6. It is evident then that the potential of the permanganate–hydrogen–manganous electrode cannot be calculated from the potentials of the manganese dioxide electrodes.

7. Since the manganese dioxide electrodes involve reactions in which there are changes in the oxygen contents, one would expect polarization to take place at the electrodes.

8. Specific directions are given for the precise determination of manganese gravimetrically.

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

TRANSFERENCE PHENOMENA AND THE EXISTENCE OF COMPLEX IONS AS INTERPRETED BY THEIR MAGNETO-CHEMICAL BEHAVIOR

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For our purpose we shall define a molecule as an entity consisting of atoms which are held together by chemical bonds. By a chemical bond we shall mean a coupling of the spin magnetic moments of a pair of equivalent electrons[1] which are held in common by two atoms. Sodium chloride, from this point of view, does not consist of molecules in the crystalline state but of sodium ions and chloride ions. On the other hand, mercuric chloride consists mostly of molecules in both the crystalline state and in solution. Hydrogen consists of molecules in the gaseous state and in the liquid.[2]

We shall extend this definition to a molecular ion. It is an ion whose atomic constituents are coupled by means of chemical bonds. We shall identify complex ions with molecular ions.

Let us consider the familiar example of the ferricyanide ion. Ferric ion in solution is strongly paramagnetic with a molal susceptibility which corresponds to five Bohr magnetons, that is, it appears to have five unbalanced electrons. If we add cyanide ion to it there is an immediate drop in its magnetic susceptibility and the resulting ferricyanide ion possesses a susceptibility corresponding to about one Bohr magneton. The magnetic moments of unbalanced electrons have been neutralized. It is natural to conclude that a number of chemical bonds have been created, that is, that a true complex (molecular) ion has been formed. It has long been recog-

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[1] Lewis, "Valence and the Structure of Atoms and Molecules," American Chemical Society Monograph Series, The Chemical Catalog Co., New York, 1923; Heitler and London, *Z. Physik*, **44**, 455–472 (1927); Heitler, *ibid.*, **47**, 835–858 (1928); London, *ibid.*, **46**, 455–477 (1928); *Naturwiss.*, **16**, 58–59 (1928).

[2] McLennan and McLeod, *Nature*, **123**, 160 (1929).

nized[3,4] that paramagnetic ions suffer a drop in their susceptibilities upon entering into complex ions.

Ordinarily, then, we should expect complex ions to form very readily whenever the metallic ion contains unbalanced electrons, that is, if it is paramagnetic. It is well known that diamagnetic ions, such as Cu^+, Zn^{++}, Ag^+, etc., form complex ions. These ions, although they are diamagnetic, are next to the paramagnetic ions in the periodic system. Their last complete electronic shells are not extremely stable (as is shown by the ease with which an electron may be removed from cuprous to form cupric ion; trivalent silver appears to exist, and trivalent gold is well known). The balance in the magnetic moments may be disrupted (the ion may become activated) and then they may recouple with other ions, such as cyanide, and produce complex ions.

In the case of such ions as sodium, potassium, magnesium, etc., whose outer electronic configurations are similar to those of the rare gases preceding the neutral atoms in the periodic table, there is no chemical evidence for their participating in complex ion formation. (In the gaseous state their electronic configurations are even more stable than those of the corresponding rare gases because the additional positive charge on the kernel attracts the electrons in the outermost shell more strongly.)

However, McBain and Van Rysselberge[5] have interpreted transference phenomena as evidence for the general existence of complex ions even among "rare gas" ions. They found, for example, that in a 0.05 M $MgSO_4$ and 0.95 M $(NH_4)_2SO_4$ solution the magnesium had actually migrated with the negative current. In a solution of 0.05 M $CaCl_2$ in 4 M NH_4Cl there appeared no net migration of the calcium ion with the positive current. They concluded that this behavior was similar to that of ferrous ion in the presence of cyanide ion and that Ca^{++}, Mg^{++}, etc., existed to a large extent in the form of complex ions. They argued from this "anomalous" electrolytic migration that undissociated molecules exist even in dilute solutions of such salts as $MgSO_4$, $CaCl_2$, etc., and hence that theories which postulate complete dissociation in such solutions are invalid.

We are reporting here a short magneto-chemical investigation which we believe will throw some light on the possibility of having such "anomalous" transference and yet having no complex ions present.

In our investigation we tried to reproduce the conditions obtaining in the work of McBain and Van Rysselberge rather closely and still make them amenable to magneto-chemical study.

Instead of magnesium sulfate we have employed manganous sulfate, with which it forms isomorphic crystals, so that those properties that are

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[3] (a) Pascal, *Ann. chim. phys.*, **16**, 359 (1909); (b) **16**, 520 (1909).

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

[5] McBain and Van Rysselberge, *ibid.*, **50**, 3009 (1928).

associated with the size and charge of the ions are very similar in both salts. However, manganous ion has five Bohr magnetons just as ferric ion. It has then five unbalanced electrons which presumably would be the first to couple upon the formation of a complex ion. Moreover, such a coupling would decrease the susceptibility of its solution.

If we can show that upon the addition of ammonium sulfate no change in the susceptibility of the manganous ion has occurred and if the manganous ion has shown no net migration with the positive current, then it has been demonstrated that transference need be no measure of the formation of a complex ion, that is, no chemical bonds have formed, no electromagnetic coupling of electrons has occurred, and the forces between the ions are purely electrostatic.

The coupling of magnetic spin moments, as a rule, produces a great change in the susceptibility. The relatively high concentration of complex ions which has been assumed to exist in mixed salt solutions such as those mentioned would make refined magnetic measurements unnecessary. Nevertheless, we made precise magnetic measurements by modifying the well-known Gouy method[4] so as to make it practically a null method and thereby we have been able to measure relative susceptibilities with unusual accuracy.

We shall state in advance that no change in the susceptibility of bivalent manganese was noted when it was present with ammonium sulfate, and that manganous ion did not show a net migration with the positive current (by changing the concentrations we were able to force a net migration in the opposite direction). Moreover, when we added cyanide ion and formed the well-known complex manganocyanide ion there was a radical decrease in the susceptibility.

Experimental

In order to determine the effect of 1.07 *M* $(NH_4)_2SO_4$ upon the susceptibility of 0.058 *M* $MnSO_4$, we employed the following method. The ordinary Gouy method consists in suspending a glass tube vertically from the stirrup of an analytical balance so that a horizontal glass partition at the center of the tube comes into the middle of the pole gap of a magnet. The substance to be investigated is placed in one compartment of the tube and the other compartment is usually evacuated. The change in weight observed when the magnetic field is excited depends upon the difference between the susceptibility of the substance in the upper and in the lower compartment. The action of the magnetic field upon the uniform glass tube is eliminated by having it extend to a field of negligible intensity on both sides of the pole gap.

We were interested primarily in comparing the susceptibility of the manganous ion when it was dissolved in a solution of ammonium sulfate with its susceptibility in pure water. We filled the upper compartment, therefore, with a solution of manganous sulfate in water and the lower compartment with a solution containing the same concentration of manganous sulfate in the ammonium sulfate.

The ammonium sulfate and water being diamagnetic, their effect was almost canceled out since diamagnetic susceptibilities are small and of about the same order of magnitude (per gram) for these substances. Hence, the balance would record principally any change in the susceptibility experienced by the bivalent manganese.

The pull in the magnetic field was very slight as only differences were involved and irregularities (which usually result from the tube being attracted to one side of the gap), temperature variations, etc., were eliminated. The method had most of the advantages of a null method.

We varied our procedure somewhat so as to eliminate the slight non-uniformity in the glass tube. The upper portion of the tube A was filled with 0.058 *M* $MnSO_4$ and it was then sealed off and a hook in the glass was made so that a string of braided silk could be attached to it with its other end fastened to the stirrup of an analytical balance. The lower portion was then filled with a solution of manganous sulfate of the same concentration.

The change in weight was then recorded for different amperages going through coils of the magnet. This change in weight registered the non-uniformity of the glass and its effect could be corrected for. The solution of 0.058 *M* $MnSO_4$ in 1.07 *M* $(NH_4)_2SO_4$ was then introduced in the lower compartment and the change in weight was observed for different currents. This procedure was repeated for a solution of 0.058 *M* $MnSO_4$ in 2.3 *M* KCN.

We determined the diamagnetic susceptibilities of the ammonium sulfate and potassium cyanide in separate runs employing the same method but having water in the upper compartment. In this way our results are practically independent of any impurities in our chemicals, which, however, were the purest obtainable in the market.

The same calibrated pipets, etc., were employed for all runs. The oxidation of the manganocyanide ion was avoided by pipetting the manganous sulfate into the potassium cyanide solution covered with xylene. The densities were measured with a pycnometer bottle to about 0.05%.

Magnetic Results

The change in weight of the tube produced by the magnetic field depends upon the difference between the susceptibility per unit volume of the upper portion and that of the lower portion. No pull corresponds to identical susceptibilities. In the table below the headings denote the material in the lower compartment.

TABLE I

THE PULL IN THE MAGNETIC FIELD

Amperes	I 0.058 *M* $MnSO_4$ in 1.07 *M* $(NH_4)_2SO_4$, mg.	II 0.058 *M* $MnSO_4$ in 2.3 *M* KCN, mg.	III 0.058 *M* $MnSO_4$, mg.	IV I corrected, mg.
25	0.43	15.40	0.07	0.04
30	.56	19.50	.06	.05
35	.66	22.70	.11	.06
40	.75	25.20	.10	.07
45	.82	27.25	.12	.08
50	.87	29.00	.11	.10

Column IV corresponds to Column I corrected for the difference in the susceptibilities of the water and ammonium sulfate. With our tube no change in susceptibility corresponds to Column III. The weights are probably accurate to within five or six hundredths of a milligram.

The table shows that the susceptibility of the manganous ion in the presence and in the absence of ammonium sulfate is identical within our limits of error. One-tenth of a milligram pull corresponds to a change in the susceptibility of about 0.2%.

The large pull induced by the potassium cyanide means that the susceptibility of the bivalent manganese in the solution of the cyanide has dropped enormously. In a short note[6] we calculated the molal susceptibility of the bivalent manganese in this solution as 1650×10^{-6}, whereas in the absence of the potassium cyanide it is $14{,}950 \times 10^{-6}$, a change of about nine-fold.

Transference

We carried out several electrolytic migration experiments in the usual manner employing a three-partition cell with a cadmium anode and a platinum cathode. We followed McBain and Van Rysselberge in taking equal volumes from the various compartments for comparison. The manganous ion was titrated with standardized permanganate solution in the presence of zinc sulfate. In the first series the same concentrations were employed as were tested magnetically, *i. e.*, 0.058 *M* $MnSO_4$ in 1.07 *M* $(NH_4)_2SO_4$. We found the same (within 0.2%) concentration in both the unchanged center and anode portions after passing seventeen milliamperes for about four hours and also after ten hours.

To test whether we could alter the conditions so that the net migration could actually be reversed, a solution containing 0.038 *M* Mn^{++} in 2.5 *M* $(NH_4)_2SO_4$ was electrolyzed. A net gain of about 0.6% in concentration was observed in the anode portion after passing seventeen milliamperes for twelve hours.

Discussion

The magnetic susceptibility of manganous sulfate was found[7] to be independent of the concentration. Such constancy is in itself excellent evidence that no complex ions are present. However, the susceptibility of many paramagnetic substances does vary with the concentration and among these substances chemical evidence also leads to the conclusion that complex ions are present. We shall give some examples of the numerous paramagnetic ions which show an immediate decrease in their susceptibilities as soon as they constitute a part of negative complex ions.

TABLE II

PARAMAGNETIC IONS AND NEGATIVE COMPLEX IONS

Metallic ion	Complex	Metallic ion	Complex
Fe^{++}	$[Fe_2(P_2O_7)_3]^{8-}$	Fe^{+++}	$[Fe_2(P_2O_7)_3]^{6-}$
	$[Fe(CN)_6]^{4-}$		$[Fe(PO_3)_6]^{3-}$
	$[Fe(CN)_5(NO)]^{4-}$		$[Fe(CN)_6]^{3-}$
Mn^{++}	$[Mn(CN)_6]^{4-}$		$[Fe(CN)_5(NH_3)]^{3-}$
	$[Mn_2(P_2O_7)_3]^{8-}$		$[Fe(CN)_5(NO_2)]^{3-}$
Ni^{++}	$[Ni(CN)_4]^{2-}$	Cu^{++}	$[CuBr_4]^{2-}$

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[6] Freed and Kasper, THIS JOURNAL, **52**, 1012 (1930).

[7] Cabrera, Moles and Marquinas, *J. chim. phys.*, **16**, 11 (1918).

Indeed, as long ago as 1909 Pascal[3a] after extensive researches on the magnetic behavior of complex ions expressed the generalization that there is a parallelism between the diminution in the analytical character (namely, the reactivity) of the metallic ion and the diminution of its magnetic susceptibility.

There is but one exception as far as we know where a paramagnetic ion does not show a marked decrease in its susceptibility when it forms a negative complex ion. This is chromic ion. Chromic ion in water, in its ammonia complex ions, and in its cyanide complexes displays nearly the same molal susceptibility.

It is highly improbable that in the case of the manganous ion we have a sulfate complex ion which would have just the same susceptibility as the manganous ion and yet its cyanide complex would have a much lower susceptibility. That is just what must occur to account for the "anomalous" transference on the assumption of complex ions and still not conflict with the magnetic behavior of the manganous ion.

Our results strongly indicate that manganous ion has not formed any magnetic bonds (any chemical bonds) with the sulfate ions. The attraction for the sulfate ions should then be regarded, with a high degree of approximation, as electrostatic only. These are the forces which Debye and Hückel considered in their famous interionic attraction theory, which postulates complete dissociation. We are inclined to believe that a comprehensive extension of their methods to concentrations which we have been employing would disclose on theoretical grounds a reversal in the direction of migration such as has been observed.

According to the interionic attraction theory every positive ion will have, on the average, a negative ion (or ions) of equal charge near it but there will be fluctuations from this average. With the types of ions that we have been considering the fluctuations will take the form of clusters of negative ions about the positive ion. The results from transference indicate that the cluster, as a whole, having an excess negative charge migrates with the negative current. The probability of this cluster is greater for those positive ions which have a greater positive charge and a smaller radius. (We realize that emphasis upon one factor is scarcely warranted because it cannot be isolated from the interacting influences which operate in so complex a phenomenon as transference, the interaction of moving charges, clusters of varying complexity and of both signs, dehydration effects, etc. However, we shall continue with our point a little further.) The fact that the net transference of magnesium ion can be reversed more readily than manganous ion and also more readily than potassium ion suggests that the reversal is a function of the charge and the radius of the ion, the very magnitudes alluded to above. It is very probable that manganous ion is somewhat larger than magnesium ion. Also potassium ion, both because of its smaller charge and because of the greater number of electrons, is larger and hence it is not altogether surprising that the migration of magnesium ion in the "wrong" direction can be forced more readily.

It is extremely probable then that ions such as Na^+, K^+, Mg^{++}, which have electronic configurations in the gaseous state like those of the rare gases retain their configurations in solution and that they do not form complex or molecular ions.

Summary

The nature of complex ions has been reviewed in terms of current theories on molecular structure as related to magnetic properties.

It has been shown that a metallic ion which does not form negative complex ions can show a net migration to the anode. It is to be concluded that the exhibition of such migration is no proof of the formation of complex ions.

A new modification of the Gouy method is described which permits the measurement of relative susceptibilities to be made easily and accurately.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE RICE INSTITUTE]

THE ATOMIC WEIGHT OF VANADIUM

BY ARTHUR F. SCOTT AND CLYDE R. JOHNSON

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The values now accepted for the atomic weight of vanadium depend upon the determinations of McAdam,[1] and Briscoe and Little.[2] These investigators have reviewed the earlier determinations, and have pointed out serious defects in all of them. Consequently, the earlier work is not given further detailed consideration here.

McAdam, from five measurements of the $NaVO_3$–NaCl ratio, obtained the average value 50.957 for the atomic weight[3] of vanadium. Briscoe and Little, rejecting two experiments in taking the final mean, derived the value 50.955 from nine measurements of the $VOCl_3$:3Ag ratio. While these results agree substantially, it may be mentioned that McAdam's investigation was intended only as a preliminary one, and cannot be given the same weight as that of Briscoe and Little. The general agreement between the results of the two series of experiments, however, practically excludes the possibility that the latter investigators, who used a distillation method in the purification of their vanadyl trichloride, were dealing with a constant boiling mixture.

In their determination of the $VOCl_3$:3Ag ratio, Briscoe and Little em-

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[1] McAdam, THIS JOURNAL, **32**, 1603 (1910).

[2] Briscoe and Little, *J. Chem. Soc.*, **105**, 1310 (1914).

[3] The antecedent atomic weights used throughout this paper are: O = 16.000; Ag = 107.880; Cl = 35.457; Na = 22.997.