

## 60. *Magnetochemistry. Part I. Introduction and Apparatus.*

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An apparatus is described for the measurement of the temperature-dependence of the magnetic susceptibility by the Gouy method from 80° to 500° K. The susceptibility of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  from 90° to 300° K is reported.

IN these two papers the magnetic susceptibilities of a number of co-ordination compounds of the transition series of elements are reported over the temperature range 80—400° K. This Part describes the equipment and indicates some general considerations which underlay the choice of compounds and the interpretation of the results.

The study of paramagnetic susceptibilities provides valuable information on the oxidation states of transition elements in co-ordination compounds. Also, if the number of unpaired electrons can be deduced from magnetic data it is often possible to infer the stereochemistry of the metal atom. Under certain conditions, even when the number of unpaired electrons is the same (*e.g.*,  $d^7$  spin-paired  $\text{Co}^{\text{II}}$  complexes), two possible shapes can be distinguished by measuring the deviation from the spin-only moment. However, it has become increasingly apparent recently that care is necessary in interpreting magnetic data if obtained at room temperature only. Thus we now recognise that intra- or intermolecular antiferromagnetic interactions may not be uncommon in complex ions. Also, spectroscopic ground-state levels of transition-metal ions usually do not conform to the simplification that no energy-level separations  $\sim kT$  from the lowest level occur. Such facts make it necessary to examine the magnetic properties in greater detail. These remarks apply particularly to the ions of the second and third transition series where antiferromagnetic interactions seem common and spin-orbit coupling is large. In a great many instances the information required for reliable deductions from magnetic data can be obtained by measuring the susceptibility over a range of temperature. In most cases the valuable information is to be obtained below room temperature and often it is sufficient to go down to the temperature of liquid air, 80° K.

The ideal paramagnetic substance obeys the Curie law  $\chi \propto 1/T$ , or rather, the closely associated Langevin-Debye expression  $\chi_M = N(\mu^2/3kT + \alpha)$  where  $\mu$  is the "magnetic moment" and  $\alpha$  is the "temperature-independent paramagnetism" or "Van Vleck high-frequency term;"  $\alpha$  is generally small compared with the term in  $\mu$ , when this exists. Exchange interactions between neighbouring spins in a paramagnetic substance (ferromagnetism and antiferromagnetism) lead to departure from the Curie law, as also do electronic ground states in which energy separations  $\sim kT$  appear. Ferromagnetism can be detected, in principle at least, by susceptibility measurements at varying field strengths, but this effect does not appear to be very common in co-ordination compounds, unless due to impurities. Antiferromagnetism results from antiparallel alignment of spins on neighbouring metal atoms; it causes a decrease in the susceptibility as compared with that expected for normal paramagnetism. At a sufficiently low temperature an antiferromagnetic compound shows a characteristic maximum in the susceptibility-temperature curve, at the Néel temperature. Above this temperature antiferromagnetism gives rise to a positive value of  $\theta$  in the Curie-Weiss law equation  $\chi_M \propto 1/(T + \theta)$ ; however, it is by no means the only cause of positive values of  $\theta$ . These can also arise from the absence of a simple electronic ground state from the ion in question. It has often been the custom to calculate a quantity  $\mu = 2.84\sqrt{[\chi_M/(T + \theta)]}$  for a substance which follows the Curie-Weiss law, in place of the relationship obtained from the Langevin-Debye expression ( $\alpha$  being ignored):  $\mu = 2.84\sqrt{(\chi_M T)}$ . Strictly, this is unjustified unless it is known that a positive value of  $\theta$  has its origin in an interaction of an antiferromagnetic nature; if this is not so it must be accepted that  $\mu_{\text{eff}}$  is a function of temperature. We adopted the latter procedure.

The form of departure from the Curie law of temperature-dependence of the magnetic susceptibility arising from non-simple electronic ground states depends on the details of the ground state; this will be discussed along with the measurements on the group of compounds pertinent to the ion under consideration. In general, the lack of simplicity of the electronic ground state of an ion is associated with incomplete quenching of the orbital angular momentum of the ion by ligand fields and also with spin-orbit coupling. Since the former effect is a function of the stereochemical environment of the ion, information on the behaviour of the magnetic susceptibility with temperature with different stereochemical arrangements is desirable.

In the second and third transition series of ions magnetic data are scanty and it seems that the influences of antiferromagnetism, unusual stereochemistries, and large spin-orbit couplings make the interpretation of data at room temperature uncertain. One of our main purposes is to find out how reliable magnetic moment measurements are at room temperature in representing the magnetic properties of the system. Little is known from direct spectroscopy of the spin-orbit coupling constants to be used in connection with ions of elements of the second and third transition series; it is necessary to obtain a value for these constants from magnetic data on suitable systems to enable the properties of other systems to be accounted for.

*Apparatus.*—The use of the Gouy method for the measurements of magnetic susceptibilities, at temperatures other than that of the room, involves disadvantages, the chief of which is keeping the required temperature uniform and constant over a comparatively large volume. Almost equally important is the need to use a magnetic field of sufficient magnitude over an even larger volume. However, the conveniences it offers over other methods in dealing with a wide range of solid and liquid chemicals led us to adapt it to our temperature-dependence measurements, overcoming the disadvantages as completely as possible. In most previous temperature-dependence measurements by the Gouy method data are lacking concerning the uniformity of temperature over the whole specimen and its constancy during reasonably long periods. Often the methods employed cannot be expected to lead to high accuracy. Indeed, many temperatures quoted in the literature in this connection are probably in error by several degrees, particularly in the region of 150° K.

With our equipment the mean temperature of the specimen is controllable to within 0.1°

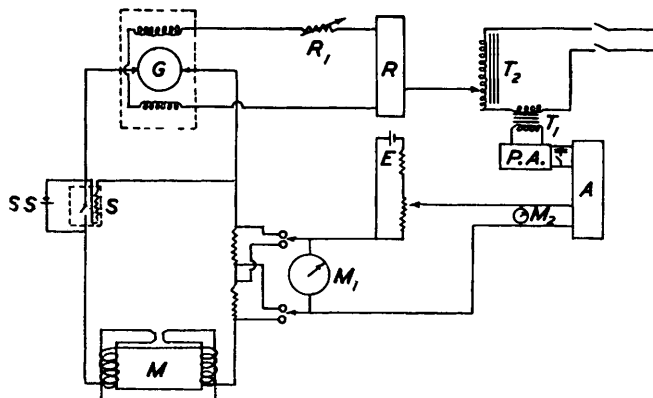
at any temperature within the range 80—500° K; the temperature gradient along the sample never exceeds 0.5° and is much less at the important low temperatures. The mean temperature can be measured to within 0.2° over the range. A magnetic field of up to 7500 oersteds is available at the lower end of the 10 cm. specimen, and is arranged to vanish at the other end of it. Gram-susceptibilities in the range  $1-500 \times 10^{-8}$  can be determined with an accuracy of about 0.5% in favourable circumstances and of about 2% in adverse ones.

As a check, the susceptibility of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  was measured; this, for single crystals, has been reported several times.<sup>2</sup>

*Description of the Apparatus.*—(1) *Magnet and balance.* The magnetic field was derived from an electromagnet of the design described by Bates and Lloyd-Evans,<sup>3</sup> supplied with the required D.C. from a motor-generator. At an exciting current of 20 A, about 7500 oersteds was developed between the pole pieces 7.5 cm. apart and 8 cm. in diameter. The current could be decreased to a minimum of 2 A, giving then about 1400 oersteds. The current was controlled through external excitation of the generator, sometimes manually by rheostats in series with the generator field coils, and in other cases automatically through a servoamplifier system

FIG. 1. Magnet current supply circuit.

*M*, Magnet. *G*, Generator. *S*, Sunvic 602 hot-wire switch. *SS*, Surge suppressor. *M*<sub>1</sub>, Magnet current meter, 0—5, 0—25 amp. *M*<sub>2</sub>, Error signal meter, 0—100 mv. *A*, D.C. amplifier, 20 w. *R*, Rectifier, to supply 100 v at 0.5 amp. *E*, 1.5 v. *T*<sub>1</sub>, Output transformer, 10,000—100 ohms. *T*<sub>2</sub>, "Variat" continuously variable autotransformer. *R*<sub>1</sub>, 100 Ohm rheostat.



feeding the field coils. These circuits are shown in Fig. 1. Control was available to within the reading accuracy of the meter, *i.e.*, 0.05 A in the range 10—25 A, and 0.01 A in the range 2—5 A. At the highest currents magnetic-field control was to within 0.1% as saturation of the magnet core was approached. However, at lower currents the field depended more or less directly on the current and the field regulation could not then be made better than 0.5%. Thus the errors in the measurements of the susceptibilities arising from field control varied from 0.2 to 1%.

The magnet current was automatically regulated by balancing the potential drop across the current-measuring meter against a potential from a standard battery. The "out-of-balance" was fed as an error signal to a Brown model 351921 D.C. amplifier, followed by a 20 w power amplifier, which delivered a 50 volt A.C. voltage of suitable phase in series with the A.C. supply to the rectifier supplying the generator field coils to alter the magnet current to reduce the error signal. The current could thus be held at a given value as accurately as could be read on the meter, as indicated above.

The balance used for measuring the forces developed was a Sartorius model S.M.10 on which each scale division was 0.1 mg. and could be interpolated to 0.01 mg. The forces encountered in the work on paramagnetism in the transition-metal compounds could be measured with an accuracy rarely worse than 1% and mostly about 0.5% or better.

The relative susceptibilities so measured are accurate to within about 1% in general, although with small forces and small magnet currents, up to 2% error may be expected. Owing to the nature of the special long, completely filled Gouy tube required in conjunction with the cryostat, the accuracy of the absolute susceptibilities determined with it were not as good as usual in the Gouy method, as the packing of solids presents problems. However, the

<sup>1</sup> Figgis and Nyholm, *J.*, 1954, 12.

<sup>2</sup> Krishnan and Mookherji, *Phys. Rev.*, 1936, **50**, 860; 1938, **54**, 533, 841; Gorter and de Haas, *Comm. Kammerlingh Onnes Lab. Leiden*, 1930, No. 210d, 39.

<sup>3</sup> Bates and Lloyd-Evans, *Proc. Phys. Soc.*, 1933, **45**, A, 425.

susceptibilities were adjusted at room temperature to the value found at that temperature on a more conventional apparatus. Calibration of the Gouy tubes was performed with 31.31% w/w  $\text{NiCl}_2$  (anhydrous) solution.<sup>4</sup>

(2) *Temperature control.* (a) *Cryostat.* This (Fig. 2) consists essentially of a chamber 1.5 cm. in diameter and 18 cm. in length in which the Pyrex glass Gouy tube (3 mm. internal diam. and 10 cm. long) is hung. This chamber is thermally insulated by a variable vacuum from a bath of liquid refrigerant (usually oxygen or nitrogen). A heating coil, spirally wound round the length of the chamber, and capable of dissipating 15 w, counterbalances the heat loss across the vacuum. A magnetic shield, consisting of a thick-walled iron tube 8 cm. long, encloses the upper end of the Gouy tube and makes the magnetic field at that point disappear. This substantially reduces the length of the Gouy tube required. A platinum wire wound

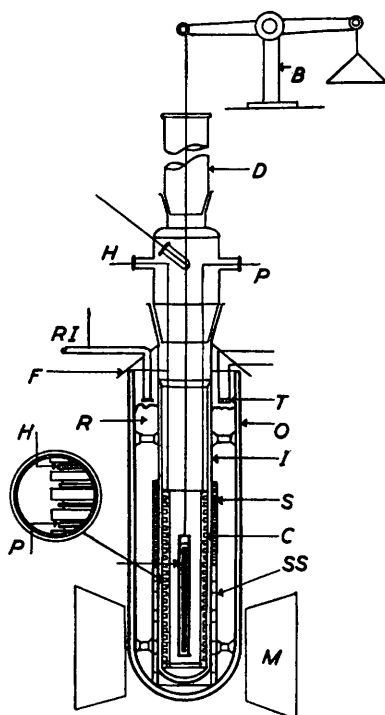


FIG. 2. *Cryostat.*

- B, Balance.
- C, Controlled block.
- D, Draught shield.
- F, Icing shield.
- H, Heater.
- I, Inner Dewar vessel.
- M, Magnet pole.
- O, Outer Dewar vessel.
- P, Platinum resistance thermometer.
- R, Refrigerant.
- RI, Refrigerant inlet.
- S, Magnetic shield.
- SS, Magnetic shield support.
- T, Thermistor.

between the spirals of the heating coil serves as a resistance thermometer for temperature control; its room-temperature resistance is about 10 ohms.

An Edwards "Speedivac" model 2S50 high-vacuum pump produced the vacuum in the inner Dewar flask, which was silvered. For operation *at*, and for about 40° *above*, the refrigerant temperature, air at atmospheric pressure was allowed to remain in the inner Dewar flask; for temperatures 40–100° *above* the refrigerant temperature the pressure in this vessel was kept at about  $10^{-3}$  mm. by a suitable leak; from there to room temperature the best vacuum of the pump was employed (about  $10^{-4}$  mm.). For operation above room temperature no refrigerant was used. A drying tube [ $\text{Mg}(\text{ClO}_4)_2$ ] at the inlet to the Dewar vessel prevented moisture from condensing in it and attacking the silvering.

The refrigerant level was kept constant in the outer Dewar vessel by means of the device set out in Fig. 3. A thermistor, of room-temperature resistance 500 ohms, was held slightly above the desired refrigerant level and heated by a coil dissipating 1 w. A Sunvic model 602 high-vacuum switch was in series with the thermistor and the combination was excited with 60 v A.C. At room temperature sufficient current was passed by the thermistor to close the switch, which then operated a small compressor to force air into a 5 l. refrigerant storage vessel.

<sup>4</sup> Nettleton and Sugden, *Proc. Roy. Soc.*, 1939, A, 173, 313.

Refrigerant was thus ejected into the outer Dewar vessel. When the refrigerant level had risen sufficiently to cool the thermistor, its increased resistance reduced the current and so switched off the compressor. A small leak dissipated the pressure in the storage vessel, and the ejection of refrigerant ceased.

The consumption of refrigerant depended upon the liquid chosen and the temperature of operation of the cryostat. For oxygen about 500 ml. were used per hour.

(b) *Temperature-control circuit.* The circuits for automatic control at any desired temperature are shown in Fig. 4. A platinum-resistance thermometer, comprising 12 feet of 32 s.w.g.

FIG. 3. Constant refrigerant level mechanism.

C, Cryostat.  
D, 5 Litre storage Dewar vessel.  
T, Theristmor.  
T<sub>1</sub>, Transformer, 240—60 v.  
S, Sunvic 602 hot-wire switch.  
A.C., Air compressor.  
V, Air escape valve.

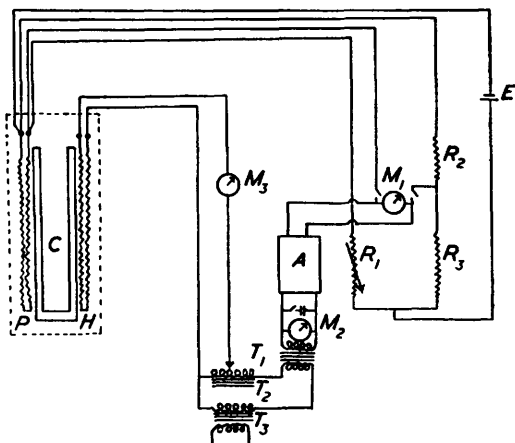
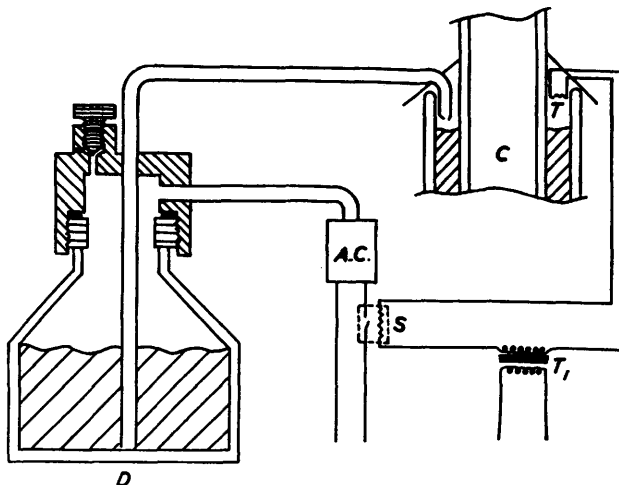


FIG. 4. Temperature-control circuit.

C, Cryostat. P, Platinum-resistance winding. H, Heater winding. R<sub>1</sub>, 5 Decade resistance box. R<sub>2</sub>, 10 Ohms. R<sub>3</sub>, 300 Ohms. E, 6 v. M<sub>1</sub>, Error-signal meter, 0—100  $\mu$ v. M<sub>2</sub>, Amplifier-output meter, 0—200 v, A.C. M<sub>3</sub>, Heater-current meter, 0—1 amp. A.C. A, D.C. amplifier. T<sub>1</sub>, Output transformer, 5000—15 ohms. T<sub>2</sub>, "Variac" continuously variable autotransformer. T<sub>3</sub>, Transformer, 240—17 v.

platinum wire, was wound on the outside of the controlled copper-block chamber, between the windings of the heating coil. The insulation from the block for the thermometer and the heating coil was a layer of 0.07 mm. thick "Teflon" foil. No particular care to avoid strain in the wire was exercised in winding the platinum as this thermometer was not used as a primary standard. The ends of the thermometer were taken to mica-insulated terminal posts on the upper end of the block. From these points current and potential leads were taken to the binding posts at the top of the cryostat. All connections at the terminals at the block and to the ends of the heating coil were silver-soldered. The leads from the block terminals to the top binding posts were spiralled inside the wall of the inner Dewar vessel to reduce heat transfer along them.

The resistance thermometer formed one arm of a Wheatstone bridge, whose other, variable, arm was a 5 decade resistance box of maximum resistance 1111.1 ohms. This bridge was

excited by 6 v D.C. The "out-of-balance" of the bridge was amplified by means of a Leeds and Northrop model R-820-1 D.C. amplifier which delivered about 150 v A.C. at 7 w to an output transformer of 15 ohms output impedance. The secondary winding of this transformer was in series with the primary of a continuously variable auto-transformer; this arrangement was fed from 17 v A.C. The output of the variable transformer was the supply for the heating coil of the cryostat. The phase of the voltage supplied by the output transformer was determined by the sign of the out-of-balance signal to the amplifier. According as this voltage was in or out of phase with the 17 v A.C. supply, it increased or decreased the power supplied to the heating coil. The phase relationship was arranged so that the change of heater power was in the direction required to reduce the error signal. Meters for reading the error signal, the amplifier output voltage, and the heater current were provided.

Operation of the temperature control was as follows. With the amplifier output voltage short-circuited by a condenser, the heater current was adjusted to maintain the required temperature with a suitable vacuum in the inner Dewar flask. The Wheatstone bridge was balanced, and the short circuit removed from the amplifier output; the temperature was then controlled at the required value.

(c) *Measurement of temperature.* The temperatures of the specimen were measured with a nichrome-constantan thermocouple so inserted that its "hot" junction was beside the mid-point of the Gouy tube, with this tube in position. When temperature equilibrium had been attained the thermocouple was withdrawn, and the susceptibility immediately measured. The thermocouple was calibrated against a platinum-resistance thermometer (not to be confused with the one in the cryostat), which had a resistance of about 2 ohms at 20° c. The resistance thermometer was calibrated at the liquid-oxygen point, the ice point, and the steam point; a check at the CO<sub>2</sub> point showed agreement to within 0.05°. The resistance of the thermometer was measured by comparing the potential drop across it, measured on a Leeds and Northrop model K2 potentiometer, with that developed across a standard 1 ohm resistance in series with it. The thermometer calibration was accurate to 0.1° or better over the range 80—500° k. The nichrome-constantan thermocouple was calibrated against this resistance thermometer by enclosing both in a 4 kg. brass block contained in a Dewar flask. Readings were taken at approximately 5° intervals. This close calibration was necessary because this thermocouple, in common with all similar combinations, may show a discontinuity in the E.M.F.-temperature curve. In this case, the discontinuity was of about 50 μv at -140° c. Use of the thermocouple within a few degrees of this point was avoided. The calibration of the thermocouple was accurate to 0.2° throughout the range. The E.M.F. of the thermocouple was measured on the same potentiometer as above.

*Performance of the Apparatus.*—With a suitable vacuum for the inner Dewar vessel any temperature from the b. p. of the refrigerant to 500° k can be attained and kept indefinitely to within 0.1° with the centre of the Gouy tube as measuring point. The temperature gradient between the ends of the Gouy tube was investigated at various temperatures by means of a differential thermocouple with a junction at each of the ends. The gradient was absent at the refrigerant temperature and rose more or less regularly with rising temperature to 0.5° per cm. at room temperature; the rise continued above this to about 1° at 400° k. With no refrigerant in the outer Dewar flask the gradient at room temperature was, of course, absent and rose steadily to about 0.5° over the length (10 cm.) of the specimen for operation at 500° k.

Thermal equilibrium of the controlled chambers is reached about 15 min. after attaining a required temperature. However, much longer was required for equilibrium to be reached with respect to the forces exerted on a specimen at a particular temperature. The period necessary for constancy of the force on the specimen varied with temperature; for all but the lowest temperatures 1 hr. was sufficient; near the refrigerant temperature about 2 hr. were required. In the course of the measurements on CuSO<sub>4</sub>·5H<sub>2</sub>O the numerical reproducibility of the apparatus was checked under the most favourable conditions of operation, *i.e.*, high magnet current and high forces; the force on a given sample at a given temperature could be reproduced to within 0.5%. This agrees with the estimates for this accuracy made from the performance of the current regulator and the balance sensitivity.

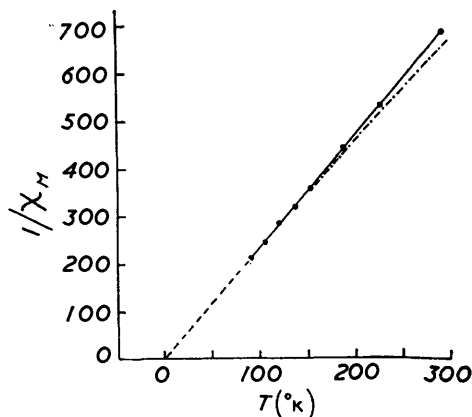
*Calibration of Gouy Tube.*—The calibration of the Gouy tube in temperature-dependence measurements presents difficulty in the assignment of the constants  $\alpha$  and  $\beta$  in the usual formula,  $10^6\chi = [\alpha + \beta(F + \delta)]/w$ , where  $\alpha$  allows for the medium (usually air) occupying the tube subsequently displaced by the specimen;  $\beta$  is dependent only on the geometry of the tube and

the magnetic field;  $\delta$  is the force exerted on the tube alone, and  $F$  that on the tube + specimen;  $w$  is the weight of the specimen.

Whereas  $\beta$  is essentially independent of temperature,  $\alpha$  and  $\delta$  are likely to be functions of it. It is possible to eliminate the correction  $\alpha$  by performing measurements in an atmosphere of nitrogen, and this was the usual procedure. The specimen chamber was evacuated and dry nitrogen admitted. A very slow flow of nitrogen was maintained across the top of the cryostat where it joins the draught shield. This prevented the diffusion of air into the specimen chamber and did not affect the operation of the balance. The correction  $\delta$  was found by measuring the

FIG. 5. Variation of the inverse of the corrected molar susceptibility of a powdered  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  specimen with temperature.

— Experimental curve,  $\chi_M$   
 - - - - - " "  $\chi'_M$   
 - - - - - Low-temperature extrapolation of  $\chi_M$



force developed on the Gouy tube in the nitrogen atmosphere over the temperature range. For a typical tube  $\delta$  decreased from 2.0 mg. at 350° K to 1.0 mg. at 90° K, apparently owing to the paramagnetic impurities in the (diamagnetic) glass.

*The Susceptibility of Copper Sulphate Pentahydrate.*—In order to check the operation of the apparatus the susceptibility of powdered  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  was measured from 90° to 300° K. This substance has an anisotropic susceptibility which obeys a Curie–Weiss law with a Weiss temperature of about 0.7°, as the mean for the three principal susceptibilities, and a mean Curie constant of 0.457.<sup>2</sup> The inverse of the molar susceptibility for our powdered specimen, corrected for the diamagnetic constitution, is plotted against temperature in Fig. 5. The broken line indicates the extrapolation to absolute zero, and also the course of the curve if no correction for the diamagnetic constituents is made. It is straight, within experimental error. The correction for diamagnetic constituents was  $74 \times 10^{-6}$ /mole. With a large Gouy tube the mass susceptibility is found to be  $6.05 \times 10^{-6}$  c.g.s. units. This is considered to be correct to better than 1½%. It agrees well with the most reliable values in the literature, namely those of Sugden<sup>5</sup> and of Gorter and de Haas<sup>2</sup> who report  $6.14 \times 10^{-6}$  and  $5.95 \times 10^{-6}$  c.g.s. units, respectively.

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<sup>5</sup> Sugden, J., 1932, 161.