obtained by evaporating the solution at room temperature under reduced pressure. The specific rotations of 0.4 and 0.2% solutions of the product so obtained were −84 and −91°, respectively. Partial racemization had taken place during the reaction.

A micro-analysis of this active product showed the formula to be $[\mathrm{Co\ en_2CO_3}]_2\mathrm{CO_3 \cdot 3H_2O}$. Calcd.: C, 22.29; H, 6.47; N, 18.92. Found: C, 21.96; H, 6.46; N, 18.94.

The two following reactions further confirm the fact that this is the levorotatory carbonato salt.

l-$[\mathrm{Co\ en_2CO_3}]_2\mathrm{CO_3} + \mathrm{HCl} \longrightarrow$ *d-cis*-$[\mathrm{Co\ en_2Cl_2}]\mathrm{Cl}$.—A sample of material obtained in the experiment outlined above was treated with alcoholic hydrogen chloride as described in a preceding paragraph. The purple powder so obtained had a specific rotation of +16° in 0.4% solution and of −33° in 0.1% solution within eleven minutes after the preparation of the solution. It racemized almost completely in two and a half hours; this is characteristic of aqueous solutions of the dichloro salt. Another sample of the product obtained from the same reaction showed a specific rotation of +14° in 0.4% solution.

l-$[\mathrm{Co\ en_2CO_3}]_2\mathrm{CO_3} + \mathrm{H_2C_2O_4} \longrightarrow$ *l*-$[\mathrm{Co\ en_2C_2O_4}]_2\mathrm{C_2O_4}$.—Only a small amount of material was available for this reaction; consequently, quantitative measurements were not attempted. The product of the reaction had the characteristic color of the oxalato salt and showed a small but distinct levo-rotation.

Summary

It has been observed that levo-dichlorodiethylenediaminocobaltic chloride reacts with potassium carbonate to give the dextro carbonato salt, but with silver carbonate to give the levo carbonato salt. This is the first indisputable example of the Walden inversion to be discovered among inorganic compounds.

Potassium oxalate and silver oxalate, reacting with levo-dichlorodiethylenediaminocobaltic chloride, yield the same product—the dextro oxalato salt.

Several other reactions of these compounds have been carried out.

These studies are being continued.

URBANA, ILLINOIS RECEIVED AUGUST 14, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Magnetic Susceptibilities of the Ions of Uranium in Aqueous Solution

BY ROBERT W. LAWRENCE

The magnetic susceptibilities of uranyl, quadrivalent, and trivalent uranium ions in aqueous solution have been determined by means of a modified Gouy method.

Magnetic measurements have been made on solid uranous oxalate and uranyl nitrate at room temperature by Bose and Bhar;[1] and on the solid oxides of uranium, also at room temperature, by Wedekind and Horst.[2] The magnetic susceptibilities of solid $\mathrm{UCl_4}$, $\mathrm{UO_2}$ and $\mathrm{U(SO_4)_2}$ from 90°K. to somewhat above room temperature have been determined by Sucksmith.[3] The only measurements in solution were by Pascal[4] who obtained, apparently as the result of a single experiment, a molal susceptibility of 3375×10^{-6} for uranous ion in 10% sulfuric acid.

Experimental Part

Method.—A modified Gouy method, described in detail by Freed,[5] was used for determining the magnetic susceptibilities of quadrivalent and trivalent uranium solutions. A glass cylinder filled with nickel chloride solution is suspended from the knife edge in a bath of the solution being examined as illustrated in Fig. 1. The end of the tube near K′ is at the center of the pole gap of an electromagnet of the Weiss type, which was described by Shaffer and Taylor.[6] The tubes used were standardized by balancing them magnetically against solutions of nickel chloride which were then analyzed to determine their nickel chloride concentration. From these data and the known susceptibilities of nickel chloride and water, the magnetic susceptibility of the solution and hence, also, the equivalent susceptibility of the tube was calculated. The equivalent susceptibilities of the tubes used are given in Table I. The calibrated tubes were then used to determine the susceptibilities of uranium salt solutions.

For calculating magnetic susceptibilities in solutions, Wiedemann's law, that the magnetic susceptibility of a solution is an additive function of the susceptibilities of the constituents of the solution, has been employed.

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(1) Bose and Bhar, *Z. Physik*, **48**, 716 (1928).

(2) Wedekind and Horst, *Ber.*, **48**, 105 (1915).

(3) Sucksmith, *Phil. Mag.*, [7] **14**, 1115 (1932).

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

(5) Freed, THIS JOURNAL, **49**, 2456 (1927).

(6) Shaffer and Taylor, *ibid.*, **48**, 843 (1926).

TABLE I

STANDARDIZATION OF TUBES—EQUIVALENT SUSCEPTIBILITY

Tube	$NiCl_2$ mole/liter	Density g./cc.	$\kappa \times 10^{6}$[a]
	A. At 20°		
1	0.5430	1.0621	+1.666
2	.3784	1.0434	+0.9425
3	.2560	1.0291	+ .4050
4	.1750	1.0205	+ .0486
5	.1268	1.0135	− .1621
6	.05935	1.0055	− .4583
7	.0391	1.0030	− .5471
	B.[b] At 0°		
2	0.3811	1.0466	+1.076
3	.2577	1.0317	+0.4945
4	.1762	1.0227	+ .1096
5	.1276	1.0155	− .1186
6	.0597	1.0073	− .4348

[a] Kappa is volume susceptibility (per cc.).

[b] Tubes 2 and 3 were calibrated at 0°; the magnetic equivalents of tubes 4, 5 and 6 at 0° were calculated on the basis of the changes in 2 and 3.

Water and nickel chloride were employed as magnetic standards. The value adopted for the specific susceptibility (χ) of water at 20° was the "I. C. T."[7] value, -0.720×10^{-6}, and for the molal susceptibility of nickel chloride at 20° Brant's[8] value of 4383×10^{-6}.

The values employed for the molal susceptibilities of the diamagnetic substances present in the solutions are: Cl^-, −22; ClO_4^-, −32; $SO_4^=$, −38; H^+, 0; Ac^- and HAc, −32.5; Na^+, −8 all $\times 10^{-6}$. The data for Ac^- and HAc are computed from Pascal's[9] determinations of the susceptibilities to be assigned to atoms appearing in organic molecules. A consideration of the data of Ikenmeyer,[10] Hocart[11] and Freed[5] in the light of Angus'[12] theoretical deductions makes the value -22×10^{-6} for Cl^- seem more probable than -20×10^{-6} which has generally been used. The remaining data were obtained from Freed's[5] diamagnetic measurements.

Materials.—The "c. p." nickel chloride was treated by the method of Ilinski and Knorre[13] to remove the 3–4% of cobalt that it contained and was then several times recrystallized. Uranic acid was used in the preparation of quadrivalent and trivalent uranium solutions. It was repeatedly washed with boiling water to remove any soluble impurities. The uranyl sulfate used was not subjected to any process of purification. These materials were then analyzed qualitatively by the systematic procedure of Noyes and Bray[14] and were further subjected to the most delicate tests available for the possible magnetic impurities—elements of the first transition group, Mo, W and the rare earths. Iron present in the $NiCl_2 \cdot 6H_2O$ was less than 0.001% by weight; in the uranic acid, H_2UO_4, 0.015%; in the uranyl sulfate,[15] UO_2SO_4, 0.003%. In the latter two there was about 0.1% of Mo which was subse-

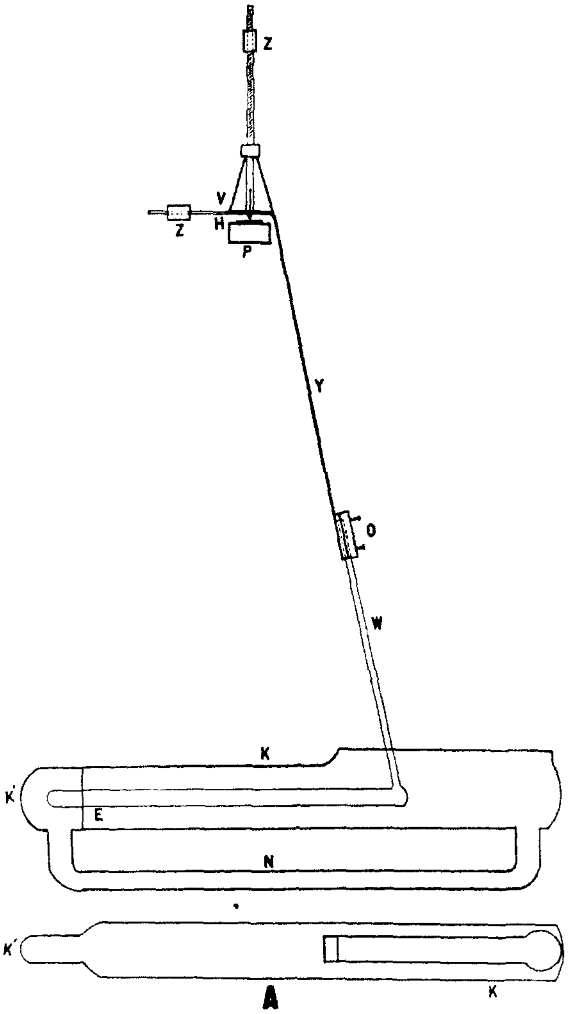

Fig. 1.

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[7] "I. C. T.," McGraw-Hill Book Co., New York, 1930, Vol. VII, p. 356, Table 3.

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

[9] Stoner, "Magnetism and Atomic Structure," E. P. Dutton & Co., New York, 1926, pp. 331–334.

[10] Ikenmeyer, *Ann. Physik*, [5] **1**, 169 (1929).

[11] Hocart, *Compt. rend.*, **188**, 1154 (1929).

[12] Angus, *Proc. Roy. Soc.* (London), **A136**, 569 (1932).

[13] Ilinski and Knorre, *Ber.*, **18**, 699 (1885).

[14] Noyes and Bray, "Qualitative Analysis for the Rare Elements," The Macmillan Co., New York, 1927.

[15] According to Wyrobouff, *Bull. soc. franc min.*, **32**, 340 (1909), uranyl sulfate crystallized from dilute sulfuric acid has the formula $2UO_2SO_4 \cdot H_2SO_4 \cdot 5H_2O$. An analysis of the material used corresponded approximately to that formula

quently removed. No other impurities could be detected. The reagents used were analyzed for iron and cobalt, which proved to be absent within the sensitivity of the tests. Corrections were made for the magnetic susceptibility of the iron present in the solutions investigated.

Analytical.—The nickel chloride solutions were analyzed for nickel electrolytically according to the procedure described by Treadwell and Hall.[16] The analyses were reproducible to 0.1–0.2%.

Solutions of uranous perchlorate and sulfate were titrated with standard 0.1 *N* potassium permanganate solution to determine their reducing power. The total uranium present in the solutions was determined by reducing the oxidized solutions in a Jones reductor and titrating with 0.1 *N* potassium permanganate, according to the method of Lundell and Knowles.[17] Titrations were reproducible to 0.1–0.2%. For the chloride solutions, 0.1 *N* potassium dichromate solution was substituted for permanganate, diphenylamine in concentrated sulfuric acid being used as indicator. The end-point was a trying one, hence the results with dichromate are less accurate than with permanganate. The dichromate solutions were standardized against the permanganate by titrating both against 0.1 *N* uranous sulfate solution, the result agreeing closely with the concentration calculated from the preparation of the solution.

Sulfate was determined by precipitation with barium chloride, corrections being made for a small amount of occlusion of uranyl chloride. Chloride was determined by titration with standard silver nitrate solution after oxidizing the uranium to the sexivalent state, precipitating it as ammonium diuranate and filtering it off.

Addition of excess uranyl sulfate to a trivalent uranium solution instantly changed the color from the reddish purple of the trivalent to the bright green of the quadrivalent, thus indicating that sexivalent and trivalent uranium do not exist together in the same solution.

Densities of the solutions were determined with a 10 cc. pycnometer, and are accurate within 0.01-0.02% for quadrivalent and sexivalent uranium solutions, but on account of hydrogen evolution only within 0.05% for trivalent uranium solutions.

Sexivalent Uranium.—Since the method used for determining the susceptibilities of quadrivalent and trivalent uranium is insufficiently sensitive for solutions more diamagnetic than 0.03 *M* $NiCl_2$, the ordinary Gouy method with a modification suggested by Dr. S. Freed was used. The method was practically the same as that used by Shaffer and Taylor[6] except that the lower half of the tube was filled with water, the upper half of the tube containing the uranyl sulfate solution. In this way the quantity measured is mainly the difference in magnetic susceptibility of water and the solution under investigation. The pole gap was about 1.5 cm., making it possible to obtain a maximum field strength of 30,000 gauss. The tube was calibrated by making a magnetic run with the upper half filled with carbon dioxide gas. Volume susceptibility of the solution is given by the equation

$$K = ((f_1 - f_2)/f_1)K_{H_2O}$$

where f_1 and f_2 are the magnetic pulls on the tube when the upper half contained carbon dioxide and uranyl sulfate, respectively.

Uranyl sulfate solutions were prepared by dissolving the hydrated salt in distilled water. Careful tests with permanganate solution showed that all the uranium was in the sexivalent state. A number of determinations were made for each solution at several field strengths.

Results of the magnetic measurements are given in Table II. No correction was made for the inherent diamagnetism of UO_2^{++}. The susceptibility obtained is in agreement with the value 57.03×10^{-6} found for UO_2^{++} in solid uranyl sulfate by Freed and Kasper.[18]

Quadrivalent Uranium

Preparation of Solutions.—Solutions of uranyl perchlorate, sulfate and chloride, prepared by dissolving uranic acid, H_2UO_4, in the appropriate acid, were reduced electrolytically to the quadrivalent state. A platinum spiral in a porous alundum cup filled with acid of the same concentration as that in the cell served for the anode and mercury as the cathode. Uranous chloride solutions were also obtained by air oxidation of previously prepared uranium trichloride solutions. The perchlorate solutions were prepared by dissolving a weighed amount of uranic acid of known uranium content in a known amount of perchloric acid to avoid the uncertainties of a tedious analysis for perchlorate.

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[16] Treadwell and Hall, "Analytical Chemistry," John Wiley and Sons, New York, 4th ed., Vol. II, p. 636.

[17] Lundell and Knowles, THIS JOURNAL, **47**, 2637 (1925).

[18] Freed and Kasper, *ibid.*, **52**, 4671 (1930).

TABLE II

MAGNETIC SUSCEPTIBILITY OF URANYL ION

t = 20°; concentrations in mole/liter

No.	UO_2^{++}	$SO_4^{=}$	H^+	Density g./cc.	$K \times 10^6$	UO_2SO_4[a] $\chi_M \times 10^6$	UO_2^{++} $\chi_M \times 10^6$
1	1.785	2.166	0.762	1.5820	−0.617	18	56
2	0.880	1.068	.376	1.2895	− .670	19	57
3	.308	0.377	.138	1.1025	− .7035	18	56
Mean						18	56

[a] (χ_M) is the susceptibility per gram mole. Correction for 0.026 mole per cent. of Fe^{+++} amounted to 4×10^{-6}.

Magnetic Measurements.—Results of magnetic measurements on quadrivalent uranium solutions are given in Tables III to VI, inclusive.

TABLE III

SUSCEPTIBILITY OF QUADRIVALENT URANIUM AS PERCHLORATE

t = 20°; concentrations in mole/liter

A. In 0.5 M $HClO_4$

Expt.	U^{++++}	UO_2^{++}	ClO_4^-	H^+	H_2O g./cc.	Density g./cc.	$K \times 10^6$	$\chi_{U^{+4}} \times 10^6$
1	0.6594	0.0264	3.20	0.51	0.8827	1.3658	+1.666	3635
2	.4610	.0225	2.39	.50	.9116	1.2658	+0.9425	3623
3	.3114	.0168	1.78	.51	.9337	1.1900	+ .4050	3631
4	.1538	.0151	1.15	.50	.9544	1.1100	− .1621	3640
5	.0722	.0115	0.81	.50	.9665	1.0676	− .4583	3630
6	.0473	.0014	.66	.47	.9704	1.0481	− .5471	3639
							Mean	3633
				B. In 3.5 M $HClO_4$				
7	.3119	.0229	4.78	3.48	0.7928	1.3524	+0.4050	3607
8	.2129	.0208	4.39	3.50	.8092	1.3057	+ .0486	3611

TABLE IV

SUSCEPTIBILITY OF QUADRIVALENT URANIUM AS SULFATE

A. At 20°; concentrations in mole per liter

No.	U^{+4}	UO_2^{++}	U^{+++}	SO_4^{--}	H^+	H_2O g./cc.	Density g./cc.	$K \times 10^6$	$\chi_{U^{+4}} \times 10^6$
1	0.2144	....	0.0002	0.86	0.86	0.9749	1.1094	+0.0486	3641
2	.1554	0.007	....	.76	.88	.9766	1.0877	− .1621	3659
				B. At 0°.					
3	0.1582	0.0125	....	0.784	0.90	0.9816	1.0988	−0.1186	3893
								Calculated to 20°	3628
								Mean 1, 2, 3	3643

TABLE V

SUSCEPTIBILITY OF QUADRIVALENT URANIUM AS CHLORIDE

t = 20°; concentrations in mole/liter

No.	U^{+4}	UO_2^{++}	Cl^-	H^+	H_2O g./cc.	Density g./cc.	$K \times 10^6$	$\chi_{U^{+4}} \times 10^6$
1	0.2130	0.0141	2.12	1.24	0.9658	1.0967	+0.0486	3700
2	.1540	.0104	1.53	0.99	.9754	1.0702	− .1621	3714
3	.0725	.0056	0.73	.43	.9876	1.0326	− .4583	3695
							Mean	3703

Hydrogen-Ion Concentration and Susceptibility of Uranous Ion.—Magnetic measurements were made on solutions with low hydrogen-ion concentrations obtained by adding sodium acetate to solutions of uranous perchlorate in dilute perchloric acid. When the hydrogen-ion concentration of a uranous solution is reduced to about 0.1–0.2 M, the color of the solution begins to change from green to brown. Thus, solutions 1 and 2 (Table VI) were quite brown, while solutions 5 and 6 showed only a slight brownish tinge. Data and results for this series of magnetic measurements are given in Table VI.

Decrease in susceptibility of uranous ion with decreasing hydrogen-ion concentration appears to be caused by the hydrolysis which may be represented by the equation

$$U^{+4} + H_2O = UO^{++} + 2H^+$$

It seems justifiable to assume this as the first step in the hydrolysis since insoluble basic salts such as $UOSO_4 \cdot 2H_2O$ have been described by Giolitti and Bucci.[19] In these uranous solutions with low hydrogen-ion concentrations the resultant paramagnetic susceptibility is presumably due to a mixture of U^{+4} and UO^{++} Relative concentrations of these two ions may be deduced from the resultant molal susceptibility given in the last column of Table VI and the values taken for molal susceptibilities of U^{+4} and UO^{++} which are, respectively, 3700×10^{-6} (from UCl_4 susceptibility) and 3110×10^{-6}, the limiting value as H^+ is reduced. Hydrogen-ion concentration was calculated by difference of positive and negative ions, except for Experiment 1 where it was calculated from the ionization constant of acetic acid, $K = 1.8 \times 10^{-5}$.

TABLE VI

MAGNETIC SUSCEPTIBILITY OF URANOUS ION: EFFECT OF HYDROGEN·ION CONCENTRATION

Concentrations in mole per liter; $t = 20°$

No.[b]	U^{IV} total	U^{+4}	UO^{++}	UO_2^{++}	ClO_4^-	Na^+	HAc	H^+	Log H^+	H_2O g./cc.	Density	$\chi_M \times 10^6$
A. $K = -0.5471 \times 10^{-6}$												
1	0.0548	0.000	0.0548	0.0000	0.256	0.173	0.146[a]	0.0001	−4.0	0.9762	1.0299	3111
2	.0549	.000	.0549	.0021	.266	.137	.137	.015	−1.82	.9778	1.0301	3107
3	.0520	.0155	.0365	.0026	.255	.082	.082	.033	−1.48	.9819	1.0278	3286
4	.0505	.0216	.0289	.0140	.3015	.040	.040	.09	−1.05	.9820	1.0315	3362
5	.0499	.0245	.0254	.0214	.333	...	...	.14	−0.85	.9830	1.0341	3400
6	.0508	.0215	.0293	.0062	.323	...	...	.17	− .77	.9837	1.0299	3360
7	.0473	.0424	.0049	.0014	.658	...	...	.48	− .32	.9704	1.0481	3639
B. $K = -0.1621 \times 10^{-6}$												
8	0.1549	0.1313	0.0236	0.0092	0.690	...	...	0.10	−1.00	0.9738	1.0819	3610
C. $K = -0.4583 \times 10^{-6}$												
9	0.0734	0.0511	0.0223	0.0198	0.424	0.105	0.105	0.03	−1.52	0.9733	1.0471	3521
10	.0732	.0569	.0163	.0092	.346	...	...	.07	−1.15	.9858	1.0401	3569

[a] Ac^- also present equal to 0.027 *M*. [b] Solution[6] 1–7 prepared by dilution of a stock solution with 0.54 *M* uranous ion and 0.35 *M* H^+. Solutions 8–10 prepared from another stock solution.

On Fig. 2 molal magnetic susceptibility of uranous ion is plotted against logarithm of hydrogen-ion concentration. From the data of Table VI a constant was estimated for the hydrolysis of uranous ion

$$K = (UO^{++})(H^+)^2/(U^{+4}) = 5 \times 10^{-3}$$

The curve in Fig. 2 was calculated on the basis of this hydrolysis constant and the magnetic susceptibilities of U^{+4} and UO^{++}. In these experiments no account has been taken of effect of ionic strength on activity coefficients. However, the data serve to show clearly that the change in magnetic susceptibility is caused by hydrolysis of the uranous ion.

Since solutions of uranous salts are readily oxidized by air to the sexivalent form at the low H^+ concentrations involved, it was necessary to protect the solutions in the bath with a thin layer of xylene. The samples, removed with pipets, were run into 10% sulfuric acid solution in which the rate of oxidation by air was found to be about 0.01% per hour.

Discussion of Magnetic Susceptibility of Quadrivalent Uranium Ion.—A series of preliminary measurements on uranous perchlorate solutions gave values about 0.5% higher than the results listed in Table IIIA. This was due to atmospheric oxidation of the uranous ion after the magnetic run was completed because the solutions were allowed to stand too long before titration.

It may be observed that Pascal's[4] result of 3375×10^{-6} for uranous ion in 10% sulfuric acid is low, probably because his solution contained a mixture of uranous and uranyl ions, and, as far as can be determined from his paper, he

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(19) Giolitti and Bucci, *Gazz. chim. ital.*, **35**, 151, 162 (1905). It may be observed in this connection that, on standing, solutions of uranous chloride or perchlorate, whose hydrogen-ion concentrations have been reduced to between 10^{-2} and 10^{-4} *M*, gradually become dark purplish-brown and quite opaque due to formation of a colloidal precipitate and after about a week deposit a purplish-brown precipitate leaving the supernatant liquid a clear green. This behavior is accelerated by heating. It is important, therefore, that the magnetic measurements be made before the hydrolysis has continued beyond the formation of UO^{++}. In the case of uranous sulfate, however, when the hydrogen-ion concentration has been reduced to about 0.01 *M*, a pale green precipitate, probably $UOSO_4 \cdot 2H_2O$, is deposited.

did not analyze his solutions to distinguish between the two, consequently assuming all the uranium to be present as uranous ion.

Quadrivalent uranium shows a parallelism with trivalent iron in its magnetic behavior. Thus, the work of Cabrera and Moles[20] showed a higher susceptibility for ferric ion as chloride than as sulfate and that its susceptibility diminishes rapidly with diminishing hydrogen-ion concentration, apparently toward the value for colloidal ferric hydroxide.

Sucksmith[3] recently determined the magnetic susceptibilities of a number of compounds in the solid state including UCl_4, UO_2, $U(SO_4)_2$ over a range from 90°K. to considerably above room temperature. Interpolation of his data gives the following molal magnetic susceptibilities at 20°: UCl_4, 4090; UO_2, 3930; $U(SO_4)_2{:}4.1\ H_2O$, 3430; and $U(SO_4)_2$, 2960; all $\times\ 10^{-6}$. It is of interest to note in connection with the last two values that as the amount of water associated with uranous sulfate increases the magnetic susceptibility tends toward the value 3643 reported in Table IV for uranous ion in uranous sulfate solution. Data in Table III show a lower susceptibility for uranous perchlorate in 3.5 *M* $HClO_4$ than in 0.5 *M*, whereas the results of Table VI indicate that the reverse would be more likely. The difference observed would be caused if too low a value were adopted for ClO_4^-.

Trivalent Uranium

Preparation of Solutions.—Trivalent uranium chloride and sulfate solutions were obtained by electrolytic reduction of the corresponding uranyl solutions (prepared as for quadrivalent uranium) according to the method described by Rosenheim and Loebel.[21] It was found that perchlorate ion is slowly reduced by U^{+3} and so the perchlorate was not prepared. To prevent oxidation of U^{+3}, carbon dioxide was bubbled through the electrolytic cell, which was packed in ice. In the first solutions prepared, U^{+3} was transformed rather rapidly to U^{+4} with evolution of hydrogen, but this difficulty was overcome by filtering the solutions through fine porous glass filters to remove small particles which might serve as nuclei for bubbles of hydrogen. The chloride solutions, being considerably more stable than the sulfate, were investigated at 20°, while the latter were maintained at 0° for the magnetic runs.

Solutions were transferred from electrolytic cell to bath via a Woulff bottle with careful precautions to prevent access of air. The bath was covered as much as possible and carbon dioxide was passed over the solution, which had a thin layer of xylene on the surface. For measurements at 0° the bath containing the solution was packed in ice inside a larger metal bath.

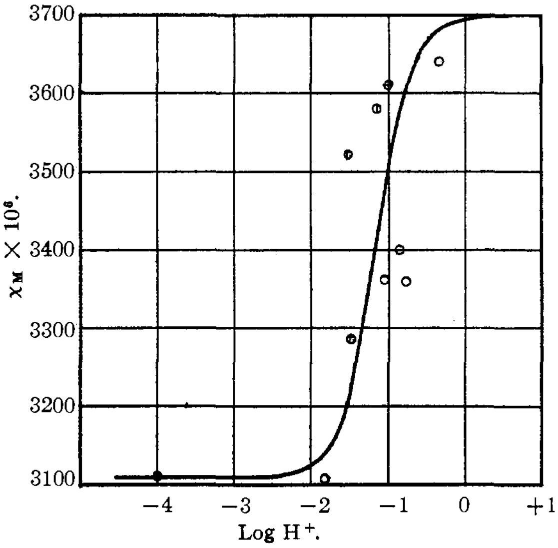

Fig. 2.—○, U^{+4} = 0.05 *M*; ⦶, U^{+4} = 0.07 *M*; ⊖, U^{+4} = 0.15 *M*; effect of H^+ concentration on magnetic susceptibility of quadrivalent uranium.

At the completion of each magnetic run, three samples were removed for determination of reducing power and three for total uranium using pipets through which carbon dioxide was passed first. The former were run into a flask containing dichromate solution in dilute sulfuric acid in excess of the amount necessary to oxidize U^{+3} to U^{+4}. A carbon dioxide atmosphere was maintained in the flasks until the uranium samples had been added. Titrations were completed as indicated under "Analytical." Correction was made for the small amount of decomposition occurring between the end of the run and the taking of each sample.

Magnetic Measurements.—Results of magnetic measurements on trivalent uranium ion are shown in Table VII.

Values obtained for the sulfates are somewhat lower than those obtained for the chlorides. In making the calculations, magnetic susceptibility of U^{+4} at 20° in the chloride solutions was taken

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(20) Cabrera and Moles. *Arch. Sci.*, [4] **35**, 425 (1913); **36**, 502 (1913).

(21) Rosenheim and Loebel, *Z. anorg. Chem.*, **57**, 234 (1908).

TABLE VII

THE SUSCEPTIBILITY OF TRIVALENT URANIUM

Concentrations in mole per liter

A. UCl_3. $t = 20°$

No.	U^{+++}	U^{++++}	Cl^-	H^+	G. H_2O/cc.	Density	$K \times 10^6$	$\chi_{U^{+++}} \times 10^6$
1	0.3538	0.0425	3.02	1.85	0.9537	1.1569	+0.9425	4338
2	.2370	.0329	2.86	2.01	.9509	1.1184	+ .4050	4339
3	.1697	.0157	2.30	1.62	.9607	1.0879	+ .0486	4309
4	.1175	.0149	.72	0.31	.9904	1.0478	− .1621	4346
5	.1622	.0278	4.80	4.20	.9082	1.1279	+ .0486	4338

B. $U_2(SO_4)_3$. $t = 0°$

No.	U^{+++}	U^{++++}	$SO_4^=$	H^+	G. H_2O/cc.	Density	$K \times 10^6$	$\chi_{U^{+++}} \times 10^6$ 0°	20°
1	0.1556	0.0351	0.512	0.54	0.9898	1.0907	+0.1096	4530	4220
2	.1107	.0281	.390	.34	.9932	1.0640	− .1186	4520	4210

as 3703×10^{-6} and in the sulfate solutions as 3643×10^{-6}. Hydrogen ion was determined by difference of charges on positive and negative ions. If account is taken of the fact that HSO_4^- is a rather weak acid, having a dissociation constant of 6×10^{-2} at 0° according to Noyes and Stewart,[22] H^+ for Experiments 1 and 2, Table VIIB, may be estimated at 0.17 and 0.10, respectively, which from Fig. 2 would give 3600 and 3500×10^{-6} for susceptibility of U^{+4} at these acid concentrations. The corresponding susceptibilities for U^{+++} at 20° would then be 4235 and 4240×10^{-6}.

Discussion of Errors.—Accuracy of the magnetic measurements is within 0.1–0.2% for solutions with uranium ions, U^{+3} and U^{+4}, at concentrations above 0.1 *M* and within 0.3% for solutions of lower concentration. Analytical accuracy is within about 0.2% for quadrivalent and 0.5% for trivalent uranium. Negative ion concentrations are considered accurate well within 2%. An error of 0.1% in the final result would be caused by an error of 2% in sulfate or perchlorate when mole ratio of negative ion to magnetic positive ion was 5 to 1, while an error of 10% in chloride concentration when the ratio Cl^-/U^{+4} is 10 to 1 would be necessary for a similar effect.

It is thought that susceptibility data for quadrivalent uranium are correct to 0.5%, Tables III, IV and V, and to 1% in Table VI. Values for trivalent uranium are probably good to 1% for the chloride and 2% for the sulfate. Since trivalent uranium sulfate decomposed with evolution of hydrogen fairly rapidly even at 0°, accurate measurements on it were difficult. These estimates do not take into account possible errors in diamagnetic corrections, or uncertainties in the values adopted for the magnetic standards.

Discussion of Results.—Magnetic moment in Bohr magnetons is given by

$$\mu = \sqrt{3RC}/5564 = 2.838\sqrt{C}$$

Magnetic susceptibilities are summarized in Table VIII. Values used for underlying diamagnetism $\times 10^6$ of uranium ions are: UO_2^{++}, −54; U^{+4}, −40; UO^{++}, −53; and U^{+3}, −46. These were estimated by rough extrapolation of Angus'[12] calculated values for a large number of negative ions. For the ions containing oxygen, -13×10^{-6} was allowed for each oxygen atom. Curie constants calculated on the assumption that the Curie law, $C = \chi T$, is obeyed in solutions and the magnetic moments calculated as above are also given in Table VIII.

TABLE VIII

MOLAL SUSCEPTIBILITY AND MAGNETIC MOMENT OF URANIUM IONS

Salt	Ion	$\chi_M \times 10^{6a}$	$\chi_M \times 10^{6b}$ Corrected	$C = \chi T$	Bohr magnetons
UO_2SO_4	UO_2^{++}	+56	+110	...	...
$U(ClO_4)_4$	U^{+4}	3633	3673	1.076	2.945
$U(SO_4)_2$	U^{+4}	3643	3683	1.079	2.95
UCl_4	U^{+4}	3703	3743	1.097	2.97
$UO(ClO_4)_2$	UO^{++}	3110	3163	0.927	2.73
UCl_3	U^{+++}	4335	4381	1.283	3.22
$U_2(SO_4)_3$	U^{+++}	4215	4261	1.248	3.17

[a] Molal magnetic susceptibility at 20°, uncorrected for diamagnetism of uranium ion, and *b* as corrected for underlying diamagnetism of uranium ion.

Spectroscopic magnetic moment of an atom or ion is given by the relation $\mu_j = g\sqrt{J(J+1)}$ where *g* is the Lande splitting factor and *J* represents the angular moment. It was suggested by Stoner[23] that the orbital component of the magnetic moment may be destroyed by inter-

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(22) Noyes and Stewart, THIS JOURNAL, **32**, 1133 (1910).

(23) Stoner, *Phil. Mag.*, **8**, 250 (1929).

actions with solvent molecules so that the spin moment alone contributes to the magnetic moment, whence $\mu_S = 2\sqrt{S(S+1)}$. However, Pauling[24] considered that the coupling between S and L might be only partially destroyed, resulting in a partial quenching of the orbital component, in which case the magnetic moment should lie between μ_S and μ_j.

TABLE IX

MAGNETIC MOMENTS—COMPARISON OF OBSERVED AND THEORETICAL

	Experimental data		Theoretical data Russell–Saunders coupling				*jj* Coupling		
Ion	Neg. ion	μ_B	Electrons	Lowest state	μ_j	μ_S		g	μ
U^{+4}	ClO_4^-	2.945	$6d^2$	$^3H_4$	3.58	2.83	2	4/5	1.96[a]
	$SO_4^{=}$	2.95					3/2, 3/2	4/5, 4/5	2.19[b]
	Cl^-	2.97	6d5f	$^3F_2$	1.63	2.83	4	117/140	3.74[a]
UO^{++}	ClO_4^-	2.73					3/2, 5/2	4/5, 6/7	3.02[b]
U^{+3}	Cl^-	3.22	$6d^3$	$^4F_{3/2}$	0.775	3.87	3/2, 3/2, 3/2	4/5, 4/5, 4/5	2 68[b]
	$SO_4^{=}$	3.17	$6d^25f$	$^4I_{9/2}$	3.62	3.87	3/2, 3/2, 5/2	4/5, 4/5, 6/7	3.35[b]

[a] Theoretical magnetic moment for probable lowest state.

[b] Assuming coupling between individual *j*'s broken

$$\mu = \sqrt{g_1^2 j_1(j_1+1) + g_2^2 j_2(j_2+1) + \ldots}$$

Quadrivalent uranium may have two and trivalent uranium three 6d electrons, although it is conceivable that one of these may be a 5f electron. In Table IX data are given showing observed and theoretical values of magnetic moment in Bohr magnetons for both Russell–Saunders and (*jj*) coupling since the latter may take the place of Russell–Saunders coupling in heavy atoms. Experimental magnetic moments for U^{+4} lie between μ_S and μ_j for a $6d^2$ electron configuration, for UO^{++} between μ_j and μ_S for 6d5f, and for U^{+3} between μ_j and μ_S for $6d^3$. Values for (*jj*) coupling show no very satisfactory agreement with experimental results. Values are also given on the assumption, analogous to that for Russell–Saunders coupling, that couplings between the individual electron *j*'s might be broken.

Experimental magneton numbers were calculated on the assumption, which may or may not be justified, that Curie's law is obeyed in solutions. Sucksmith[3] obtained data for $U(SO_4)_2 \cdot 4.1\ H_2O$ indicating a Δ term (*cf.* the Weiss law $C = \chi(T + \Delta)$) of 85 and a magnetic moment of 3.20 magnetons. If the values given for the sulfate in Table IV of 3893 for U^{+4} at 0° and 3650 at 20° are used in the Weiss equation, a Δ term of 27 is obtained and a magnetic moment of 3.06 magnetons is calculated. However, the accuracy of the data is such that it seems preferable to average the data as was done.

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Summary

Magnetic susceptibilities of uranyl ion, UO_2^{++}, of the quadrivalent uranium ions, U^{4+} and UO^{++}, and of trivalent uranium ion, U^{+++}, have been determined for aqueous solutions.

The effect of varying the hydrogen-ion concentration on the susceptibility of quadrivalent uranium has been investigated.

Magnetic susceptibilities obtained have been converted to magnetic moments expressed in Bohr units which were then compared with theoretical spectroscopic magnetic moments. Experimental magnetic moments in Bohr magnetons are 2.97 for quadrivalent uranium as chloride, and 2.95 for corresponding sulfate and perchlorate; 2.73 for UO^{++}; and 3.22 for trivalent uranium ion as chloride.

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(24) Pauling, THIS JOURNAL, 53, 1392 (1931).