

## The Diamagnetism of Gaseous Nitrosyl Chloride

Carrol M. Beeson and Charles D. Coryell

Citation: [The Journal of Chemical Physics](#) **6**, 656 (1938); doi: 10.1063/1.1750146

View online: <http://dx.doi.org/10.1063/1.1750146>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/6/10?ver=pdfcov>

Published by the [AIP Publishing](#)

---

### Articles you may be interested in

#### [Nitrosyl Chloride Structure](#)

J. Chem. Phys. **34**, 2195 (1961); 10.1063/1.1731857

#### [On the Ionicity of Gaseous Thallous Chloride](#)

J. Chem. Phys. **22**, 573 (1954); 10.1063/1.1740126

#### [The Structure of Nitrosyl Chloride from the Microwave Absorption Spectrum](#)

J. Chem. Phys. **18**, 1514 (1950); 10.1063/1.1747527

#### [The InfraRed Spectrum of Nitrosyl Chloride](#)

J. Chem. Phys. **18**, 1411 (1950); 10.1063/1.1747486

#### [The Free Energy and Entropy of Nitrosyl Chloride](#)

J. Chem. Phys. **6**, 335 (1938); 10.1063/1.1750262

---



Judging from the spectra we have been led to assign rather permanent, discrete geometrical configurations to the fields about the ions of europium notwithstanding the fact that such configurations have long been imagined characteristic of non-electrolytes. This behavior is not limited to salts of europium. It is not due to some singular electronic distribution which europium possesses,<sup>6</sup> since europium ion acts in its salts and solutions like the *spherically* symmetrical gadolinium ion ( $^8S$ ). Salts of these two ions are almost inseparable by fractional crystallization; they are next to each other in the periodic table.

The model for the structure of these electrolytes which the spectra seem to place before us has little resemblance to the model evolved by the interionic attraction theory. There is, for example, no sign of a diffuse ionic atmosphere changing continuously in extent and field intensity with dilution. The spectra give no suggestion that at greater dilution discrete structures will disappear. The fact is that when one discrete structure disappears another as discrete and fixed takes its place.

There may, of course, be somewhat similar phenomena with bivalent ions but there seems little likelihood that they are prominent in univalent ions where the Debye-Hückel theory has been so conspicuously successful. However, with simple trivalent ions in the range of concentrations we have investigated, there are, it seems, sufficient reasons for expecting the Debye-Hückel theory to be in disagreement with the experimental results.

SIMON FREED

G. H. Jones Laboratory,  
University of Chicago,  
Chicago, Illinois,  
September 9, 1938.

<sup>1</sup> S. Freed and S. I. Weissman, J. Chem. Phys. (1938).

<sup>2</sup> S. Freed and H. F. Jacobson, J. Chem. Phys., in this issue.

<sup>3</sup> H. Bethe, Ann. der Physik 3, 133 (1929).

<sup>4</sup> The osmotic coefficients of the salts of those rare earths which have been measured (C. M. Mason, J. Am. Chem. Soc. 60, 1638 (1938)) differ extremely little. The isomorphism of the crystals, their miscibility with each other, the slight differences in the ionic sizes and in the molal volumes and especially the great difficulty of separating them by fractional crystallization.

<sup>5</sup> International Critical Tables.

<sup>6</sup> The exceptionally sharp lines, that is, the exceptionally weak coupling which  $\text{Eu}^{++}$  has with the oscillations, rotations, etc., of the environment, may, perhaps, be related to the zero value of the angular momentum of the electronically activated state, i.e.,  $J=0$ . The basic state of  $\text{Eu}^{++}$  is actually  $J=0$  and the thermally activated states are  $J=1$  etc. Transitions between these and an activated state  $J=0$  are very probable.

### The Separation of the Carbon Isotopes by Diffusion

The results to be described were obtained with a battery of 51 Hertz-type pumps as modified by Professor W. Bleakney of Princeton.<sup>1</sup> Preliminary experiments on mixtures of argon-helium, carbon dioxide-nitrogen and carbon dioxide-argon permitted the determination, for these mixtures, of the best operating conditions in respect to applied

heat and working pressure. With respect to the latter, our results confirm those of Barwich.<sup>2</sup> As for the question of the presence or absence of a capillary between the pump units we have found that the yield is better without a capillary. For the two mixtures carbon dioxide-argon and carbon dioxide-nitrogen we have obtained separation factors of 2.4 and 5.4 respectively. From these values it is possible to calculate, for methane, a theoretical separation factor of 1.18. Experimentally we found that, for methane, better separation of the carbon isotopes could be obtained with higher heats than in the cases of the above mixtures. In spite of this, however, the experimental separation factor is less than the theoretical value, in agreement with the data of Sherr.<sup>1</sup> At the present time, with an adequate system of purification and circulating a large volume of methane, we have obtained in thirty hours of pumping a yield of 300 cc of methane at 1.8 mm Hg pressure and containing from 30 to 32 percent of carbon 13. This is indicated by the relative intensities of the Swan bands  $\text{C}^{12}-\text{C}^{12}$ ,  $\text{C}^{12}-\text{C}^{13}$  and  $\text{C}^{13}-\text{C}^{13}$  reproduced in Fig. 1.

We wish particularly to thank Messrs. Breyre and Coppens of the Institut National des Mines at Paturages, who placed at our disposal specially purified methane.

P. CAPRON  
J. M. DELFOSSE  
M. DE HEMPTINNE  
H. S. TAYLOR

Institut de Physique,  
Université de Louvain,  
Louvain, Belgium,  
September 15, 1938.

<sup>1</sup> R. Sherr, J. Chem. Phys. 6, 251 (1938).

<sup>2</sup> Barwich, Zeits. f. Physik 100, 166 (1936).

### The Diamagnetism of Gaseous Nitrosyl Chloride\*

In a recent paper Jahn<sup>1</sup> suggested that nitrosyl chloride ( $\text{NOCl}$ ) exists in a triplet normal state, perhaps with a low-lying singlet state, in order to explain the apparent excess entropy of  $R \ln 3$  or  $R \ln 4$  calculated from equilibrium measurements over that calculated from structural and spectroscopic information. This triplet ground state would lead to paramagnetism of the substance. Wilson<sup>2</sup> made magnetic measurements on liquid nitrosyl chloride and found it to be diamagnetic. There remains, however, the possibility that polymerization of the molecules in the liquid state might reduce the paramagnetism of the substance, as is the case with oxygen at sufficiently

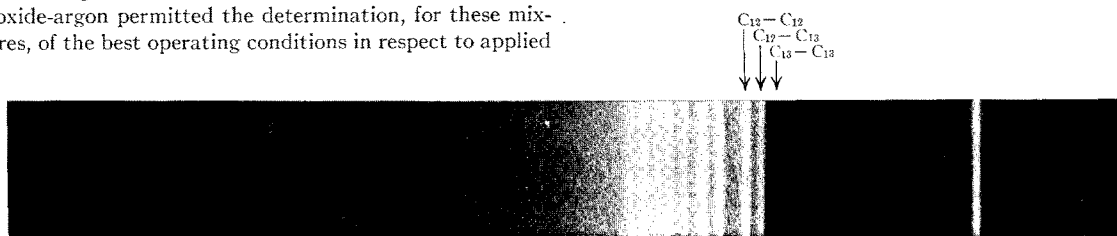


FIG. 1.

low temperatures. We have therefore carried out measurements on the gaseous compound.

The susceptibility was measured at 25° by the Gouy method, making comparison with oxygen as the substance of known paramagnetism ( $\kappa = +0.142 \times 10^{-6}$  c.g.s.m. at 20°).<sup>3</sup> A glass tube of 19 mm diameter was separated into two compartments by a glass septum and equipped at either end for sealing off. This was suspended from the arm of an analytical balance, and the apparent change in weight ( $\Delta w$  in mg) of the tube was determined when the magnet was excited with two different currents. The absolute values of the magnetic fields obtained were 8080 and 9350 oersteds at 9.00 and 14.00 ampere readings. With both ends evacuated there were found for the corresponding readings  $\Delta w = +0.10$  and 0.16 (average of at least two determinations); with the upper end evacuated and dried tank oxygen at 701 mm pressure at 25° in the lower end,  $\Delta w = -8.29$  and  $-11.08$ ; with the upper end evacuated and pure nitrosyl chloride at 790 mm pressure at 25° in the lower end,  $\Delta w = +0.11$  and 0.14. The probable error in the determination of  $\Delta w$  is of the order of  $\pm 0.05$  mg. The nitrosyl chloride was prepared from nitric oxide and chlorine which had been carefully purified for use in equilibrium measurements. A large excess of nitric oxide was allowed to react with the chlorine, and the nitrosyl

chloride was then frozen out in the tube and pumped free from volatile impurities.

The predicted values of  $\Delta w$  for nitrosyl chloride in a  $^3\Sigma$  state at the pressure and temperature of measurement are  $-9.3$  and  $-12.5$ ; the predicted values for equipartition between three  $^3\Sigma$  and one  $^1\Sigma$  states (quantum weight four) are  $-7.0$  and  $-9.3$ ; the predicted values for a singlet state (diamagnetic), taking into account the estimated molecular diamagnetism of  $-30 \times 10^{-6}$ , are  $+0.19$  and  $0.28$  respectively. Correction for an estimated dissociation of 0.5 percent<sup>4</sup> into chlorine and paramagnetic nitric oxide would lower the diamagnetic values to  $+0.15$  and  $+0.24$  respectively. The observed  $\Delta w$  values are in satisfactory agreement with this last prediction. We conclude therefore that nitrosyl chloride is diamagnetic and in a singlet state.

CARROL M. BEESON

CHARLES D. CORYELL

Gates and Crellin Laboratories of Chemistry,  
California Institute of Technology,  
Pasadena, California,  
August 23, 1938.

\* Contribution from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, No. 663.

<sup>1</sup> F. P. Jahn, J. Chem. Phys. **6**, 335 (1938).

<sup>2</sup> E. B. Wilson, Jr., J. Am. Chem. Soc. **56**, 747 (1934).

<sup>3</sup> *International Critical Tables*, VI, 354 (1929).

<sup>4</sup> Extrapolation of unpublished equilibrium data of C. M. Beeson and D. M. Yost.