## 648. *Solutions for the Calibration of Gouy Equipment.*

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The magnetic susceptibilities of solutions of $Cs_2CoCl_4$ in water have been found to obey the relationship, $10^6\chi = 21{\cdot}71x - 0{\cdot}720(1 - x)$, at 25°, within an accuracy of $0{\cdot}2_5$%, where $x$ is the weight fraction of $Cs_2CoCl_4$ in the solutions. These solutions are suggested as calibrants for Gouy magnetic susceptibility apparatus.

Apparatus employing the Gouy method for the measurement of magnetic susceptibility is usually calibrated by reference to a substance of known susceptibility. Most frequently, a solid substance is employed for work with paramagnetic compounds, for example, $HgCo(CNS)_4$,[1] $(NH_4)_2Fe(SO_4)_2,6H_2O$,[2] or $Ni(en)_3(S_2O_3)_2$.[3] More accurate calibration is possible if a liquid is employed, since packing inhomogeneity is eliminated. Liquids used in this connexion are water [4] and aqueous solutions of nickel(II) chloride.[5]

Water is of accurately known susceptibility,[4] but the magnitude of the susceptibility ($\chi = -0{\cdot}720 \times 10^{-6}$ c.g.s. at 25°) is so much smaller than that of most paramagnetic substances that accurate comparison of the forces developed by the water calibrant and the unknown substance may be difficult. Aqueous solutions of nickel(II) chloride can be made up with suceptibility as large as $10 \times 10^{-6}$ c.g.s. units, and provide more convenient calibrants from that point of view. However, these solutions suffer from the disadvantage that their composition must be determined by chemical analysis. Besides being inconvenient, the analysis introduces additional error into the calibration process.

An ideal calibrant solution should possess the following characteristics. (1) The susceptibility should be accurately known as a function of concentration, and should be fairly large. (2) The solution should be easily made up to any required susceptibility from readily obtainable starting materials, without the necessity for chemical analysis. (3) The change of susceptibility with temperature should be a simple function, and should

[1] Figgis and Nyholm, *J.*, 1958, 4190.
[2] Selwood, "Magnetochemistry," Interscience, New York, 1956, p. 26.
[3] Curtis, *J.*, 1960, 4409.
[4] Piccard and Devaud, *Arch. sci. phys. et nat.*, 1920, **2**, 455.
[5] Nettleton and Sugden, *Proc. Roy. Soc.*, 1939, *A*, **173**, 313.

be known as a function of concentration. (4) Unless the starting materials are very readily available, they should be easily recovered in high purity from the solutions.

It is believed that aqueous solutions of the compound $Cs_2CoCl_4$ fulfil these requirements better than any others which have been studied. Accordingly, the susceptibilities of these solutions have been measured between the concentration limits 0·17 and 0·43 w/w $Cs_2CoCl_4$ at 25°. The magnetic susceptibility of the solutions (see Table) covers the range 3·0—9·0 × $10^{-6}$ c.g.s. units.

The magnetic susceptibility of solutions of $Cs_2CoCl_4$ in water.

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Wt. fraction $Cs_2CoCl_4$ | 0·4318 | 0·4151 | 0·3922 | 0·3550 | 0·3098 | 0·2871 | 0·2727 | 0·2681 |
| $10^6\chi$ .................... | 8·978 | 8·612 | 8·113 | 6·785 | 6·234 | 5·740 | 5·372 | 5·293 |
| Wt. fraction $Cs_2CoCl_4$ | 0·2476 | 0·2332 | 0·2328 | 0·2099 | 0·2066 | 0·1877 | 0·1831 | 0·1701 |
| $10^6\chi$ .................... | 4·806 | 4·499 | 4·543 | 3·974 | 3·917 | 3·480 | 3·389 | 3·093 |

The susceptibilities of the solutions can be expressed as a combination of two terms, one due to the paramagnetism of the cobalt compound, the other to the diamagnetism of the water. At 25·0°,

$$10^6\chi = 21{\cdot}71(\pm 0{\cdot}06)x - 0{\cdot}720(1 - x),$$

where $x$ is the weight fraction of $Cs_2CoCl_4$ in the solution.

The magnetic susceptibility of solutions of cobalt(II) chloride in water, of concentration with respect to cobalt comparable to the present solutions, has been reported as a function of temperature in the vicinity of 25°.[6] The paramagnetic contribution to the susceptibility was found to obey a Curie–Weiss law [$\chi_{Co} \propto (T + \theta)^{-1}$], with a Weiss constant, $\theta$, which varied somewhat with concentration, but was fairly small. From those results a value of $\theta$ of 18° may be estimated to account for the variation of the susceptibility over the range of temperature 15—35° at any of the concentrations of $Cs_2CoCl_4$ covered in the present study. There are small variations in the susceptibility of water with temperature ($d\chi/dt = -1 \times 10^{-4}/°$)[7] and with dissolved oxygen, but these are not sufficient to warrant an alteration in the second term of the expression at any temperature near ambient. The preceding expression can be put in the form

$$10^6\chi = [6867x/(T + 18)] - 0{\cdot}720(1 - x),$$

where $T$ is the absolute temperature.

The magnetic moment for the cobaltous ion in the solutions is, on the basis of the first term in the above formula, 5·00 B.M. at 25°. That value is in good agreement with the value reported for the solutions of cobalt(II) chloride of comparable cobalt concentration, 5·04 B.M.,[6] and is typical of the value for an octahedral spin-free bivalent cobalt complex ion with water ligands.

The compound $Cs_2CoCl_4$ is readily prepared in high purity. It can be recovered unchanged from the aqueous solutions simply by evaporation.

## Experimental

Filtered, redistilled water, saturated with air, was used in connexion with all the measurements. Cæsium chloride and $CoCl_2,6H_2O$ were of analytical reagent grade.

$Cs_2CoCl_4$ was prepared by slow evaporation of filtered aqueous solutions of $CoCl_2,6H_2O$ and cæsium chloride in 1 : 2 mole ratio. After about 90% of the material had separated out as deep blue crystals the mother-liquor was removed at the pump and the substance dried at 120°. Three preparations were made.

The solutions of $Cs_2CoCl_4$ were prepared by adding water to a weighed amount of $Cs_2CoCl_4$ in a stoppered vessel; the less concentrated solutions being obtained by the dilution. A total of 16 solutions were studied, made up from the three preparations of the substance, covering the weight fraction range 0·17—0·43 in $Cs_2CoCl_4$.

[6] Lallemand, *Ann. Physique*, 1935, **3**, 97.
[7] Auer, *Ann. Physik*, 1933, **18**, 593.

The magnetic susceptibility of the solutions was measured at 25° by the Gouy method, with water as the standard substance. The Gouy tube was 0·75 $cm.^2$ in cross-section and about 12 cm. in length. The tube was constricted at the top to facilitate the reproduction of the volume of liquid employed. Thermostated water was circulated around the tube. An electromagnet producing a magnetic field of 10,000 gauss over a pole diameter of 10 cm. was employed with manual control of the current, which was measured with a high-precision ammeter. A semi-micro chemical balance sensitive to 0·01 mg. determined the forces developed. The force of the empty Gouy tube was −11·23 mg. The force on water in the tube was −25·07 (±0·02) mg. Forces on the solutions varied from 100 to 550 mg.

The solubility of oxygen in water is 0·0038 g./100 g./atm. at 25°. The magnetic susceptibility of oxygen, $\chi = 106 \times 10^{-6}$ c.g.s. units, is sufficient to raise the susceptibility of air-free water from [4,7] $-0{\cdot}7205 \times 10^{-6}$ to $-0{\cdot}7198 \times 10^{-6}$ at 25°.

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