

110. The Magnetic Susceptibility of Cadmium Compounds.

By WINIFRED R. A. HOLLENS and JAMES F. SPENCER.

DURING the course of an investigation into the nature of the so-called sub-compounds of cadmium (J., 1934, 1062), the scarcity of information concerning the magnetic properties of cadmium compounds was noticed.

Some 30 of these compounds, including the "sub-chloride," were therefore prepared, and measurements of their mass susceptibilities made by the modified Gouy method (Sugden, J., 1932, 161; Trew and Watkins, *Trans. Faraday Soc.*, 1933, 29, 1310). All the compounds measured were diamagnetic; and the atomic susceptibility of cadmium was also diamagnetic, in keeping with the fact that its atom has a closed configuration. The molecular susceptibility was calculated for each compound, and from it the gram-ionic susceptibility, χ_A , of cadmium. In order to calculate the latter, it was necessary to measure the susceptibilities of other substances, since the values of certain anions required are not recorded in the literature. A mean value of $\chi_A = -24.85 \times 10^{-6}$ was obtained from 30 results. It is interesting to note that the "sub-chloride" gives a value of χ_A which is very close to the mean value above, and this is in accordance with the result (*loc. cit.*) that the substance is a solid solution of metal in cadmic chloride.

EXPERIMENTAL.

Preparation of Materials.—The compounds measured were prepared and purified by the usual methods from Kahlbaum's pure cadmium or A. R. cadmium sulphate. They were all shown to be free from iron by the thioglycolic acid reaction, and from nickel by dimethylglyoxime. The 8-hydroxyquinoline derivative was prepared by Berg's method (*Z. anal. Chem.*, 1927, 71, 369). The borofluoride, which has not hitherto been described, was obtained by the action of the acid on the carbonate; it was very soluble in water, but sparingly soluble in alcohol and ether. It crystallised as heptahydrate in highly deliquescent needles; dehydration over phosphoric oxide was very slow, requiring about a year for completion. The anhydrous acetate was obtained by refluxing a mixture of cadmium nitrate and acetic anhydride (Späth, *Monatsh.*, 1912, 33, 235). Cadmium was estimated in the majority of compounds examined by conversion into the sulphate and electrolysis of the solution with a rotating platinum cathode, a current of 1.4—1.6 amps. being used. No compound was employed which gave a cadmium content differing by more than 0.2% from the calculated value.

Measurement of Susceptibility.—This was carried out at atmospheric temperature; six closely agreeing measurements were made with fresh packings in each case, and the mean value recorded. The results are included in Table I, in which χ is the mean measured mass susceptibility, χ_M the g.-mol. susceptibility, δ the susceptibility value of the groups attached to the metallic ion, and χ_A is obtained by subtracting δ from χ_M . Where possible, δ was obtained from values quoted in the "International Critical Tables," VI, 349, and Stoner "Magnetism and Atomic Structure," 1926, p. 122.

TABLE I.

(All values are negative throughout.)

Substance.	χ .	χ_M .	δ .	χ_A .	Substance.	χ .	χ_M .	δ .	χ_A .
Cd	0.167	18.77	0.00	18.77	Cd ₃ (PO ₄) ₂	0.302	159.20	70.80	29.46†
CdO	0.239	30.70	4.61	26.09	CdC ₂ O ₄	0.265	53.13	28.50	24.60
Cd(OH) ₂	0.277	40.60	15.30	25.30	CdH ₂ C ₂ O ₄ ·2H ₂ O...	0.336	80.90	60.60	20.30
CdCO ₃	0.271	46.72	22.20	24.52	Cd(C ₂ H ₅ O ₂) ₂	0.413	119.90	93.10	26.80
CdS	0.343	49.57	15.60	33.97	CdC ₂ H ₃ O ₄	0.307	58.50	33.70	24.80
CdSO ₄	0.284	59.23	33.60	25.63	CdC ₂ H ₃ O ₄ ·H ₂ O ...	0.331	68.98	46.70	22.28
CdSO ₄ ·H ₂ O	0.341	77.25	46.60	30.65	Cd(C ₂ H ₅ O ₂) ₂ ·2H ₂ O	0.476	184.90	162.80	22.10
3CdSO ₄ ·8H ₂ O	0.374	95.94	68.60	27.34	Cd(C ₂ H ₃ O ₂) ₂	0.363	83.66	60.00	23.66
CdCl ₂	0.375	68.74	40.00	28.74	Cd(C ₂ H ₅ ·NH ₂) ₂ I ₂	0.426	236.00	221.12	14.88
CdCl ₂ ·H ₂ O	0.428	86.10	53.00	33.10	CdSO ₄ ·(N ₂ H ₅) ₂ SO ₄	0.367	135.90	107.60	28.30
Cd ₂ Cl ₇	0.357	249.30	140.00	27.32*	Cd(C ₂ H ₅ ON) ₂ ·2H ₂ O	0.518	226.10	210.61	15.49
CdBr ₂	0.320	87.10	62.00	25.10	Cd(BF ₄) ₂	0.351	100.40	81.74	18.66
CdI ₂	0.320	117.20	90.00	27.20	Cd(ClO ₃) ₂ ·2H ₂ O ...	0.272	85.76	78.00	7.76
CdF ₂	0.270	40.61	12.60	28.01	Cd(BrO ₃) ₂ ·H ₂ O ...	0.308	119.00	95.22	23.78
Cd(NO ₃) ₂	0.233	55.10	28.40	26.70	Cd(IO ₃) ₂	0.235	108.40	90.00	18.40
Cd(NO ₃) ₂ ·4H ₂ O ...	0.371	114.50	80.40	34.10					

* *I.e.*, $\frac{1}{2} \times 109.30$.

† *I.e.*, $\frac{1}{3} \times 88.40$.

The mean value of χ_A from all the above results is -24.85×10^{-6} .

The data given in Table II were obtained with the object of calculating χ_A in those cases where the literature did not supply the appropriate value of δ . In the determination of δ , the values of gram-atomic susceptibility, $K^* = -11 \times 10^{-6}$, $Na^* = -9.2 \times 10^{-6}$, $H = -3.04 \times 10^{-6}$, were obtained from the same source as δ (above).

TABLE II.

Substance.	χ .	χ_M .	Correction.	Group.	δ .
$C_6H_5NH_2 \cdot HI$	-0.514	-113.60	-3.04	$(C_6H_5 \cdot NH_2 + I')$	-110.56
KBF_4	-0.412	-51.87	-11.00	BF_4'	-40.87
$Na_2C_3H_2O_4$	-0.352	-52.10	-18.40	$CH_3(COO)_2'$	-33.70
$N_2H_4 \cdot H_2SO_4$	-0.437	-56.84	-3.04	$N_2H_5 \cdot SO_4'$	-53.80
C_6H_5NOH	-0.657	-95.35	-3.04	C_6H_5ON	-92.31
HIO_3	-0.267	-48.04	-3.04	IO_3'	-45.00
$KBrO_3$	-0.312	-52.11	-11.00	BrO_3'	-41.11

SUMMARY.

1. The mass susceptibilities of 30 cadmium compounds are recorded.
2. The atomic susceptibility of cadmium is found to be -24.85×10^{-6} .
3. Cadmium borofluoride is described.
4. Susceptibility values for the groups $(C_6H_5 \cdot NH_2 + I')$, BF_4' , $CH_2(COO)_2'$, $N_2H_5 \cdot SO_4'$, C_6H_5ON , IO_3' , BrO_3' are given.

The authors thank the Imperial Chemical Industries Ltd., and the Chemical Society for grants.

BEDFORD COLLEGE, N.W. 1.

[Received, March 7th, 1935.]