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Inorganic Chemistry

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TOPIC:-UNIT II, MAGNETIC PROPERTIES, METHODS OF DETERMINING MAGNETIC SUSCEPTIBILITY GOUY'S METHOD

METHODS OF DETERMINING MAGNETIC SUSCEPTIBILITY

Measurements of magnetic properties have been used to characterize a wide range of systems such as oxides, metallic alloys, solid state materials, and coordination complexes containing metals. Most of the organic and main group element compounds have all the electrons paired and these are diamagnetic molecules with very small magnetic moments. All of the transition metals have at least one oxidation state with an incomplete d sub shell. Magnetic measurements, particularly for the first row transition elements, give information about the number of unpaired electrons. The number of unpaired electrons provides information about the oxidation state and electron configuration. The determination of the magnetic properties of the second and third row transition elements is more complex.

The magnetic moment is calculated from the magnetic susceptibility, since the magnetic moment is not measured directly. There are several ways to express the degree to which a material acquires a magnetic moment in a field. The magnetic susceptibility per unit volume is defined by:

$$K = \frac{I}{H}$$

Where I is the intensity of the magnetization induced in the sample by the external magnetic field, H. The extent of the magnetic induction (I) depends on the sample. The induction may be visualized as an alignment of dipoles and/or by the formation of charge polarization in the sample. H is the strength of the external magnetic field in units of oversteds (Oe). The K is unit less.

Generally, it is more convenient to use mass units, therefore, the mass or gram susceptibility (χ_g) is defined as:

$$\chi_g = \frac{\kappa}{d}$$

Where d is the density of the solid. The molar susceptibility (χ_m) is the mass susceptibility multiplied by the formula weight (F.W.).

$$\chi_m = \chi_g \text{ (F.W. in g mol}^{-1}\text{)}$$

The terms κ, χ_g and χ_m are all measures of the magnetic moment of a substance in a magnetic field. There are various methods to measure magnetic susceptibility which are dicussed in the next section.

GOUY'S AND QUINCKE'S METHOD

Gouy's method

Gouy's balance named after the scientist who devised it generally to be used to measure paramagnetism. In this method, finely powdered substance or solution is taken in a pyrex cylindrical glass tube called Gouy tube the substance is weighed first without magnetic field and then in the presence of magnetic field (Figure 3.2). A paramagnetic substance will weigh more in the presence of a magnetic field than in its absence, the increase in weight gives a quantification of paramagnetism of the substance. More the number of unpaired electrons in a substance; greater will be the increase in its weight under a magnetic field. The magnetic susceptibility is measured from the difference in weight of the sample with and without magnetism.

Determination of magnetic moment measurement with standard substance

The apparatus can be calibrated by measuring the values of a substance whose susceptibility is accurately known. The standard substance commonly used for calibration is mercury tetrathiocyanatocobaltate; Hg[Co(CNS)4]. Its magnetic susceptibility is $16.44 \times 10^{-6} at\ 20^0C$.

I. Weigh the empty tube with and without magnetic field in gram

Weight of empty tube without magnetic field = A

Weight of empty tube with magnetic field = B

Difference in weights of emty tube = B-C

II. Weigh the tube filled with standard substance in presence and in absence of magnetic field in gram

Weight of tube filled with the standard in absence of magnetic field = D

Weight of tube filled with the standard in presence of magnetic field = E

Difference in weight of tube filled with standard = E-D

III. Difference in the weight of standard (Δw_s) = (E-D) – (B-A)

IV. Weight of standard in absence of magnetic field (w_s) = D-A

Measurement with unknown substance

I. Weigh the empty tube with and without magnetic field in gram

Weight of empty tube without magnetic field = F

Weight of empty tube with magnetic field = G

Difference in weights of emty tube = G-F

II. Weigh the tube filled with substance in presence and in absence of magnetic field in gram

Weight of tube filled with substance the in absence of magnetic field = H

Weight of tube filled with the substance in presence of magnetic field = I

Difference in weight of tube filled with substance = I-H

III. Difference in the weight of substance (Δw) = (I-H) – (G-F)

IV. Weight of substance in absence of magnetic field (w) = H-F

If magnetic susceptibility of the standard is χ_s then the magnetic susceptibility of the substance will be

$$\chi = \chi_s \frac{w_s}{\Delta w_s} \times \frac{\Delta w}{w}$$

$\chi_m = \chi$ x molecular weight of the substance

The Gouy method is a convenient method for measuring magnetic susceptibility. The sample is suspended (in a cylinder) in a non homogeneous magnetic field and the force exerted on the sample can be determined by weighing it. The force acting on the sample is

$$F = \frac{1}{2}AH^2\kappa$$

Where A is the cross sectional area of the cyclinder; H is the intensity in the central homogenous part of the magnetic field and κ is volume susceptibility

The above equation is valid only when the measurements are taken in vacuum. However, if the sample is surrounded by air, then the air susceptibility (κ') must be subtracted from the measured susceptibility. Now the equation becomes:

$$F = \frac{1}{2}AH^2(\kappa - \kappa')$$

Where κ' is the volume susceptibility of air

The Gouy tube itself produces a force which is always present. Therefore, actual force acting on the sample can be calculated by subtracting the force acting on the Gouy tube (δ) from the observed force. This force will be negative because of the diamagnetic material of the tube. Now the equation becomes:

$$F = \frac{1}{2}AH^2(\kappa - \kappa') + \delta$$

For a sample with constant length and cross sectional area, the factor A H^2 will be constant. If the sample density is introduced, the above equation can be written as:

$$10^6\chi = \frac{\alpha + \beta F}{w}$$

Where α is a constant for the displaced air = 0.029 x specimen volume and expressed in mg; w is the weight of sample in gram; F is the force on the sample and β = tube calibration constant.

The apparatus can be calibrated by measuring the values of a substance whose susceptibility is accurately known. The standard substance commonly used for calibration is mercury tetrathiocynatocobaltate; Hg[Co(CNS)4]. Its magnetic susceptibility is 16.44 $\times$ 10^{-6} $at\ 20^0C$. By taking measurements with this standard substance, the constant β is first calculated. By substuting the values of α, β, δ and F F on a sample of weight w, the susceptibility (χ) of the substance can be calculated

The forces are large because the amount of sample taken in the Gouy's tube is quite large and therefore, a chemical balance can also measure the changes in mass. The disadvantage of this method is that it requires perfect uniform packing of the substance in the Gouy's tube. Therefore, correct results can not be obtained if the Gouy's tube has not been packed uniformly.