518. The Accuracy of Determination of the Magnetic Susceptibility of Solids by the Gouy Method.

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The errors incurred in the determination by various differences in experimental procedure (particularly in methods of packing) and in other factors are examined.

It has frequently been assumed that the accuracy of determination of the magnetic susceptibility of solids, other than homogeneous specimens containing no air or other inclusion, *e.g.*, metal rods, is necessarily appreciably less than that of liquids. This has been ascribed largely to difficulties in packing solids uniformly throughout the volume of the susceptibility tube. However, other factors for which allowance must be made have also been noted, the most important of these being (*a*) a meniscus correction, when a liquid is used to determine the volume of the susceptibility tube, and (*b*) a correction for the presence of air enclosed in the packed solid. The former is considered in detail by Nettleton and Sugden (*Proc. Roy. Soc.*, 1939, *A*, **173**, 313), who, however, do not mention a correction for air present, *i.e.*, they do not differentiate between d, the true density of the solid, and W/V, where W is the weight of solid packed in a volume V of the susceptibility tube. This, as will subsequently be shown, may give rise to appreciable errors. Hoare (*ibid.*, 1934, *A*, **147**, 88) derived an equation substantially the same as equation (2). His method is, however, open to criticism, in that he assumed that the specific susceptibility of the solid was equal to the measured volume susceptibility of the material in the tube (which may contain an appreciable amount of air) divided by the true density of the solid. Angus and Hill (*Trans. Faraday Soc.*, 1943, **39**, 185), on the other hand, employ the apparent density (W/V) of any solid measured. Michaelis and Granick (*J. Amer. Chem. Soc.*, 1943, **65**, 1752), however, make allowance for the presence of air even when paramagnetic solids are under investigation, although the correcting term will here be relatively small. The importance of these various factors, and a simple equation by which they may be taken into account, are discussed below. The method of packing solids is also examined.

Air enclosed in Packed Solid.—If W is the weight of solid of density d packed uniformly into a volume V c.c. of tube, then this volume will contain W/d c.c. of solid and $(V - W/d)$ c.c. of air. If κ is the susceptibility of 1 c.c. of the solid–air mixture in the tube, then provided the field strength at the top of the specimen is zero, the observed pull F on the specimen of cross-sectional area A will be related to the field strength H at the bottom by the equation $F = \frac{1}{2}(\kappa - \kappa_{\text{air}}) . AH^2$. Eliminating A and H from this equation by using a standard substance of known volume susceptibility κ_s, specific susceptibility χ_s, and density d_s, on which the pull under the same conditions is F_s, we have

$$F_s = \tfrac{1}{2}(\kappa_s - \kappa_{\text{air}}) . AH^2$$
$$= \tfrac{1}{2}(d_s\chi_s - \kappa_{\text{air}}) . AH^2$$

whence

$$\kappa = (d_s\chi_s - \kappa_{\text{air}}) . F/F_s + \kappa_{\text{air}}$$

Included in this equation is a contribution of $\kappa_{\text{air}}(1 - W/Vd)$, due to the air enclosed in each c.c. of solid–air mixture. Hence the volume susceptibility of the solid itself is

$$\kappa_{\text{solid}} = (d_s\chi_s - \kappa_{\text{air}}) . F/F_s + \kappa_{\text{air}} - \kappa_{\text{air}}(1 - W/Vd)$$
$$= (d_s\chi_s - \kappa_{\text{air}}) . F/F_s + \kappa_{\text{air}} . W/Vd$$

This is the susceptibility of W/V g. of solid, whence the specific susceptibility per g. will be given by

$$\chi = (\chi_s - \kappa_{\text{air}}/d_s) . FVd_s/F_sW + \kappa_{\text{air}}/d \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Meniscus Correction.—Equation (1) can be used without further modification if V is determined directly, by measurement of the cross-sectional area (which must be uniform) and length of tube to a fixed filling mark. Frequently, however, V is determined from the weight of standard liquid filling the tube to this mark. In this case, Vd_s cannot be equated simply to W_s, since the volume of solid packed to the mark will be less than that of the standard liquid by an amount equal to the volume of the meniscus, *i.e.*, $Vd_s = W_s - c$, where W_s is the weight of the standard liquid filling the tube to the mark, and c is the correction for the meniscus effect. Thus, on substitution in equation (1) for Vd_s, we have

$$\chi = (W_s - c)(\chi_s - \kappa_{\text{air}}/d_s) \, . \, F/F_sW + \kappa_{\text{air}}/d \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

Now both the meniscus correction and the ratio of the weight W_s to the length h of the column of liquid filling the tube are functions of the internal radius of the tube (in addition to other variables). It is found that corrections calculated from the Table (based on the data of Bashforth and Adams) given in the International Critical Tables (Vol. I, p. 73, Table 3) may be represented as an approximately linear function of W/h, at least in the cases of water, acetone, and benzene, the three liquids commonly used for calibration, and for tubes of radius between 2 and 4 mm., normally employed. Hence the correction for a particular tube can be obtained graphically, or by means of a suitable empirical equation for the particular liquid used; *e.g.*, for benzene (with W_s in g. and h in cm.) from the data in the International Critical Tables (*loc. cit.*), $c = 0{\cdot}0854W_s/h - 0{\cdot}0037$. This meniscus correction has an appreciable effect on the calculated susceptibility of both dia- and paramagnetic substances, and is illustrated in a typical example in the Table.

Density of Solid.—The assumption is frequently made that the density of a solid may be represented by the ratio W/V, where W is the weight of solid packed as tightly as possible into a volume V of the tube. In the case of paramagnetic solids, except in work of extreme accuracy, the error introduced in making this assumption is generally, though not always, negligible. For example, Michaelis and Granick (*loc. cit.*) give as an example of their method of calculation, their results for Wurster's blue perchlorate, which has a true density of 1·398. However, the apparent density calculated from the weight of solid packed into the susceptibility tube is only 0·308, on account of the loose packing used by these authors. The difference in the calculated value of the susceptibility obtained by using the true and apparent densities is $0{\cdot}0736 \times 10^{-6}$ for this compound ($\chi = 4{\cdot}18 \times 10^{-6}$). With diamagnetic solids the error introduced in making this assumption is frequently appreciable, as illustrated in the Table. Whenever possible, therefore, it is desirable to determine the density of the solid by an independent experiment, and to use this value in the appropriate term of equation (2).

Method of Packing.—It is noteworthy that in spite of widely different methods of packing employed by different workers, the values obtained for magnetic susceptibility are often in remarkably good agreement. The reason for this becomes apparent on examination of equation (2). This shows that F/W is the factor having the greatest effect on the value of the susceptibility. Since χ, the susceptibility per g. of solid, must, from its definition, be independent of tightness of packing, then theoretically F/W must also be independent of tightness of packing, since the other terms in equation (2) are unaffected by it. (This assumes, of course, that the true density d of the solid is used for the calculation, since otherwise tightness of packing will influence the magnitude of the W/V term.) Hence the experimentally determined susceptibility should be the same for all methods of packing, provided this is uniform. These conclusions, and the importance of the various factors examined above, are borne out by the data in the following table, which gives values of $10^6\chi$ for a specimen of potassium nitrate (not specially purified).

$V = 4{\cdot}08$ c.c.; $h = 12$ cm.; $F_s = 7{\cdot}94$ mg.; $W_s = 3{\cdot}599$ g.; $\chi_s = -0{\cdot}702 \times 10^{-6}$ (benzene); $c = 0{\cdot}022$ (from graph); $d = 2{\cdot}1$ g./c.c.

		Series 1. Mean $F = 6{\cdot}34$ mg. Mean $W = 6{\cdot}391$ g. $F/W = 0{\cdot}992$		*Series* 2. Mean $F = 5{\cdot}69$ mg. Mean $W = 5{\cdot}730$ g. $F/W = 0{\cdot}993$	
Density value	" W_s " value	$-10^6\chi$	Error	$-10^6\chi$	Error
d	$W_s - c$	0·315	0·000	0·315	0·000
W/V	$W_s - c$	0·310	−0·005	0·308	−0·007
d	W_s	0·317	+0·002	0·317	+0·002
W/V	W_s	0·312	−0·003	0·310	−0·005

In series 1 the powder was packed by ramming it into the tube in successive, small, approximately equal layers. In series 2 it was loosely packed by tapping the bottom of the tube on the bench after addition of each layer. Although in the second series there is approximately 10% less solid in the tube, there is no significant difference in the F/W ratio. Nevertheless, it frequently appears easier to obtain uniform packing by the method of tight ramming than by other methods, although this may be a personal factor. It is clear, however, that the object of the method adopted must be to obtain uniformity, and not, as is often believed, to remove as much air from the interstices as possible. Correction for the latter factor can be made as previously indicated.

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