(d) Magnetism

Magnetization, M, (magnetic dipole moment per unit volume) of a sample in a magnetic field, H, is proportional to magnitude of H, and the proportionality constant, χ, depends on the sample.

$$M = \chi H \tag{6.3.1}$$

χ is the volume susceptibility and the product of χ and the molar volume V_m of a sample is the **molar susceptibility** χ_m. Namely,

$$\chi_m = \chi V_m \tag{6.3.2}$$

All substances have diamagnetism, and in addition to this, substances with unpaired electrons exhibit paramagnetism, the magnitude of which is about 100 times larger than that of diamagnetism. **Curie's law** shows that paramagnetism is inversely proportional to temperature.

$$\chi_m = A + \frac{C}{T} \tag{6.3.3}$$

where T is the absolute temperature and A and C are constants. In the Gouy or Faraday

methods, magnetic moments are calculated from the change of weight of a sample suspended between magnets when a magnetic field is applied. In addition to these methods, the highly sensitive SQUID (superconducting quantum interference device) has been used recently to carry out such measurements.

Paramagnetism is induced by the permanent magnetic moment of an unpaired electron in a molecule and the molar susceptibility is proportional to the electron spin angular momentum. Paramagnetic complexes of d-block transition metals have unpaired electrons of spin quantum number 1/2, and a half of the number of unpaired electrons is the total spin quantum number S. Therefore, the magnetic moment based only on spins can be derived theoretically.

$$\mu = 2\sqrt{2S(S+1)}\mu_B = \sqrt{n(n+2)}\mu_B$$

Here μ_B = 9.274 x 10^{-24} JT^{-1} is a unit called the Bohr magneton.

Many 3d metal complexes show good agreement between the magnetic moments of

agreement between the magnetic moments of paramagnetic complexes measured by a magnetic balance with the values calculated by the above formula. The relationship between the number of unpaired electrons and magnetic susceptibility of a complex is shown in Table 6.3. Because of this agreement with theory, it is possible to determine the number of unpaired electrons from experimental values of magnetic measurements. For example, it can be assumed that a Fe^{3+} d^5 complex with a magnetic moment of about 1.7 μ_B is a low-spin complex with an unpaired spin but a Fe^{3+} d^5 complex with a moment of about 5.9 μ_B is a high-spin complex with 5 unpaired electrons.

Some paramagnetic solid materials become **ferromagnetic** at low temperatures by forming **magnetic domains** in which thousands of electron spins are aligned parallel to each other. The temperature at which the paramagnetic-ferromagnetic phase transition occurs is called the **Curie temperature**. When spins are aligned antiparallel to each other, the material changes to an **antiferromagnetic substance**, and this transition temperature is called the **Néel temperature**. The material becomes ferrimagnetic when the spins are incompletely canceled. Recently, attempts have been made to synthesize polynuclear multi-spin complexes with special ligands that make paramagnetic metal ions align to induce ferromagnetic interactions between the spins. This effect is impossible in mononuclear complexes.