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# THE MAGNETIC PROPERTIES OF ODD MOLECULES

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The magnetic behavior of a substance is of fundamental chemical importance on account of its intimate relation to the electron motions in the constituent atoms. An electron moving in its orbit is like an electric current flowing in a circular or elliptical conductor, and by analogy it possesses a magnetic moment. In the helium atom the two electrons have annulled each other's magnetic moment by a process of mutual orientation, so that helium is said to be "diamagnetic." In fact, practically all known organic compounds contain an even number of electrons and are diamagnetic like helium. Most inorganic compounds behave similarly, although many of the compounds of the iron, the palladium, and the rare-earth transition groups show paramagnetism.

This striking coincidence of even electron number in a molecule and appearance of diamagnetism led Professor G. N. Lewis[1] to state this as a "first law of chemical affinity that electrons in an atom or molecule tend to pair with one another in such a manner as to eliminate magnetic moment." Substances possessing an odd number of electrons cannot pair them completely and, consequently, "odd molecules should have a magnetic moment, and should, therefore, represent the highest degree of chemical unsaturation." It has been the object of the present research to test this prediction that odd molecules are paramagnetic.

The high degree of reactivity possessed by odd molecules is an indication that this idea is correct. Only rarely are they found in the free state. The commonly known substances of this class are nitric oxide, nitrogen dioxide, chlorine dioxide, organic free radicals, amalgams of metals having an odd-numbered valence, such as thallium amalgam or sodium amalgam, and liquid ammonia solutions of alkali or alkali-earth metals such as sodium or calcium. All of these substances possess an odd number of electrons per molecule. In the last case cited the odd molecule is not the sodium or calcium ion, but rather the solvated electron which is responsible for the color and high conductivity of such solutions. Soné[2] has shown that nitric oxide and nitrogen dioxide are paramagnetic. They have 15 and 23 electrons, respectively. He gives the following values for the molal susceptibility at 20°: nitric oxide, $1465 \times 10^{-6}$; and nitrogen dioxide, $207 \times 10^{-6}$. It is interesting to note that all the other oxides of nitrogen are diamagnetic (that is, they possess no residual magnetic moment).

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[1] Lewis, "Valence and the Structure of Atoms and Molecules," American Chemical Society Monograph, The Chemical Catalog Company, New York, **1923**, p. 148.

[2] Soné, *Science Repts. Tôhoku Imp. Univ.*, **11**, 139 (1922).

Soné gives these values: nitrous oxide, —18.9; $N_2O_3$ (l), —15.9; nitrogen tetroxide (l), —25.6; nitrogen pentoxide (s), —35.6. The factor "$\times 10^{-6}$" is to be added to each of these values.

In the present research the other free radicals were studied at room temperature. The apparatus consisted essentially of a very large electromagnet giving a field of 25,000–30,000 gauss over an air gap of about 1.5 cm. distance and with a pole face diameter of 2.5 cm. Samples for investigation were placed in a long glass tube which hung from a sensitive analytical balance above the magnet in such a way that the lower boundary of the sample was in the most intense part of the field and the upper end was in zero field. With this arrangement the magnetic pull ($P$) on the sample is given by the expression, $P = \frac{1}{2}\chi H^2\sigma$, where $\chi$ represents the susceptibility of the material per unit volume, $H$ is the strength of the field, and $\sigma$ gives the cross-sectional area of the tube. The apparatus and method have been described in another article.[3] In the early studies in magnetism in this Laboratory the strength of the field was measured by means of the change of resistance of a bismuth spiral and also the use of a search coil and a ballistic galvanometer. It was found to be simpler, however, to rely on relative measurements, using pure water in the same tube under identical conditions, comparing the magnetic pull on water and on the substance being studied and making use of the susceptibility value of water which is known with fairly high accuracy. The volume susceptibility of pure water measured against ordinary laboratory air at 20° is $-0.749 \times 10^{-6}$. Against a vacuum it is $-0.720 \times 10^{-6}$.

The magnetic pull was usually obtained for currents of 10 amperes and of 15 amperes in the magnet coil. On account of the hysteresis in the magnet it was necessary always to follow the same current-time cycle in magnetization. The details of each experiment will now be given.

**Chlorine Dioxide.**—This material was prepared by the action of solid potassium chlorate on oxalic acid crystals in the presence of a small amount of water, as recommended by Bray.[4] The gas was bubbled through water and then dried by passing through phosphorus pentoxide. It was then absorbed in cold carbon tetrachloride up to about 1 or 2% solution by weight. After the magnetic measurement the solution was analyzed by addition of potassium iodide and titration of the free iodine with standard 0.1 $N$ sodium thiosulfate solution. Preliminary measurements were made on five different solutions of chlorine dioxide in carbon tetrachloride. Their compositions varied from 0.375 to 1.63% of $ClO_2$ as based on total oxidizing power of the solution. In these analyses no account was taken of the chlorine content of the solution, but later work showed it to be about 10% of the chlorine dioxide present. All of these five solutions were para-

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

[4] Bray, *Dissertation*, Leipzig, **1906**.

magnetic, or at least less diamagnetic than the pure carbon tetrachloride. The paramagnetic pull due to chlorine dioxide was, on the average, about 0.03 g. The molal susceptibilities of chlorine dioxide at 20°, calculated from the results, were 1368, 1322, 1426, 1268 and 1380 $\times 10^{-6}$.

A more accurate analysis of the chlorine dioxide content was then made on a new solution by titrating in a neutral and also in an acid medium, so that the reactions are as follows.

$$ClO_2 + \tfrac{1}{2}Cl_2 + 6I^- + 4H^+ = 3I_2 + 2Cl^- + 2H_2O \qquad (1)$$
$$3ClO_2 + \tfrac{1}{2}Cl_2 + 6I^- = 2I_2 + 4Cl^- + 2IO_3^- \qquad (2)$$

The chlorine content can thus be determined. Data are given herewith for a 2.77% solution of chlorine dioxide, having an assumed density of 1.58 g. per cc. The volume susceptibility of the substance had been previously determined to be —0.692 $\times 10^{-6}$.

| | |
|---|---|
| Magnetic pull on solution | 0.0126 g. |
| Magnetic pull on $CCl_4$ in the same tube | − .0489 g. |
| Correction due to $CCl_4$ present in solution | − .0475 g. |
| Magnetic pull due to $ClO_2$ | .0601 g. |

Volume susceptibility of $ClO_2$ in solution $= 0.0601/-0.0489 \times (-0.692 \times 10^{-6})$
$= .8502 \times 10^{-6}$

Volume susceptibility $= .8502 \times 10^{-6} \times \dfrac{100}{2.77}$
$= 30.69 \times 10^{-6}$

Molal susceptibility $= 30.69/1.58 \times 10^{-6} \times 67.46 = 1310 \times 10^{-6}$

If allowance were made for the inherent diamagnetism of chlorine dioxide due to all the electron pairs present, the correction, according to Pascal,[5] would be —21 $\times 10^{-6}$ for chlorine and —4.8 $\times 10^{-6}$ for each oxygen atom, that is, —30.6. The molal susceptibility due to the free electrons in chlorine dioxide would then be 1341 $\times 10^{-6}$. This value is probably correct to within 5%.

The result is of great interest because it shows that chlorine dioxide is definitely paramagnetic. Further, the value obtained is of the same order of magnitude as that of nitric oxide (1465 $\times 10^{-6}$). It may be that the state of the electron giving rise to the observed magnetic effects is the same in both cases. The lower value for chlorine dioxide may be due to some slight formation of dichlorine tetroxide.

**Thallium Amalgam.**—It was suggested by Professor Lewis that metals of odd valence dissolved in mercury might be paramagnetic. Thallium, because of its high solubility, was chosen for these experiments. Solid thallium is diamagnetic but, because of the disturbing influence of crystal structure, no reliable conclusion can be drawn from this fact regarding the magnetic characteristics of the thallium atom alone.

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[5] Pascal, *Ann. chim. phys.*, [8] **29**, 2 (1913).

Pure thallium and mercury were made up into liquid amalgams (in an atmosphere of nitrogen) and the magnetic pulls determined for various field strengths. The amalgam was then analyzed by adding a known volume of standard 0.025 *N* sulfuric acid, and bubbling oxygen through the solution, forming thallium hydroxide. This neutralized a part of the sulfuric acid and the excess was determined by addition of standard 0.025 *N* sodium hydroxide. The magnetic data are given herewith. The densities of the amalgams were taken from a paper by Richards and Daniels.[6]

| | Magnetic pull | | Vol. | G. of metal per cc. | Atomic $\chi$ of Tl, |
|---|---|---|---|---|---|
| | (15 amps.) | (10 amps.) | $\chi \times 10^6$ | of amalgam | $\times 10^6$ |
| $CCl_4$ | −0.0510 g. | −0.0472 g. | −0.692 | | |
| Hg | − .1920 g. | − .1713 g. | −2.64 | 11.14 | |
| Tl amalgam No. 1 | − .1395 g. | − .1299 g. | −1.945 | 2.08 | 22.3 |
| Tl amalgam No. 2 | − .1470 g. | − .1364 g. | −2.048 | 1.85 | 24.8 |

In calculating these volume susceptibilities a correction was of course made for the magnetic pull on the air in the lower half of the tube. The results show fairly definitely that thallium dissolved in mercury is paramagnetic. If all of the thallium were present in the free state, however, so as to contribute to the paramagnetism, the atomic susceptibility would probably be about $1400 \times 10^{-6}$ as it is for chlorine dioxide and for nitric oxide. It seems very likely, therefore, that most of the thallium exists as thallium ion, $Tl^+$. Since thallium ion contains an even number of electrons it would show diamagnetism. It is to be expected that the alkali metals dissolved in mercury would also lose their valence electrons and, in fact, compounds with mercury are well known.

**Organic Free Radicals.**—The highly abnormal chemical and physical properties of organic free radicals have been ascribed to their being "odd molecules." Professor Lewis suggested that they might possess paramagnetism because of the extra electron. This was tested on a benzene solution of $\alpha$-naphthyl-diphenylmethyl, the chloride of which was very kindly supplied by Professor M. Gomberg. The free radical was produced by the action of finely divided silver on a benzene solution of this chloride in absence of air, and it was then siphoned into a previously evacuated glass tube which was used for the magnetic measurements. The solution was analyzed by absorption of standard bromine solution and titration of the excess of bromine with standard sodium thiosulfate solution. Great care must be taken to avoid exposure to air. On account of the small dissociation of the hexa-aryl compound at high concentrations only about a 7% solution of the free radical was used. This, combined with a high molecular weight so that only a small fraction of a mole of free radical was present in the solution, made accurate measurements very difficult. The data for the best run are given herewith.

[6] Richards and Daniels, This Journal, **41,** 1745 (1919).

Current in magnet coils 15 amps.

Magnetic pull due to benzene $-0.0663$ (1)

Magnetic pull due to solution $-.0626$ (2)

Per cent. composition of solution: ($C_6H_6$) 92.8

Free radical 7.2

Correction due to dissolved benzene $-.0615$ (3)

Magnetic pull due to free radical (2) − (3) = $-0.0011$ g.

Vol. $\chi$ of benzene $= -0.651 \times 10^{-6}$

Vol. $\chi$ of this free radical $= 0.0011/0.0663 \times (-0.651 \times 10^{-6}) = -0.0108 \times 10^{-6}$

From data at 10 amps.:

Vol. $\chi$ of free radical $= -0.0106 \times 10^{-6}$

Average $= -0.0107 \times 10^{-6}$

Assume solution has same density as pure benzene (0.88)

Hence, $0.072 \times 0.88 = 0.0634$ g. per cc. Free radical has a susceptibility equal to $-0.0107 \times 10^{-6}$

Hence, specific $\chi$ of free radical $= (-0.0107 \times 10^{-6})/0.0634 = -0.169 \times 10^{-6}$

Molal $\chi = -0.169 \times 10^{-6} \times 294 = -49.6 \times 10^{-6}$

In one other solution of the same free radical in benzene the concentration was only about 1% and was too low for accurate analysis. The change in magnetic pull due to replacement of benzene in the tube by the solution was definite but was only about 1 mg. Consequently, too much weight must not be given to this set of data. The molal susceptibility computed from these data is $-122 \times 10^{-6}$.

The diamagnetic susceptibility values given by Pascal for carbon and for hydrogen are $-60 \times 10^{-7}$ and $-29.3 \times 10^{-7}$, respectively. The susceptibility computed similarly for α-naphthyl-diphenylmethyl is $-190 \times 10^{-6}$. The odd electron is thus seen to confer a definite paramagnetic effect of about $(190-50) \times 10^{-6} = 140 \times 10^{-6}$, and since the compound used for experiment was only about one-third dissociated[7] the paramagnetic correction for a mole of the free radical would be about $570 \times 10^{-6}$. This is markedly less than the values obtained for chlorine dioxide and nitric oxide, but the small effects which were measured hardly justify quantitative comparisons.

**Sodium in Liquid Ammonia.**—Commercial ammonia gas was condensed over sodium and allowed to stand for some time until it was thoroughly dry and the characteristic blue solution had formed. The ammonia was then distilled in a vacuum onto a number of small sticks of sodium which were contained in glass tubes open at the ends. The tube containing this solution was then sealed off. The solution was "bronze," showing typical metallic reflection. After the magnetic pull at room temperature had been determined, the solution was frozen in liquid air, the tip broken off and the solution allowed to warm slowly so that the ammonia which boiled off could be collected in *N* sulfuric acid. The dry sodium remaining was then absorbed in a mixture of alcohol and water and titrated with *N*

[7] Compare Gomberg, *Chem. Rev.*, **1**, 104 (1924).

sulfuric acid. The analysis gave 32.5% of sodium and 67.5% of ammonia by weight. The magnetic pull on the bronze solution at 15 amps. was —0.0081 g., and at 10 amps. was —0.0072 g.; the pull on liquid ammonia (same tube) at 15 amps. was —0.0515 g., and at 10 amps. —0.0480 g.

It should be noted that these pulls are against air. The pull due to the solution or to ammonia alone would be approximately 0.0025 g. less, at 15 amperes, namely, —0.0055 g. for the solution and —0.0490 g. for the ammonia. In a solution containing 67.5% by weight of ammonia the diamagnetism due to ammonia would be 0.675 × (—0.0490) = —0.0330 g. Consequently, there is a paramagnetic correction of —0.0055 − (—0.0330) = 0.0275 g. due to the presence of the sodium. This value is, of course, not exact because no account is taken of the density of the solution, and the assumption is made that it has the same density as liquid ammonia at the same temperature, but it would be necessary for the ammonia to expand to four times its original volume on addition of sodium in order to account for the large paramagnetic correction. Gibson and Argo,[8] and Kraus,[9] have shown that the valence electron supplied by sodium or by any alkali or alkali-earth metal attaches itself to the solvent molecules which form an aggregate about it. The experiments here reported give strong indication that this solvated electron is a magnet.

## Summary

The theory that magnetic forces play an important role in chemical affinity has been tested by measuring the magnetic susceptibility of several "odd" molecules, chlorine dioxide, thallium dissolved in mercury, an organic free radical (α-naphthyl-diphenylmethyl) and a solution of sodium in liquid ammonia. All of these substances show definite paramagnetism.

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[8] Gibson and Argo, *Phys. Rev.*, **7**, 33 (1916).

[9] Kraus, THIS JOURNAL, **43**, 749 (1921).