reliable, in terms of what happens kinetically during evaporation from a concave surface.

The surface tension of water has been estimated from height of rise in capillaries of graded sizes down to about 6.7 μ radius, and the data show that there is no appreciable difference in surface energy from that of a flat surface.

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Paramagnetism and the Molecular Field of Neodymium

BY P. W. SELWOOD[1]

Previous work by the writer has shown that concentration changes in solutions of neodymium compounds are accompanied by changes in the characteristic absorption spectrum, the molar refraction[2] and in the magnetic susceptibility[3] of the neodymium ion.

The object of the present work was to establish if possible an experimental relation between the above-mentioned effects and the Weiss molecular field constant Δ in the Weiss law $\chi = C/(T + \Delta)$ where χ is the magnetic susceptibility, C the Curie constant, and T the absolute temperature. For reasons to be discussed later it proved scarcely possible to examine Δ over a very wide concentration of neodymium salts in solution, but measurements were made on several compounds of varying "magnetic dilution" and on certain intimate mixtures of neodymium oxide and the diamagnetic and isomorphous lanthanum oxide.

It was also hoped that these measurements would serve to test the theoretical relations established by Van Vleck[4] and his co-workers for the magnetic susceptibility of neodymium and its temperature dependence.

Although recent theoretical work tends to show that the molecular field may in many cases have no real physical significance,[5] it has nevertheless been the subject of much fruitful investigation especially in study of the paramagnetism of the elements of the first transition series. Many estimates of Δ in a few compounds of neodymium and other rare earths are available and they show an astonishing variety. In order for any worth while conclusions to be drawn it seems essential that measurements should be made on the same original material where different compounds are being investigated. Of the available information on the molecular field,

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(1) Part of this work was done while the writer was a National Research Fellow.

(2) Selwood, THIS JOURNAL, **52**, 3112 (1930); **52**, 4308 (1930).

(3) Selwood, *ibid.*, **53**, 1799 (1931).

(4) Van Vleck, "Theory of Electric and Magnetic Susceptibilities," Oxford, 1932, hereafter referred to simply as Van Vleck.

(5) Penney and Schlapp, *Phys. Rev.*, **41**, 194 (1932).

the mass of data on many substances from the Leiden laboratory[6] shows that Δ is in general a function of the magnetic concentration. Gorter, de Haas, and v. d. Handel[7] find Δ for $Pr_2(SO_4)_3 \cdot 8H_2O$ = 32°, $Pr_2(SO_4)_3$ = 45°. Cabrera and Duperier[8] give for Pr_2O_3 Δ = 65.5°. The latter also find for $Nd_2(SO_4)_3$ Δ = 18.3° and for Nd_2O_3 Δ = 26.0°. Owing to the (in the writer's opinion) somewhat arbitrary method used by Cabrera and Duperier in calculating Δ it is impossible to compare their values with those of others. Gorter[6] gives for $Nd_2(SO_4)_3 \cdot 8H_2O$ Δ = 45.0°. Williams[9] gives for Nd_2O_3 Δ = 44°. No estimates of Δ in other neodymium compounds either solid or in solution seem to have been made. Measurements on solutions are difficult because of the limited temperature range available.

Experimental Part

It was necessary during this work to use two types of magnetic balances because the very sensitive apparatus required for dilute solutions was not adapted for solids. The magnet available for the measurements was scarcely adequate inasmuch as with an interspace of 3.8 cm. between the truncated conical pole-pieces a maximum field of only 2630 gausses was attainable with 8 amperes through the coils. Any larger current resulted in excessive heating. As this field was, as shown in Fig. 1, insufficient to saturate the pole-pieces, readings were taken with the field reversed. The mean reading was then more nearly independent of the hysteresis characteristics of the iron. The current was controlled by means of a sensitive ammeter and shunted rheostats. For the case of the Gouy balance, if I is the current through the magnet and W the increase in weight of a substance because of the field, then dW/dI at I = 8 amp., times ∂I, the maximum probable error in reading the ammeter, was less than half the maximum probable error in weighing the quantity W.

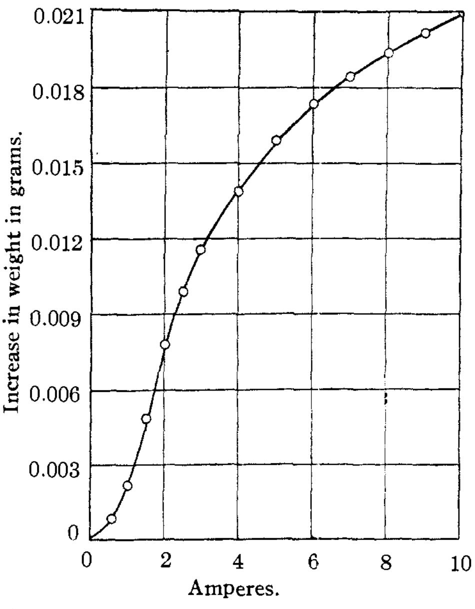

Fig. 1.—Change of weight increase with current through magnet.

Gouy Method.—For solids the well-known method of Gouy was used, Fig. 2.[10] In this method a glass tube containing the substance under investigation is suspended with its axis perpendicular to a homogeneous magnetic field. One end is in the field and the other in a region where the field

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[6] Admirably summarized by Gorter, Leiden Dissertation, 1932, or Archives du Musee Teyler, III, **7**, 183 (1932).

[7] Gorter, de Haas and v. d. Handel, *Akad. Wetenschappen Amsterdam*, **34**, 1249 (1931).

[8] Cabrera and Duperier, *Compt. rend.*, **188**, 1640 (1929).

[9] Williams, *Phys. Rev.*, **12**, 158 (1918).

[10] See, for instance, Stoner, "Magnetism and Atomic Structure," Methuen, 1926.

is negligible. The force on the tube is $F = {}^1/_2(K_1 - K_2)A(H_1 - H_2)^2$ where K_1 and K_2 are the volume susceptibilities of the tube and the surrounding medium, respectively. A is the cross-sectional area of the tube, H_1 is the intensity of the field, and H_2 is the intensity of the field at the other end of the tube in case it is not negligible. In the present work the tube was surrounded by dry nitrogen whose susceptibility is quite negligible compared to that of the substances being measured. Hence the expression for the mass or specific susceptibility reduces to $x = 2gW/dAH^2$ where g is the gravitational constant, W the change in weight on application of the field, and d the apparent density of the substance in the field. Correction must of course be made for the magnetism of the glass tube. The chief difficulty in this otherwise very convenient method lies in introducing powdered crystals into the glass tube so that they will have a uniform apparent density throughout.

The glass tube was suspended in a slightly larger tube by means of a silk thread attached to one pan of an analytical balance. The outside tube was itself surrounded by a Dewar flask shaped as shown in the figure to fit between the poles of the magnet. This flask was used for holding the bath liquids for maintaining desired temperatures and was provided with a stirrer, heating coil, and thermocouple. Dry nitrogen was slowly led through the bath in a spiral glass tube and was allowed then to pass up over the sample being measured. After having been at liquid air temperature the nitrogen was warmed to well above the dew point before escaping into the air, thus avoiding accumulation of moisture on the silk thread. The glass tube for holding the samples was 14 cm. long and had an interior cross-sectional area of 0.282 sq. cm. The balance was sensitive to 0.05 mg. Except in one or two cases mentioned below all measurements were made at four temperatures, liquid air, carbon dioxide–ether, 0 and 100°. The temperatures were measured to 0.1° by means of a four junction copper–constantan thermocouple. The thermocouple was calibrated against a platinum resistance thermometer provided with a Bureau of Standards certificate, and checked against an oxygen vapor thermometer at the lowest temperature. The glass tube used was diamagnetic and slightly affected by temperature as follows:

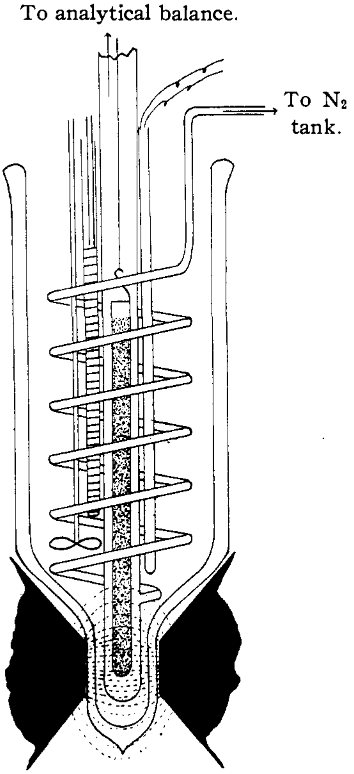

Fig. 2.—Gouy magnetic balance.

Temperature	Room	Liquid air
Change in weight, g	−0.00040	−0.00030

The apparatus was calibrated with solutions of neodymium nitrate and of nickel chloride. Solutions of neodymium nitrate had previously been investigated by the writer[3] and the susceptibility compared by the capillary rise method with that of water, which was taken as -0.720×10^{-6} at 20°. The results obtained were in good agreement with those of Decker.[11] A solution of neodymium was therefore prepared as

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(11) Decker, *Ann. Physik*, **79**, 324 (1926).

before. It was analyzed by direct evaporation and ignition to oxide. The analyses checked to within 0.05% of 54.19% $Nd(NO_3)_2$ by weight. The density was 1.693. The specific susceptibility of this solution was taken as 7.695×10^{-6} at 20°.

The magnetic susceptibility of nickel chloride solutions has been carefully investigated by Miss Brant,[12] whose results agree with those of Cabrera, Moles and Guzman,[13] and of Weiss and Bruins.[14] The molar susceptibility of nickel chloride at 20° was taken as 4383×10^{-6}. The solution was prepared from C. P. nickel nitrate from which the cobalt was first removed as cobaltinitrite. The nickel was deposited electrolytically on a platinum dish from an ammoniacal sulfate solution, was redissolved in redistilled nitric acid, evaporated and ignited to the oxide, dissolved in redistilled hydrochloric acid, recrystallized, and finally made up to approximately 30% $NiCl_2$ by weight. The only impurity which could be detected after this procedure was a faint trace of ferric iron. The solution was analyzed with dimethylglyoxime and checked to within 0.4% to contain 31.10% $NiCl_2$. The density was 1.364 which is a little lower than as near as may be interpolated from the results of Miss Brant. The specific susceptibility of the solution was given by $\chi_s = 4383/129.6 \times 0.3110 - (0.72 \times 0.6890) \times 10^{-6} = 10.02 \times 10^{-6}$ at 20°.

The apparatus constant k worked out from the relation $k = 2g/AH^2 = \chi_s d/W$ where the quantities have the same significance as before, was from the neodymium nitrate $k = 1.007 \times 10^{-3}$, and from the nickel chloride $k = 1.012 \times 10^{-3}$. The constant was taken as $k = 1.01 \times 10^{-3}$.

It may be of interest to mention results obtained incidentally on a few other substances: manganese pyrophosphate, χ_s at 20° $= 106.5 \times 10^{-6}$. Foëx[15] gives 101.3 to 102.5×10^{-6}. Water gave $\chi_s = -0.7 \times 10^{-6}$ and mercury -0.21×10^{-6} both at 20°. For the latter the "International Critical Tables" give $\chi_s = -0.19 \times 10^{-6}$. Purified anhydrous oxalic acid was carefully investigated for reasons which will appear below. The specific susceptibility, which does not seem to have been measured before, was -0.6×10^{-6} and quite independent of temperature from -190 to 100°.

The data given below are believed to be accurate to 0.1×10^{-6} units of susceptibility except for highly magnetic substances such as neodymium oxide at low temperatures with which some difficulty was experienced in finding the increase in weight to the limit of sensitivity of the balance. The glass tube empty, and also several of the compounds, for instance, lanthanum oxide, were investigated for ferromagnetic impurity by comparing the susceptibility at low field intensity with that at high. But in no case was any field dependence of the susceptibility found. The data given are the mean of two measurements, one with falling and the other with rising temperature; in most cases a freshly prepared batch of material being used for the two measurements. In all cases the temperature was maintained constant for half an hour before a reading was taken although equilibrium appeared to be reached in about ten minutes.

Torsion Method.—As it was hoped to be able to measure the molecular field in the case of dilute solutions a method of fairly high sensitivity was required. The torsion method used by Decker[11] was decided on. The apparatus consisted of a small glass rod, hereafter called the "test-piece," suspended parallel to the field between the poles of a magnet by a quartz fiber which was attached to a torsion head as shown in Fig. 3. The test-piece was attached to the fiber by means of a very thin glass rod 15 cm. long, near the top of which a small mirror was attached. The solution being investigated was made the medium to surround the test-piece, only about 2 cc. being required. The test-piece was first placed at an angle of 45° to the direction of the field with the field off be-

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(12) Brant, *Phys. Rev.*, **17**, 678 (1921).

(13) Cabrera, Moles and Guzman, *Arch. Sci. Phys. Nat.*, **37**, 325 (1914).

(14) Weiss and Bruins, *Proc. Acad. Sci. Amsterdam*, **18**, 346 (1915).

(15) Foëx, *Ann. phys.*, **16**, 174 (1921).

cause the maximum couple may be exerted at this angle. Then on application of the field the test-piece turned and was brought back to its original position by turning the torsion head until a spot of light from the mirror mentioned above returned to a fixed point on a glass scale. It was possible to return the test-piece to its original position within 0.01 cm. on a scale 1 meter distant from the mirror. The retorsion angle was read by means of a telescope fixed to the torsion head.

We have[16] $M_M = (K_0 - K)H^2C_1$ where M_M is the moment acting on the test-piece by virtue of the field, K_0 and K are the volume susceptibilities of test-piece and surround medium, respectively, H is the field intensity, and C_1 a constant. We also have $\phi = M_TC_2$ where ϕ is the torsion (or retorsion) angle, M_T the torsion moment on the test-piece, and C_2 the fiber torsion constant. At equilibrium $M_M = M_T$, hence $C_2 = (K_0 - K)C_1H^2$ or $K_0 - K = \phi C$ for constant field.

The apparatus might therefore be calibrated with two known substances, or better with one known and with the apparatus evacuated so that $K = 0$. The torsion head was connected through a packing gland so that the apparatus could be evacuated readily. The quartz fiber was sufficiently removed from the temperature bath so that there was no danger of the torsion constant C_2 varying. Furthermore, the constant C_1 depends only upon the form of the magnetic field and of the test-piece, so that the final constant C should be completely independent of external conditions as long as H remains constant. Nevertheless, the apparatus required frequent calibration in order to give consistent results. The temperature and field controls were similar to those previously described. The test-piece was 12 mm. long and 3 mm. thick. It was, of course, diamagnetic and its susceptibility depended on the temperature. The calibration was done with water and with the apparatus evacuated. A typical calibration was as follows: at 20° for water $\chi_s = -0.720 \times 10^{-6}$ and $K = \chi d = -0.719 \times 10^{-6}$. K for vacuum is zero. Then $K_0 = \phi_{\text{vac.}}C = 884C$, where 884 is the reading given by the telescope attached to the torsion head. Also $K_0 + 0.719 \times 10^{-6} = \phi_{H_2O}C = 78C$, hence $C = -0.719 \times 10^{-6}/806 = -8.92 \times 10^{-10}$. The negative sign depends merely on which direction for the torsion head is considered positive.

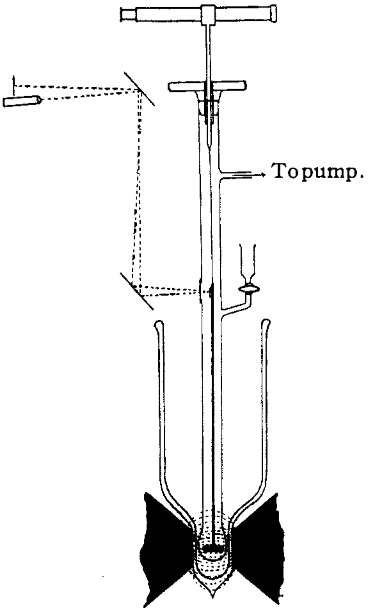

Fig. 3.—Torsion magnetic balance.

It was of course necessary to determine K_0, the volume susceptibility of Pyrex glass over the complete range of temperature. Data for K_0 are given below. Temperature dependence of the susceptibility of glass is discussed by Gerlach and Little[17] and must be due to traces of some paramagnetic constituent in the glass.

When the apparatus was calibrated in vacuum there was some danger of the test-piece being at a temperature different from the bath. A convenient check was to admit dry oxygen, the susceptibility of which is well known.

As the field was of necessity not homogeneous it was necessary to return the test-piece to the same position for every reading. However, the readings could be greatly facilitated if the spot of light from the mirror could be returned conveniently near

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(16) For rigorous derivation see Stoner, Ref. 10, p. 273.

(17) Gerlach and Little, *Z. Physik*, **52**, 464 (1928).

Table I

Volume Susceptibility of Pyrex Glass

Temp., °C.	20	0	−20	−40	−60	−80
$K_0 \times 10^6$	−0.784	−0.778	−0.766	−0.752	−0.731	−0.701
Temp., °C.	−100	−120	−140	−160	−180	
$K_0 \times 10^6$	−0.662	−0.615	−0.560	−0.495	−0.420	

its zero point and then a small correction applied to the torsion head reading. In order to justify such a procedure it was necessary to examine the relation between displacements on the two scales, which will be called the mirror scale and the telescope scale. This amounts to examining the relation between the moment M_M and angular displacement of the test-piece. Figure 4 shows this relation to be nearly but not quite a straight line. It was found safe to correct for small displacements on the mirror scale provided they did not exceed 1 cm. For solutions in which K_0 and K were nearly identical, this method was most convenient. The relative measurements by the torsion method are believed accurate to 0.001 × 10^{-6} units of susceptibility although the absolute accuracy is doubtless considerably less.

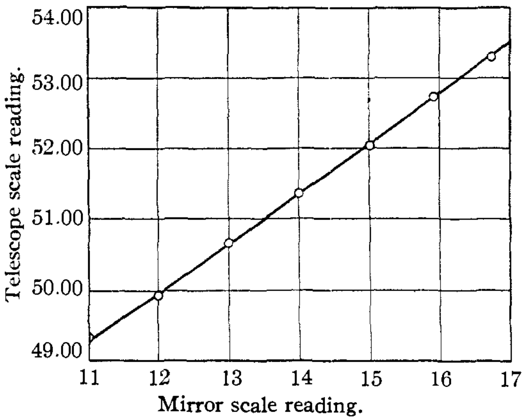

Fig. 4.—Relation between test-piece position and the magnetic couple acting on it.

Preparation of Materials.—The preparation and purity of the neodymium have been described previously. In the preparation of the neodymium and lanthanum compounds described below all reagents were specially purified unless otherwise mentioned. The mineral acids were invariably redistilled. As oxalic acid was used for precipitation of the oxalate preparatory to ignition to oxide, considerable care was taken to ensure its purity. The oxalic acid was repeatedly recrystallized from redistilled hydrochloric acid until the supernatant liquid became quite colorless. The crystallization was then repeated from distilled water until no test for chloride remained. The compounds of neodymium examined were the oxide, octahydrated sulfate, and the anhydrous sulfate, nitrate, perchlorate, and fluoride.

The oxide was prepared as mentioned above. The ignition was carried out at nearly white heat for twelve hours. This intense and prolonged ignition was found necessary if results were to be duplicated.

The hydrated sulfate $Nd_2(SO_4)_3 \cdot 8H_2O$ was prepared from the oxide. A paste made from Nd_2O_3 and H_2SO_4 was heated to drive off excess water and acid. The resulting nearly anhydrous sulfate was dissolved in ice-water, filtered, and heated to boiling. The crystalline precipitate which appeared was dried at 80°, ground to a fine powder, placed in a vacuum desiccator over saturated $Nd_2(SO_4)_3 \cdot 8H_2O$ solution for twenty-four hours and finally allowed to stand in a balance case for another twenty-four hours. This procedure is somewhat similar to that described by Freed[18] for $Sm_2(SO_4)_3 \cdot 8H_2O$. The material was analyzed for neodymium by precipitation as oxalate and ig-

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[18] Freed, This Journal, **52**, 2702 (1930).

nition to oxide. The results checked the theoretical to within 0.2%. This method of analysis was used in preference to direct ignition because of the long and very intense ignition necessary to decompose the sulfate.

The anhydrous sulfate was prepared from the hydrated sulfate by heating it for twelve hours at about 400°. No analysis was carried out. The material dissolved in cold water to give a clear solution, showing the absence of decomposition to oxide.[19]

The anhydrous nitrate was prepared as previously described by the writer.[3] It was analyzed merely by ignition to the oxide and checked the theoretical to 0.2%.[20]

Anhydrous neodymium perchlorate does not appear to have been prepared before. The hydrated salt was made from Nd_2O_3 and $HClO_4$ (redistilled under reduced pressure). The anhydrous salt was then made by raising the temperature slowly to 200° while a high vacuum was applied. The salt was removed and finely powdered several times during the dehydration. Any higher temperature than 200° resulted in partial decomposition. The material as prepared dissolved in water to give a clear solution which showed only a faint opalescence with silver nitrate. It was analyzed by the oxalate-oxide method and checked the theoretical to 0.4%. The results indicated that the dehydration might not have been quite complete. The compound had several properties of interest. Like the anhydrous nitrate it was quite hygroscopic. On gentle warming with a Bunsen burner it began to decompose so violently as to heat itself to incandescence. The product of decomposition was probably an oxychloride, as it contained much chloride, was insoluble in water and cold nitric acid, but soluble in hot acid. Prolonged ignition yielded the pure oxide.

Anhydrous rare earth fluorides have been prepared by Hirsch,[21] who covered the hydrated fluoride with absolute alcohol and heated to 200°. It was decided to attempt the toluene method[22] for this preparation. Gelatinous hydrated neodymium fluoride was precipitated from a chloride solution by adding insufficient hydrofluoric acid (not specially purified). This was centrifuged and washed with water several times. It was dried at 100° and then covered with purified toluene which was distilled off. The fluoride was finally heated to about 200° in a vacuum for a short time. The final product appeared to be quite anhydrous. It should be mentioned that it was essential to have very pure toluene. The analysis was less accurate because of the difficulty in getting the fluoride into solution. This was done by digesting it with sulfuric acid in a platinum crucible. The analysis was completed by the oxalate-oxide method. The analyses which checked themselves fairly well were a few per cent. low, indicating perhaps incomplete dehydration but more likely partial loss of material during the analysis.

In order to determine the effect of magnetic dilution while holding the crystalline field practically constant, measurements were made on various mixtures of neodymium oxide and lanthanum oxide.[23] Although lanthanum oxide is known to be diamagnetic, the material available was paramagnetic and a long process of purification became necessary. The elements it was required to remove were bismuth, cerium, praseodym-

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(19) The statement which sometimes appears that the oxides of the cerium group rare earths are somewhat soluble in water is not true in any ordinary sense. Prolonged boiling of Nd_2O_3 in water followed by filtering through fine sintered glass yields no spectroscopic trace of neodymium in the filtrate.

(20) A well-known method of separating rare earths from one another is by heating the nitrate mixture to about 250°, then dissolving in water and boiling until a precipitate appears. It has long been thought that a partial decomposition took place on heating and that this was the cause of the precipitate. However, the writer finds that as far as neodymium is concerned a neutral solution of the nitrate prepared by any method will yield a precipitate by hydrolysis on boiling. There is no decomposition of the dry neodymium nitrate provided the temperature does not rise above 250–260°.

(21) Hirsch, *J. Ind. Eng. Chem.*, **3**, 885 (1911).

(22) Coparisow, *Nature*, **128**, 838 (1931).

(23) The writer is indebted to Dr. B. S. Hopkins of the University of Illinois for the use of both lanthanum and neodymium in this work.

ium, and manganese, the last of which was purposely added during the removal of cerium. Bismuth was removed as sulfide from a chloride solution. Cerium was precipitated as basic ceric nitrate after oxidation with potassium permanganate and the procedure was repeated until no test by the hydrogen peroxide–ammonia method was obtained. Praseodymium, the presence of which was detected spectroscopically, was removed by repeated fractional precipitation of the oxalate after fractional precipitation with magnesium oxide had proved less satisfactory. Both these are standard methods. By this means a sample was obtained which showed no praseodymium absorption spectrum through a 5-cm. layer of saturated nitrate solution. The manganese, which was not removed by repeated oxalate precipitations, was completely eliminated by precipitation of the hydrated lanthanum sulfate $La_2(SO_4)_3 \cdot 9H_2O$ from a boiling solution of the anhydrous sulfate.[24] The lanthanum was precipitated as hydroxide by passing ammonia gas into the boiling solution, and it was finally dissolved in nitric acid and precipitated as oxalate for ignition to oxide.

During this process the magnetic susceptibility of the lanthanum steadily improved; but even after repeating the whole purification procedure it continued to show some dependence on temperature.

TABLE II

Susceptibility of the Lanthanum Oxide

Temperature, °C.	100	0	−77	−188
$\chi_s \times 10^6 \pm 0.05$	−0.25	−0.25	−0.20	−0.15

Alkali salts remain as possible impurities but they too are diamagnetic. The only other measurement on lanthanum oxide at low temperatures seems to be that of Williams quoted in the "International Critical Tables" as -0.4×10^{-6} at room temperature and apparently independent of temperature. During the introduction of the oxide to the glass tube a certain amount of paramagnetic air must have entered between the individual particles. In order to see whether this was responsible for the temperature dependence, the air in the tube was pumped off while the lanthanum in the tube was heated, and nitrogen was allowed to take the place of the air. No change in the susceptibility could be observed. The oxalic acid used in the final precipitation was also examined with the results described above.

In spite of the elaborate purification procedure the writer is scarcely willing to believe that the susceptibility of pure lanthanum oxide is not strictly independent of temperature, and as praseodymium remained the most likely impurity it was of interest to calculate what amount of praseodymium could be responsible for the observed temperature dependence. This was done as follows: we have the relation $\chi_m = \chi_{La} p_{La} + (C_{Pr}/(T + \Delta_{Pr}))\ (1 - p_{La})$ where χ_m is the susceptibility of the mixture, χ_{La} that of the La_2O_3, p_{La} the fraction of La_2O_3 present, C_{Pr} the Curie constant of Pr_2O_3, and Δ_{Pr} the molecular field constant of Pr_2O_3. Taking C_{Pr} as $11{,}000 \times 10^{-6}$ per gram, and Δ_{Pr} as 70° we have for the measurements at 20° and −188°, respectively.

$$-0.25 \times 10^{-6} = \chi_{La} p_{La} + \frac{11{,}000 \times 10^{-6}}{293 + 70} (1 - p_{La}) \quad \text{and}$$

$$-0.15 \times 10^{-6} = \chi_{La} p_{La} + \frac{11{,}000 \times 10^{-6}}{85 + 70} (1 - p_{La})$$

whence $p_{La} = 99.8\%$ and $\chi_{La} = -0.29 \times 10^{-6}$. It is not impossible that 0.2% Pr_2O_3 could have escaped detection. Assuming that the specific susceptibility is -0.29×10^{-6}, the molar susceptibility of the lanthanum ion may be estimated as -28×10^{-6} after correction for the molar diamagnetism of the oxygen as follows:

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[24] The writer wishes to thank Mr. Nelson Allen for suggesting this most satisfactory procedure.

$[(-0.29 \times 10^{-6} \times 325.8) - 39 \times 10^{-6}]/2 = -28 \times 10^{-6}$. The theoretical estimate of Pauling[25] is -38×10^{-6}. No further purification of the lanthanum was attempted.

In the preparation of mixtures of lanthanum and neodymium oxides a mechanical mixture was in no sense sufficient. It was essential that the neodymium should be in solid solution in the lanthanum. Freshly ignited samples of the respective oxides were weighed out, mixed, dissolved in nitric acid, precipitated as oxalate, and ignited. The oxalate precipitation was carried out rapidly with a large excess of oxalic acid in order to avoid partial separation. Mixtures were made up containing 50, 10 and 2% Nd_2O_3 by weight.

In the work on solutions it was decided to use alcoholic solutions of anhydrous neodymium nitrate rather than aqueous solutions because of the wider and more favorable temperature range available. This part of the work was not very satisfactory because the more concentrated solutions became too viscous to measure at low temperatures, while for reasons stated below the data on dilute solutions could not be applied to the problem in hand. Furthermore, as anhydrous neodymium nitrate is not very soluble in absolute ethyl alcohol, it was necessary to water the alcohol to the extent of about 10%. This was fairly satisfactory as a solvent. Anhydrous neodymium sulfate was found to be quite insoluble in alcohol.

The densities of the solutions were determined pycnometrically, and the concentrations by evaporation and ignition of weighed samples. Data on the C_2H_5OH + 10% H_2O solvent used are as follows: K_1 and K_2 are the volume susceptibilities for two separate determinations, calculated as indicated above, $\chi = K/d$ = the specific susceptibility.

TABLE III

SUSCEPTIBILITY OF ALCOHOL SOLVENT

Temp., °C.	$-K_1 \times 10^6$	$-K_2 \times 10^6$	Mean $K \times 10^6$	Density	$-\chi \times 10^6$
40	0.593	0.588	0.591	0.7875	0.750
20	.597	.592	.595	.8041	.740
0	.601	.598	.600	.8217	.730
−20	.607	.606	.607	.8392	.723
−40	.617	.618	.618	.8565	.722
−60	.630	.633	.632	.8738	.723
−80	.648	.652	.650	.8910	.730

It is not known whether the observed variation of χ with temperature has any real significance. Solutions were made up containing 41.42, 4.62, and 0.522% $Nd(NO_3)_3$ by weight.

Results

Interpretation of the experimental results involves calculation of χ_{Nd}, the susceptibility per gram ion (hereafter the three plus signs will be omitted from Nd^{+++}), and of Δ, the molecular field constant. These calculations are based on the familiar Wiedemann law $\chi_m = \chi_1 p_1 + \chi_2 p_2 + \dots$ For the pure neodymium compounds the experimental values were converted first to molar susceptibilities, and then corrections were applied for the diamagnetism of the acid radical, for the water of crystallization (if any), and for the underlying diamagnetism of the neodymium ion. The susceptibilities of the oxide and sulfates have to be halved because of the two neodymium ions present. The various correc-

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(25) Pauling-Van Vleck, Ref. 4, p. 252.

tions, mostly Pascal's values taken from Stoner, p. 122, are given in Table IV.

TABLE IV

DIAMAGNETIC CORRECTIONS

Group	Molar susceptibility × 10^6	Authority
$O^=$	−13	Same as water
$SO_4^=$	−37	Pascal
NO_3^-	−18	Pascal
ClO_4^-	−37?	Estimated same as $SO_4^=$
F^-	−11.5	Pascal
H_2O	−13	$x_{H_2O} = -0.72 \times 10^{-6}$
Nd	−30	See below

All these corrections are small compared with the paramagnetism of the neodymium ion which is about 5000×10^{-6} at 20°. Correction for the diamagnetism of neodymium is based on the experimental value -28×10^{-6} for lanthanum which it resembles except for the three 4f electrons whose contribution to the diamagnetism is probably slight. This point is discussed by Van Vleck, p. 252.

The reciprocal of the susceptibility per gram ion obtained as above was then plotted against the absolute temperature and a straight line (or in some cases a smooth curve) was drawn through the points. In general the experimental points did not lie off the straight line by more than 0.5%. The results given below for $1/\chi_{Nd}$ are values read off the straight line, and the other quantities given were calculated from this mean value of $1/\chi_{Nd}$. The method of calculation for the oxide mixtures and for the solutions was similar, a correction being made for the experimentally determined diamagnetism of the lanthanum and alcohol, respectively.

In the following tables the temperatures are in degrees K., χ_s is the specific susceptibility, χ_M the molar susceptibility, and χ_{Nd} the paramagnetic susceptibility per gram ion of neodymium corrected as described above. Δ is given in degrees.

TABLE V

T, °K.	$\chi_s \times 10^6$	$\chi_M \times 10^6$	$\chi_{Nd} \times 10^6$	$\frac{1}{\chi_{Nd}} \times 10^{-4}$	$\chi_{Nd}(T + \Delta)$
	Nd_2O_3		$\Delta = 59$		
373	25.2	8480	4290	2.33	1.85
293	30.9	10400	5260	1.90	1.85
223	38.8	13060	6580	1.52	1.86
153	52.9	17800	8930	1.12	1.89
83	89.4	30100	15100	0.66	2.14
	NdF_3		$\Delta = 56$		
373	20.0	4030	4100	2.44	1.76
293	24.7	4980	5050	1.98	1.76
223	30.9	6220	6290	1.59	1.75
153	41.4	8330	8400	1.19	1.76
83	66.7	13430	13500	0.74	1.88

TABLE V (*Concluded*)

T, °K.	$\chi_s \times 10^6$	$\chi_M \times 10^6$	$\chi_{Nd} \times 10^6$	$\frac{1}{\chi_{Nd}} \times 10^{-4}$	$\chi_{Nd}(T + \Delta)$
	$Nd(NO_3)_3$		$\Delta = 49$		
373	12.3	4050	4130	2.42	1.74
293	15.2	5020	5100	1.96	1.74
223	19.2	6330	6410	1.56	1.74
153	25.9	8540	8620	1.16	1.74
83	39.6	13020	13100	0.76	1.73
	$Nd(ClO_4)_3$		$\Delta = 48$		
373	9.10	4030	4170	2.40	1.76
293	11.3	5010	5150	1.94	1.76
223	14.3	6310	6450	1.55	1.75
153	19.3	8560	8700	1.15	1.75
83	39.7	13160	13300	0.75	1.74
	$Nd_2(SO_4)_3 \cdot 8H_2O$		$\Delta = 45$		
343	12.7	9160	4720	2.12	1.83
293	14.6	10500	5410	1.85	1.83
223	18.5	13320	6800	1.47	1.82
153	25.0	18060	9170	1.09	1.82
83	39.3	28320	14300	0.70	1.83
	$Nd_2(SO_4)_3 \cdot 8H_2O$ begins to decompose a little above 80°				
	$Nd_2(SO_4)_3$		$\Delta = 42$		
373	13.9	8030	4100	2.44	1.70
293	17.3	9990	5080	1.97	1.70
223	22.0	12650	6410	1.56	1.70
153	30.1	17370	8770	1.14	1.70
83	47.2	27200	13700	0.73	1.71

In the following table showing the results on lanthanum–neodymium oxide mixtures, a column has been added to show the specific susceptibility χ_m of the mixture.

TABLE VI

T, °K.	$\chi_m \times 10^6$	$\chi_s \times 10^6$	$\chi_M \times 10^6$	$\chi_{Nd} \times 10^6$	$\frac{1}{\chi_{Nd}} \times 10^{-4}$	$\chi_{Nd}(T + \Delta)$
	50% Nd_2O_3 in La_2O_3				$\Delta = 55$	
373	12.52	25.3	8520	4310	2.32	1.85
293	15.52	31.3	10540	5320	1.88	1.85
223	19.55	39.3	13240	6670	1.50	1.85
153	26.50	53.2	17920	9010	1.11	1.87
83	46.12	92.4	31100	15600	0.64	2.15
	10% Nd_2O_3 in La_2O_3				$\Delta = 32$	
373	2.32	25.5	8600	4350	2.30	1.78
293	2.95	31.8	10720	5410	1.85	1.76
223	3.92	41.0	13800	6900	1.45	1.76
153	5.44	56.2	18940	9520	1.05	1.76
83	10.06	102.0	34300	17200	0.58	1.98

TABLE VI (*Concluded*)

T, °K.	$\chi_m \times 10^6$	$\chi_s \times 10^6$	$\chi_M \times 10^6$	$\chi_{Nd} \times 10^6$	$\frac{1}{\chi_{Nd}} \times 10^{-4}$	$\chi_{Nd}(T + \Delta)$
	2% Nd_2O_3 in La_2O_3				$\Delta = 30$	
373	.26	25.8	8680	4390	2.3	1.8
293	.40	32.3	10880	5490	1.8	1.8
223	.63	41.5	13980	7040	1.4	1.8
153	.96	57.9	19500	9800	1.0	1.8
83	1.86	95.4	32100	16100	0.62	1.8

In the case of the solutions data for only one of which are given here, $\chi_{sol.}$ is the specific susceptibility of the solution and d the density.

TABLE VII

T	d	$\chi_{sol.} \times 10^6$	$\chi_s \times 10^6$	$\chi_M \times 10^6$	$\chi_{Nd} \times 10^6$	$\frac{1}{\chi_{Nd}} \times 10^{-4}$	$\chi_{Nd}(T + \Delta)$
	41.42% $Nd(NO_3)_3$ in C_2H_5OH					$\Delta = 45$	
313	1.196	5.438	14.18	4685	4769	2.095	1.71
293	1.216	5.813	15.05	4972	5056	1.980	1.71
273	1.236	6.198	16.00	5290	5374	1.860	1.71
253	1.258	6.645	17.07	5640	5724	1.750	1.71
233	1.279	7.200	18.41	6080	6164	1.620	1.71

The solution became too viscous to go below −40°.

In the case of the more dilute solutions containing 4.62 and 0.522% $Nd(NO_3)_3$, χ_s at 20° was found to be 13.85 and 13.98 × 10^{-6}, respectively. Furthermore the $1/\chi$–T relation was far from a straight line. These anomalous results may have been due to unsuspected errors in theory or calibration. However, they are quite outside the range of any known probable error. The point will be investigated further at the first opportunity. It may be mentioned that Quartaroli[26] found anomalous results for the susceptibility of ferric chloride at low concentrations in dry alcohols and ether. The problem is also discussed by Cabrera[27] and mentioned by Kunz.[28] On the other hand, Decker[11] found the susceptibility of neodymium nitrate in very dilute aqueous solution to be quite independent of concentration.

It is of interest to compare the above results with earlier work. Values available up to 1926 are summarized by Zernike and James.[29] Important work since that time has been published by Cabrera and Duperier,[8] by Gorter and de Haas,[30] and by Sucksmith.[31] Data are available only on the oxide and the two sulfates. Values given by Zernike and James are for the gram ion corrected for anion and crystal water but apparently not for the diamagnetism of the neodymium. But the values quoted for the oxide

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[26] Quartaroli, *Gazz. chim. ital.*, **46**, 371 (1916).

[27] Cabrera, *J. chim. phys.*, **16**, 442 (1918).

[28] Kunz, *Bull. Nat. Research Council*, "Theories of Magnetism," 1922, p. 201.

[29] Zernike and James, THIS JOURNAL, **48**, 2827 (1926).

[30] Gorter and de Haas, *Akad. Wetenschappen Amsterdam*, **34**, 1243 (1931).

[31] Sucksmith, *Phil. Mag.*, [VII] **14**, 1115 (1932).

have not been corrected at all. Cabrera and Duperier do not give values for the susceptibilities directly, but these may be calculated from their equation $\chi' + K = C/(T - \Theta)$ and from the published values of K, C and Θ. Gorter and de Haas give results corrected for anion and crystal water but not for the diamagnetism of the neodymium. Sucksmith does not state what corrections, if any, were made. For purposes of comparison all data are converted (interpolated where necessary) to specific susceptibility at 20° with no corrections.

TABLE VIII

COMPARISON OF EXPERIMENTAL RESULTS

		$\chi_s \times 10^6$	
	Nd_2O_3	$Nd_2(SO_4)_3$	$Nd_2(SO_4)_3 \cdot 8H_2O$
Urbain	28.7	..	..
Wedekind	..	..	14.5
Williams	29.6	..	..
S. Meyer	..	..	14.6
Cabrera	..	..	15.4
Zernike and James	..	..	14.5
Cabrera and Duperier	29.6	18.3	..
Gorter and de Haas	..	..	13.08
Sucksmith	28.2	..	..
Selwood	30.9	17.3	14.6

The writer's value for neodymium oxide may be too high although the necessity for strong ignition has been discussed above. Sucksmith's oxide seems to have been contaminated with carbonate. The writer's value for the anhydrous sulfate is probably low, as it yielded the lowest Curie constant of any of the compounds. The value for the hydrated sulfate seems to be quite accurate.

Discussion of Results

By means of quantum mechanics Van Vleck has derived the following expression for the volume susceptibility of a gas in which the multiplet intervals are small compared to kT

$$\chi = (N\beta^2/3kT)\,[4S(S+1) + L(L+1)] \qquad (1)$$

where N is the number of molecules per unit volume, β is the Bohr magneton, and S and L are the resultant spin and orbital moments, respectively. The other quantities have their usual significance. Unfortunately, there are few if any monatomic paramagnetic vapors whose susceptibility may be measured accurately.

In the case of the rare earths the 4f electrons responsible for the paramagnetism are shielded from external forces or, to put it in another way, their orbital wave functions but slightly overlap those of neighboring atoms even in the solid. Questions of orbital distortion such as commonly arise in liquids and solids are therefore absent or much reduced and, as experiment shows, the theory developed for gases may almost equally well be applied to the paramagnetic rare earth ions. In the case of gadolinium the orbital contribution is completely lacking by virtue of the ion being in an ^{8}S state and gadolinium is found to obey the simple Curie law $\chi = C/T$ to the lowest temperatures. Generally, however, the multiplet intervals in the rare earths are large compared with kT. The susceptibility in this case is given by

$$\chi = \frac{Ng^2\beta^2J(J+1)}{3kT} + N\alpha \tag{2}$$

where g is the Lande splitting factor, J is the resultant of the spin and orbital moments, and α is a constant. For samarium and europium neglect of the multiplet intervals introduces large discrepancies into the theoretical susceptibilities. But for the case of neodymium a calculation by Miss Frank[5] shows that correction for the higher multiplet levels adds only three per cent. to the susceptibility at room temperature. The constant $N\alpha$ (for details of which the reader must be referred to Van Vleck, p. 233) contributes a small temperature independent part to the susceptibility. The diamagnetic part is, of course, neglected throughout this discussion. Gorter, de Haas, and van den Handel[7] estimate $N\alpha$ for neodymium at room temperature to be about 4% of the temperature dependent part of the susceptibility.

Many substances follow the Weiss law $\chi = C/(T + \Delta)$ in preference to $\chi = C/T$ and numerous attempts have, therefore, been made to find a theoretical basis for Δ. That of Weiss which is best known of the classical theories is based on the mutual action of the elementary magnets on one another.

The significance of Δ in quantum mechanics is three-fold.[32] First, when magnetic atoms or ions are close together the Heisenberg exchange interaction has the effect of introducing a very strong coupling between the respective spins. Analysis yields the expression

$$\chi = 4N\beta^2S(S+1)/3k(T - T_c) \tag{3}$$

for the susceptibility above the Curie point which, of course, is the only case in which we are interested here. This expression is of the same form as the experimental Weiss law. It was formerly thought that even diamagnetic atoms would have strong mutual magnetic interactions[33] but it has been shown by Van Vleck and by Slater[34] that atoms or ions with closed shells (and hence diamagnetic) have no exchange interaction. This point is of special interest in connection with the lanthanum–neodymium oxide mixtures.

Second, Δ may appear from the multiplet intervals being neither very small or very large compared with kT. In this case there will be a Boltz-

(32) This question is discussed by Gorter, *Physik. Z.*, **14**, 546 (1932), as well as at length by Van Vleck.

(33) Terry, Bull. Nat. Research Council, "Theories of Magnetism," p. 159.

(34) Slater, *Phys. Rev.*, **35**, 509 (1930).

mann statistical distribution between the various levels and the Curie constant itself will change with temperature. Δ therefore will have no real significance and will probably not remain constant over a very large temperature interval. Except to the small extent mentioned above this effect does not enter into the case of neodymium.

The third source of Δ is the effect of inhomogeneous electric fields produced by neighboring ions or oriented solvent dipoles on the orbital moments of the 4f electrons. Measurements at low temperatures are of particular interest because they show the order of magnitude of the interatomic forces tending to orient the 4f orbits. Penney and Schlapp have examined theoretically the influence of crystalline fields on the susceptibilities of praseodymium and neodymium. They show that in this case the field causes a splitting of the multiplet levels and consequent redistribution of the magnetic moment. At ordinary temperatures kT is of the same order as the energy separations produced by the field and the susceptibility actually appears to follow the Weiss law over a wide range of temperatures although here again Δ has no real significance. At low temperatures the $1/\chi-T$ relation should bend toward the T axis.

The fact that for neodymium Δ remains about 40 or 45° at even the highest magnetic dilution indicates that while the exchange interaction becomes negligible, the field of oriented solvent dipoles (or water of crystallization) remains constant and fairly large. Attempts to apply equation 2 are, therefore, not entirely satisfactory even for dilute solutions and are much less so for the oxide. Sucksmith, however, gives for the gram ion at 20° in the oxide $\chi_{\text{calcd.}} = 5760 \times 10^{-6}$, Cabrera = 4910, Sucksmith = 4790. The value 5410 obtained by the writer from the hydrated sulfate is in considerably better agreement with the theoretical. As for the constant paramagnetic part $N\alpha$ in (2), Sucksmith finds $1/\chi-T$ for Nd_2O_3 is practically a straight line from 90°K. to room temperature but shows a satisfactory bending toward the T axis at higher temperatures. If $N\alpha$ amounts to 4% of the temperature dependent part at room temperature it should have been detected in the writer's work, but no deviation above about 150°K. was found.

Turning now to a consideration of the molecular field, it is difficult to distinguish between the exchange interaction and the crystalline field effect. Δ is the same in solution as in the hydrated sulfate and increases with the tightness of atomic binding in the salts studied although the low value for $Nd_2(SO_4)_3$ is a definite discrepancy. It was hoped that the behavior of the oxide mixtures would clear up this point and more accurate measurements on such mixtures should be valuable. In the 50% mixture Δ is nearly the same as in pure Nd_2O_3. The fact that it falls below 40 or 45° in the dilute mixtures may have no significance because of the high probable error. In oxide mixtures the crystalline field surely cannot vary nearly as much as say between fluoride and hydrated sulfate, while as has been mentioned there can be no exchange interaction involving a diamagnetic group. We are therefore forced to the surprising conclusion that practically all the change in Δ in the different salts is due to exchange interaction.

On the other hand, there is almost equally strong evidence that the crystalline fields do vary strongly from one compound to another. As mentioned above Penney and Schlapp find theoretically a bending of the $1/\chi-T$ relation toward the T axis at very low temperatures and their results are in excellent agreement with the measurements of Gorter and de Haas on $Nd_2(SO_4)_3 \cdot 8H_2O$. The writer's measurements were not carried low enough to show this bending for $Nd_2(SO_4)_3 \cdot 8H_2O$ but it is apparent for Nd_2O_3, NdF_3 and the 50% La–Nd oxide mixture in which the crystalline fields might be expected to be more intense than in the other compounds.

It was previously shown that the susceptibility of $Nd(NO_3)_3$ in aqueous solution decreased about 2% over a concentration range 0.3 to 3.0 molar. Such a change could be accounted for by an increase of Δ by about 7°. However, as Δ for anhydrous $Nd(NO_3)_3$ is only 4° higher than that in solution, it is probable that most of the concentration change in Δ was produced by other causes.

The writer is at a loss to explain the changes in Curie constant from one compound to another. Such changes are by no means uncommon. For instance, Theodorides[35] finds as follows for the Curie constant of manganese: $MnSO_4$, −4.267; $MnCl_2$, −4.097; MnO, −3.808 and 3.534.

There seems to be a definite relation between the molecular field and the shift of absorption bands, although measurements of absorption in the solid are scanty. The writer found a shift of about 10 Å. toward the red in the case of the sharp 4270 Å. band of neodymium in going from the dilute solution to crystalline $Nd(NO_3)_3 \cdot 6H_2O$. Until rare earth absorption spectra are more thoroughly understood it will be difficult to establish any theoretical relation between Δ and the spectral shifts.

The writer wishes to thank Dr. Charles P. Smyth for his interest in this work.

Summary

Measurements on magnetic susceptibility over the temperature range −190° to about 100° have been made for the compounds Nd_2O_3, NdF_3, $Nd(NO_3)_3$, $Nd(ClO_4)_3$, $Nd_2(SO_4)_3$, $Nd_2(SO_4)_3 \cdot 8H_2O$, La_2O_3 and certain mixtures of lanthanum and neodymium oxides. Data are also given on a solution of neodymium nitrate in ethyl alcohol from −40 to 40°, on oxalic acid and on Pyrex glass from −190 to 100°. These results are compared with other work and are discussed with reference to Van Vleck's quantum mechanical theory of paramagnetism and especially with reference to the

(35) Theodorides, *J. Phys. Radium*, [VI] **3**, 1 (1933).

so-called Weiss molecular field and its dependence on crystalline field and exchange interaction. In general the theory is supported although discrepancies are noted. Preparation and properties are given for anhydrous neodymium perchlorate.

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The Behavior of Dichlorodifluoromethane and of Chlorotrifluoromethane in the Electric Discharge

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Dichlorodifluoromethane under ordinary conditions is a very stable, relatively inert gas. Midgley and Henne[2] report that it reacts slowly with metals and with water at 175°; in each case they describe some attack upon the chlorine–carbon bond, but the fluorine remained attached to carbon. Our experiments with pure metals at higher temperatures confirm this result. It was difficult to obtain any extensive reaction under controlled conditions, and the side reactions of intermediate products with the glass walls of the containing tubes made it difficult to determine the course of the main reaction.

In a high-tension electric discharge, however, this rather inert substance is easily broken up to form products of higher and lower volatility. Chief among these are chlorine, chlorotrifluoromethane and carbon tetrafluoride. Considerable quantities of dichlorotetrafluoroethane and less volatile substances, including slightly volatile solids not soluble in any ordinary solvent, also are obtained. And there is good evidence that tetrafluoroethylene is produced in small quantities. These result are satisfactorily explained by supposing that the molecular fragments CF_2, F and Cl are present in the discharge; it is supposed that they combine in random fashion outside the region of activation. After this first combination, secondary reactions may occur: any free fluorine would displace chlorine, and any double bonds would soon be saturated by the chlorine. It is probable that most of the dichlorotetrafluoroethane is formed in this way. Fragments containing less than two fluorine atoms may account for some of the heavier products.

Chlorotrifluoromethane, a substance which seems to be about as inert as dichlorodifluoromethane, may be decomposed in like manner, to produce chlorine, very good yields of carbon tetrafluoride, and small quantities of dichlorodifluoromethane. In this case, no light substances less volatile

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[1] This paper is taken from a thesis presented by Nannie V. Thornton in June, 1932, to the Faculty of the Division of the Physical Sciences of the University of Chicago in part fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Midgley and Henne, *Ind. Eng. Chem.*, **22**, 543 (1930).