An Improved Technique for Determination of Magnetic Susceptibilities of Solids by the Gouy Method.

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A new technique for measuring magnetic susceptibilities of solids by the Gouy method has been developed. The method has been tested with a crystalline solid and a fine powder and shown to give greater reproducibility than previous methods, especially in the case of the powder. Improved magnetic-susceptibility values have been obtained for potassium chloride and carbon tetrachloride.

Attention has been directed recently to possible sources of error in the determination of the magnetic susceptibility of solids by the Gouy method in which the finely powdered solid is packed into a cylindrical tube. The chief source of error lies in non-uniform packing of the specimen, and the problems of obtaining uniform packing.are similar to those found in packing chromatographic columns. It was noted some years ago that this error tends to be particularly high with fine powders and microcrystalline solids, where the usual method of ramming the specimen into the tube tends to produce alternating zones of compressed and lightly packed material. It is generally recognised that reproducibility of results for solid substances is less than that for measurements in the liquid state or in solution. With careful technique and crystals of approximately uniform size, results of any one investigator are usually reproducible within about 1%, but greater divergences may occur, especially between those of different investigators.

French and Harrison (*J.*, 1953, 2538) have moreover drawn attention to the necessity for correcting susceptibility measurements of solids, made by the Gouy method, for the air remaining in the interstices of the packed solid and for the meniscus effect of the calibrating liquid, if such is used. They have also pointed out, with a few figures in support, that uniformity rather than tightness of packing is the limiting factor governing reproducibility. They did not, however, investigate the problem of attaining uniformity of packing, and do not record the number of individual measurements made or the mean error obtained.

The following modification effects a considerable improvement in the uniformity of packing: the susceptibility tube is filled with the solid under investigation by gradual sedimentation under a column of the reference liquid used in calibrating the magnetic balance. By tapping and rotating the tube during sedimentation, and centrifuging slowly at intervals, a high degree of reproducibility was obtained even with finely powdered solids. A number of measurements have been made on the same solid to check the method in detail. Pure potassium chloride was selected as it has been used as a standard for calibration. Some measurements have also been made on a fine powder, thallic oxide being chosen, as some earlier unsatisfactory results, obtained by the ramming technique, were available for comparison.

Experimental

Measurements of the specific susceptibility have been made with two calibrating liquids, various field strengths, and susceptibility tubes of different cross-sectional area. After completion of each set of measurements the liquid was evaporated and a final measurement made with air in the interstices of the solid. Benzene and carbon tetrachloride, in which the inorganic salts under investigation are insoluble, were used as the standard liquids. Benzene has a high susceptibility and has been used for some time as a calibrating standard, while carbon tetrachloride affords a useful alternative for testing the method owing to its low susceptibility and high density. The method of measurement of the magnetic susceptibility and the magnetic balance used have been described previously (Trew and Watkins, *Trans. Faraday Soc.*, 1933, **29**, 1310; French and Trew, *Trans. Faraday Soc.*, 1945, **41**, 439). The volumes of the susceptibility tubes and densities (d_4^{20}) of the liquids and of the solids were determined. Measurements were made of the diamagnetic thrust on the tube alone and filled to the mark with the standard liquid, before each set of measurements, and these calibrations were repeated after the final measurement with air in the interstices of the material. To pack the tube it was filled about two-thirds of the way to the mark with the standard liquid; the finely powdered solid, after being sieved through a stretched cotton gauze of approx. 40-mesh, was dropped into the tube from a weighing bottle. The tube was lightly tapped and rotated during the addition of solid to ensure even sedimentation. The most reproducible packing was obtained when slow centrifugation was used after about each 0·5-cm. length had been filled. Centrifugation was continued for a minute at 2000 r.p.m., giving a force of 200 *g* at the top and 500 *g* at the base of the tube. The adjustment of the solid to the upper mark of the standard apparatus was somewhat critical and was best achieved by levelling off at the mark, under the liquid, with a glass rod of dimensions just smaller than those of the tube, while viewing the interface with a strongly magnifying lens. The level of the liquid meniscus was then adjusted with the tube suspended in a thermostat at 20°. Magnetic measurements were made at room temperature, which rarely varied within the magnet enclosure by more than a degree from 20°. In determinations of the thrust on the mixture the mean of at least six readings was taken for each packing. In some experiments the mixture was then centrifuged again, and again filled to the mark and the thrust re-measured. Some measurements were made at different field strengths, as described in a previous paper (Trew, *Trans. Faraday Soc.*, 1953, **49**, 604), and two sets included were carried out by Dr. S. A. Husain using a different magnet with smaller field and larger susceptibility tubes. The diamagnetic susceptibility of benzene as a standard is well established, but it was found necessary to remeasure that of carbon tetrachloride. Four different field strengths and both susceptibility tubes were used to obtain a mean value of

TABLE 1.

W_{KCl}	W_m	F_m	F_s	χ_m ($\times -10^6$)	χ_{KCl} ($\times -10^6$) (*A*)	χ_{KCl} ($\times -10^6$) (*B*)	F_a	χ_{KCl} ($\times -10^6$) (*C*)
(*a*) Tube 1; packed under benzene. $W_s = 2·7289$ g. $V_1 = 3·104$ ml. $l_s = 8·014$ cm.								
2·7327	4·2403	16·54	12·95	0·5832	0·5175	0·5144	9·56	0·5207[1]
3·1685	4·4003	15·89	12·18	0·5702	0·5188	0·5087	10·26	0·5092
3·2599	4·5511	15·90	11·86	0·5715	0·5196	0·5206	10·41	0·5240[2]
3·2354	4·5332	15·87	11·88	0·5725	0·5186	0·5186	10·29	0·5226
2·9617	4·3797	15·41	11·86	0·5750	0·5138	0·5136	10·50	0·5084
3·3521	4·5974	15·83	11·86	0·5634	0·5118	0·5113		
3·3967	4·6223	15·91	11·86	0·5632	0·5131	0·5125		
(*b*) Tube 2; packed under benzene. $W_s = 3·2674$ g. $V_2 = 3·7242$ ml. $l_s = 9·01$ cm.								
3·4560	5·1755	17·04	13·18	0·5794	0·5182	0·5142	10·26	0·5166[3]
3·4560	5·1755	16·76	12·97	0·5790	0·5177	0·5137	10·08	0·5154[4]
3·4560	5·1755	16·49	12·75	0·5796	0·5186	0·5145	9·89	0·5144[5]
(*c*) Tube 1; packed under carbon tetrachloride. $W_s = 4·9505$ g.								
3·2344	5·6350	16·51	13·24	0·4795	0·5132*	0·5194	10·10	0·5179
			11·86	0·4798	0·5137			
3·2344	5·6237	16·50	13·24	0·4803	0·5144	0·5194		
			11·86	0·4804	0·5147			
3·3251	5·6048	16·52	13·24	0·4825	0·5157	0·5149	—	—
			11·86	0·4827	0·5158			
(*d*) Tube 2; packed under carbon tetrachloride. $W_s = 5·9362$ g.								
4·0159	6·7657	18·26	14·55	0·4827	0·5164*	0·5186	11·41	0·5139
			13·04	0·4813	0·5136			
4·0159	6·7565	18·26	14·55	0·4832	0·5173	0·5186		
			13·04	0·4819	0·5146			
(*e*) Tube 3; packed under benzene. $W_s = 6·6411$ g. $V_3 = 7·5549$ ml.								
8·5678	11·4061	8·94	6·56	0·5640	0·5181	0·5176	—	—
8·6399	11·4655	8·98	6·56	0·5637	0·5183	0·5192	—	—

Mean values $\chi_{KCl}\,(A) = -0·5164 \pm 0·0021 \times 10^{-6}$
$\chi_{KCl}\,(B) = -0·5159 \pm 0·0029 \times 10^{-6}$
$\chi_{KCl}\,(C) = -0·5163 \pm 0·0040 \times 10^{-6}$

* Calc. relative to carbon tetrachloride as standard (upper row), and benzene as standard (lower row).

[1, 2, 3, 4, 5] Length of residual column slightly contracted, to 7·91, 8·00, 8·84, 8·84, and 8·84 cm. respectively.

$-10^6\chi = 0{\cdot}4341 \pm 0{\cdot}0006$ e.m.u. per g., in agreement with an earlier value of $0{\cdot}4340 \pm 0{\cdot}0011$ (French and Trew, *loc. cit.*).

The specific mass susceptibility χ_m of the mixture of solid and liquid was calculated from the relation :

$$\left(\chi_m - \frac{kV}{W_m}\right) \Big/ \left(\chi_s - \frac{k}{d_s}\right) = F_m W_s / F_s W_m$$

an expression used in earlier work with liquids (Trew, *loc. cit.*) but with the ratio of the densities replaced by that of the weights in volume V. χ_s is the specific mass susceptibility of the standard liquid, k the volume susceptibility of air ($0{\cdot}0294 \times 10^{-6}$), and d_s the density of the standard liquid. F_m and F_s are the thrusts in mg. on the column of mixture filling the volume V, and W_m and W_s are the corresponding weights in grams corrected in each case for the meniscus correction of the liquid. This correction was calculated from Bashford and Adams's tables in The International Critical Tables (Vol. I, p. 73).

The specific mass susceptibility χ of the salt then follows by application of the mixture law, *i.e.*, $\chi_m = [p\chi + (1 - p)\chi_s]$, where p is the weight fraction of solid in the mixture. Values of the susceptibility χ_{KCl} (A), calculated in this manner, are recorded in column 6 of Table 1. To test the extent of possible errors introduced by incorrect adjustment of liquid to the mark when the tube is packed with solid, the results χ_{KCl} (B) in column 7 were evaluated. The volume of liquid in the interstices of solid and hence total weight of mixture were here calculated from the known weight and density of solid used and the volume of the tube. The last two columns show the thrust, F_a, obtained on the solid after evaporation of the standard liquid, and the resulting susceptibility χ_{KCl} (C) calculated by means of French and Harrison's formula (*loc. cit.*) with corrections for the meniscus effect and the residual air in the interstices of solid.

A similar set of experiments was carried out with finely powdered thallic oxide, prepared by oxidation of a nearly saturated solution of pure thallous nitrate in 25% aqueous sodium hydroxide by means of 5% hydrogen peroxide at 80°. The resultant precipitated oxide was washed repeatedly by decantation and dried and the thallium estimated as chromate (Found, 89·8. Calc. : 89·5%). The susceptibility results for six determinations with the new technique are recorded in Table 2, where are given also the summarised results of some unsatisfactory earlier measurements (ramming method in air).

TABLE 2.

$W_{Tl_2O_3}$	W_m	F_m	χ_m ($\times -10^6$)	$\chi_{Tl_2O_3}$ ($\times -10^6$)	$W_{Tl_2O_3}$	W_m	F_m	χ_m ($\times -10^6$)	$\chi_{Tl_2O_3}$ ($\times -10^6$)
$W_s = 3{\cdot}2369$ g. $F_s = 12{\cdot}70$ mg. $V_4 = 3{\cdot}6865$ cm.									
7·5716	10·064	16·67	0·2997	0·1672	8·0767	10·556	17·07	0·2930	0·1673
7·6284	10·112	16·42	0·2938	0·1608	8·1624	10·543	17·04	0·2929	0·1718
7·7934	10·273	16·67	0·2936	0·1634	8·2658	10·728	17·05	0·2879	0·1645

Mean $\chi_{Tl_2O_3} = -0{\cdot}1658 \pm 0{\cdot}0029 \times 10^{-6}$.

Previous values packed in air by ramming; mean of eleven readings, $-0{\cdot}176 \pm 0{\cdot}026 \times 10^{-6}$, with individual readings ranging from $0{\cdot}137$ to $0{\cdot}206 \times 10^{-6}$.

DISCUSSION

For potassium chloride the figures in Table 1 show a much greater reproducibility than is generally found by other methods of packing. The agreement of the mean from columns 6 and 7 shows that with care the error in filling the liquid to the mark is negligible. In addition the mean value from the figures in column 9 affords a striking confirmation of the method. Here, however, the variation between individual results is rather greater as no especial precautions were taken to prevent displacement of the solid during evaporation of the standard liquid, or to see that air entirely replaced all the vapour of the liquid in the interstices. It was noted that uniformity of packing was still the most critical factor in obtaining reproducibility of results. Two sets of figures, one for the solid packed under benzene and one under carbon tetrachloride, in which sedimentation of the potassium chloride was allowed to take place without centrifugation, gave low results and were discarded.

The figures for thallic oxide show that the new technique gives much greater reproducibility on fine powders. The earlier value of $\chi = -0{\cdot}176 \pm 0{\cdot}026 \times 10^{-6}$ is replaced by the figure of $-0{\cdot}166 \pm 0{\cdot}003 \times 10^{-6}$, a ten-fold improvement in the mean error. The mean specific mass susceptibility of potassium chloride, $-10^6\chi = 0{\cdot}5164 \pm 0{\cdot}0021$, gives a molar susceptibility of $-10^6\chi_M = 38{\cdot}50$. Both this figure and that for carbon tetrachloride supply useful additional standards for diamagnetic measurements. The new method of packing the susceptibility tube should be equally applicable to measurements on paramagnetic solids.

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