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THE EFFECT OF COMPLEX ION FORMATION UPON THE MAGNETIC SUSCEPTIBILITY OF PARAMAGNETIC SALTS IN AQUEOUS SOLUTION

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Introduction

In the field of organic chemistry Pascal[2] has made a very great contribution to our knowledge of magnetic properties by pointing out the existence of an additivity law and by recognizing the influence of certain types of bonds. Among inorganic compounds, there are many variables, such as valence, crystal structure and complex formation; and although a large number of investigators have worked in this field there are still several factors whose influence is not clearly understood. Unfortunately, much of the earlier work is of doubtful accuracy. The literature on the subject of magnetic susceptibility is extensive. It is not our purpose in this paper to give a general review of the whole problem of magnetic susceptibility and chemical constitution, but rather to present some of our own results on the influence of complex-ion formation. We have, therefore, confined our references to those articles which bear on this field only, and purposely left out mention of many excellent papers which would undoubtedly be discussed in a general review.

It has been found by Cabrera, Moles and Guzman,[3] by Weiss and Bruins,[4] and by Brant[5] that the magnetic susceptibility per gram molecule

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[1] The material presented here was submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of California in May, 1925.

[2] Pascal, *Ann. chim. phys.*, [8] **29,** 218 (1913). "L'Additivité des Propriétés Diamagnétiques," A. Hermann et fils, Paris, **1913.**

[3] Cabrera, Moles and Guzman, *Arch. Sci. Phys. Nat.*, **37,** 325 (1914).

[4] Weiss and Bruins, *Proc. Acad. Sci. Amsterdam,* **18,** 246 (1915).

[5] Brant, *Phys. Rev.*, [2] **17,** 678 (1921).

of simple salts of nickel in aqueous solution is constant and independent of the concentration. Weiss and Frankamps[6] have shown that the same applies to simple ferrous salts, while Cabrera and his co-workers[7] have found that salts of chromium give constant values. Under certain experimental conditions simple cobaltous salts have been found to have a constant molal susceptibility by Trumpler[8] and by Brant.[5]

On the other hand, variation of the susceptibility with the concentration has been found in some cases. Cobaltous salts have been found to have a variable susceptibility by Cabrera and his co-workers,[9] while Piccard and Cherbuliez,[10] and Cabrera and Moles[11] have found that the susceptibility of cupric salts varies with the concentration. The latter authors have also found that the susceptibility of ferric salts depends upon the concentration of hydrogen ion in the solution. Weiss and Bruins[4] and Jacobsohn[12] have shown that ammonia lowers the susceptibility of solutions of nickel and copper salts, while Pascal[13] has shown that the susceptibility of complex iron phosphates is lower, the more stable the complex. The present paper deals with the effect of the formation of certain complex ions on the susceptibility of cupric and nickelous salts.

Method and Apparatus

The method employed is the so-called "cylinder" method described by Gouy.[14] The essential feature of the method is the determination of the weight of a cylinder suspended from one arm of a balance in such a way that the lower end of the cylinder is situated between the poles of an electromagnet, while the upper end extends far enough out to be practically in zero field. The difference in weight when the exciting current is on and off is the force due to the magnetic field acting on the cylinder, the force being directly proportional to the susceptibility. The method may be used either for absolute measurements of susceptibility or for measurements relative to some standard substance of known susceptibility. We have used the latter method, using water as the standard.

The experimental arrangement is shown in Fig. 1.

A yoke A of soft iron supports pole pieces H, also of soft iron, which pass through yoke and coils. The softest and purest iron obtainable was used for this construction in order to reduce hysteresis to a minimum. The outer ends of the pole pieces are threaded and provided with heavy brass collars, also threaded, to permit adjustment of

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[6] Weiss and Frankamps, *Proc. Acad. Sci. Amsterdam*, **18**, 254 (1915).

[7] Cabrera and Marquina, *Anales soc. españ. fís. quím.*, **15**, 199 (1917).

[8] Trumpler, *Thesis*, Zurich, **1917**.

[9] Cabrera, Jimeno and Marquina, *Anales soc. españ. fís. quím.*, **14**, 367 (1916).

[10] Piccard and Cherbuliez, *Arch. Sci. Phys. Nat.*, [4] **42**, 324 (1916).

[11] Cabrera and Moles, *ibid.*, [4] **35**, 425 (1913); **36**, 502 (1913); **37**, 324 (1914).

[12] Jacobsohn, *Thesis*, Zurich, **1916**.

[13] Pascal, *Ann. chim. phys.*, [8] **16**, 520 (1909).

[14] Gouy, *Compt. rend.*, **109**, 935 (1889).

the pole gap. The coils C are wound with insulated, square copper wire, and are water-cooled by means of a system of brass tubing. This magnet was constructed under the personal supervision of Mr. G. F. Nelson, chief mechanician of the Research Laboratory, whose suggestions also were very helpful in its design.

The tube which holds the solution to be investigated is shown at D in Fig. 1a, and on a larger scale in Fig. 1c. The tube is of circular cross section, 30 cm. long, and of 0.5 sq. cm. cross-sectional area. It is sealed off in the center, E in Fig. 1c, so that the solution filling the upper half of the tube ends in the center of the magnetic field. The air gap in which the tube hung was kept constant throughout the experiments, the distance between the pole faces being 1.2 cm. and the area of each pole face about 6 sq. cm. The solution thus hung with one end in a large uniform field. The tube is continued through the field in order that it shall be symmetrical with respect to the field, and hence experience no force when empty. This eliminates the correction for the force on the tube itself. The lower end F of the tube is open to the air. In the upper end of the tube, at G in Fig. 1c, is a thermometer sealed to the tube with de Khotinsky cement, so that its bulb is immersed in the solution. A hook at the top of the thermometer enables the whole to be suspended by a silk thread from one arm of an analytical balance, which stands upon a wooden shelf directly above the magnet, the silk thread passing through a hole in the floor of the balance case.

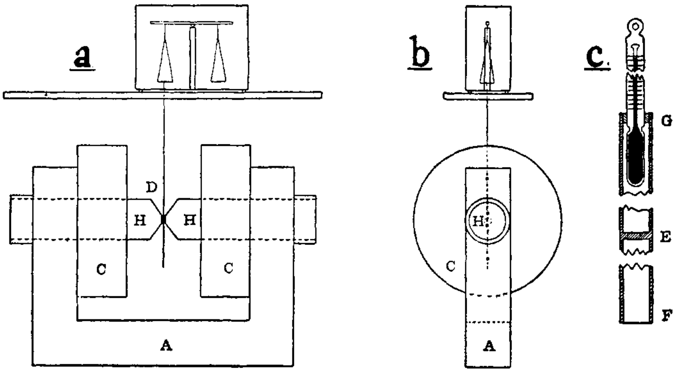

Fig. 1.—Arrangement of apparatus.

Each of the coils of the magnet was built in two sections connected in parallel, with water cooling between. Current was supplied to the two coils, connected in parallel, by a 17.5 kilowatt, direct current, motor-generator set, and controlled by rheostats, not shown in the figures. The current was measured by two ammeters, one on each coil, which could be read to tenths of amperes, and the mean of the two readings was used in the calculations. The ammeters were placed far enough from the magnet to be unaffected by its magnetic field, which was mapped in the vicinity and found to fall off very rapidly in passing away from the magnet.

The field of the magnet was calibrated using a bismuth spiral and found to range from 22,000 to 27,000 gauss with currents of from 5 to 18 amperes in each coil. A smooth and reproducible curve was obtained by plotting field strength against current.

Routine of the Experiments

The solutions used were prepared from chemically pure salts and reagents, filtered and stored in glass-stoppered bottles. Samples of the solutions were measured from a weight buret and analyzed electrolytically, a check being run on each analysis, an agreement of a few tenths of one per cent. being obtained. The amount of added substances was determined by weighing out the required amount of the pure substance, or in some cases by adding a measured amount of a standard solution of the substance. The solution after being made up was weighed, and this weight, together with the density, gave the volume for computing the molality of the added constituents. The density of the solutions was obtained by the use of a 10cc. pycnometer bottle, the results being reproducible to within 0.1%.

The solution to be examined was placed in the dry specimen tube, filling the upper half of it to within 2 cm. of the top. The thermometer was then inserted and sealed in with de Khotinsky cement. The tube was then hung from the balance and adjusted by means of a brass adjusting screw so that the lower end of the solution was exactly in the center of the pole gap. The weight was then determined to within 0.1–0.2 mg. A current of 17 amperes was passed through each coil for one minute, then reduced to 15 amperes and a weighing made. The current was further reduced and a second weighing made. This was repeated four times, giving four values of the force due to four different field strengths. The temperature was read as each weighing was completed. The current was then shut off and the zero weight checked.

In the case of strongly paramagnetic solutions the tube tended to swing over against one of the pole faces because of inhomogeneities in the field above the field gap. This was prevented by a device consisting of a tightly stretched horizontal wire through which a small alternating current was passed. This wire, placed 5 cm. below the pole gap, was in strong enough magnetic field so that it vibrated rapidly with a small amplitude. It was adjusted by a screw adjustment so that it barely touched the specimen tube and provided a slight horizontal agitation which prevented friction against the pole face and allowed accurate weighings to be made.

Having obtained the force on the tube filled with the solution due to a certain exciting current, we may divide this by the force on the tube filled with water for the same current and multiply by the susceptibility of water to obtain the susceptibility of the solution. This value is given as χ^v_{sol} in the tables. The susceptibility of water is known very accurately from work by Seve,[15] Piccard[16] and Piccard and Devaud,[17] to be -0.720×10^{-6} measured against a vacuum and, subtracting the susceptibility of air given by Soné,[18] we obtain, for the susceptibility of water against air, -0.749×10^{-6}.

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[15] Seve, *J. phys.*, [5] **3,** 8 (1913).

[16] Piccard, *Arch. Sci. Phys. Nat.*, [4] **35,** 340 (1913).

[17] Piccard and Devaud, *ibid.*, [5] **2,** 455 (1920).

[18] Soné, *Phil. Mag.*, [6] **39,** 305 (1910).

Using Wiedemann's law[19] that the susceptibility of a solution is an additive property of its constituents, we may write

$$\chi^{v}_{\mathrm{sol}} = \chi^{v}_{\mathrm{air}} + \left(\chi^{m}_{\mathrm{H_2O}} \times \frac{W_{\mathrm{H_2O}}}{1000}\right) + \sum\left(\chi^{m}_{n} \times \frac{W_n}{1000}\right) + \left(\chi^{m}_{\mathrm{salt}} \times \frac{W_{\mathrm{salt}}}{1000}\right) \tag{1}$$

from which we obtain

$$\chi^{m}_{\mathrm{salt}} = \frac{1000}{Mm}\left[\chi^{v}_{\mathrm{air}} + \chi^{v}_{\mathrm{sol}} - \left\{\left(\sum \chi^{m}_{n} \times \frac{W_n}{1000}\right) + \left(\frac{1000\,d - (Mm + W_n)}{1000}\right)\chi^{m}_{\mathrm{H_2O}}\right\}\right] \tag{2}$$

where M is the concentration of the solute in moles per liter of solution, m is the molecular weight of the solute, W_n is the mass of any added substance per liter of solution, χ^{v}_{sol} is the volume susceptibility of the solution, and χ^{m} is the specific, or mass, susceptibility obtained by dividing the volume susceptibility by the density.

Discussion of Errors

Uniformity of the Magnetic Field.—The field was found to be uniform between the pole faces by exploration with the bismuth spiral. Also, a crystal of a paramagnetic salt hung between the poles and entirely within the uniform portion of the field showed no tendency to move toward either pole face. It was further found that in weighing, the specimen tube with the field on it could be allowed to move up and down with the swing of the analytical balance without any change in the force on it so long as the lower end of the solution did not actually move from between the pole faces.

Reproducibility of the Field.—It was found that by always using the same cycle of magnetization, as described under **Routine of Experiments,** a perfectly reproducible field was obtained. This was checked from time to time.

Effect of Field on Balance.—The balance was shielded from the magnet by a sheet of iron and was unaffected by the field.

Actual Measurement of Force.—The measurement of the force on the tube could be made very accurately. The weight of the tube filled with solution was about 40 g. The smallest changes of weight due to the application of the field were a few hundredths of a gram. These could be measured to 0.1 mg. The larger changes of weight were of the order of a gram and could be measured to within 1 mg.

Temperature of the Solution.—The measurements on the solutions were made at room temperature. The temperature was read on the thermometer at the moment of weighing, the bulb of the thermometer being immersed in the solution. The thermometer was calibrated and accurate to 0.2°. The variations in temperature were never over 3°. If no account were taken of this the error would be about 1%, assuming Curie's

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[19] Wiedemann, *Pogg. Ann.*, **126,** 1 (1865).

law to hold. The mean temperature was, however, used in our calculations and correction made to 293.1° A.

Purity of Salts and Reagents.—The substances investigated were free from iron, cobalt and other impurities. Tests with ammonium thiocyanate, when compared with blanks containing known amounts of iron and cobalt, showed that these impurities were present in amounts far less than 0.1%. The salts studied were all paramagnetic so that even several tenths of one per cent. of a paramagnetic impurity would cause an error less than the experimental error.

Results

The results are given in terms of the molal susceptibility at 20°C., the molecule for which the calculation has been made being indicated in each case. The results are corrected to 20° assuming Curie's law to hold over the narrow temperature range used.

Table I

Nickelous Chloride Solutions

Molal concn.	D.	Added subs., *M*	Temp., ° A.	$\chi^v_{\text{sol}} \times 10^6$	$\chi^{20°}_{\text{NiCl}_2} \times 10^6$
2.907	1.3297	0	292.6	12.530	4553
1.4473	1.1698	0	290.9	5.933	4579
0.205	1.202	1.42 $K_2C_2O_4$	294.6	0.094	4390
.106	1.118	0.81 $K_2C_2O_4$	295.1	− .333	4260
.055	1.051	0.37 $K_2C_2O_4$	295.2	− .534	4370
.3206	1.0107	3.81 NH_4OH	292.6	.622	4241
.2598	0.9930	5.20 NH_4OH	292.7	.339	4137
.1469	.9918	3.55 NH_4OH	292.5	− .130	4165
.114	.9285	12.6 NH_4OH	296.2	− .270	4123
.207	.9529	9.26 CH_3NH_2	296.8	.142	4008
2.801	1.3404	0.44 KCl	293.2	12.383	4678
0.515	1.1374	2.87 KCN	...	−0.781	−44.6
.351	1.0957	2.02 KCN	...	− .776	−54.1
.256	1.103	0.79 KCN 6.30 NH_3	287.9	− .474	1295
.182	0.994	0.22 KCN 4.49 NH_3	291.2	− .195	2981
.203	0.941	0.13 KCN 5.0 NH_3	292.3	.019	3690

The results of Table I show that the susceptibility of nickelous chloride is lowered in all cases by substances which form stable complex ions with the nickel ion. In the case of the nickel ammonia complex an equilibrium between at least two molecular species is indicated by the lower values obtained with larger concentrations of ammonia. Potassium cyanide alone renders nickelous chloride diamagnetic, its effect when added to solutions of nickelous chloride in ammonium hydroxide being proportional to its concentration.

The values for the specific diamagnetic susceptibility of the added substances in Table I were determined by measurements of concentrated aqueous solutions to be as follows:

Subs.	$K_2C_2O_4$	NH_3[a]	CH_3NH_3	KCl	KCN
Dia. sus., × 10^6	−0.415	−0.948	−0.754	−0.466	−0.500

[a] The value for NH_3 is taken from the work of Weiss and Bruins, Ref. 4.

TABLE II

NICKELOUS BROMIDE SOLUTIONS

Concn.	D.	Added M subs.	Temp., °A.	$\chi^{v}_{\text{sol}} \times 10^6$	$\chi^{20°}_{\text{NiBr}_2} \times 10^6$
0.5385	1.1053	0	292.8	1.629	4393
.6080	1.3523	4.25 HBr	291.9	1.944	4495
.6097	1.2323	2.11 HBr	294.3	1.941	4423

The susceptibility of hydrobromic acid was determined by measurement of two solutions with the following results for the gram susceptibility: 14.11 M HBr, —0.378 × 10^{-6}; 5.50 M HBr, —0.389 × 10^{-6}. The mean of these values was used in the calculations.

TABLE III

CUPRIC NITRATE SOLUTIONS

Concn.	D.	Added M subs.	Temp., °A.	$\chi^{v}_{\text{sol}} \times 10^6$	$\chi^{20°}_{\text{Cu(NO}_3)_2} \times 10^6$
4.063	1.5716	0	293.8	5.701	1584
2.202	1.3214	0	298.3	2.708	1567
1.059	1.1570	0	295.0	0.947	1579
0.902	1.1342	0	298.1	.682	1585
.358	1.0533	0	295.1	− .175	1586
.782	1.4395	12.3 HNO_3	294.0	.559	1574
.795	1.2120	3.10 HNO_3	296.0	.527	1584
.795	1.1374	0.62 HNO_3	297.0	.525	1588

The specific susceptibility of nitric acid was determined by measurement of a concentrated solution to be —0.306 × 10^{-6}.

TABLE IV

CUPRIC BROMIDE SOLUTIONS

Concn.	D.	Added M subs.	Temp., °A.	$\chi^{v}_{\text{sol}} \times 10^6$	$\chi^{20°}_{\text{CuBr}_2} \times 10^6$
2.91	1.5417	0	293.5	3.732	1516
2.57	1.4737	0	298.3	3.156	1517
2.344	1.4437	0	302.4	2.799	1537
1.455	1.2813	0	293.4	1.538	1551
1.393	1.2651	0	295.3	1.401	1557
0.390	1.0749	0	298.2	−0.142	1559
.0738	1.0142	0	296.6	− .557	1591
.549	1.8072	12.74 HBr	297.3	− .148	1379
.576	1.4912	7.07 HBr	300.7	− .029	1404
.596	1.3415	4.40 HBr	297.9	.088	1497
.604	1.1739	1.17 HBr	297.6	.174	1545
.596	1.1270	0.21 HBr	297.1	.174	1551

TABLE IV (*Concluded*)

Concn.	D.	Added M subs.	Temp., °A.	$\chi^{v}_{sol} \times 10^6$	$\chi^{20°}_{CuBr_2} \times 10^6$
.558	1.1095	0.02 HBr	298.1	.115	1553
1.24	1.5390	6.41 HBr	297.0	.967	1413
1.22	1.3871	3.08 HBr	298.5	1.066	1511
1.233	1.2974	1.44 HBr	297.6	1.140	1535
1.232	1.2653	0.80 HBr	294.5	1.145	1526
1.229	1.2454	.095 HBr	296.0	1.154	1544
1.178	1.2257	.019 HBr	299.3	1.064	1547
1.427	1.3005	.627 KCl	294.3	1.464	1539
1.411	1.3180	.56 KBr	301.4	1.393	1544
1.450	1.3003	.266 KBr	301.8	1.449	1534
1.457	1.2863	.067 KBr	302.0	1.472	1548
1.216	1.4056	1.08 $CaBr_2$	294.7	1.076	1526
1.414	1.3075	0.22 $CaBr_2$	295.5	1.430	1520
1.439	1.2899	.07 $CaBr_2$	296.4	1.479	1546

The specific susceptibilities of potassium chloride and bromide and calcium bromide were measured in aqueous solution and found to be as follows: potassium chloride, —0.466 $\times 10^{-6}$; potassium bromide, —0.343 $\times 10^{-6}$; calcium bromide, —0.370 $\times 10^{-6}$.

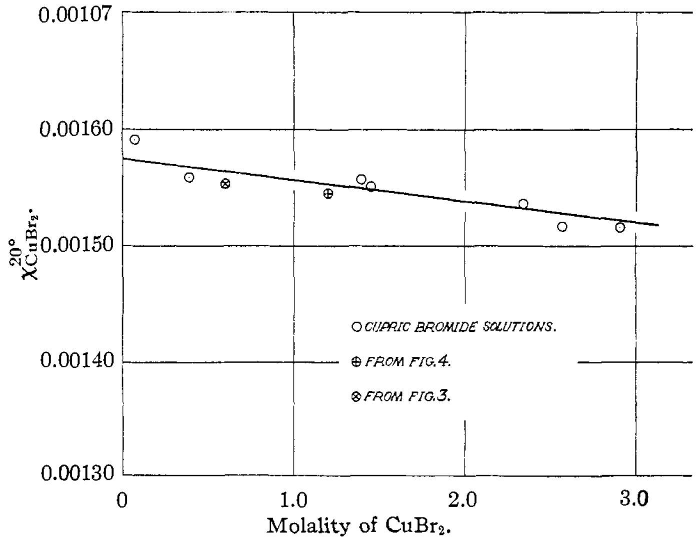

Fig. 2.—Variation of the magnetic susceptibility of cupric bromide with concentration.

The data of Table IV for the effect of concentration on the cupric bromide are shown in Fig. 2. Points for the susceptibility of cupric bromide with no hydrobromic acid added have been taken from Figs. 3 and 4 as indicated. The effect of hydrobromic acid on the susceptibility of cupric bromide solutions is shown in Figs. 3 and 4, where we have plotted the molal susceptibility of cupric bromide as abscissas against the ratio of hydrobromic acid to cupric bromide as ordinates. Here we see the marked decrease in the susceptibility caused by large amounts of hydrobromic acid. In Table IV we see that calcium bromide is the only other substance causing a decrease in the susceptibility.

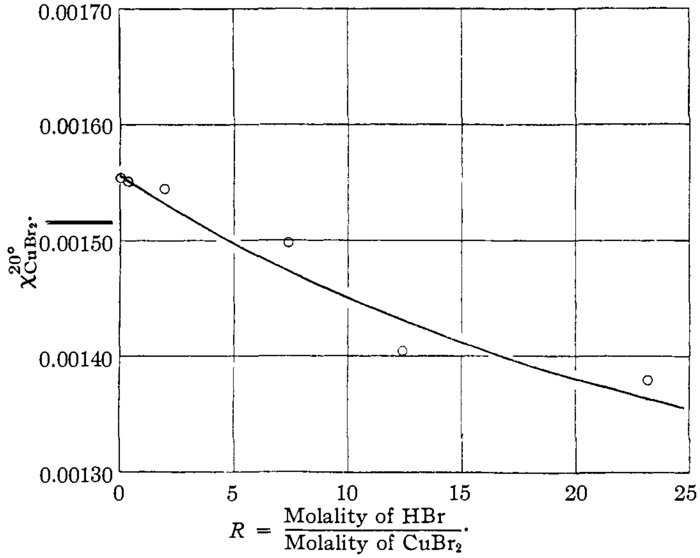

Fig. 3.—Effect of hydrobromic acid on the magnetic susceptibility of 0.6 *M* cupric bromide.

Discussion

The lowering of the susceptibility of a salt by complex ion formation seems to be roughly parallel to the firmness of the bonds between the metal atom and the atoms or groups in the coördination position. There are at present no quantitative data of any accuracy on the dissociation constants of these complexes and, therefore, we must rely on deductions from chemical stability, heat of formation and so forth. This parallelism between chemical and magnetic properties has been pointed out by Pascal[2] in the case of the complex pyro- and metaphosphates of iron. He has shown that as "the analytical properties of the iron become feebler the paramagnetism diminishes."

The interesting color changes in cupric bromide solutions have long been the subject of investigation and speculation. Dilute solutions of cupric bromide are green and this changes in passing to more concentrated solutions through greenish-brown to brown. The addition of bromide ion causes a deepening of this brown color, while the addition of hydrobromic acid causes a very deep red color, the solution becoming almost opaque.

Denham[20] has measured the transference number of cupric ion in various concentrations of cupric bromide. As the concentration of the salt is increased, the transference number of the cupric ion diminishes and, passing through zero, becomes negative. The negative value indicates that the copper has become a negatively charged complex ion and is leaving the cathode space.

G. N. Lewis[21] found that while the brown color of cupric bromide solutions was enhanced by additions of the bromides of the alkali metals, the deepening of the brown color was not proportional to the concentration of bromide ion furnished by the added salt, but more nearly proportional to the lowering caused in the activity of the water. Thus, lithium bromide produces the greatest deepening of the brown color of a cupric bromide solution, although it gives the least bromide ion of any of the salts tried. The addition of lithium bromide to water, however, lowers its vapor pressure more than does any other salt used. Lewis suggests that the equilibrium involved is that between hydrated cupric ion and cupric ion in which bromide has displaced the water from the coördination positions, in the following way: $[Cu(H_2O)_4]^{++} + nBr^- = [Cu(H_2O)_{(4-n)}Br_n]^{+2-n} + nH_2O$. This theory is corroborated by other evidence. The formation of complex ions is less exothermic than the formation of hydrates, as is indicated by the fact that solutions of cupric bromide are browner at higher

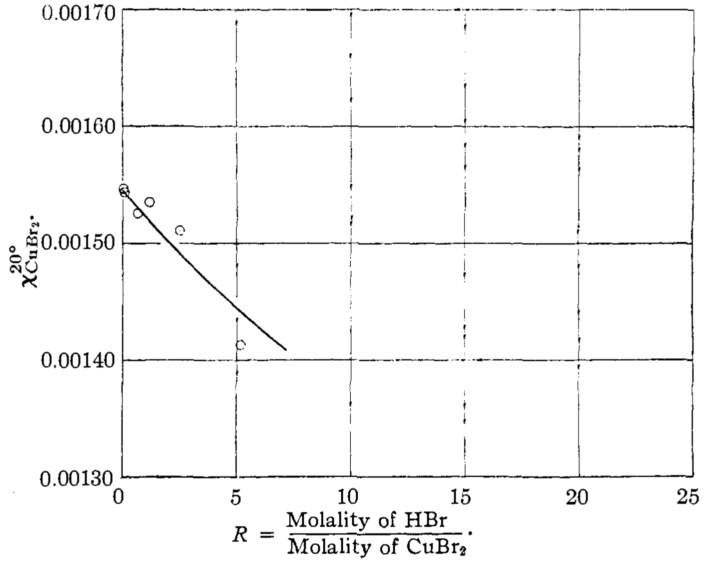

Fig. 4.—Effect of hydrobromic acid on the magnetic susceptibility of 1.2 *M* cupric bromide.

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[20] Denham, *Z. physik. Chem.*, **65**, 64 (1909); *J. Chem. Soc.*, **115**, 1269 (1919).

[21] Lewis, *Z. physik. Chem.*, **56**, 223 (1906); **52**, 222 (1905).

temperatures, corresponding to the breaking down of the hydrate and the formation of the complex bromide ion.

Conclusions

These results may be summarized in the statement that the formation of a chemical bond lowers the susceptibility of a paramagnetic ion and that the lowering of the susceptibility is proportional to the firmness of the bond formed. This is essentially the same conclusion as that arrived at by Pascal[2] that the lowering of the magnetic susceptibility of an ion by complex formation is proportional to the diminution of the analytical properties of the ion. We may conclude from this either that chemical bonds are partly or wholly magnetic in character, or that the bonds are formed by the same electrons which give rise to the magnetic properties. G. N. Lewis[22] has suggested that two electron orbits in forming a chemical bond may pair in such a way that their magnetic fields may partly or wholly compensate. This assumption will explain the effects here observed.

Weiss[23] has calculated the number of magnetons in various paramagnetic ions from susceptibility measurements in aqueous solutions with a view to proving the existence of a definite unit of magnetic moment, namely, 1123.5 c.g.s. units. The results of this research show clearly that such calculations can be only qualitative unless exact knowledge is available of all the hydrated ions, complex ions or other molecular species present in any solution and of their equilibrium concentrations.

This research was undertaken at the suggestion of Professor G. N. Lewis, whose continued interest has been a source of inspiration to the authors.

Summary

The paramagnetic susceptibilities of aqueous solutions of nickelous chloride, nickelous bromide, cupric nitrate and cupric bromide have been determined by use of the "cylinder" method. The effect of the addition of various diamagnetic substances such as hydrogen ion, chloride ion, bromide ion, cyanide ion, ammonia and methylamine on the susceptibility of these salts was studied. A definite reduction of paramagnetism was observed in all cases where complex ions of considerable stability were known to form. We may conclude from this that the bonds associated with this formation are at least partly magnetic in character.

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[22] Lewis, *Chem. Rev.*, **1**, 231 (1924).

[23] Weiss, *J. phys.*, **7**, 249 (1908); **6**, 661 (1907); [4] **5**, 129 (1924).