

THE WEISS CONSTANT OF PARAMAGNETIC IONS IN THE S-STATE.

Part I—Aqueous Solutions of Manganous Salts.

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1. Introduction.

IN several recent papers, Van Vleck¹ and others have discussed theoretically the influence of crystalline and molecular fields on the magnetic behaviour of paramagnetic ions. For ions in the S-state, *e.g.*, Mn^{++} , Fe^{+++} , whose magnetic moments are due wholly to the *spin* moments of the electrons (the contributions from the *orbital* moments of the electrons being absent), the theoretical deductions are simple. One important result is that for these ions the Weiss constant θ appearing in the well-known relation $\chi = C/(T - \theta)$ is zero; that is, the susceptibilities of the S-state ions conform to the simple Curie law of inverse dependence on temperature. This result has been verified experimentally by Jackson² and others in the case of manganous and ferric salts *in the solid state*. But, for manganous salts *in aqueous solution*, in which state one would *a fortiori* expect this result to hold true, the experimental data at present available do not confirm it; they yield large values for θ , *viz.*, between 24 and 28 for the Mn^{++} ion in aqueous solutions of $MnCl_2$, and between 22 and 27 for the ion in $Mn(NO_3)_2$ solutions.³

In view of this apparent anomaly the present writer undertook extensive measurements on the susceptibilities of some S-state ions in aqueous solutions of different concentrations and at different temperatures. In the present Part of this paper an account is given of the measurements on manganous salts.⁴ Studies on the magnetic behaviour of Fe^{+++} ions will form the subject-matter of Part II.

¹ See *Theory of Electric and Magnetic Susceptibilities*, Chap. XI.

² *Roy. Soc. Proc. (A)*, 1923, 104, 671.

³ See *International Critical Tables*, 6, 351. (In Table 13 on page 351, the signs prefixed to the values of θ for Mn^{++} ion should be *positive*.)

⁴ A preliminary short report of the results was published in *Nature*, Feb. 10, 1934.

2. Principle of the Experimental Method.

The measurements were made by the well-known Gouy weighing method. The solution whose susceptibility is to be determined is contained in a long test-tube of uniform bore, and it is suspended from one arm of an analytical balance in such a way that the lower end of the tube is in a uniform, horizontal magnetic field, and the upper level of the solution in the tube is well outside it. The lower part of the tube, where the cross-section of the column of solution varies, lies wholly in the uniform part of the field, while in the regions where the field is non-homogeneous the column of solution has uniform cross-section. If, under these conditions, w_1 be the weight of the solution when the magnetic field is on, and w_2 be the weight when the current through the magnet is switched off (w_1 and w_2 having been corrected for the weights of the empty tube with and without the field respectively), it can be shown that

$$w_1 - w_2 = \frac{1}{2} A (k - k') (H^2 - H_r^2 - H_0^2), \quad \dots \quad (1)$$

where A is the area of cross-section of the column of solution, k is its volume susceptibility, and k' that of air, and H is the uniform field in the region occupied by the lower portions of the test-tube when the current through the magnet is on, H_r is the residual field in the same region when the current is switched off, and H_0 is the field in the region of the upper level of the solution when the magnetic current is on. $H_r^2 + H_0^2$ is naturally very small in comparison with H^2 . The above relation enables us to calculate k when the other constants are known.

In the actual measurements, however, instead of determining the susceptibility of the solution directly in this manner, it was found more convenient to compare it with that of a standard liquid whose absolute susceptibility had already been determined by the above method. The comparison of the two susceptibilities was made by weighing successively the solution and the standard liquid in the field, under identical conditions. If K is the volume susceptibility of the standard liquid, and if W_1 and W_2 are its weights when the current through the magnet coils is on and off respectively (after correction for the weights of the empty tube), the corresponding weights for the solution being w_1 and w_2 , the volume susceptibility of the solution, k , is given by the relation

$$\frac{k - k'}{K - k'} = \frac{w_1 - w_2}{W_1 - W_2} \dots \dots \dots (2)$$

3. Description of the Apparatus.

A sketch of the experimental arrangement used is given in Fig. 1. A pyrex glass test-tube, which was slightly diamagnetic, was filled up to a

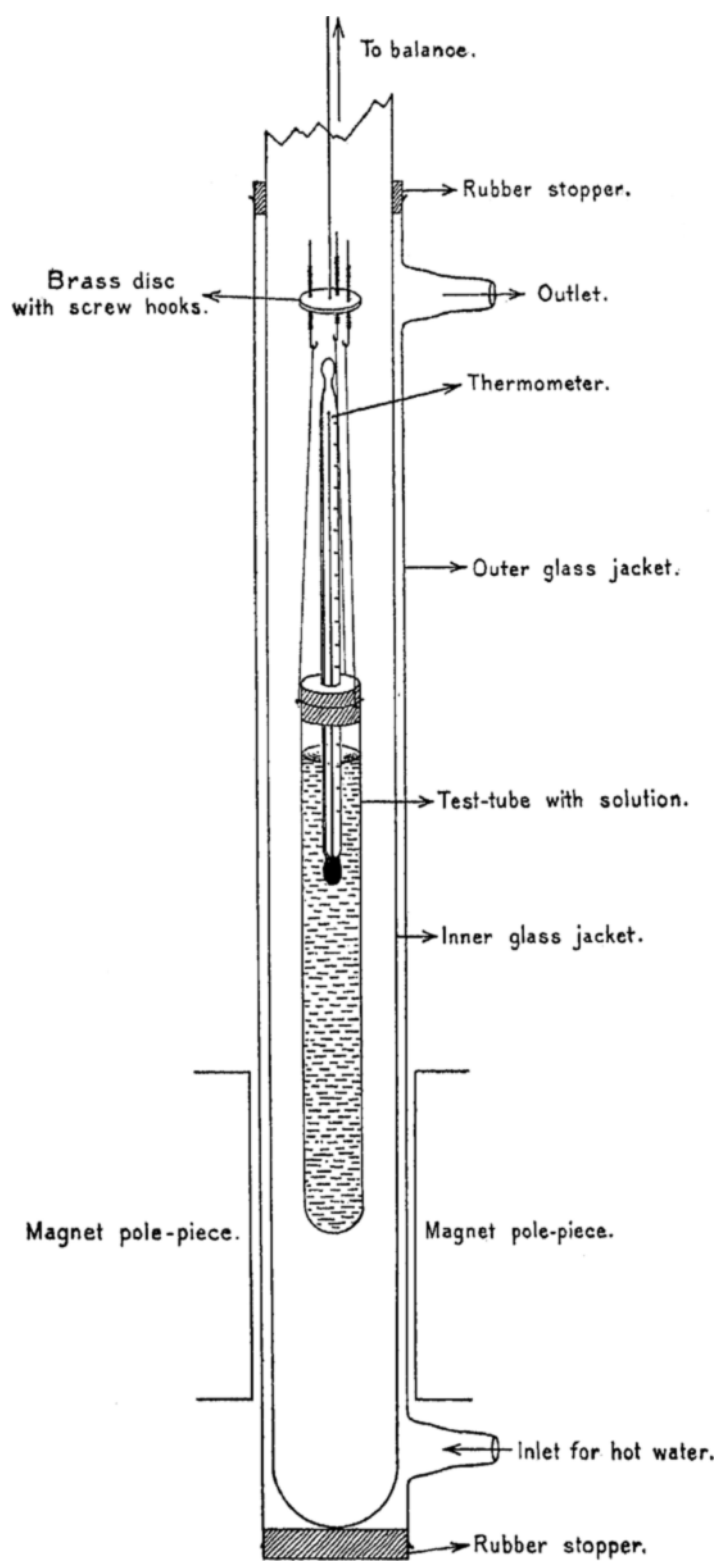


FIG. 1.

certain mark with the solution to be investigated, and was closed with an air-tight rubber stopper, through which was inserted a light, short, standardised mercury thermometer. The tube was suspended vertically by three pieces of thread from three vertical brass rods which could be screwed up and down in a horizontal brass disc. By adjusting the screws we could make the tube exactly vertical. The above combination was suspended by a piece of thread from one arm of an analytical balance, placed on a platform above the magnet. The test-tube was about 15 cms. long and of 1.5 cms. diameter, and was suspended as mentioned previously with its lower end in the centre of the magnetic field. The magnet pole-pieces had a large face area, of about 180 sq. cms., and the field near the centre was quite uniform; this was tested by placing a quantity of the paramagnetic solution in the test-tube so as to fill up its lower portions where the area of cross-section was not uniform, and weighing it with and without the magnetic field. The difference between the two weights was found to be practically the same as that due to the empty test-tube.

In order to prevent all convection currents, the test-tube and the part of the suspension outside the balance case were enclosed in a long glass tube with its lower end sealed off, and the upper end, which reached up to the balance case, closed by a sheet of asbestos with a small hole in the centre, through which passed the suspension thread leading to the balance arm.

Temperature control.—The long glass tube was surrounded by a jacket tube of slightly larger diameter. Through the space between the two tubes was allowed to circulate hot water from a thermostat of large capacity. It was thus possible to keep the solution whose susceptibility was to be measured, at any desired temperature. When steady conditions had been reached, it was found that the maximum variation of temperature in the region occupied by the test-tube was less than 0.1°C. The pole-pieces of the magnet were insulated from the heating arrangement by sheets of asbestos.

4. The Standard Liquid.

The standard liquid with which the solutions were compared for susceptibility, was an aqueous solution of nickel chloride of density 1.321 at 26°C. On chemical analysis by the dimethyl glyoxime method, it was found to contain 28.40 gms. of NiCl_2 per 100 gms. of solution.

The susceptibility measurements for this solution gave the following results:—

H	= 4378 gauss.
H_r	= 25 „
H_0	= 150 „

$$A = 0.1431 \text{ sq. cm.}$$

$$W_1 - W_2 = 0.1634 \text{ gm. at } 27^\circ.3 \text{ C.,}$$

after correcting for the force, *viz.*, $-.0034$ gm.,
due to the field acting on the empty suspended system.

From these data the susceptibility of the standard NiCl_2 solution comes out as 11.69×10^{-6} per c.c. at $27^\circ.3 \text{ C.}$,

and its temperature co-efficient was found to be about

$$-0.04 \times 10^{-6} \text{ per c.c. per } 1^\circ\text{C. rise of temperature.}$$

The susceptibility of NiCl_2 solutions has been studied extensively by Miss Brant,⁵ Cabrera, Moles and Guzman,⁶ Weiss and Bruins⁷ and others, and the value obtained here agrees well with the results of their measurements. Their values for a solution of 28.40% NiCl_2 at $27^\circ.3 \text{ C.}$ are as follows:—

Brant	11.69
Cabrera and others	11.71
Weiss and Bruins	11.74

5. Results.

The results of our measurements are collected together in Tables I to IX. c gives the concentration of the anhydrous salt in gms. per gm. of the

TABLE I.

MnCl_2 solution : $c = .3671$.
 $W_1 - W_2 = .1688 \text{ gm. at } 32^\circ.2 \text{ C.}$

T	$w_1 - w_2$	$k \times 10^6$	ρ	$k_m \times 10^6$	$\chi \times 10^4$	χT	Deviation from the mean value
305.8	.8404	57.14	1.397	112.6	142.2	4.35	.00
319.7	.7983	54.27	1.390	107.6	135.9	4.35	.00
330.2	.7694	52.31	1.384	104.2	131.6	4.35	.00
340.8	.7436	50.56	1.377	101.2	127.9	4.36	+ .01
341.9	.7382	50.19	1.377	100.5	126.9	4.34	— .01
353.0	.7113	48.36	1.370	97.40	123.1	4.35	.00
367.4	.6812	46.32	1.367	93.56	118.2	4.34	— .01
						Mean=4.35	

⁵ *Phys. Rev.*, 1921, 17, 678.

⁶ *Arch. de Geneve*, 1914, 37, 325.

⁷ *Proc. Amst. Acad.*, 1926, 18, 246.

TABLE II.

MnCl₂ solution : $c = .3671$.
 $W_1 - W_2 = .0775$ gm. at 27°·8 C.

T	$w_1 - w_2$	$k \times 10^6$	ρ	$k_m \times 10^6$	$\chi \times 10^4$	XT	Deviation from the mean value
300·8	·3866	58·14	1·400	114·4	144·4	4·34	—·01
306·3	·3796	57·09	1·396	112·6	142·2	4·36	+·01
313·0	·3710	55·80	1·392	110·3	139·3	4·36	+·01
316·9	·3660	55·05	1·390	109·0	137·6	4·36	+·01
320·8	·3590	53·99	1·388	107·1	135·2	4·34	—·01
325·8	·3534	53·15	1·385	105·7	133·4	4·35	·00
331·9	·3470	52·19	1·382	104·0	131·3	4·36	+·01
333·0	·3455	51·97	1·381	103·7	130·9	4·36	+·01
337·4	·3394	51·05	1·378	102·1	128·9	4·35	·00
343·0	·3339	50·22	1·375	100·7	127·2	4·36	+·01
353·0	·3226	48·52	1·369	97·78	123·5	4·36	+·01
358·6	·3172	47·71	1·366	96·39	121·7	4·36	+·01
363·0	·3118	46·90	1·363	94·98	120·0	4·36	+·01
368·0	·3068	46·15	1·360	93·69	118·4	4·36	+·01
						Mean=4·35	

solution. $W_1 - W_2$ denotes the force acting on the standard NiCl₂ solution due to the field (after correcting for that on the empty suspended system). The first column in the Tables gives the temperature T of the solution in degrees Kelvin and the second the force acting on the solution due to the field, namely $w_1 - w_2$ (in gms.) after correcting for that acting on the empty tube. Column 3 gives the volume susceptibility k and column 4 the density, ρ , of the solution. The next column gives the mass susceptibility, k_m , of the anhydrous salt, calculated from that of the solution on the basis of the additive law. This value is then corrected for the diamagnetism of the anion, and the susceptibility of the Mn⁺⁺ ion is calculated *per gm. ion*;

TABLE III.

MnCl₂ solution: $c = .2784$. $W_1 - W_2 = .1632$ gm. at 26°·7 C.

T	$w_1 - w_2$	$k \times 10^6$	ρ	$k_m \times 10^6$	$\chi \times 10^4$	XT	
296·9	·5708	·4096	1·283	116·6	147·2	4·37	
373·0	·4393	·3153	1·247	92·7	117·1	4·37	
						Mean=4·37	

TABLE IV.

Mn(NO₃)₂ solution: $c = .5948$. $W_1 - W_2 = .0775$ gm. at 27°·8 C.

T	$w_1 - w_2$	$k \times 10^6$	ρ	$k_m \times 10^6$	$\chi \times 10^4$	XT	Deviation from the mean value
298·6	·5570	83·76	1·746	81·14	145·6	4·35	·00
306·3	·5406	81·29	1·739	79·08	142·0	4·35	·00
311·9	·5278	79·37	1·734	77·44	139·1	4·34	-·01
318·0	·5182	77·93	1·729	76·26	137·0	4·36	+·01
323·0	·5076	76·33	1·724	74·91	134·6	4·35	·00
328·6	·4988	75·01	1·719	73·85	132·6	4·36	+·01
336·3	·4840	72·79	1·712	71·96	129·2	4·35	·00
339·7	·4786	71·97	1·709	71·28	128·1	4·35	·00
344·7	·4696	70·62	1·704	70·15	126·0	4·34	-·01
350·2	·4612	69·36	1·700	69·09	124·1	4·35	·00
354·1	·4544	68·34	1·696	68·23	122·6	4·34	-·01
361·3	·4442	66·80	1·680	66·94	120·3	4·35	·00
368·0	·4344	65·33	1·684	65·71	118·1	4·35	·00
						Mean=4·35	

TABLE V.

Mn(NO₃)₂ solution : $c = .5690$. $W_1 - W_2 = .1632$ gm. at $26^\circ.7$ C.

T	$w_1 - w_2$	$k \times 10^6$	ρ	$k_m \times 10^6$	$X \times 10^4$	XT
298.0	1.091	78.27	1.701	81.43	146.2	4.36
373.0	.8342	59.84	1.634	64.91	116.6	4.35
						Mean=4.36

TABLE VI.

Mn(NO₃)₂ solution : $c = .4334$. $W_1 - W_2 = .1632$ gm. at $26^\circ.7$ C.

T	$w_1 - w_2$	$k \times 10^6$	ρ	$k_m \times 10^6$	$X \times 10^4$	XT
297.7	.7216	51.77	1.481	81.59	146.5	4.36
373.0	.5544	39.78	1.426	65.30	117.3	4.37
						Mean=4.37

TABLE VII.

MnSO₄ solution : $c = .3755$. $W_1 - W_2 = .1632$ gm. at $26^\circ.7$ C.

T	$w_1 - w_2$	$k \times 10^6$	ρ	$k_m \times 10^6$	$X \times 10^4$	XT
295.5	.7524	53.97	1.491	97.60	147.7	4.36
373.5	.5778	41.46	1.452	77.23	117.0	4.37
						Mean=4.37

TABLE VIII.

MnSO₄ solution : $c = .3241$. $W_1 - W_2 = .0775$ gm. at 27°·8 C.

T	$w_1 - w_2$	$k \times 10^6$	ρ	$k_m \times 10^6$	$X \times 10^4$	XT	Deviation from the mean value
296·3	·2882	43·35	1·404	96·78	146·6	4·34	—·02
301·9	·2836	42·66	1·401	95·46	144·6	4·37	+·01
307·4	·2788	41·93	1·399	93·97	142·3	4·37	+·01
317·4	·2668	40·13	1·394	90·34	136·8	4·34	—·02
322·4	·2632	39·59	1·391	89·30	135·3	4·36	·00
328·6	·2578	38·78	1·388	87·70	132·8	4·36	·00
333·6	·2532	38·09	1·386	86·30	130·7	4·36	·00
341·9	·2456	36·94	1·381	84·02	127·3	4·35	—·01
346·9	·2426	36·49	1·378	83·20	126·0	4·37	+·01
351·9	·2380	35·80	1·375	81·85	124·0	4·36	·00
358·6	·2326	34·99	1·371	80·22	121·6	4·36	·00
364·1	·2280	34·30	1·367	78·89	119·5	4·35	—·01
368·0	·2254	33·91	1·365	78·14	118·4	4·36	·00
						Mean=4·36	

TABLE IX.

MnSO₄ solution : $c = .2773$. $W_1 - W_2 = .1632$ gm. at 26°·7 C.

T	$w_1 - w_2$	$k \times 10^6$	ρ	$k_m \times 10^6$	$X \times 10^4$	XT	
295·5	·4934	35·41	1·335	97·51	147·6	4·36	
373·0	·3778	27·11	1·296	77·29	117·1	4·37	
						Mean=4·37	

denoting this gm. ionic susceptibility by χ , the values of χ are given in column 6, while column 7 gives the product χT . As will be seen, χT is practically constant, *i.e.*, independent of temperature. The deviation of the actual value of χT at any particular temperature from the mean value is given in the last column of the Table; these values serve to show how closely the susceptibility of the Mn^{++} ion follows the simple Curie law.

6. *Temperature Dependence of Susceptibility.*

It is clear from the Tables that for all the solutions χT is practically independent of temperature: for any given solution the maximum variation of χT from its mean value is less than one-half of one per cent., which is about the order of the experimental errors. We can therefore conclude that, within the limits of our experimental errors, the susceptibility of the Mn^{++} ion in these solutions does obey the Curie law. This, as we have already mentioned in the introduction, is in conformity with the theoretical predictions.

7. *The Magnetic Moment of the Mn^{++} Ion.*

The absolute values of χT are also the same for the different solutions. They are collected together in Table X. The last column in the Table gives the corresponding magnetic moment μ of the Mn^{++} ion in terms of the Weiss magneton (assumed to be equal to 1123.5 c.g.s. e.m.u. per gm. ion).

The theoretical value of μ , calculated on the assumption that the Mn^{++} ion is in the ${}^6S_{5,2}$ state, is 29.4.

TABLE X.

Salt	c	χT	μ
MnCl ₂ ..	.3671	4.35	29.3
	"	4.35	29.3
	.2784	4.37	29.4
Mn(NO ₃) ₂ ..	.5948	4.35	29.3
	.5690	4.36	29.4
	.4334	4.37	29.4
MnSO ₄ ..	.3755	4.37	29.4
	.3241	4.36	29.4
	.2773	4.37	29.4

Summary.

Recent theoretical studies by Van Vleck and others on the magnetic behaviour of paramagnetic ions in the S-state, *e.g.*, Mn^{++} , predict that their susceptibilities should follow the simple Curie law of temperature dependence. The available experimental data for aqueous solutions of manganous salts, however, do not verify this result, the data conforming to the Weiss relation $\chi=C(T-\theta)$ where θ , instead of being zero as required by theory, has a value as high as 22 to 28. The present paper gives an account of some fresh measurements on aqueous solutions of $MnCl_2$, $Mn(NO_3)_2$ and $MnSO_4$ of various concentrations, by a convenient form of Gouy's method. The susceptibility data for the Mn^{++} ion obtained from these measurements do conform to the simple Curie law, as predicted by theory. Further the Curie constant of the Mn^{++} ion is found to be practically the same for all the solutions, being independent of the nature of the salt and of its concentration, and it corresponds to a magnetic moment of 29.3 to 29.4 Weiss magnetons, in agreement with the theoretical value for the ${}^6S_{5/2}$ state, *viz.*, 29.4.

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