu^2 / 3kT$, where N_0 is Avogadro's number, μ_0 is the vacuum permeability, and k is the Boltzmann constant. The molar susceptibility can be written

$$\chi_M = N_0 \mu_0 \xi + \frac{N_0 \mu_0 \mu^2}{3kT} \quad (6)$$

where ξ is the magnetizability and $\mu_0 \xi$ is the small (negative) diamagnetism per molecule. We can write this equation in the form

$$\chi_M = N_0 \mu_0 \xi + \frac{C}{T} \quad (7)$$

where C is called the *Curie constant* for the substance concerned. If C is determined by experiment, the magnetic dipole moment of the atom, molecule, or ion is obtained from it with the equation

$$\mu = \left(\frac{3kC}{N_0 \mu_0} \right)^{1/2} \quad (8)$$

Expressing this result in Bohr magneton units, we obtain

$$\mu = 797.8 \sqrt{C} \text{ Bohr magneton} \quad (9)$$

where C is in SI units ($\text{m}^3 \text{ mol}^{-1} \text{ K}$).

Transition-Metal Complexes. The present experiment is largely concerned with complex ions of transition-group metals, such as hexahydrated or ammoniated ferrous or ferric ions and ferro- or ferricyanides. Here each metal ion is surrounded by a number of negative or neutral groups called *ligands*. This number is six in the cases cited and in other common cases may be four or eight.

Two distinct groups of complexes can be distinguished on the basis of experimental paramagnetic susceptibilities. *High-spin complexes* are those for which the effective magnetic moment is very close to the spin-only value for the free (gaseous) transition ion. *Low-spin complexes* have much lower moments than would be predicted for the free metal ion and can even be diamagnetic.

The early theory of transition-metal complexes, due largely to Pauling,² involved an explanation based on distinguishing between essentially ionic and essentially covalent bonding between the metal ion and its ligands. Where the number of unpaired electrons in the complex as deduced from the measured susceptibility is the same as that expected for the free metal ion (high-spin case), the bonding with the ligands was considered to be ionic (i.e., due to Coulomb attraction as in $[\text{Fe(III)F}_6]^{3-}$ or due to electrostatic polarization of neutral ligands by the central ion as in $[\text{Co(III)(H}_2\text{O)}_6]^{3+}$). Where the number of unpaired electrons found in the complex is considerably less than the free-metal-ion value (low-spin case, as in most complexes with cyanides, ammonia, carbon monoxide, etc.), the bonding was considered to be covalent. It is assumed that the electrons are paired owing to the necessity of accommodating, in the atomic orbitals, some additional electrons donated by the ligands for forming electron-pair bonds. Thus in $[\text{Co(III)(NH}_3)_6]^{3+}$ the six electrons outside the argon shell of Co^{3+} are augmented by 6 electron pairs from the ligands, giving 18 electrons. Of these 12 electrons (or 6 pairs) are shared with the ligands to form 6 octahedral covalent bonds, using two $3d$, one $4s$, and three $4p$ orbitals of cobalt. The other 6 electrons are paired in the remaining three $3d$ orbitals. Since all electrons are paired with spins opposed, salts of this complex are diamagnetic.

The "crystal-field" or "ligand-field" theory of transition-metal complexes, first proposed by Van Vleck³ and subsequently developed extensively,⁴ has proven to be of great value in the interpretation of a wide range of properties. This theory explains transition-metal complexes in terms of the splitting of the five-fold-degenerate d level into two or more levels of different energy by perturbations due to the ligands. In the simplest version, this splitting is due purely to the electrostatic crystal field of the ligands. However, it is often necessary to consider also the metal-ligand orbital overlap (so-called adjusted crystal-field theory⁴). In any case, ligand-field theory is an adequate description as long as the d orbitals of the metal ion are well defined. If there is strong mixing between metal ion and ligand orbitals (as in metal carbonyls), a molecular-orbital theory is required.†

We shall discuss ligand-field theory in the one-electron approximation, in which a one-electron d state is split by the ligand field and the individual states are then filled by the d electrons of the central ion (taking account of interactions). As an example, consider a d^6 complex with octahedral symmetry; Fig. 1 shows the situation for Co(III) complexes. For weak ligand fields, the splitting Δ is small and the electrons distribute themselves according to Hund's first rule. Thus a complex such as $[\text{Co(III)F}_6]^{3-}$ is a high-spin complex with four unpaired electrons. The energy of this configuration can be written as $(-\frac{2}{5}\Delta + P)$, where P is the average energy required to form an electron pair. When the ligand field is strong enough (Δ sufficiently large), the energy difference between the levels can no longer be overcome by the electron-unpairing tendency of Hund's rule. Thus a complex such as $[\text{Co(III)(NH}_3)_6]^{3+}$ is a low-spin complex: the six d electrons of the cobalt ion fill the lower

†As shown by Van Vleck,³ Pauling's theory is a special case of the more general MO theory.

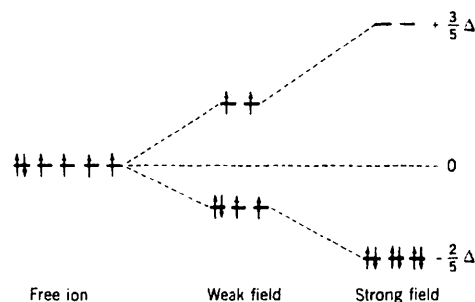


FIGURE 1
Weak field, e.g., $[\text{Co(III)F}_6]^{3-}$, and strong field, e.g., $[\text{Co(III)(NH}_3)_6]^{3+}$, splitting of the 3d level of Co(III) due to ligands with O_h symmetry. The splitting between the low-lying triplet and the upper doublet is defined as Δ . In the weak-field case, there are four unpaired spins; whereas all the spins are paired in the strong-field case.

triplet state with spins paired and the complex is diamagnetic. The energy of this configuration is $(-\frac{12}{5}\Delta + 3P)$. Analogous arguments can be applied to d^4 , d^5 , and d^7 complexes.

Thus ligand-field theory allows one to understand both high-spin and low-spin complexes. In particular low-spin complexes can be explained without assuming a covalent electron-pair bond between the metal ion and the ligand. Indeed there is no clear-cut distinction made between ionic and weak covalent character. According to the ligand-field theory, a low-spin complex simply means that the ligand field strength (and thus the splitting Δ) is greater than some critical value. It should be stressed that this critical value will be different for different complexes and one cannot equate increasing ligand field strength with increasing "covalency" in any simple way.

METHOD

Most methods for the determination of a magnetic susceptibility depend upon measuring the force resulting from the interaction between a magnetic field gradient and the magnetic moment induced in the sample by the magnetic field.⁵ Assuming for simplicity that H varies only as a function of x , the x component of this force, per unit volume of the sample, is

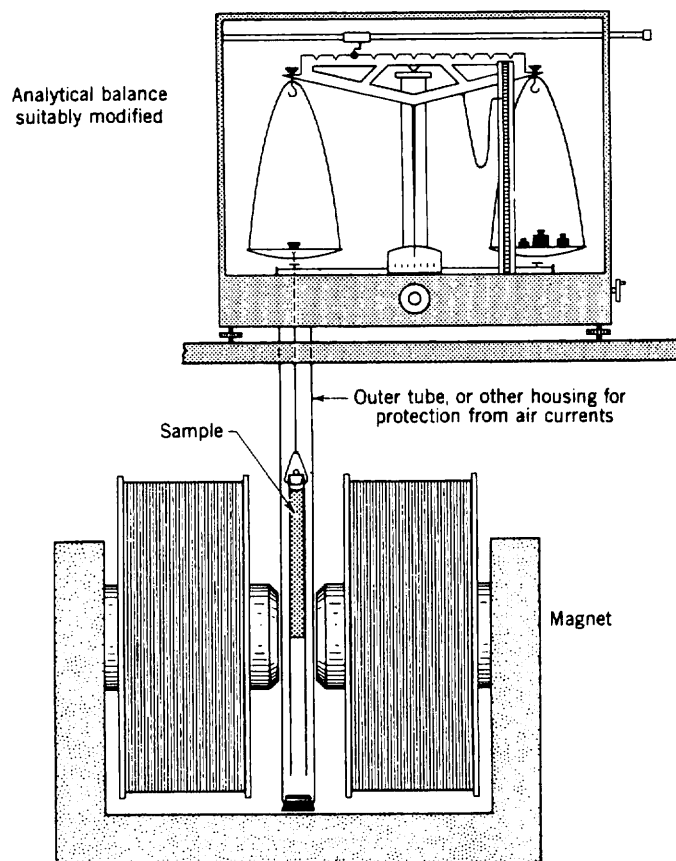
$$f_x = \mu_0 M \frac{dH}{dx} = \chi \mu_0 H \frac{dH}{dx} \quad (10)$$

where M is the magnetization and μ_0 is the vacuum permeability, equal to $4\pi \times 10^{-7}$ N A^{-2} ($\text{N} = \text{newton}$, $\text{A} = \text{ampere}$). This force is such as to tend to draw the sample into the strongest part of the field if the sample is paramagnetic (χ positive) or repel it into the weakest part if the sample is diamagnetic (χ negative). The work done on the system when a volume dV of the sample is carried from a point of field strength H_1 to a point of field strength H_2 is

$$\begin{aligned} dw &= dV \int f_x dx = dV \chi \mu_0 \int H \frac{dH}{dx} dx = dV \chi \mu_0 \int_{H_1}^{H_2} H dH \\ &= \frac{1}{2} \chi \mu_0 (H_2^2 - H_1^2) dV \end{aligned} \quad (11)$$

The Gouy Balance.⁵ In the Gouy balance (Fig. 2), a long tube, divided into two regions by a septum, is suspended from one side of an analytical balance so as to hang

FIGURE 2
Gouy balance.



vertically in a magnetic field. The septum is in the strongest part of the field and the two ends of the tube are in regions of essentially zero field strength. The part of the tube above the septum is filled with the sample to be investigated, and the part below is empty.

In addition to the downward gravitational force acting on the tube, a force is exerted by the magnetic field. Let us calculate the work done in *lowering* the tube, with cross-sectional area A , by an amount $|\Delta x|$. This is equivalent to bringing a volume $A|\Delta x|$ of the specimen from a region of zero field strength to a region of field strength H . Thus, ignoring gravitational work,

$$w = \frac{1}{2}\chi\mu_0 H^2 A |\Delta x| = f |\Delta x|$$

Therefore the *downward force* f on the tube due to its interaction with the magnetic field is†

$$f = \frac{1}{2}\chi\mu_0 H^2 A \quad (12)$$

†In case the top of the tube is not at zero field strength, we should write

$$f = \frac{1}{2}\chi\mu_0 (H_{\max}^2 - H_{\min}^2) A$$

Note that this force f as defined is a positive quantity for a paramagnetic sample, whereas f_x is negative when the positive x direction is taken to be upward.

In making a measurement, the "apparent weight" W is determined in the absence of a field and then with a field present, and the difference is equated to f :

$$(W_{\text{field}} - W_{\text{no field}}) = f = \frac{1}{2}\chi\mu_0 H^2 A \quad (13)$$

The weight W in each case is a *force* (in newtons) obtained by multiplying the mass of the weights used (in kg) by the acceleration due to gravity (in m s^{-2}).

The magnet should provide a field of at least 0.4 T (=4 kgauss) and preferably 0.6 T or more. The field should be reasonably homogeneous over a region considerably larger than the diameter of the tube. For a sample tube up to 15 mm in diameter, a magnet with a gap of 1 in. and a pole diameter of at least 3 in. is convenient.

To obtain the weights in the presence and absence of a field, it is most convenient to have an electromagnet, the field of which can easily be turned on and off. Such a magnet, with a regulated power supply, has the disadvantage of being rather expensive. A permanent magnet is usually less expensive, but special arrangements for making the no-field measurements are required. If the magnet is mounted on rails or on a pivot, it can be rolled or swung in and out of its normal position. If the magnet is stationary, the Gouy tube can be hung at two different levels (Fig. 3). If the latter method is to be used, the septum should be in the strongest part of the field in the lower position and in essentially zero field in the upper position. The sample tube should be long enough that in either position the bottom end is in an essentially zero-field region *below* the strong part of the field.

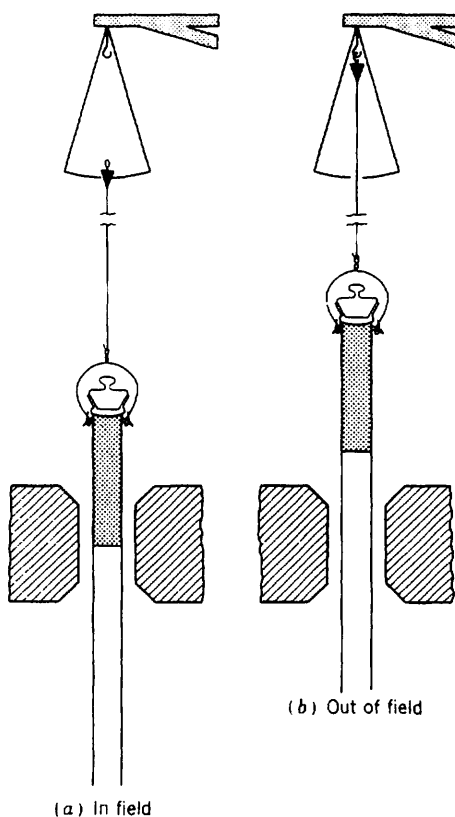


FIGURE 3
Positioning of Gouy tube
for (a) in-field and
(b) out-of-field weighings
when a stationary
permanent magnet is used.

A suitable analytical balance is mounted on a sturdy table over the magnet as shown in Fig. 2. Displayed is a two-pan balance but an electronic single-pan balance such as the Mettler model AE 100 can also be used and is simpler to operate. The Gouy tube is supported by a nonmagnetic wire or nylon thread that passes through a hole drilled in the base of the balance. If an electromagnet is used, the left-hand pan may be dispensed with and the wire attached directly to the stirrup. If, instead, a permanent magnet is used with the scheme shown in Fig. 3, a hole must be drilled in the pan so that the wire can pass through it to a hook that is attached to the stirrup for the no-field weighing or allowed to rest on the pan for the in-field weighing. The Gouy tube should be protected against air currents. Provision should also be made for mounting a thermometer near the Gouy tube.

EXPERIMENTAL

The procedure to be used in operating the Gouy balance will necessarily depend on the details of construction and cannot be given here with any completeness; a set of instructions should be compiled by the instructor and posted near the apparatus. The balance should be operated in the normal manner; the beam must be off the knife edges when the Gouy tube is being mounted, demounted, or changed in position. It is important to **remove your watch** when working near the magnet and to keep steel and iron tools or instruments out of the way.

In order to determine the "apparatus constant" $\mu_0 H^2 A/2$ that appears in Eq. (13), measurements are made on a material of known susceptibility. For this purpose, a common standard is an aqueous solution of nickel chloride, about 30 percent NiCl_2 by weight. Prepare 100 mL of such a solution with an accurately known weight fraction of NiCl_2 in air-free distilled water. When this and other solutions are weighed on the Gouy balance, record the ambient temperature.

Solutions of the following salts† in air-free distilled water should be studied. In each case the concentration (~ 0.5 molar) must be known precisely. If possible, prepare the solutions in advance, since some of these salts dissolve quite slowly.

KMn(VII)O_4 , potassium permanganate (*Note:* This is soluble only to ~ 0.4 molar)

Mn(II)SO_4 , manganous sulfate

$[\text{Fe(II)(H}_2\text{O)}_6](\text{NH}_4)_2(\text{SO}_4)_2$, ferrous ammonium sulfate (*Note:* This is subject to slow air oxidation)

$\text{K}_4[\text{Fe(II)(CN)}_6]$, potassium ferrocyanide

$\text{K}_3[\text{Fe(III)(CN)}_6]$, potassium ferricyanide

It is important to know the densities of all solutions. A satisfactory procedure is to weigh the Gouy tube empty and then filled with water to a fiducial mark near the top. From

†Magnetic measurements may be made on powdered crystalline salts rather than on aqueous solutions. The volume susceptibilities are very much larger (an attractive feature if a strong magnet is not available), but the molar susceptibilities are not so easily interpretable in terms of atomic moments, owing to interaction effects in the crystalline state. In place of Eq. (7), we write (neglecting the diamagnetic term)

$$\chi_M = \frac{C}{T - \Delta}$$

This is called the *Curie-Weiss law*. The constant Δ may be positive or negative and for most compounds is less than 75 K in magnitude. To obtain a value of the Curie constant from which an atomic moment can be calculated, it is necessary to measure χ_M at more than one temperature. When the reciprocal of χ_M is plotted against absolute temperature, the slope is the reciprocal of the Curie constant C . The density ρ required in the calculations is not the crystal density but an effective powder density determined in the manner described for solutions.

the known density of water at this temperature, calculate the volume. Then fill the tube with the solution to be studied up to the same fiducial mark and weigh it. (All these weighings are in the absence of a magnetic field.) Alternatively the density of each solution can be determined with a Westphal balance⁶ or a good hydrometer.

CALCULATIONS

Calibration. The mass susceptibility of an aqueous nickel chloride solution is given by⁷

$$\chi_{\text{mass}} = \left[\frac{10\,030p}{T} - 0.720(1 - p) \right] \times 4\pi \times 10^{-9} \text{ m}^3 \text{ kg}^{-1} \quad (14)$$

where p is the mass fraction of NiCl_2 and T is the absolute temperature. The second term in the brackets is the correction for the diamagnetism of the water used as solvent. This expression assumes that the solution is free of dissolved atmospheric oxygen.

From the χ_{mass} given by this expression and the density of the NiCl_2 solution, the volume susceptibility χ can be calculated from Eq. (2). With this and the measured weight difference, determine and report the apparatus constant $\mu_0 H^2 A/2$ appearing in Eq. (13).

Measurements on Unknown Solutions. The mass susceptibility of a solution in which the solute has molar mass M is related to the molar susceptibility by

$$\chi_{\text{mass}} = \frac{\chi_M(\text{solute})}{M} p - 0.720 \times 4\pi \times 10^{-9} (1 - p) \text{ m}^3 \text{ kg}^{-1} \quad (15)$$

where p is again the mass fraction of solute. If the concentration c of the solute in units of mol L^{-1} is known, we can write the volume susceptibility directly in the form

$$\chi = 1000c\chi_M - 0.720 \times 4\pi \times 10^{-9} (\rho - 1000cM) \quad (16)$$

where χ_M , ρ , and M are all expressed in SI units ($\text{m}^3 \text{ mol}^{-1}$, kg m^{-3} , kg mol^{-1} , respectively). From the experimental weight difference, χ is determined by use of Eq. (13) and the known apparatus constant $\mu_0 H^2 A/2$. The solute molar susceptibility χ_M is obtained from Eq. (16).

If the material is paramagnetic (χ_M positive), the small negative diamagnetic term $N_0 \mu_0 \xi$ can be neglected in Eq. (7) and the constant C can be determined. The atomic moment μ can then be calculated from Eq. (9). With neglect of any orbital contribution, the number of unpaired electrons can be found approximately with Eq. (4). Calculate the number of unpaired electrons for each paramagnetic substance studied.

DISCUSSION

In potassium permanganate Mn(VII) has no unpaired electrons and thus no permanent magnetic moment. However, the magnetic field induces a small, temperature-independent paramagnetism because the field couples the ground state to paramagnetic excited states.⁴ The other four compounds illustrate high- and low-spin cases of octahedral d^5 and d^6 complexes. (Neutral solutions of manganese sulfate are very pale pink and contain $[\text{Mn(II)(H}_2\text{O)}_6]^{2+}$ ions.) In the case of Fe(III) and the isoelectronic Mn(II) , the 6S ground

state of the free ion has no orbital angular momentum and no effective coupling to excited states. Thus the magnetic moment of their high-spin complexes should be very close to the spin-only value. Comment on the spin type and ligand-field strength of each complex studied.

SAFETY ISSUES

None.

APPARATUS

Gouy balance (comprising a magnet, power supply if needed, suitably modified analytical balance); glass-stoppered Gouy tube; several 100-mL volumetric flasks and glass-stoppered 200-mL flasks; 0 to 30°C thermometer; Westphal balance or hydrometer (optional).

NiCl_2 (40 g); MnSO_4 (10 g); KMnO_4 (10 g); $\text{K}_4\text{Fe}(\text{CN})_6$ (25 g); $\text{K}_3\text{Fe}(\text{CN})_6$ (20 g); $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (20 g); or a solution of each salt of an accurately known concentration (100 mL).

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