THE MAGNETIC MOLECULAR SUSCEPTIBILITY OF SALTS OF THE IRON GROUP.

By O. Liebknecht and A. P. Wills.[1]

GUSTAV WIEDEMANN was the first to undertake magneto-chemical investigations in regard to the behavior of the paramagnetic salts of the metals: chromium, manganese, iron, cobalt, nickel and copper. He used a torsion method with a non-uniform field.[2] He found that the quantity defined by him as the "Molecularmagnetismus" is nearly independent of the solvent, the concentration, and especially of the nature of the anions for a given temperature and cation of a given valency. The differences always exceeded the experimental errors and amount in general to 2 or 3 per cent. Therefore he found a mean value for a given cation and called it the "Atommagnetismus." The atomic magnetisms of the manganous, ferrous, cobaltus and nickelous salts were as $a + 2b$, $a + \frac{3}{2} b$, $a + b$, a, where $b = 1.15a$; that of the ferric salts exceeds that for the ferrous salts by about 15 per cent.

Not long since G. Jäger and St. Meyer[3] published some striking measurements made with a modification of the Quincke manometric method. They drew the conclusion that the atomic magnetisms of manganese, iron, cobalt, nickel are as $6:5:4:2$; this agrees with the proportion given above if $a = b$. Their results were obtained from the chlorides, sulphates and nitrates; with manganese, cobalt and nickel, only the bivalent salts could be used; on the other hand the value for iron was taken as the mean of the results for ferric chloride, ferrous sulphate and ferric nitrate.

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[1] The chief results were communicated to the Physikalische Gesellschaft on the 30th of June, 1899; many results were still outstanding.

[2] G. Wiedemann, Pogg. Ann., 126, p. 1, 1865; 135, p. 177, 1868; Wied. Ann., 5, p. 45, 1878; P. Plessner, Wied. Ann., 39, p. 336, 1890; G. Quincke, Wied. Ann., 24, p. 392, 1885. G. Wiedemann, Lehre von der Elektricität, 2. Aufl. 3, §§ 1266–1291, 1895. J. Koenigsberger, Wied. Ann., 66, p. 698, 1898.

[3] G. Jäger und St. Meyer, Wien. Ber. (2), 106, pp. 594, 623, 1897; 107, p. 5, 1898.

In later articles Jäger and St. Meyer use for ferrous chloride the relative number 3 instead of 5 as above; further, they obtain from chromic chloride and chromic sulphate the number 2.5 for chromium.

In the light of these results it seemed to us desirable to make new determinations using a different method. We have made quantitative determinations upon 36 salts of the five metals of the iron group and of copper. Great stress was laid upon the procuring of the purest material possible, and all salts in which there was danger of rapid decomposition were discarded. In general, we have studied the sufficiently soluble fluorides, chlorides, bromides, iodides, sulphates and nitrates; for the reason just mentioned, it was not possible to study many of the iron and chromium compounds. The accuracy of our final results may vary between 2 and 5 parts in 1,000, according to the method used in the chemical analysis.

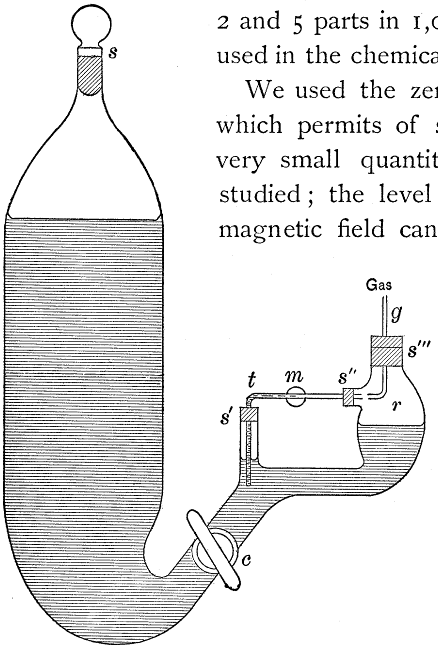

Fig. 1. ¼ natural size.

We used the zero method of Prof. du Bois,[1] which permits of successful manipulation with very small quantities of the substances to be studied; the level of the capillary tube in the magnetic field can be so adjusted that the unmagnetic solution can be prepared with great precision so as to be well within the limits of error in the subsequent chemical analysis. Briefly, the procedure is as follows: A conveniently strong paramagnetic solution is prepared and then diluted with the diamagnetic solvent until the solution is unmagnetic. The practicability of the method is only limited by the susceptibility and solubility of the salt. Sometimes the method is inadmissible on this account as, for example, in the case of potassium chromate and bichromate and of

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[1] H. du Bois, Wied. Ann., 35, p. 154, 1888; 65, p. 38, 1898.

potassium and calcium permanganate. These peculiarly constituted salts are well known to be but weakly paramagnetic; the similarly constituted dry K_2FeO_4 proved to be much more paramagnetic; the alkali solution decomposed so quickly that we were prevented from making a quantitative determination.

As a criterion for the unmagnetic condition of the solution, the behavior of its meniscus in a Quet's[1] capillary tube *t* in a magnetic field was observed (Fig. 1). The large mixing vessel had a capacity of about 600 ccm.; it could be closed by means of a glass stopper *s*, and could be separated from the rest of the apparatus by means of the glass stopcock *c*; the arm connected with the mixing vessel was so formed that fresh capillary tubes could be suitably introduced and fixed by means of the rubber stoppers at s' and s''. The space beyond the meniscus in the capillary tube and the space *r* could be filled with washed moist illuminating gas.[2] This apparatus was fixed to a suitable stand permitting a rotation about a horizontal axis perpendicular to the plane of the figure. The inclination of the capillary tube could be thereby regulated by means of a suitable adjusting screw; and, moreover, by means of a vigorous rotation of the apparatus about this axis a thorough mixing of the solution could be attained. At *m* is represented the end view of the truncated conical pole piece of the ring electro-magnet.

With a little practice a very short time sufficed to prepare an unmagnetic solution with an accuracy of one part in 1,000, so that upon excitation of the electro-magnet no noticeable motion of the meniscus took place. At each dilution the mixing apparatus was, of course, well shaken and each part well washed with the diluted solution, so that the solution should have in all parts the same concentration as at the meniscus. Any possible local change in the concentration due to magnetic influences would scarcely have time to be effected; furthermore, though such an effect theoretically

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[1] Quet, Comp. Rend., 38, p. 562, 1854; E. Verdet, Oeuvres, 1, p. 199

[2] The susceptibility of illuminating gas was neglected; as far as known it amounts at a pressure of one atmosphere to less than one thousandth of that of water; compare M. Faraday, Exp. Res., 3, p. 502, 1855; G. Quincke, Wied. Ann., 34, p. 445, 1888; A. Toepler u. R. Hennig, Wied. Ann., 34, p. 796, 1888. An absolutely unmagnetic gas can be made after the manner of an unmagnetic solution by mixing a little oxygen with a diamagnetic gas; compare du Bois, l. c., p. 167; of course it is here tacitly supposed that the permeability of a vacuum serves as the unit in the usual conventional way.

exists, it has not been unmistakably shown experimentally.[1] In case the capillary is inclined toward the horizontal by a fraction of a degree, it is possible with a field of 40,000 c. g. s. units, to detect a differential susceptibility which does not exceed a hundred thousandth of that of water. On account of the above mentioned limits of error in the chemical analysis, it was useless to try for such accuracy as this, so that as a rule a much less sensitive adjustment was employed.

The procuring and cleaning of the capillary tubes offered at first some difficulties. Finally the freshest possible tubes from Thüringer glass were used, these being kept under water until required.[2] With these the mobility of the meniscus was satisfactory. Any influence of the breadth of the capillary tube used upon the concentration of the unmagnetic solution contained therein, could not be detected. This furnished, as is easy to see, an indirect proof that the capillary constants of unmagnetic solutions are quite unaltered in the magnetic field.

This independence of the surface tension of magnetic influences seems to obtain in general.

Brunner and Mousson[3] have fruitlessly sought such an action, whereby they seem to have overlooked the well known-Quincke effect of elevation (or depression) in the magnetic field, which, however, W. Wertheim[4] probably observed. Quincke[5] first undertook drop experiments with strong paramagnetic manganese and iron solutions; he found that the weight of a drop was unaltered by a uniform magnetic field and assumed, therefore, the constancy of the surface tension of such solutions. On the other hand, in a non-uniform field between conical pole pieces the drops of manganese chloride as of iron chloride were larger or smaller upon the excitation of the magnetism according as they formed under or above the shortest lines of force.

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[1] Compare with G. Wiedemann, Electricität, 2, Aufl. 3, § 1205, 1895.

[2] Compare P. Volkmann, Wied. Ann., 66, p. 194, 1898.

[3] C. Brunner u. A. Mousson, Pogg. Ann., 79, p. 141, 1850.

[4] W. Wertheim, Comp. rend., 44, p. 1022, 1857; Pogg. Ann., 102, p. 595, 1857.

[5] G. Quincke, Pogg. Ann., 160, p. 586, 1877; Wied. Ann., 24, p. 375, 1885. Compare also Durchflussbeobachtungen by H. Dufour, Lum. Electr., 23, p. 337, 1887; likewise G. Jäger u. St. Meyer, Wied. Ann., 67, p. 711, 1889.

For a further investigation of these phenomena we constructed an apparatus (Fig. 2) by means of which the formation of the drop could take place at the nozzle n which was of about 1 mm. inside breadth, and at the proper pressure and at different rates, and moreover either in a uniform field of about 18,000 c. g. s. units between surface pole pieces, or in a non-uniform field of about 40,000 c. g. s. units between conical pole pieces M and M' and while the nozzle was placed in the position of greatest field intensity. The vessel A was in connection through S with the reservoir B in which the level of the liquid could be regulated. The space r, r could be connected through the cock c with a pump; the pressure regulated in this manner was read off on the manometer m. A number of experiments were carried out with this apparatus and, briefly stated, the results are as follows :

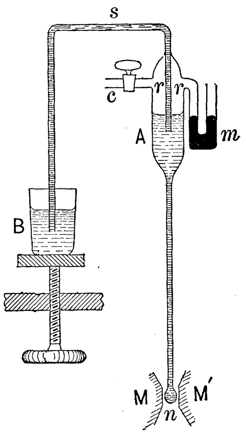

Fig 2. ⅙ natural size.

Paramagnetic solutions show in a uniform field, an increased rate of dropping when the magnetic force upon the liquid column acts downwards ; through diminution of the pressure the original rate being again approximately established,[1] the weight of the drop suffers no change. On the other hand, we observe an enlargement of the drop in a non-uniform field; the form of the drop is then changed and depends upon the particular distribution of the field as regards the sense and manner in which it happens. These experiments confirm Quincke's results and conclusions.

Diamagnetic water shows in a uniform field a slower rate of dropping when the magnetic force is directed upwards and, therefore, against the hydrostatic pressure; under proper conditions the dropping may be quite stopped through excitation of the field. If the original rate of dropping be restored through increase of the pressure the weight of the drop suffers no change. In a non-uniform field the weight appeared less with the arrangement used, and more so the less uniform the field.

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[1] This must be done because, as well known, the rate under ordinary conditions exerts a small secondary influence upon the weight of the drop.

Unmagnetic solutions are not at all influenced, as regards the magnitude of the drop, through excitation of the field if the drops fall in an atmosphere of illuminating gas. Toward air they behave, naturally, like a weakly diamagnetic liquid. This simple criterion has an application in the preparation of unmagnetic solutions; in accuracy this procedure is inferior to the method already described and the one, as a rule, used by us.

THEORY OF THE METHOD.

The extension of our knowledge of magnetic phenomena might be expected, from the first, in a thorough investigation of the thermo-magnetic and magneto-chemical processes. It would seem then to be not superfluous to give in this place, concisely as possible, the elementary conceptions connected with calculations on this subject. The reference of the magnetic moment to the unit of mass, once much employed, has been quite displaced in consequence of the advanced development of the mathematical theory of electromagnetism, because in mathematical physics the reference to the unit of volume is simpler. Professor du Bois[1] has shown that in some cases it is desirable to return to the original method, because the results are in many respects more easily comparable when the variable density is eliminated. Since magnetic processes are essentially molecular it is still better to refer them for stoichiometrical purposes to molecular masses.

In what follows m means molecular weight; M, mass; $\mathfrak{M}$, magnetic moment; $\mathfrak{S}$, specific magnetization, *i. e.*, moment per unit of mass; $\mathfrak{H}$, field intensity; i, specific susceptibility defined by the relation $i = \frac{\mathfrak{S}}{\mathfrak{H}}$.[2] The molecular susceptibility i_m is now defined by the equation

$$i_m = mi = \frac{m\mathfrak{S}}{\mathfrak{H}}.$$

In what follows, the subscripts l, w, s refer respectively to the solution, solvent and salt. On account of the additive properties,

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[1] H du Bois, Phil. Mag. (5), 29, p. 293, 1890.

[2] If we designate, as customary, the density with D, the magnetization with $\mathfrak{J}$, the susceptibility according to the ordinary definition with κ, then is $\mathfrak{S} = \frac{\mathfrak{J}}{D}$ and $i = \frac{\kappa}{D}$. Compare J. Koenigsberger, Wied. Ann., 66, p. 698, 1888.

first shown by G. Wiedermann, of the quantities here coming into consideration, the following equation obtains for a solution in a uniform field

$$\mathfrak{M}_l = \mathfrak{M}_w + \mathfrak{M}_s.$$

The influence of form as well as the therewith connected magnetic interaction of the separate similar or dissimilar volume elements may be with the strongest paramagnetic solutions disregarded since the square of the susceptibility in comparison with unity is quite negligible. In particular for an unmagnetic solution $\mathfrak{M}_l = 0$ therefore $\mathfrak{M}_s = -\mathfrak{M}_w$, or $\mathfrak{S}_s M_s = -\mathfrak{S}_w M_w$. After division by $\mathfrak{H}$ we get

$$(1) \qquad \frac{i_s}{i_w} = -\frac{M_w}{M_s}$$

and the relative molecular susceptibility $\frac{i_m}{i_w}$ of the salt becomes finally

$$(2) \qquad \frac{i_m}{i_w} = -m\frac{M_w}{M_s},$$

i. e., equal to the negative product of the molecular weight into the mass ratio of the solvent and salt. This value of i_m holds not only for the particular concentration of the unmagnetic solution but quite generally;[1] whether, considering the accuracy of our new method, it is quite independent of the kind of solvent can only be decided by a special series of experiments; it changes markedly with the temperature.

Professor du Bois has shown that the behavior of an unmagnetic solution in fields of different intensities permits a conclusion as to the constancy of the susceptibility and has shown this constancy to exist with fields up to 10,000 c. g. s. units.

If the constitution of the unmagnetic solution measured by $\frac{M_w}{M_s}$, is independent of the field intensity, then it follows directly from equation (1) that the relative susceptibility with reference to water $\frac{i_s}{i_w}$ is also independent of the field.

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[1] According to the results of various investigators; compare with J. Koenigsberger, l. c., p. 708.

[2] H. du Bois, Wied. Ann., 35, p. 155, 1888.

In fact, such a dependency was not found for any of the unmagnetic solutions investigated, and this holds for the extended range of fields between 2,000 and 40,000 c. g. s. units. Now it can be asserted with a probability bordering upon certainty that the variations of the susceptibility of water would not be followed exactly proportionately by those of the different salts. Therefore, the constancy of the absolute susceptibility of the dissolved salt, as of water, within the specified range of fields, follows from the constancy of the susceptibility of the dissolved salt relative to water.

Furthermore, it is very improbable that the susceptibility for weaker fields would be variable.[1] In the results to follow the constant susceptibility of water enters everywhere as a principal factor. We have the following determinations for this factor which have been recalculated so as to refer to a temperature of 18°, and to a vacuum ; the susceptibility of air at one atmosphere pressure and 18° was taken as 0.023×10^{-6}.[2]

TABLE I.

	Temperature 18°.	Toward Vacuum.
1885	G. Quincke (most accurate value)	$\kappa = -0.797 \times 10^{-6}$
1888	H. du Bois	-0.831 "
1892	S. Henrichsen	-0.727 "
1895	P. Curie (mean value)	-0.788 "
1896	J. S. Townsend	-0.735 "
1898	J. Koenigsberger	-0.785 "
1899	G. Jäger–St. Meyer (mean value)	-0.645 "
	Mean value	$\kappa = -0.758 \times 10^{-6}$
Since $D_{18^\circ} = 0.9987$, i_w becomes -0.759×10^{-6}		

In consideration of the obvious uncertainty of the value of the fundamental constant i_w and its temperature coefficient we have for the present designated it by x and taken the molecular

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[1] Compare Vgl. F. Auerbach in Winkelmann's Handbuch der Physik, 3, 2 Abth., p. 217. Breslau, 1895.

[2] G. Quincke, Wied. Ann., 24, p. 404, 1885 ; H. du Bois, Wied. Ann., 35, p. 167, 1888 ; S. Henrichsen, Wied. Ann., 45, p. 53, 1892 ; P. Curie, Thése Nr. 840, p. 31, Paris, 1895 ; J. S. Townsend, Proc. Roy. Soc., 60, p. 186, 1896 ; Beibl. 20, p. 796, 1896 ; J. Koenigsberger, Wied. Ann., 66, p. 703, 1898 ; G. Jäger und St. Meyer, Wied. Ann., 67, pp. 427 u. 707, 1899. The old determinations of M. Faraday, E. Becquerel, J. Schuhmeister and the value of Théodore Wahner's which falls so far out are not considered.

susceptibility relative to it; and then in order to obtain approximate absolute values we have taken provisionally $x = -0.75 . 10^{-6}$. A thorough discussion of the above values and further accurate new determinations would be desirable. So soon as these can be carried through with the accuracy with which the relative values $\frac{i_m}{x}$ are determined, the reduction of the latter to absolute numbers may be easily accomplished.

The constitution of an unmagnetic solution is variable with the temperature; we have therefore carefully maintained a normal room temperature of 18°C.[1] The unmagnetic solutions prepared according to this are then at higher (lower) temperatures somewhat diamagnetic (paramagnetic) because the temperature coefficient for the salt is always greater than for the water.

In case the latter were accurately known, the former for different salts could easily be determined.[2]

The Chemistry Details.

Most of the salts were pure preparations from Kahlbaum or Merck, and were, when possible, many times recrystallized before use. Most of the fluorides, bromides and iodides were prepared by one of us from pure carbonates. The nickel salts were procured from Kahlbaum as "cobalt-free" and the cobalt salts as "nickel-free"; the influence of the chemically unrecognizable impurities present cannot make a difference in the molecular susceptibility fonnd of more than 0.5-per-cent. solutions, which especially incline to decomposition, *e. g.*, MnF, MnCl, FeSo, FeCl, FeBr, were usually treated with a free acid; this was without noticeable influence on the results since the susceptibility of the acid added differs little from that of water; the ferrous iodide contained some free iodine. Where a gradual decomposition was to be feared, the solution was analyzed as soon as prepared; quickly decomposable solutions were not investigated, as already remarked; of course,

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[1] Compare F. Kohlrausch und L. Holborn, Leitvermögen der Elektrolyte, Leipzig, 1898.

[2] In such measurements, an unmagnetic atmosphere should bound the liquid. The marked dependence of the susceptibility of oxygen relative to air upon the temperature, which has already been mentioned, would otherwise bring in a considerable error.

care was taken that no dilution or concentration change should take place after the solution was once prepared. The gravimetric analysis was carried out for the chromium salts by precipitating them with ammonia as hydroxides. The manganese solutions were precipitated with phosphorus-free hydrogen peroxide and ammonia as oxides and weighed as mangano-manganic oxides. The iron salts were determined in part with potassium permanganate by titration and in part precipitated with ammonia as hydroxides. Finally, the cobalt, nickel and copper were electrolytically precipitated, the two first in a neutral solution with ammonium oxalate and the copper in a solution of sulphuric acid containing a little nitric acid.

RESULTS.

Our quantitative results are collected into Table II. q designates the valency of the cation of the salt; a the atomic weight; the metals are arranged according to their increasing atomic weights.[1] The position of cobalt and nickel in the series is reversed, however, after mature consideration. For, according to the collective properties in the metallic or amalgamated condition, and in the condition as a paramagnetic compound, cobalt stands nearer to iron than does nickel; likewise for the chemical properties. In the column before the last is given the relative molecular susceptibility x, which is calculated from the equation given above. In the last column the absolute value is given under the provisional assumption $x = -0.75 \times 10^{-6}$ which number may be a number of per cent. false.

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[1] The atomic weights are from those collected by the German Chemical Society (Chem. Ber., 31, p. 2761, 1898; Wied. Beibl., 23, pp. 69 und 315, 1899, whereby $O = 16.00$). The question as to the atomic weight of cobalt and nickel is still a subject of chemical discussion; compare Cl. Winkler, Zeitsch. anorg. Chem., 17, p. 236, 1898; Th. W. Richards and G. P. Baxter, l. c., 21, 251 and 22, p. 221, 1899; St. Meyer, Wied. Ann., 69, p. 263, 1899, hints at the possibility of an inverted order in the series.

[2] Recalculated according to the collection of W. Ostwald, Stoichiometrie, 2. Aufl., p. 512, Leipsig, 1891.

Table II.

Temperature 18°C. $x = -0.75 \times 10^{-6}$

	Name of Salt in Water Solution.	q	Formula.	O = 16.00		$\frac{M_w}{M_s}$	$-\frac{i_m}{x}$	$+i_m$
				a	m			
1	Chromium Sulphate.	3	$Cr_2(SO_4)_3$	52,1	392,38	40,73	2×7990	0,00599
2	Chromium Potass. Alum.	3	$CrK(SO_4)_2$	52,1	283,37	29,63	8400	0,00629
3	Chromium Amm. Alum.	3	$CrNH_4(SO_4)_2$	52,1	262,30	30,77	8070	0,00605
4	Chromium Nitrate.	3	$Cr(NO_3)_3$	52,1	238,22	35,28	8400	0,00629
5	Manganous Fluoride.	2	MnF_2	55,0	93,00	215,71	20060	0,01504
6	Manganous Chloride.	2	$MnCl_2$	55,0	125,90	163,10	20530	0,01540
7	Manganous Bromide.	2	$MnBr_2$	55,0	214,92	94,63	20340	0,01524
8	Manganous Iodide.	2	MnI_2	55,0	308,70	65,49	20220	0,01516
9	Manganous Sulphate.	2	$MnSO_4$	55,0	151,06	133,65	20190	0,01514
10	Manganous Ammon. Sul.	2	$Mn(NH_4)_2(SO_4)_2$	55,0	283,28	71,04	20130	0,01509
11	Manganous Nitrate.	2	$Mn(NO_3)_2$	55,0	179,08	114,37	20480	0,01536
12	Ferrous Iodide.	2	FeI_2	56,0	309,70	55,18	17090	0,01282
13	Ferrous Sulphate.	2	$FeSO_4$	56,0	152,06	111,72	16990	0,01272
14	Ferrous Ammon. Sul.	2	$Fe(NH_4)_2(SO_4)_2$	56,0	284,28	59,42	16890	0,01268
15	Ferric Chloride.	3	$FeCl_3$	56,0	162,35	111,14	18040	0,01356
16	Ferric Bromide.	3	$FeBr_3$	56,0	295,88	66,77	19750	0,01482
17	Ferric Sulphate.	3	$Fe_2(SO_4)_3$	56,0	400,18	101,06	2×20200	0,01515
18	Ferric Ammon. Alum.	3	$Fe(NH_4)(SO_4)_2$	56,0	266,20	75,64	20140	0,01510
19	Ferric Ammon. Oxalate.	3	$Fe(NH_4)(S_2O_4)_2$	56,0	250,08	81,75	20450	0,01533
20	Ferric Nitrate.	3	$Fe(NO_3)_3$	56,0	242,12	74,48	18030	0,01352
21	Cobaltous Fluoride.	2	CoF_2	59,0	97,00	142,60	13830	0,01037
22	Cobaltous Chloride.	2	$CoCl_2$	59,0	129,90	108,21	14060	0,01054
23	Cobaltous Bromide.	2	$CoBr_2$	59,0	218,92	63,13	13820	0,01036
24	Cobaltous Iodide.	2	CoI_2	59,0	312,70	44,08	13790	0,01034
25	Cobaltous Sulphate.	2	$CoSO_4$	59,0	155,06	87,65	13590	0,01019
26	Cobaltous Nitrate.	2	$Co(NO_3)_2$	59,0	183,08	76,62	14030	0,01052
27	Nickelous Fluoride.	2	NiF_2	58,7	96,70	61,50	5950	0,00446
28	Nickelous Chloride.	2	$NiCl_2$	58,7	129,60	46,02	5960	0,00447
29	Nickelous Bromide.	2	$NiBr_2$	58,7	218,62	27,00	5900	0,00442
30	Nickelous Iodide.	2	NiI_2	58,7	312,40	18,62	5820	0,00436
31	Nickelous Sulphate.	2	$NiSO_4$	58,7	154,76	37,39	5790	0,00435
32	Nickelous Nitrate.	2	$Ni(NO_3)_2$	58,7	182,78	32,31	5910	0,00443
33	Cupric Chloride.	2	$CuCl_2$	63,6	134,50	16,33	2200	0,00165
34	Cupric Bromide.	2	$CuBr_2$	63,6	223,52	9,40	2090	0,00157
35	Cupric Sulphate.	2	$CuSO_4$	63,6	159,66	13,72	2190	0,00164
36	Cupric Nitrate.	2	$Cu(NO_3)_2$	63,6	187,68	11,54	2170	0,00163

From the series of numbers in the foregoing table we may draw the following conclusions: The molecular susceptibility shows the well-known increase from chromium to manganese and iron and then a gradual decrease to copper. The four halogen salts could be investigated unobjectionably as bivalent salts only, in the case of manganese, cobalt and nickel; there occurs here again a regular increase from the fluoride to the chloride with a following decrease to the iodide. Simple additive or subtractive properties are obviously not present.

The approximate coincidence of the chlorides and nitrates is striking throughout; in connection with the ferric compounds it is noticeable that the bromides, sulphates, oxalates, give values which are 12 per cent. higher than those which the ferrous compounds furnish; this agrees with the results found by G. Wiedemann. Moreover, the difference among the separate salts amounts to 5 per cent., so that the introduction of a fixed atomic susceptibility for the cation cannot be allowed without considerable arbitrariness. That this quantity exerts by far the chief influence upon the value of the molecular susceptibility has, of course, never been doubted. We have investigated the sulphates of six metals. These are suitable for comparison with earlier observed values and with the proposed algebraic relations which are collected in Table III.

TABLE III.

Observer.	**Cr‴**	**Mn″**	**Fe″**	**Fe‴**	**Co″**	**Ni″**	**Cu″**
Liebknecht–Wills (from exp.)	7990	20190	16990	20200	13590	5790	2190
" " ($Ni'' = a$)	$1.38a$	$3.49a$	$2.93a$	$3.49a$	$2.35a$	a	$0.38a$
" " ($b = 1.25a$)	——	$3.50a$	$2.88a$	——	$2.25a$	a	——
G. Wiedemann (exp. $Ni'' = a$)	$1.34a$	$3.29a$	$2.74a$	$3.26a$	$2.26a$	a	——
Jäger–Meyer: ($Ni'' = a = b$)	——	$3a$	$2.5a$	——	$2a$	a	——

Our values for the sulphates of Mn, Fe, Co and Ni may be approximately represented by Wiedemann's proportion, whereby $b = 1.25a$; of course, only two of the latter numbers are independent since Mn and Ni serve to determine the parameters a and b; putting $a = b$ does not give an agreement with our results. Finally, these are with respect to nickel everywhere larger than those of Wiedemann, also than those of Jäger and Meyer; the departure can only be explained in case the nickel compounds investigated by these observers should have contained cobalt; this, in our judgment, must have been the case.

We wish to thank Dr. W. Meyerhoffer for his kind assistance in carrying out numerous analyses. The investigations were carried out in the laboratory of Professor H. du Bois, to whom our cordial thanks are due.

Berlin, December, 1899.