

Symmetries of the Fields About Ions in Solution and Electrolytic Dissociation

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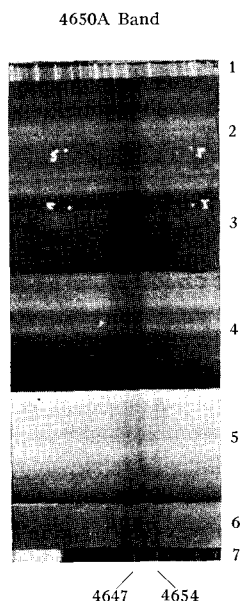


FIG. 1. 1-Fe arc. 2-EuCl₃ .0025 M. 3-EuCl₃ .95 M. 4-Eu(NO₃)₃ .0025 M. 5-Eu(NO₃)₃ .009 M. 6-Eu(NO₃)₃ .95 M. 7-Fe arc.

separate patterns remain unchanged from about 1.5 M to about 0.01 M as observed with a 21-ft. grating. On diluting to 0.0007 M, we could discover no change in the pattern of the chloride but when the nitrate was diluted to 0.0007 M, its group which had consisted of three lines now had changed over to four, indistinguishable in character from those of the chloride. At concentrations between 0.01 M and 0.0007 M, the nitrate showed both spectra and with increased dilution the chloride pattern gained intensity at the expense of the nitrate pattern. (See Fig. 1.)

Europium nitrate in aqueous solution has then distributed itself between two discrete configurations in equilibrium corresponding to different symmetries of the fields about the europium ions. There is some resemblance here to the situation in which two allotropic modifications of a crystal are present together, with this difference, that the equilibrium in the solution of the nitrate takes place within one phase.

In a forthcoming note it will be shown that europium nitrate and europium chloride are strong electrolytes similar to and of the same order of strength as lanthanum nitrate and lanthanum chloride which have served as standard salts in thermodynamic studies of trivalent ions. Because of the close resemblance of europium to other rare earths, we regard the existence of discrete forms of different symmetry as no rare phenomenon—among trivalent ions, at any rate.

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September 2, 1938.

¹ S. Freed and S. I. Weissman, *J. Chem. Phys.* **6**, 297 (1938).

² Since the publication of the previous note, we have discovered that G. Urbain (*J. Chem. Phys.* **4**, 243 (1906)) had observed differences between the spectrum of europium nitrate and of europium chloride in aqueous solution.

Symmetries of the Fields About Ions in Solution and Electrolytic Dissociation

Recent experiments¹ have shown that the fields about the ions of trivalent europium in aqueous solution are sharply defined in their intensities and orientations and that these differ with the nature of the solution. However, with a solution of a given salt, the structures in the spectra which respond to changes in the fields are not affected when the solution is diluted. The wave-lengths of the lines, their sharpness, relative intensities, the spacings within the multiplet, all remain unchanged, from concentrated to dilute solutions. Europium chloride has four lines in a particular group in the blue region. No change could be observed in the character of the lines when the concentration was varied from about 1.5 M to 0.0007 M. Corresponding to this group of lines, europium nitrate has three lines, altogether different in quality from the four of the chloride. These lines experience no change when the solution is diluted, even though a new additional form makes its appearance² at about 0.01 M. The spectrum of the new form is indistinguishable from that of the chloride. As dilution proceeds the "chloride-structure" of the nitrate becomes more intense relative to the original "nitrate-structure." Nevertheless, even though the total intensity of each structure varies, the relative intensities within the structure, the sharpness, and the intervals remain invariable throughout dilution.

The theory of Bethe³ prescribes into how many components a particular energy level will be decomposed by an electrical field of given symmetry. The magnitude of the intervals between the components is a measure of the strength of the fields. We have found that the spectrum of a crystal of hydrated europium nitrate contains three lines in its blue group, having roughly the same intervals as originate from a solution of the nitrate. We are then to conclude that the fields about the europium ions in the crystal are roughly of the same intensity as the fields about the ions in solution. Furthermore this intensity does not change with dilution.

A natural assumption to make at this point is that the salts of europium are revealing bonds which are permanently oriented. If that description is to be correct, it must not exclude the electrolytic dissociation of the salts since, as we shall show, salts of europium are strong electrolytes in about the same measure as the salts of lanthanum. The latter have repeatedly served to illustrate and test the inter-ionic attraction theory.

There is such a mass of different data on the close resemblance among the ions of the rare earths⁴ that there can be little doubt concerning the resemblance with respect to ionization also. As a final check on these inferences, which, to be sure, involve little interpolation, Mr. I. M. Klotz of this laboratory measured the electrical conductivities of solutions of europium nitrate and of europium chloride and found them to be nearly of the same magnitude as those of the corresponding lanthanum salts. Mr. Klotz will publish his data shortly. As to thermodynamic behavior—the freezing point lowering of lanthanum nitrate at 0.01 M is 3.35 times⁵ that of the same concentration of mannose and at 0.001 M it is 3.75 times.

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,⁶ 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.

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September 9, 1938.

¹ S. Freed and S. I. Weissman, *J. Chem. Phys.* (1938).

² S. Freed and H. F. Jacobson, *J. Chem. Phys.*, in this issue.

³ H. Bethe, *Ann. der Physik* **3**, 133 (1929).

⁴ 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.

⁵ *International Critical Tables*.

⁶ The exceptionally sharp lines, that is, the exceptionally weak coupling which 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 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.¹ 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.² 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.¹ 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.

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¹ R. Sherr, *J. Chem. Phys.* **6**, 251 (1938).

² Barwich, *Zeits. f. Physik* **100**, 166 (1936).

The Diamagnetism of Gaseous Nitrosyl Chloride*

In a recent paper Jahn¹ suggested that nitrosyl chloride (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. Wilson² 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

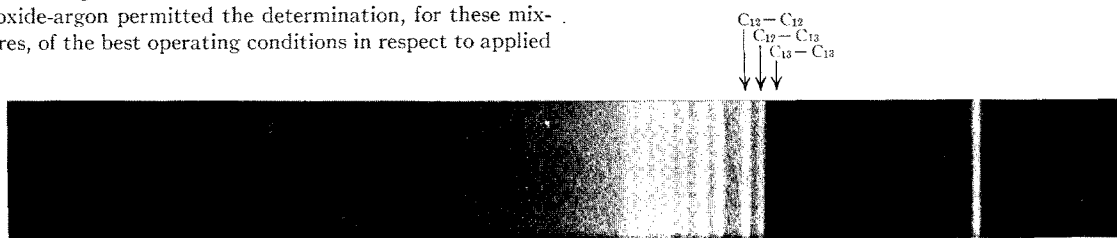


FIG. 1.