

Determination of Magnetic Susceptibilities between 81 and 295°K by Means of a Modified Sucksmith Balance

Studies in Magnetochemistry 24*

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A detailed description is given of the construction and use of a Sucksmith ring balance, which is operated according to a compensation principle: The current exiting the electromagnet is regulated until the magnetic force exerted upon the sample exactly compensates the removal of a known weight from the elastic phosphor bronze ring, which constitutes the sensitive part of the balance. By introduction of the compensation principle errors due to changes in the elasticity of the ring have been eliminated. An electromagnetically operated weight manipulator, which may be charged with three ring-formed weights at a time, allows 13 different loads to be applied to the phosphor bronze ring. A set of six interchangeable ring weights cover the scale from less than 1 mg to about 80 mg. A cryostat arrangement is also described. The sample is surrounded by a double walled glass tube, which is immersed in liquid air. When the space between the walls of the glass tube has been suitably evacuated, the sample may be given any temperature between 81 and 295°K by heating the inner wall of the tube electrically. Examples of the reliability of the apparatus during actual measurements both at room temperature and at lower temperatures are given.

Several methods of measuring the magnetic gram susceptibility, χ_g , rest upon the relation

$$K = \chi_g m H \frac{\delta H}{\delta z} \quad (1)$$

where K is the force exerted upon a sample of mass m , which is suspended in an inhomogeneous magnetic field H with the gradient $\delta H/\delta z$ perpendicular to the magnetic lines of force. Accurate determinations of $\delta H/\delta z$ are rather difficult, measurements of the gram susceptibility are therefore often relative. That is, the magnetic force exerted upon the sample under investigation is

* No. 23 appeared in *Acta Chem. Scand.* 12 (1958) 939.

compared with that exerted upon some standard substance placed in the same position in the magnetic field. The measuring problem is thus essentially reduced to that of measuring the force K .

A very convenient apparatus for measurements of magnetic susceptibilities over a wide range of temperatures is the ring balance originally designed by Sucksmith^{1,2} and later modified by Jackson³, v. Oort⁴, and others^{5,6}. The essential features of the ring balance are as follows (*cf.* Fig. 1): An elastic ring made of phosphor bronze is clamped at the top, while a quartz capillary carrying the sample is attached to the diametrically opposite point. Two small mirrors facing each other are fixed to the ring. The light from a distant lamp passing a lens is reflected from the mirrors and focused on a vertical scale. When the magnetic field is switched on, the force acting on the sample deforms the ring and so causes a displacement of the light spot upon the scale, which may be calibrated in terms of the force acting on the sample.

When the balance is used in this manner, it needs rather frequent recalibration, probably due to small changes in the elasticity of the ring. This difficulty is circumvented if the ring balance, as mentioned by Cooke and Duffus⁵, is used as a pure zero instrument. The current exiting the electromagnet is regulated until the effect of removing a known load from the ring is exactly compensated. By this means all the facilities connected with a compensation method are introduced. In order to obtain the necessary flexibility in the choice of loads to be compensated, a weight manipulator has been constructed. In the following sections the constructional details of the balance and its accessories together with a description of the operating procedure and the calibration are given.

THE APPARATUS

In Fig. 1 the main features of the apparatus are shown. The ring A, which is made from a strip of phosphor bronze 0.1 mm thick and 3 mm wide, is clamped at the top in vertical position. The diameter of the ring is 60 mm.

The perfectly straight quartz capillary B, which carries the sample C is attached to the lowest point of the ring by means of an aluminium clamp D. The external diameter of the capillary is 1 mm.

Two flat spiral springs pasted to the quartz capillary with a drop of shellac at E_1 and E_2 effectively prevent lateral movements of the sample. In a special experiment it was demonstrated that the spirals reduce the lateral movements of a strongly paramagnetic sample to less than 0.1 mm under the influence of the strongest field obtainable with the magnet. In the absence of the spirals the sample suddenly adhered to the pole pieces even when moderate fields were applied. The spirals are cut from a sheet of phosphor bronze of 0.05 mm's thickness.* They only diminish the sensitivity of the balance 1—2 %.

The quadratic mirrors F_1 and F_2 ** of 10 mm edge and 1 mm thickness are made from optically plane glass and coated on the front side with a reflecting layer of aluminium. They are pasted with shellac to small pieces of phosphor

* The author is thanks due to Mr. O. Gram Jeppesen for the design of the spirals. †

** The mirrors were obtained from Messrs. I. G. Müller GmbH Wedel, Holsten, who guarantee a planarity of at least 600 m.

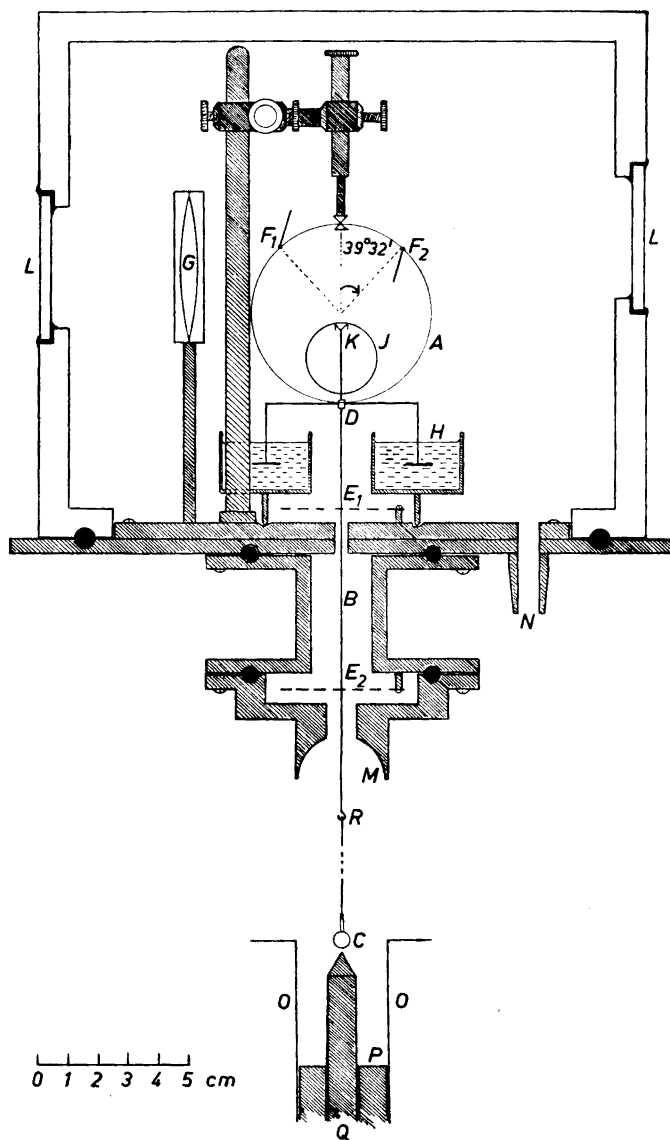


Fig. 1. General view of the apparatus.

bronze and bolted to the ring at the points, where the angular deflection is calculated to be a maximum^{1,7}.

A mated glass plate illuminated from behind serves as a source of light. A transparent glass plate with an engraved fine cross is pressed against the

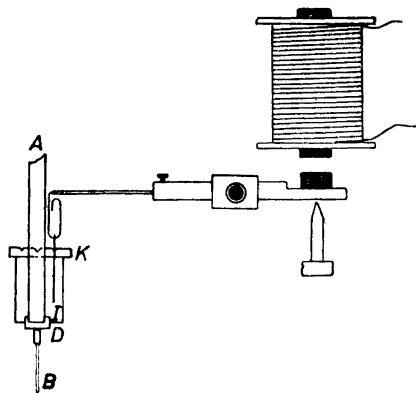


Fig. 2. Side view of a single unit of the weight manipulator.

mated plate. When the light has passed the lens G and has been reflected from the mirrors, the sharp shadow of the cross is easily observed by a low power microscope. The microscope is provided with a cross hair in the ocular. For a given load on the ring the exact position of the reflected light beam is indicated by setting the microscope so that the centers of the shadow cross and the ocular cross coincide. This zero-position is very stable and reproducible. The ring may be loaded and unloaded several times before slight readjustment is necessary.

The elastic ring is extremely sensitive to vibrations, which completely blur out the shadow cross and render the setting of the zero-position impossible. The balance is therefore placed on a large cement block in the basement of the laboratory building, and supported adequately by thickwalled rubber tubes. However, occasional heavy traffic in the building still causes severe blurring. An aluminium damping vane H immersed in Apiezon oil reduces these disturbances to a tolerable level.

The balance is loaded by placing ring formed weights J on the beam K (cf. also Fig. 2). Six carefully calibrated ring weights ranging from 4 to 40 mg have been prepared from platinum wires.

The loading and unloading of the balance is performed by means of a weight manipulator, which can be operated electromagnetically from the observers table. For the sake of simplicity the weight manipulator, which can be charged with three ring loads at a time, is not shown on Fig. 1. A single of the three identical units of the manipulator is shown, slightly schematically on Fig. 2. The capital letters on the latter figure have the same meaning as those on the former.

From the six platinum weights available 20 sets of three weights can be selected. Each set may be combined to 13 different loads, *viz.* 7 sums and 6 differences. The differences may be utilized in the following way: A given load is placed on the rider beam and the zero-position is adjusted. The load is then exchanged with another lighter one. The magnetic force necessary to reestablish the zero-position is equal to the difference between the two loads. The 260 possible combinations give 116 different loads, which cover a scale from less than 1 mg to about 80 mg.

The balance is enclosed in a cubic box of plexiglas provided with plane glass windows L. During the measurements the sample is surrounded by a glass tube (not shown) connected to the balance compartment by a spherically ground joint M. The temperature is measured by a calibrated copper-constantan thermocouple placed immediately below the sample. When measurements at lower temperatures are performed, the glass tube is replaced by the cryostat tube described below. The balance compartment may be evacuated through N and refilled with a suitable gas.

The electromagnet is mounted on a turning table provided with three levelling screws by means of which the magnet can be moved vertically. Plane cylindrical pole pieces O of 10 cm diameter ensure a sufficiently large volume, where $H\delta H/\delta z$ may be considered constant. The width of the pole gap is always kept at exactly the same value, 27 mm, by a brass block P inserted between the pole pieces. With an exiting current of about 10 A, a maximum value of $H\delta H/\delta z$ of about 1.2×10^7 Gauss²/cm is obtained. The electric current is taken from the 220 volts main lines and regulated by a system of rheostats. The current is read on a Siemens & Halske precision ammeter.

OPERATING PROCEDURE

Only finely powdered substances are measured. The powder is packed in the spherical part of the pyrex phial shown in Fig. 3 a. After thoroughly cleansing of the capillary the phial is evacuated and the bulb is sealed off and pasted to a quartz capillary by a minimum of wax (Fig. 3 b and c.). The quartz capillary is then in turn cemented rigidly to the balance system at R (Fig. 1.). The bulbs usually contain 100—200 mg of powder.

It is very essential that all samples are placed accurately in the rather narrow region of the magnetic field where $H\delta H/\delta z$ has a rather flat maximum. That is, where the current necessary to compensate the removal of a given load is a minimum. This position must be found by trial for each particular sample under investigation. During this procedure the vertical position of the sample is controlled by the brass rod Q, which defines the vertical axis of the magnetic field. A brass cylinder (not shown) with a drill, which fits to Q controls the horizontal position of the sample by means of a horizontally

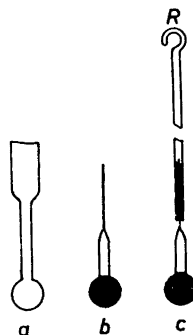


Fig. 3. Preparation of the sample.

- a) The empty phial.
- b) The filled, evacuated and sealed-off bulb.
- c) The bulb pasted to the quartz capillary.

moving fine screw. The presence of this device in the pole gap has no detectable influence upon the field characteristics. Five independent settings of the same sample gave the following compensation currents in amperes: 8.36, 8.37, 8.36, 8.38, 8.37. It has been verified that the position of the maximum of $H\delta H/\delta z$ is independent of the field strength.

The final measurements are carried out in the following manner. A suitable weight is placed on the rider beam, and the zero-position is adjusted. After removal of the weight the magnetic field is switched on and three readings of the compensation current are taken. The zero-position is checked at once. Changes are rarely observed. The mean value of the three readings is taken as the result of a single measurement. This procedure is repeated twice and the mean value of the three mean values constitutes the final result of the measurements at that particular field strength. The spread of the ammeter readings is illustrated by two typical examples from the measuring book.

Fe(NH ₄) ₂ (SO ₄) ₂ · 6H ₂ O	No. VI	Ni(NH ₄) ₂ (SO ₄) ₂ · 6H ₂ O	No. II
Mass of substance	134.6 mg	Mass of substance	209.3 mg
Force in dynes	39.20	Force in dynes	23.20
Compensation current, A:		Compensation current, A:	
Direct readings:	Mean:	Direct readings:	Mean:
8.13 -14 -13	8.13	9.01 -02 8.99	9.01
8.14 -14 -13	8.14	8.98 -97 -98	8.98
8.16 -14 -14	8.15	8.99 9.00 -01	9.00
Mean of mean:	<u>8.15</u>	Mean of mean:	<u>9.00</u>
8.15 A ~ 8.993 × 10 ⁶ Gauss ² /cm		9.00 A ~ 10.54 × 10 ⁶ Gauss ² /cm	
$\chi_g \times 10^6 = \frac{39.20}{8.993 \times 0.1346} = 32.38$		$\chi_g \times 10^6 = \frac{23.20}{10.54 \times 0.2093} = 10.52$	
Temperature 20.0°C		Temperature 19.0°C	

METHOD OF CALIBRATION

By a series of measurements on samples of Fe(NH₄)₂(SO₄)₂ · 6H₂O, Mohr's salt, the relation between the compensation current and $H\delta H/\delta z$ was established. Three different samples from a preparation of Mohr's salt, which has served as a magnetic standard in this laboratory for several years, were measured at as many values of $H\delta H/\delta z$ as were permitted by the possible load combinations. The gram susceptibility of the standard was put equal to $9\,500 \times 10^{-6}/(T+1)$, (T = abs. temperature)^{8,9}. $H\delta H/\delta z$ was then calculated from eqn. (1) and plotted against the observed compensation currents. The plot comprehended 80 points, through which a smooth curve could be drawn. The calibration has been checked several times through more than a year, but no change has been observed. These latter measurements then reflect the reproducibility of independent measurements on the same substance. The standard deviation from the calculated value was 0.3 %.

Since the measurements are made on powdered substances, appropriate corrections must be applied for the force exerted upon the glass container. For this purpose eqn. (1) is rewritten

$$K = H \frac{\delta H}{\delta z} (m \chi_g + m^{\text{glass}} \chi_g^{\text{glass}}) \quad (2)$$

The gram susceptibility of the glass sort used for the bulbs has been determined separately with a Gouy balance to -0.285×10^{-6} . The mass of the bulb is about 0.03 g. The correction for the diamagnetism of the container is thus small. In the two examples mentioned above the corrected values for the gram susceptibilities are 32.45×10^{-6} and 10.56×10^{-6} , respectively.

With the purpose of tracing possible systematic errors either in the calibration of the apparatus or in the measuring method, the susceptibilities of some simple substances were measured. The substances selected for this test represent a rather wide scale of susceptibilities. The results of the measurements are collected in Table 1 together with some relevant results taken from the literature. The value of a comparison of results obtained in different laboratories is severely limited by the difficulty of obtaining materials of high magnetic purity. Nevertheless the general accordance between the susceptibilities found and those quoted from the literature can scarcely be accidental, so it is concluded that systematic errors are scarcely present.

Table 1. Magnetic gram susceptibilities of various substances at 22.0°C.

Substance	$\chi_g \times 10^6$ found	$\chi_g \times 10^6$ literature
FeSO ₄ · 7H ₂ O	41.80	40.70 ^a 42.04 ¹⁰
Mn(NH ₄) ₂ (SO ₄) ₂ · 6H ₂ O	37.05	37.11 ¹¹
Fe(NH ₄) ₂ (SO ₄) ₂ · 6H ₂ O	32.14	32.09 ^b
NiSO ₄	26.12	26.27 ^b
NiSO ₄ · 7H ₂ O I	15.35	15.24 ¹²
NiSO ₄ · 7H ₂ O II	15.56	15.85 ^b 15.53 ^a
Ni(NH ₄) ₂ (SO ₄) ₂ · 6H ₂ O	10.45	10.38 ^b
CuSO ₄ · 5H ₂ O	5.89	5.76 ¹³ 5.85 ¹⁴

The susceptibilities have been adjusted to 22.0°C by means of the temperature dependence given in the literature.

Concerning the materials used for the test is stated: NiSO₄ was prepared by quantitative conversion of a very pure Ni-bis-acetylacetonate into the sulphate. The hydrated sulphates were the finest c.p. chemicals available, which were recrystallized to constant susceptibility. The double sulphates were prepared from the above mentioned recrystallized simple sulphates and (NH₄)₂SO₄ c.p. The preparate of Mohr's salt used for the test was thus independent of that used for the calibration.

Each susceptibility listed in Table 1 is the mean value of measurements at several different values of $H\delta H/\delta z$. Field strength dependence of the susceptibility was not traced in any case. In Table 2 are shown two arbitrarily selected examples of the values of χ_g found at different $H\delta H/\delta z$ values. The standard deviation only measures the precision of the physical method.

Table 2. Magnetic gram susceptibilities at different values of $H\delta H/\delta z$.

NiSO ₄ at 22.0°C		FeSO ₄ · 7H ₂ O at 21.5°C	
$H\delta H/\delta z \times 10^{-6}$ Gauss ² /cm	$\chi_g \times 10^6$	$H\delta H/\delta z \times 10^{-6}$ Gauss ² /cm	$\chi_g \times 10^6$
4.730	26.06	5.166	42.05
5.331	26.10	5.579	41.83
6.860	26.01	5.647	41.80
8.323	26.17	5.987	41.72
8.560	26.06	8.213	41.80
10.02	26.19	8.597	41.84
11.51	26.22	11.19	41.96
Mean	26.12	Mean	41.86
Stand. dev.	0.08	Stand. dev.	0.11

MEASUREMENTS AT LOW TEMPERATURES

The value of a magnetochemical investigation is considerably enhanced if it is extended over a range of temperatures. In the following section a fairly simple device, which allows measurements at any temperature in the range 81 to 295°K, is described.

The cryostat arrangement shown on Fig. 4 consists of a silvered Dewar vessel A and a cryostat tube B. The latter is connected to the balance com-

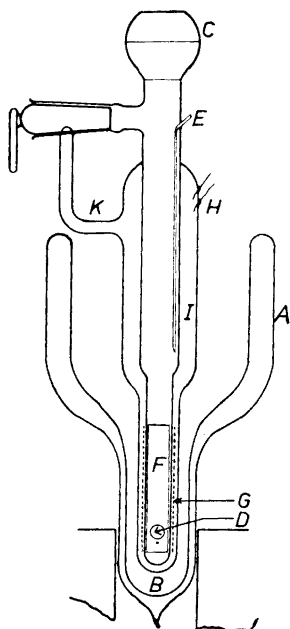


Fig. 4. General view of the cryostat arrangement.

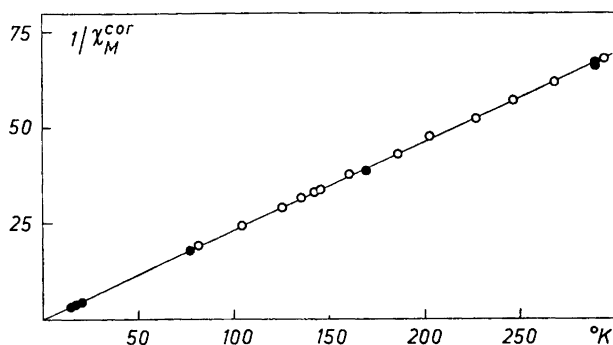


Fig. 5. Reciprocal, corrected molar susceptibility of $\text{Mn}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$.
 ○ Present author. ● Jackson and Kamerlingh Onnes¹¹

partment by the spherically ground joint C. The position of the sample inside the inner tube is indicated by a circle D. The point immediately below the circle indicates the position of the measuring junction of the copper-constantan thermocouple. The thermocouple is introduced through the narrow tube E and kept in a fixed position by a sheet of phosphor bronze F. The tube E is sealed with Apiezon wax. A coil G of 0.1 mm \varnothing constantan wire is wound around the inner tube and connected to a variable transformer by means of the sealed-in wires H. When the space I is evacuated and liquid air is poured into the Dewar vessel, any temperature between 81 and 295°K may be established by application of a suitable heating current in the coil. Only slight regulation of the heating current is necessary to keep the temperature constant within half a degree.

In actual laboratory work two cryostat tubes are used. One, which has been evacuated to a few mm and sealed off at K, covers the temperature scale from 81 to 145°K by application of a maximum heating effect of 1.1 W in the coil. The temperatures from 140 to 295°K are established by means of a second cryostat tube, which must be evacuated to less than 10^{-4} mm the day before use. A permanently evacuated tube like the first one would indeed have been more convenient. The insulated wire of the heating coil, however, cannot be effectively outgassed, so that the necessary high vacuum cannot be maintained for more than a couple of days at a time. The maximum heating effect used in this cryostat tube is 0.8 W.

The thermocouples have been compared *in situ* with a thermocouple, which in turn has been compared with a standard resistance thermometer at 80.5, 195.5 and 293.0°K. The EMF's of the thermocouples are determined by compensation. The detailed EMF/temperature relation for the cryostat thermocouples has been established magnetically by means of the relation

$$(T - \Theta) \chi_g = C. \quad (3)$$

Mohr's salt again served as a reference substance ($\Theta = -1$). The temperatures determined magnetically nicely supplement the above mentioned fix point values to a temperature scale which is considered reliable within at least one degree.

The effectivity of the entire apparatus was finally checked by a series of measurements on $\text{Mn}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, which has been investigated magnetically by Jackson and Kamerlingh Onnes¹¹. The result of these measurements is shown in Fig. 5, where the reciprocal corrected molar susceptibilities are plotted against the absolute temperature (open circles). For comparison the measurements of Jackson and Kamerlingh Onnes are also shown, appropriately corrected for the diamagnetism (full circles). The accordance is considered very satisfactory.

In conclusion just a few remarks concerning the details of the operating procedure should be given. During all measurements at low temperatures the apparatus is filled with hydrogen. Measurements are taken at both falling and raising temperatures during the same investigation, and the results are carefully inspected for signs of temperature hysteresis. Measurements at a single temperature usually take one hour. In the course of 10 min the temperature in question is established. 20 min later the first series of measurements is taken. After another 20 min interval the measurements are repeated. In a special experiment it was found that the sample came to thermal equilibrium with the surroundings within less than 10 min. All later experiences during actual measurements confirm this.

It should be mentioned that even 295°K may be established by means of the cryostats set-up, that is with liquid air in the Dewar vessel and a suitable heating of the coil. Results obtained under these conditions are in wholly accordance with those obtained in a more straightforward manner.

Acknowledgment. The author is very much indebted to the head of the laboratory professor R. W. Asmussen for having suggested this work and for valuable criticism.

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Received March 3, 1958.