8. Excited mercury atoms can decompose a formic acid molecule in two ways.

PRINCETON, NEW JERSEY

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

THE MAGNETIC SUSCEPTIBILITIES OF THE POSITIVE IONS OF VANADIUM

BY SIMON FREED

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The view of Lewis[1] that the magnetic moments associated with the electrons in atoms or molecules usually neutralize each other in pairs has been confirmed by magnetochemical observations and by the analyses of spectra.[2,3,4] No atom or molecule containing an odd number of electrons is known to be diamagnetic.[5] However, there are numerous examples of paramagnetic atoms and molecules which contain an even number of electrons. Aside from the oxygen molecule, all such cases are to be found toward the centers of the long periods of the Periodic Table. The ions of vanadium investigated here occur in the first of these periods.

Hund's[6] remarkable success in arriving at the magnetic moments of the ions of the rare earths in solution, from spectroscopic information alone, has raised the hope that the electronic configurations of all ions in solution might be determined and that an insight into their behavior might be obtained from spectroscopic data and the quantum theory.

A word should be said upon the relation of spectra to magnetic moments. In the evaluation of spectral lines it has been found possible to assign definite quantities of angular momentum to the electron (or electrons) in each orbit. The angular momentum of an electron is intimately related to its magnetic moment. More recently, the electron itself is pictured as spinning and the ratio in Bohr units of its magnetic moment to its mechanical moment is two. In general, the ratio between the magnetic moment and the resultant mechanical moment is some simple rational fraction, a value deduced in each case from observations on the anomalous Zeeman effect.

Hund[6] supposed that the regularities found in the spectra of other ions existed in the spectra of the rare earths. This assumption led him to

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[1] Lewis, THIS JOURNAL, **38**, 762 (1916); "Valence and the Structure of Atoms and Molecules," Chemical Catalog Co., New York City, **1923**.

[2] Lewis, *Chem. Reviews*, **1**, 231 (1925).

[3] Kemble, "Molecular Spectra in Gases," p. 304, *Bul. Nat. Res. Council*, **1926**, No. 57.

[4] Sommerfeld, "Three Lectures in Atomic Physics," Methuen and Co., London **1926**, Lecture III.

[5] Taylor and Lewis, *Proc. Nat. Acad. Sci.*, **11**, 456 (1925).

[6] Hund, *Z. Physik*, **33**, 855 (1926).

assign in an unbroken sequence the character of the basic term of each ion, that is, the net angular momentum of the ion in its most stable state. Then, by applying the rules holding universally in the anomalous Zeeman effect, he calculated the magnetic moment of the ion in the gas. These values were almost identical with the values obtained from the crystals and from solution.[7]

Laporte and Sommerfeld[8] have extended Hund's ideas to apply to the series of the elements from scandium to copper. Their predictions demand a knowledge of the energy intervals between the multiplet levels of the basic terms of the ions. Because of the complexity of these atoms such a knowledge will not be obtained for a considerable time. Moreover, the work to be herein described will show their conclusions to be highly improbable.

Magnetic Measurements in Solution

Magnetic susceptibilities of many substances have been measured but most of the results obtained have been vitiated by the magnetic impurities in the samples investigated. Recently some accurate work has been done.

Among the measurements that deserve the highest confidence are those of water and those of nickel chloride solutions—both of which were taken as standards for this investigation. The value adopted for the gram susceptibility of water at 20° was -0.720×10^{-6}, based upon the elaborate determination of Piccard and Devaud,[9] who obtained -0.7199×10^{-6} with a probable relative error of 0.01%.[10]

The value 4383×10^{-6} was used for the molal susceptibility of $NiCl_2$ at 20.0°. This is the value obtained by Brant[10] and was found to be constant over a 3000-fold change in concentration with a claimed accuracy of 0.1% in the portion of the range used here as standard.[11]

Principle of Method

The method used was an adaptation of the Gouy method which depends upon having a cylinder with one end in a uniform field and the other end in a field of negligible intensity. The force on the cylinder depends upon the difference between the susceptibility per unit volume of the medium surrounding the cylinder and the susceptibility of the cylinder.

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[7] Decker, *Ann. Physik,* **79,** 324 (1926).

[8] Laporte and Sommerfeld, *Z. Physik,* **40,** 333 (1926).

[9] Piccard and Devaud, *Arch. sci. phys. Nat.,* **5,** 2 (1920).

[10] Brant (*Phys. Rev.,* **17,** 678 (1921)), whose values for nickel chloride were used here, by assuming the above value for water, checked the susceptibility of air obtained by Soné (*Phil. Mag.,* March, 1920, p. 345) within 0.1%. Seves' (*Ann. chim. phys.,* [8] **27,** 189, 425 (1912)) value for water was -0.720×10^{-6}. Weiss and Piccard (*Compt. rend.,* **155,** 1234 (1912)) obtained -0.7193×10^{-6}.

[11] The results obtained by Miss Brant checked well with those of Cabrera, Moles and Guzman (*Arch. Sci. Phys. Nat.,* **37,** 325 (1914)) and those of Weiss and Bruins (*Proc. Acad. Sci. Amsterdam,* **18,** 346 (1915)), whose accuracy was probably within 1%.

A null method utilizing this fact was suggested by Professor G. N. Lewis. Cylinders of various susceptibilities were balanced horizontally against liquids of known susceptibility. These cylinders were then used to determine the unknown susceptibilities of the solutions under investigation.

Various devices were tried out to realize the advantages of such a null method. In the earlier experimentation on the method the writer had the benefit of the coöperation of Dr. S. S. Shaffer.

Apparatus

EW is a Pyrex glass tube, 11 mm. in diameter at E and about 1 mm. at W. It is filled with nickel chloride solution and sealed at O where it is fastened by means of a strip of compressed paper and screws to a brass rod Y grooved to give the rod lightness and rigidity. The latter is fastened above to an angled brass frame which has an agate knife-edge H. The knife-edge rests on a polished horizontal agate plate fastened to a heavy brass bar. The latter is screwed to 4″ × 4″ uprights which are in turn bolted to the iron base of a powerful electromagnet. ZZ are nuts with which the center of gravity of the swinging system can be adjusted for its optimum sensitivity.

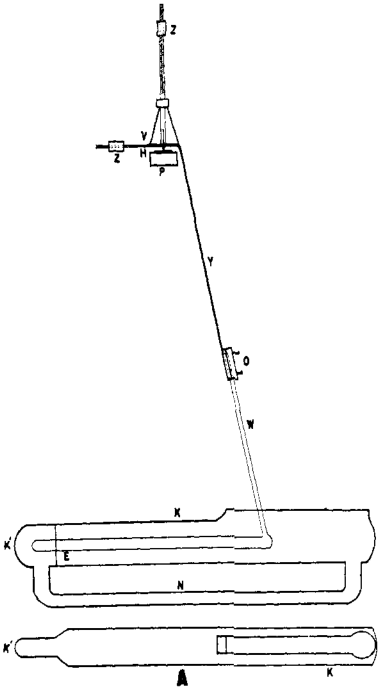

Fig. 1.

The "bath" in which the tube E is immersed is shown with its top view at A. The tube N about 12 mm. in diameter permits the circulation and mixing of the solution, which is done by a stirrer (not drawn) in the extreme right end of the bath, above the tube N. The portion EK′ fits between the pole pieces of the magnet. The latter is of the Weiss type. It produces a field of about 19,000 gauss in a pole gap 2 cm. in diameter and 2 cm. long.

Materials

All the vanadium salts used were made from the same sample of hydrated vanadium pentoxide. The latter and the nickel chloride used for standardization were analyzed by the systematic analytical procedure of Noyes and Bray[12] and of Noyes, Bray and Spear[13] for the common and rarer elements. The sensitive color reactions for Fe, Co, Mn, Cr, Ni, Mo and Ti were taken advantage of and comparison was made with color standards in water or ether or, in the case of vanadium, in the vanadium solutions themselves, so as to eliminate any influence of the dissolved substances upon the sensitivity of the tests.

Sodium chloride was tested only for iron before its diamagnetic measurements Perchloric acid and sulfuric acid were analyzed only for the commoner substances.

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[12] Noyes and Bray, This Journal, **29**, 137 (1907).

[13] Noyes, Bray and Spear, *ibid.*, **30**, 481 (1908).

The hydrated vanadium pentoxide was found to contain 0.35 mole of sodium in the form of vanadate and 0.015 mole of acetate for every mole of vanadium in the sample. The amounts of potassium permanganate used to oxidize the same sample of vanadium pentoxide twice in succession after it had been reduced with sulfur dioxide were practically identical.

Because of its diamagnetism the effect of the acetate upon the results was neglected.

Analysis

The quantitative analysis of vanadium in its different valence states was made by titrating with standard potassium permanganate solution, which oxidized all of the vanadium to the quinquivalent condition. Then through the resulting solution sulfur dioxide gas from a cylinder was passed which reduced all of the vanadium to the quadrivalent state. By reoxidizing this quadrivalent vanadium with the standard potassium permanganate solution the total vanadium was found. These two titrations were sufficient to determine the concentrations of vanadium of two different valences. It was assumed that not more than two can coëxist in the solution because of their extreme reactivity.

Rutter[14] has reported the rapidity with which these ions interact.

The reduction of vanadium by sulfur dioxide for its quantitative determination was highly recommended by Treadwell and Hall,[15] Hillebrand[16] and Lundell and Knowles,[17] whose precautions were strictly followed.

The sulfate present in solutions containing quadrivalent vanadium (VO^{++}) was found to be quantitatively precipitated by barium chloride solution. In the analyses for sulfate, the trivalent and bivalent vanadium solutions were left exposed to the air to be oxidized to the quadrivalent state before the sulfate analyses were made.

Mode of Operation and Standardization of Tubes

Five tubes such as EW were filled with different concentrations of nickel chloride solution and sealed at O. Each tube was standardized by filling the bath in which the tube was immersed with pure nickel chloride solution and by adjusting its concentration until the tube would swing neither in one direction nor in the other when the magnetic field was on. After the balance had been reached in a field of about 19,000 gauss, samples were taken out of the bath and analyzed. The density of the solution was taken and also its temperature.

In the case of unstable substances, calibrated pipets were "washed" with carbon dioxide until they touched the bath. The pipet filled with the solution was allowed to drain to the mark and then into a flask filled with carbon dioxide and containing sulfuric acid solution and a known amount of potassium permanganate. As the pipet was being drained into the flask, a stream of carbon dioxide was passed just over the top of the pipet.

During the standardization of the tubes the effect of one drop of water in 175 cc. of solution in the bath could be detected when the more concentrated solutions (about 0.20 molal nickel chloride) were being measured.

In the following table are the concentrations of nickel chloride which balanced each tube and the corresponding susceptibilities per unit volume. These values were

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[14] Rutter, *Z. anorg. Chem.*, **52,** 368 (1907).

[15] Treadwell and Hall, "Analytical Chemistry," John Wiley and Sons, Inc., New York City, 4th edit., Vol. II, p. 636.

[16] Hillebrand, "Analysis of Silicates," United States Geological Survey Bulletin, No. 78.

[17] Lundell and Knowles, THIS JOURNAL, **43,** 1560 (1921).

computed by taking —0.720 × 10^{-6} as the susceptibility of a gram of water and 4383 × 10^{-6} as the susceptibility of a mole of nickel chloride at 20°.

A variation of 3° had no measurable effect upon the concentration necessary to balance each tube.

Independent magnetic measurements of the same tube gave identical results as far as analyses could disclose, that is, within 0.2%.

TABLE I

STANDARDIZATION OF TUBES

Tube	Molal concn., $NiCl_2$	Density	$\frac{\text{G. } H_2O}{\text{cc. soln.}}$	$\chi_{cc.}^{20°} \times 10^{6}$ [a]
1	0.2766	1.0310	0.9951	+0.4958
2	.2191	1.0242	.9958	+ .2433
3	.1618	1.0176	.9966	− .0083
4	.1119	1.0115	.9970	− .2275
5	.07927	1.0076	.9973	− .3707

[a] $\chi_{cc.}^{20°}$ is the susceptibility per cc. at 20°.

Diamagnetic Measurements

All of the constituents of the solution have associated with them definite amounts of diamagnetism. The diamagnetism of the magnetic ions will be discussed later. The diamagnetism of all the other ions was determined by the Gouy method described by Shaffer and Taylor.[18]

Wiedemann's law of the additivity of ionic susceptibilities was used in these evaluations as well as in the paramagnetic ones. To determine the susceptibilities of single ions the diamagnetism of one of the ions had to be known from some other source. The value —20 × 10^{-6} was taken for the atomic susceptibility of Cl^-. This value is in accord with the theoretical considerations on diamagnetism of Joos,[19] who obtained —19.5 × 10^{-6}, and the experimental work of Pascal,[20] who obtained —20 × 10^{-6} from his magnetic work on organic compounds and on chlorine gas.

The following table gives the diamagnetic susceptibilities. They are the mean of a number of measurements and are good to about 5%.

TABLE II

DIAMAGNETIC MEASUREMENTS

Subs.	Times measured	Molality	Density	$\frac{\text{G. } H_2O}{\text{cc. soln.}}$	$\chi_{\text{cc. soln.}}^{20°}$	$\chi_{\text{moles}}^{20°}$ solute
$NaClO_4$	4	5.47	1.3866	0.670	−0.740	−41 × 10^{-6}
NaCl	5	4.63	1.1730	.901	− .800	−32.6 × 10^{-6}
$HClO_4$	3	9.04	1.522	.613	− .720	−31 × 10^{-6}
H_2SO_4	2	0.993	1.0580	.961	− .732	−41 × 10^{-6}
H_2SO_4	2	17.9	1.8323	.0733	− .752	−39 × 10^{-6}

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[18] Shaffer and Taylor, THIS JOURNAL, **48**, 843 (1926).

[19] Joos, *Z. Physik*, **19**, 347 (1923).

[20] (a) Pascal, *Ann. chim. phys.*, [8] **16**, 520 (1909); (b) **19**, 1 (1910); (c) **25**, 289 (1912); (d) **29**, 218 (1913).

From Table II the following values were adopted, $\chi^{20°}_{ClO_4^-} = -28 \times 10^{-6}$; $x_{SO_4^{--}} = -37 \times 10^{-6}$; $\chi_{Na^+} = -12 \times 10^{-6}$.

Quadrivalent Vanadium Ion

The basic idea which was constantly kept in mind was to introduce a minimum of foreign matter into the solutions so as to keep the corrections as small as possible. All solutions were prepared at room temperature or below to avoid hydrolysis and other complications that might accompany higher temperatures. It appears that if cobalt chloride solution be warmed its molal susceptibility thereafter varies with the concentration but it remains constant if not warmed.

To minimize the danger of the formation of complex ions Professor G. N. Lewis suggested that the perchlorates should be used whenever feasible.

Preparation of Solution.—$VO(ClO_4)_2$ solution was prepared by suspending the hydrated vanadium pentoxide in a solution of perchloric acid containing a known amount of the acid. Hydrogen sulfide gas made by dilute sulfuric acid reacting with iron sulfide was washed in water and then conducted slowly into the solution. The liberated sulfur was filtered off through a Jena porous-glass filter and then the excess of hydrogen sulfide was pumped off at room temperature with a Nelson vacuum pump. Some of the blue $VO(ClO_4)_2$ solution was taken and carbon dioxide was passed through it and then into very dilute potassium permanganate solution for five minutes without decolorizing the pink solution.

As some authors claim that vanadium pentoxide reduced with hydrogen sulfide requires a little more potassium permanganate for its reoxidation than vanadium pentoxide reduced with sulfur dioxide, the $VO(ClO_4)_2$ solution freed from hydrogen sulfide was shaken with solid vanadium pentoxide and then filtered. Upon titrating the resulting solution with potassium permanganate solution, reducing with sulfur dioxide and titrating again, about 0.5% of quinquivalent vanadium was found in the solution. The amount of the latter increased to 0.9–1.0% by the time the last of the magnetic measurements on quadrivalent vanadium were finished.

The effect of so small an amount of diamagnetic[21] substance was negligible.

The solution was diluted to a definite volume before any had been removed for detecting unevaporated hydrogen sulfide in order to fix the concentration of ClO_4^-. The concentration of total vanadium was determined in this volume and since the total number of moles of perchloric acid was known, a definite ratio of the concentrations of total vanadium to total perchlorate was fixed. This ratio remained unaltered

TABLE III

SUSCEPTIBILITY OF QUADRIVALENT VANADIUM ION

	Molal concn., VO^{++}	Concn. $Na^+ \times VO^{++}$	Concn. total $ClO_4 \times VO^{++}$	Concn. $H^+ \times VO^{++}$	$\frac{\text{G. } H_2O}{\text{cc. soln.}}$	Density of soln.	$\chi \times 10^6$, cc. soln.	$\chi_{20°} \times 10^6$ Moles VO^{++}
I	0.9555	0.35	2.57	0.214	0.900	1.2152	+0.4958	1275
II	.7553	.35	2.57	.214	.920	1.1695	+ .2433	1277
III	.5585	.35	2.57	.214	.941	1.1255	− .0083	1276
IV	.3858	.35	2.57	.214	.957	1.0855	− .2275	1274
V	.2739	.35	2.57	.214	.971	1.0618	− .3707	1274

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[21] Ref. 20 a, p. 565.

throughout the various magnetic runs as it obviated the repeated analyses for ClO_4^-. The concentration of total vanadium in any solution automatically gave the concentration of total perchlorate.

Magnetic Measurements.—The data obtained on quadrivalent vanadium ion are given in the preceding table.

Trivalent Vanadium Ion

Preparation of Solution.—Rutter's[14] suggestion that platinized platinum serve as the cathode in the electrolytic reduction of quadrivalent vanadium to trivalent vanadium was adopted.

As perchlorate ion is reduced by trivalent vanadium ion, the sulfate was used.

Vanadyl sulfate, prepared as described in the preceding section, was reduced in an electrolytic cell of about 200 cc. capacity. The latter consisted of a cathode of platinized platinum and of an anode of platinum wire. The latter was dipped into a dilute sulfuric acid solution in an alundum thimble. Carbon dioxide at least 99% pure, which was passed through potassium permanganate solution and then through distilled water, was bubbled through the electrolyte.

The color changed gradually from a bright blue to a greenish-brown. This brown solution was filtered in an atmosphere of carbon dioxide through a Jena porous-glass filter.

Magnetic Measurements.—The data of the magnetic measurements are given in the following table.

TABLE IV

SUSCEPTIBILITY OF TRIVALENT VANADIUM ION

Brown variety, assuming trivalent present only as VO^{+}[a]

	Molal concn., VO^{+}	Concn. VO^{++}	Concn. V^{++}	Concn. Na^{+}	Concn. SO_4^{--}	$\frac{\text{G. } H_2O}{\text{cc. soln.}}$	Density	$\chi \times 10^6$, cc. soln.	$\chi_{20°} \times 10^6$, VO^{+}
I	0.3216	0.1116	....	0.1520	0.614	0.985	1.0765	+0.4958	3382
II	.2559	.08011	....	.1220	.476	.987	1.0580	+ .2433	3405
III	.1942	...	0.0086	.0710	.284	.991	1.0337	− .0083	3415
IV	.1289	.0534	....	.0638	.259	.992	1.0308	− .2275	3331

Green variety, assuming trivalent present only as V^{+++}[b]

	Molal concn. V^{+++}	Concn. VO^{++}	Concn. H^{+}	Concn. Na^{+}	Concn. SO_4^{--}	$\frac{\text{G. } H_2O}{\text{cc. soln.}}$	Density	$\chi \times 10^6$, cc. soln.	$\chi_{20°} \times 10^6$, V^{+++}
V	0.2160	0.0163	0.33	0.0813	0.544	0.988	1.0538	−0.0083	3261
VI	.1528	.0081	.21	.0563	.370	.991	1.0366	− .2275	3208
VII	.1076	.0073	.15	.0402	.264	.994	1.0261	− .3707	3216

[a] If an attempt were made to calculate the susceptibility on the basis of V^{+++}, that is, disregarding the contradiction of inequality of positive and negative constituents, all values of magnetic moments would be about 0.3% higher.

[b] The deficiency in sulfate to form just a neutral solution if V^{+++} were assumed is: I, 0.053 molal; II, 0.046 molal; III, 0.050 molal; IV, 0.019 molal. (The greater the deficiency, the less the H^{+} concentration.)

A few remarks are necessary here. The brown solution of the preceding paragraph was measured magnetically and then analyzed. It was found to be a mixture of trivalent and quadrivalent vanadium; but the amount of sulfate present, known to within 1%, did not agree with the formula

V^{+++} for trivalent vanadium but accorded well with the assumption that the trivalent vanadium was present chiefly as VO^+.

In the literature trivalent vanadium is described as green and its formula is usually given as V^{+++}. Indeed, the crystals of $V_2(SO_4)_3$ have been isolated out of a solution containing six-molal sulfuric acid.

A little more sulfuric acid was added in the next electrolytic reduction and the color of the final product was pure green as was expected.

The first four solutions tabulated were prepared independently; the green solutions were dilutions from one electrolytic reduction. An attempt to make the electrolyte even less acid than in I, II and III resulted in the gradual settling out of a greenish-gray precipitate.

The brown variety oxidized in the bath rapidly, although there was a heavy stream of carbon dioxide constantly entering the paraffin pocket.

In II an innovation was introduced. Xylene was put over the solution in the bath until it formed a layer 5 mm. thick. Moreover, the stream of carbon dioxide was not interrupted. Under these conditions, the deflection of the balance was the same before and after two minutes of rapid stirring, that is, the oxidation was sufficiently slow.

It should be observed that the results with xylene are the same as the one without xylene.

The Use of Xylene

Twenty cc. of xylene did not affect the color caused by one drop of 0.03 *N* potassium permanganate although the mixture was vigorously agitated. Ten cc. of xylene in contact with V^{++} for a day, as well as several cc. in contact with the trivalent for a week behaved similarly.

Benzene dissolves in water only to about 0.08% by volume. Toluic acid is given in the tables as less soluble in water than benzoic.[22] Saturated aliphatic compounds are less soluble than aromatic. From the work of Conant and Cutter[23] on the action of bivalent vanadium on organic substances, it was concluded that its reduction of xylene was nil or negligible. Even if xylene were reduced, the product formed would be less soluble than xylene itself. Its diamagnetic effect could certainly be ignored, particularly as the difference in its diamagnetism from that of water would have to be considered. *Henceforth xylene was always used over the bath.*

The effect of carbon dioxide was also neglected. Its diamagnetism is quite high, -0.42×10^{-6} per gram according to Soné.[24]

The difference between this value and that of water is involved. A correction would amount to less than 0.1% in the magnetic moment.

Bivalent Vanadium

Preparation of Solution.—Bivalent vanadium was prepared from $VOSO_4$ in the same way as trivalent vanadium, except that a mercury cathode was used instead of a platinum one. The solution was surrounded with ice but in order to avoid local heating a low current density was used.

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[22] Hertz, *Ber.*, **31**, 2671 (1898).

[23] Conant and Cutter, This Journal, **48**, 1016 (1926).

[24] Stoner, "Magnetism and Atomic Structure," Dutton and Co., New York, **1926**, p. 268.

The color changed in some cases from the blue of the vanadyl to a brownish-green, then to a lavender, and in others from the blue to a deep brown with a greenish hue and then to lavender. The variation through the trivalent state depended upon the original acid concentration. The acid concentration was kept low and in every case a fine precipitate formed as the reduction passed through the trivalent state, a precipitate which did not redissolve.

The first attempt to prepare the bivalent vanadium resulted in a solution containing some of this precipitate and it catalyzed the decomposition of water to such an extent as to decompose 23 to cc. out of 150 cc. in fifteen minutes.

The tube through which the carbon dioxide was bubbled into the cell was later used to siphon the solution through a porous-glass filter into a filter flask connected to a vacuum pump. The filter was in a Gooch funnel which reached to the bottom of the filter flask, in which there were about 10 cc. of xylene. The system was filled with carbon dioxide before evacuation began. In its passage from the electrolytic cell, which was constantly in operation and evolving hydrogen, to the filter flask the bivalent vanadium did not come in contact with the atmosphere.

The concentration of the acid was reduced and a solution of bivalent vanadium was finally prepared which could be handled with comparative ease.

Magnetic Measurements.—The following table (V) gives the results. As will be observed, the bivalent vanadium was contaminated with a considerable amount of trivalent vanadium. If the trivalent had been assumed to be of the form V^{+++}, there would still have been a surplus of SO_4 to account for the H^+ tabulated. It was then obvious that the trivalent vanadium present was of the "green variety" considered under "Trivalent Vanadium."

For purposes of correction, the average of the three green solutions of trivalent vanadium was used, that is, 3228×10^{-6} as the molal susceptibility of V^{+++} at 20°.

TABLE V

SUSCEPTIBILITY OF BIVALENT VANADIUM ION

	Molal concn., V^{++}	Concn. V^{+++}	Concn. H^+	Concn. Na^+	Concn. SO_4^{--}	Density	$\frac{\text{G. } H_2O}{\text{cc. soln.}}$	$\chi \times 10^6$, cc. soln.	$\chi_{20^\circ} \times 10^6$, molal
I	0.1890	0.01616	0.066	0.072	0.281	1.0347	0.996	+0.4958	6204
II	.1381	.0315	.13	.059	.279	1.0310	.994	+ .2433	6290
III	.1018	.0247	.080	.044	.208	1.0225	.995	− .0083	6255
IV	.07217	.01651	.074	.031	.148	1.0158	.996	− .2275	6129
V	.04614	.02065	.044	.0234	.111	1.0116	.997	− .3707	6175
VI[a]	.1833	.0218	.096	.072	.310	1.0364	.995	+ .4958	6297

[a] Preliminary run included to show that the peculiar increase in grams H_2O per cc. of solution was probably real. In the preliminary run, the solution was heated to evaporate the excess of sulfur dioxide gas in the reduced vanadium pentoxide solution. It was then cooled in ice and electrolyzed. The regular solutions were never heated.

In the calculations, the presence of carbon dioxide in the solution was ignored, as was done previously.

Aside from the experiments whose results have been tabulated, only one other complete magnetic run on the vanadium ions was made. This was rejected because of a poor check in the analyses.

Discussion of Errors

The cumulative effect upon the susceptibility of the quadrivalent vanadium ion of all the substances ignored in the calculations, such as dissolved air, carbon dioxide, etc., is probably not more than 0.3% (or 0.15% in the magnetic moment). The effect of each substance is in general to reduce the apparent susceptibility because of the very high diamagnetic susceptibility of one gram of water.[25]

The errors in the analysis of quadrivalent vanadium are probably not greater than 0.2%, those of trivalent vanadium not greater than about 0.5% and those of the bivalent ion not greater than about 0.8%. In the two latter cases, the reflection of these analytical errors upon the susceptibilities is not as serious as it appears to be. The concentration of total vanadium even here was determined within about 0.3% and a decrease in the bivalent vanadium (if that be the ion under consideration) due to an analytical error would increase the trivalent ion impurity and so the resultant error would involve the differences in the susceptibilities of these two constituents and not one only.

More serious sources of error are the diamagnetic corrections and the correction for V^{+++} in V^{++} solutions.

The uncertainty in the value of e/m is of vital importance when the magnetic moments are considered, especially in the case of quadrivalent vanadium ion.

Discussion of Results

Change of susceptibility with change in acid concentration is common. It is usually attributed to the formation of complex ions. The latter probably result from the pairing of unbalanced electrons. It is not surprising then that the susceptibility of the trivalent ions should decrease with increasing H^+ concentration. The variation in susceptibility of the bivalent vanadium ions might be due almost entirely to the accompanying trivalent vanadium ions. As previously mentioned, it was the constant aim to have a minimum of acid present.

Langevin[26] arrived at the following formula connecting the susceptibility of a paramagnetic gas with its magnetic moment for ordinary field strengths and at room temperature

$$\chi T = \frac{M^2}{R}\overline{\cos^2\Theta}$$

where M is the magnetic moment of a mole of the gas, R is the gas constant, T is the absolute temperature and $\overline{\cos^2\Theta}$ is the mean of the square

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[25] The content in water was determined by the difference between the calculated weight of the dissolved substances in 1 cc. listed in the tables and the specific gravity of the solutions.

[26] Langevin, *Ann. chim. phys.*, [8] 5, 70 (1905).

of the cosines of the angle which the axis of the electronic orbit makes with the direction of the magnetic field.

The magnetic moment considered above applies only to the paramagnetism of the gas and not to the diamagnetism induced by the field, which reacts upon the susceptibility actually measured. Corrections for this diamagnetism must be estimated. Its amount is small and the error introduced in the estimation is not serious. Thus, potassium ion has a molal susceptibility of -15×10^{-6}, whereas calcium being a bivalent ion[27] has a smaller susceptibility, in fact -6×10^{-6}. VO^{++} because of its oxygen content is probably a little more diamagnetic than the latter.[28] As a rough estimate -13×10^{-6} per mole was taken. In the same way, -20×10^{-6} was taken as the molal diamagnetic susceptibility for VO^{+}. That of V^{+++} and V^{++} was neglected. If the VO^{++} had been considered to have zero for its diamagnetic susceptibility, the magnetic moments tabulated would have been lowered by 0.5%.

One-half of one per cent. is about the uncertainty in our knowledge of the exact value of e/m. The value of the latter as given by Sommerfeld is employed, that is, 1.769×10^7. Consequently, the Bohr unit of magnetic moment

$$\frac{1}{4\pi} Nh \frac{e}{m} = 5584 \text{ gauss cm. per mole}$$

From this value and the Langevin equation as modified by Sommerfeld's[29] application of the quantum theory, the following table was calculated.

According to the quantum theory only discrete orientations of the magnetic moments with respect to the field are permissible. If the lowest term of the ion is an S term, the orientations depend only upon the resultant mechanical moment of the ion.[30]

Table VI

Units of angular momentum	Bohr magnetic units	Average squared cosines
$^1/_2$	1	1
$^2/_2$	2	$^2/_3$
$^3/_2$	3	$^5/_9$

For all S terms, the ratio of the magnetic moment to the mechanical moment is exactly two. For basic levels other than S the ratio is in general non-integral. Using the $\overline{\cos^2\Theta}$ listed in each table, the following values were obtained for the magnetic moments.

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[27] Ref. 24, p. 271.

[28] Pascal, ref. 20, found that O in organic compounds has the atomic susceptibility of -4.6×10^{-6}.

[29] Sommerfeld, *Z. Physik,* **19,** 221 (1923).

[30] Sommerfeld, "Atombau und Spektrallinien," Vieweg and Son, Braunschweig, **1922,** 4th ed., p. 639.

TABLE VII

MAGNETIC MOMENTS OF THE POSITIVE IONS OF VANADIUM

Quadrivalent Bohr Magnetons—$\overline{\cos^2\Theta} = 1$

Run no.[a]	I	II	III	IV	V
Moments	1.004	1.004	1.004	1.003	1.003

Trivalent—$\overline{\cos^2\Theta} = {}^2/_3$

Brown—low acid concentration

Run no.	I	II	III	IV
Moments	1.997	2.004	2.007	1.982

Green—higher acid concentration

Run no.	V	VI	VII
Moments	1.956	1.939	1.942

Bivalent—$\overline{\cos^2\Theta} = {}^5/_9$

Run no.	I	II	III	IV	V	Preliminary
Moments	2.954	2.975	2.966	2.936	2.947	2.976

[a] Refers to tables of susceptibilities.

From the measurements of Cabrera[31] it appears that Cr^{+++} has 3 (within 1%) and Cr^{++} has 4 (within 2%) Bohr magnetons. The generalization of Kossel[32] that the atomic moments of all ions having the same number of electrons are equal has been found to hold ($V^{++} - Cr^{+++}$).

The three ions of vanadium and the two of chromium form a remarkable series of integral values,[33] values which would never be expected from the theory of Laporte and Sommerfeld.[8] The values anticipated by them would be non-integral and, *a fortiori*, not a regular sequence of integral values.

Sommerfeld's modification of Langevin's equation is based upon the anomalous Zeeman effect, as observed on *atoms* and atomic ions. Why the application of such an equation to *molecular* ions in solution such as VO^{++} and VO^{+} should yield integral numbers of Bohr magnetons is not at all clear.

The striking resemblance in the character of electronic levels of molecules (and molecular ions) to that of electronic levels in atoms (and atomic ions) of the same number of "valence" electrons[34] has caused the electronic levels of molecules to be classified as S, P, D, etc., levels in analogy to the energy levels of atoms. To determine how strict this analogy is will require much further work in band spectra.

It is highly probable that even in the case of "simple" atomic ions, such as those discussed here, the ionic individuality includes the water

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[31] Cabrera, *Anales soc. españ. fís. quím.*, **15**, 199 (1917), given by Weiss, *J. phys. radium*, **5**, 141 (1924).

[32] Kossel, *Ann. Physik*, **49**, 229 (1916).

[33] Mn^{++} and Fe^{+++} also constitute members of this series as each of them appears to have five Bohr magnetons. (Ref. 29, p. 639.)

[34] (a) Mulliken, *Phys. Rev.*, **26**, 561 (1925). (b) Mecke, *Naturwissenschaften*, **13**, 698 (1925). (c) Birge, *Nature*, **117**, 300 (1926).

molecules of coördination.[35] The atomic ions in long periods of the Periodic Table should then be considered as of the molecular type. Presumably magnetic influences on band spectra (Zeeman effect, Paschen-Back effect) should be invoked to study them and not the anomalous Zeeman effect on atomic ions as has been done heretofore.

The writer expresses with pleasure his deep obligation to Professor G. N. Lewis for his suggestions and interest in this research. He also wishes to thank Professor W. F. Giauque for his interest in this work.

Summary

1. A new method has been developed for measuring magnetic susceptibilities.

2. The magnetic susceptibilities of the positive quadrivalent, trivalent, and bivalent ions of vanadium have been measured.

3. It appears that: (*a*) the quadrivalent vanadium ion has 1 integral Bohr magneton; (*b*) the trivalent vanadium ion has 2 integral Bohr magnetons; (*c*) the bivalent vanadium ion has 3 integral Bohr magnetons.

4. The above results do not agree with any current theory based upon the quantum theory and anomalous Zeeman effect. A reason for this discordance is suggested.

5. Some measurements on diamagnetic substances are included.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY]

STUDIES OF METHANOL CATALYSTS. I

BY HUGH STOTT TAYLOR AND GEORGE B. KISTIAKOWSKY[1]

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During the past few years the technique of hydrogenation catalysis in industry has undergone a revolutionary development. Until recently, hydrogenation catalysts were confined practically exclusively to a very restricted series of metals, among which platinum, nickel, copper and iron were the most important. With the industrial development of methanol synthesis, this series of catalysts has expanded fundamentally in that it has been shown that a variety of hydrogenation processes may be carried out in contact with various oxides or mixtures of the same. This extension

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[35] Such a condition undoubtedly obtains among the ions having their outer electronic shells incompletely filled. On the other hand, among the ions of the rare earths the electrons responsible for the magnetic moments are far within the kernel and are surrounded by shells having their full complement of electrons. Under such conditions, the water molecules do not form an integral part of the ions and apparently their influence is slight, as is shown by the close agreement between the values calculated from spectroscopic studies and those observed in solution.

[1] International Research Fellow.