[Contribution from the Chemical Laboratory of the University of Illinois]

DEFORMATION OF ELECTRON SHELLS. I.
ABSORPTION SPECTRUM, MOLECULAR VOLUME AND REFRACTION OF NEODYMIUM PERCHLORATE

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The object of this work was to investigate the relations existing between the absorption spectrum and other properties of certain rare earth salts. As pointed out by Foex[1] in a recent article on the "Different Magnetic States of an Ion:" "If each magnetic state corresponds to a special structure of the outer electron layer, it may be expected that all of the properties of the ion which depend on that outer layer will change with the changes that occur in this layer. For example, the refraction of the ion, the absorption bands, the magnetic rotation, polarization, etc., would change when the magnetic state changes. These changes and co-relations have not as yet been investigated."

During the course of work on the absorption spectra of the rare earths by Quill, Selwood and Hopkins,[2] it was observed that the spectrum of neodymium and other rare earth salts in solution could be altered by the addition of excess of a common ion or merely by changing the concentration. In general, the absorption bands of neodymium salts and, to some extent, those of other rare earths investigated were shifted toward the red end of the spectrum by increased concentration.

Regarding the possible mechanism of these absorption band shifts, the authors have this to say, "It is known that even in the case of strong electrolytes the oppositely charged ions in solution may approach close enough to one another to cause distortion of the outer electron shells. It is probable that the distortion may be communicated in part, as small energy changes, to the electrons composing the inner sub-group which is thought to be the seat of the spectrum bands in the visible region. Recent observations by Ephraim and Bloch on the ammonia complexes of praseodymium chloride have been successfully explained by them on the basis of their theory of the deformation of the inner electron shell."

The relation between molecular volume and absorption spectrum has received considerable attention from Ephraim and co-workers.[3] Briefly, the object of their investigations has been to determine whether the deformation of the outer electron shell resulting from chemical union is transmitted to the inner shells. The rare earths are ideal for such an investigation. Ephraim maintains that a chemical union which is attended by a

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[1] Foex, *Trans. Am. Electrochem. Soc.*, **55**, 97 (1929).

[2] Quill, Selwood and Hopkins, This Journal, **50**, 2929 (1928).

[3] Ephraim and Bloch, *Ber.*, **59B**, 2629 (1926); *ibid.*, **61B**, 65, 72, 80 (1928); Ephraim and Ray, *ibid.*, **62B**, 1509, 1520, 1639 (1929).

diminution of molecular volume results in compression of the electron shells, bringing about a shorter period of vibration and a corresponding shift to the violet in the absorption bands. No matter what the theoretical interpretation of Ephraim's results, there can be no question that the extension of his observations to solutions of rare earth salts should provide valuable confirmatory evidence for the deductions which may be drawn from absorption and refraction.

A basis for the work on molecular refraction has been established by Fajans and co-workers.[4] Taking as his primary postulate that the familiar Lorentz–Lorenz expression $R = \frac{n^2 - 1}{n^2 + 2} \times \frac{M}{d}$ is strictly additive unless changes occur in the electron shell, he considers deviations of R as being measures of such changes. Fajans maintains that the close proximity of an anion to a cation will result in an increase in the refraction of the latter proportional to the charge on the anion and to the polarizability of the cation. Conversely, the refraction of an anion is diminished by the approach of a cation.

From the standpoint of the classical Clausius–Mosotti theory of dielectrics, a shift of the absorption bands toward the red should be attended with an increase of molecular refraction. To be sure, absorption bands have to do with only a few electrons in the cation, while refraction has to do with all the electrons in cation, anion and solvent molecule as well; but as pointed out by Fajans, some means are available for the estimation of these various effects.

Experimental

Preparation of Solutions.—The measurements described here were carried out on solutions of neodymium perchlorate. When the work was started neodymia was the only rare earth available in sufficient quantity (about 1000 g.) for the purpose. The neodymium had been prepared by fractional crystallization of the double magnesium nitrate by the writer and others during the past two years. The rich blue color of the oxide and the absence of absorption spectrum bands of other rare earths were taken as evidences of purity.

Perchlorate was chosen because, as has been pointed out by several workers, the refraction of the perchlorate ion is only slightly influenced by concentration or other external influence.[5]

More than sufficient neodymium oxide to prepare 100 cc. each of seven

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[4] Fajans, *Naturwissenschaften*, **11**, 165 (1923); *Trans. Faraday Soc.*, **23**, 357 (1927); Fajans and Joos, *Z. Physik*, **23**, 1 (1924); Fajans, *Z. physik. Chem.*, **130**, 724 (1927); Fajans, Kohner and Geffcken, *Z. Elektrochem.*, **34**, 1 (1928); Fajans, *ibid.*, **34**, 1 (1929); *Z. Physik*, **50**, 531 (1928); *Z. physik. Chem.*, **A137**, 361 (1928); *Z. Krist.*, **66**, 321 (1928).

[5] Mazzucchelli and Vercillo, *Gazz. chim. ital.*, **55**, 498 (1925).

solutions from about 2 to 7 N in neodymium perchlorate was treated with insufficient perchloric acid to effect complete solution. The mixture was subjected to prolonged boiling and was then filtered. The clear filtrate was analyzed for neodymium content and appropriate quantities were removed and evaporated down to the desired concentration. The solutions finally obtained were clear and neutral to litmus.

Analytical Procedure.—Preliminary tests indicated two methods which might be used for the analysis of the solutions. These were, first, precipitation of the neodymium as oxalate with standard oxalic acid, filtering, and back-titration of the excess oxalic acid in the filtrate with standard permanganate; and, second, ignition of the oxalate to oxide which may be weighed directly. Neither of these methods was very satisfactory, and they do not compare in accuracy with the other measurements necessary in the determination of molecular refraction. Both methods were conveniently run on the same weighed sample of solution. The possible oxidation of oxalic acid by the liberated perchloric acid was investigated by standardizing the former against permanganate first in sulfuric acid solution and then in perchloric acid. No difference could be detected, so it was assumed that dilute perchloric acid had no effect on oxalic acid.

The weighed samples of the neodymium perchlorate solutions were acidified with a few drops of dilute sulfuric acid, diluted with water and heated just to boiling. Standard oxalic acid solution to the extent of about one and one-quarter times the amount required to precipitate all the neodymium was added and the mixture was allowed to cool, and if convenient to stand overnight. The mixture was then filtered, the precipitate thoroughly washed, the filtrate was heated to boiling and quickly titrated with standard potassium permanganate solution after the addition of 5 cc. of 6 N sulfuric acid. The neodymium oxalate was dried and ignited in porcelain to constant weight over the full heat of a Méker burner. This required several hours. The oxide was allowed to cool in a carbon dioxide-free desiccator and was weighed. No tendency to increase in weight was observed.

The results obtained by the oxide method were, in general, 1% higher than those by the permanganate method. Good checks were secured by both methods although the oxide checks were better. When the oxide results were plotted against refractive index, the curve obtained was much smoother than when the permanganate results were used. The neodymium oxide when dissolved in nitric acid gave no test for chloride, thus eliminating the possibility of oxalo-perchlorate formation. In view of these facts, and the more direct procedure involved in the oxide method, the results obtained by that method were used exclusively in the calculation of refractions and volumes. The compositions of the solutions given are believed to be accurate to 0.2%. The irregularities in the refraction and volume curves are believed by the writer to be attributable to the unavoidably high probable error in the analytical work. A single determination by weighing the oxalate in a sintered glass crucible after drying at 125° gave an excellent check with the oxide determination on the assumption that the oxalate was associated with one molecule of water. The reliability of this method is, however, said to be open to serious question.[6]

Densimetry.—The densities of the solutions were determined pycnometrically and

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[6] Little (Friend), "Textbook of Inorganic Chemistry," Vol. IV, 1921.

by Archimedes' principle. The temperatures were read to 0.1° on a mercury thermometer calibrated against a Bureau of Standards thermometer. In the case of the most concentrated solution which had the largest temperature coefficient, 0.1° was approximately equivalent to 0.1 mg. on the balance pan, so that nothing could have been gained by more sensitive temperature control. The density of each solution was determined at at least four different temperatures. The densities were plotted against temperature, and the value at the temperature at which the refractive indices were determined was found by interpolation. The maximum probable error is believed to be about 0.02%. The values obtained by the two methods agree within this amount.

Refractometry.—The refractive indices of the solutions were measured on an Eykmann refractometer. The large number of intense absorption bands in the spectrum of neodymium salts rendered it possible that anomalous dispersion would completely mask the small deviations it was hoped to detect. It became necessary, therefore, to plot the refractive index of a concentrated solution over a range of wave lengths in the neighborhood of the yellow and red portions of the spectrum. Figure 1 shows the refractive index of a nearly saturated (about 10 *N*) solution of neodymium nitrate from 4554 to 6708 Å. Most of the wave lengths were obtained from salts of barium placed in the positive crater of a carbon arc. The very slight deviation of the hydrogen C line is attributed to a small change in the position of the source when the change was made from an arc to a Geissler tube. Otherwise the refractive indices lie on a smooth curve, and any anomalous dispersion, if present, must be within the observational error. These results are in accord with those of Elias,[7] who found very slight anomalous dispersion in the region of the intense neodymium band in the yellow.

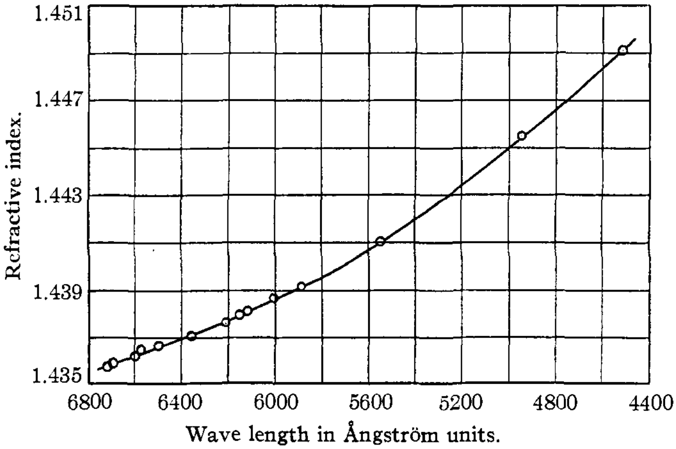

Fig. 1.—Dispersion of saturated $Nd(NO_3)_3$ solution.

The refractive indices used in estimating molecular refraction were all found for the hydrogen C line (6563 Å.) which is in a region comparatively free from absorption. The measurements were made at room temperature, which was read to 0.1° on a calibrated thermometer suspended directly in the solution. The refractive indices were corrected to vacuum and are believed to be accurate to 0.003%.

Absorption Spectrum.—Although some investigators have stated that solutions of neodymium salts obey Beer's laws throughout considerable ranges of concentration, it has been shown elsewhere that this is not true. The present paper indicates that

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[7] Elias, *Ber. Physik. Ges.*, 955 (1910).

absorption band shifts may be found in even the moderate concentrations (about 7 *N*) obtainable with neodymium perchlorate.

For the purpose of this work the absorption spectrum of the highest concentration of neodymium perchlorate prepared (6.63 *N*) through a 3-mm. layer was compared with that of a 0.1989 *N* solution through the equivalent thickness of 100 mm. In the case of the more dilute solution it was believed that the rare earth ions were completely surrounded by water molecules, or their electron shells, at any rate, were shielded from the influence which produces absorption band shifts. Unpublished work by the writer indicates that Beer's law is rigorously obeyed by solutions of rare earth salts from about 0.2 *N* down. The spectra were registered photographically on a Hilger E 1 quartz prism spectrograph, using a quartz system throughout. The light source was a tungsten ribbon incandescent lamp which gave a steady light and a fairly uniform continuous spectrum in the region involved. The curves shown in Fig. 4 are tracings of the curves obtained from the photographic plate on a recording microphotometer.

The longer absorption cell was a glass tube fitted with quartz windows. In order to reduce the relatively large error possible in measurements of 10 mm. or less, the shorter cell was made of brass, gold-plated and ground to the proper dimensions. It was also fitted with quartz windows.

The most serious difficulties in connection with the spectrographic work were the location of satisfactory reference points from which to compare the two microphotometric curves, and the establishment of the highest possible degree of uniformity in exposure and development of the plate.

The first difficulty was readily solved by placing a solution of europium nitrate in the optical train before the slit of the spectrograph. The sharp, intense absorption lines of this element at about 4650 and 5250 Å. are indicated in Fig. 4.

The method used by Jones[8] for procuring uniformity of exposure through long and short absorption cells was one of trial and error where the time of exposure was varied until approximately equivalent blackening of the photographic plate was obtained. In view of the very slight deviations expected in this work, such a method did not seem satisfactory to the writer. Resort was, therefore, made to the following arrangement. Both the long and short cells were left in place throughout both exposures. In the first case the longer cell was filled with the more dilute solution and the shorter cell with water and the plate was then exposed for five minutes. In the second case the longer cell was filled with water and the shorter one with the more concentrated solution. The exposure was again for five minutes. In this way the only possibility of error was in variations in intensity of the light source. The intensity was controlled as closely as possible, and plates wherein it had appeared to vary were rejected. In order further to insure uniformity, the two spectra were taken as near together as possible on the same plate, and the usual precautions were taken in developing and fixing.

Results

The apparent molecular volume of neodymium perchlorate in solution calculated from the simple mixture law is shown in Fig. 2. The values given are the averages of several determinations at 29.5°, and they show about a 14% increase with increasing concentration. Owing, however, to the fact that no account has been taken of the possibility of change in the specific volume of the solvent, the writer does not care to attach much importance to these results other than in a qualitative sense. As such

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[8] Jones, "Absorption Spectra of Solutions," Carnegie Institute of Washington Publications, No. 130, No. 160.

they suggest an agreement with Ephraim's theory which requires an increase in molecular volume to be associated with a decrease of characteristic spectral frequency.

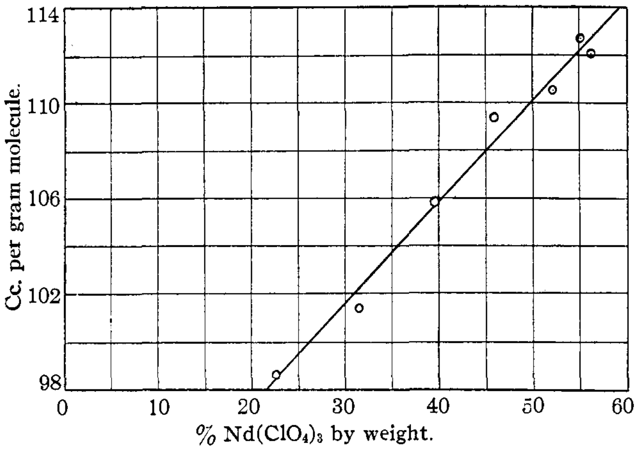


Fig. 2.—Apparent molecular volume of neodymium perchlorate in aqueous solution.

The values for the molecular refraction of neodymium perchlorate are indicated in Fig. 3. These were calculated from the refractive indices

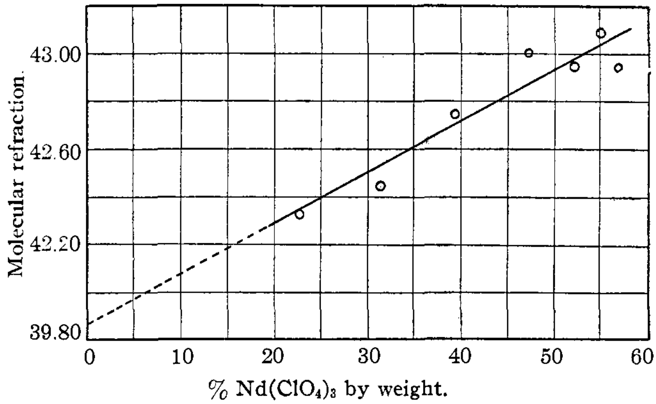
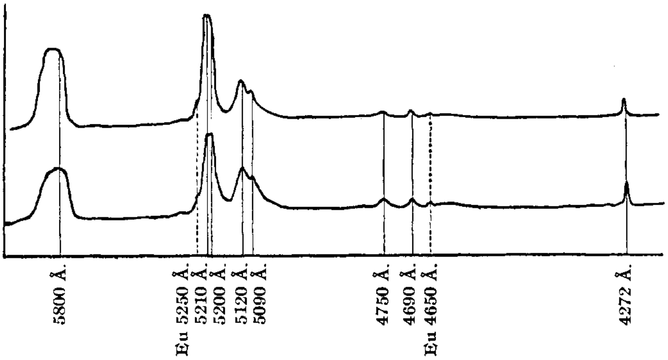


Fig. 3.—Molecular refraction of neodymium perchlorate in aqueous solution.

corrected to vacuum, the absolute densities and the percentage composition by weight, by means of the simple mixture law

$$R = \frac{100\,M}{P}\left[\left\{\frac{n^2-1}{n^2+2}\cdot\frac{1}{d}\right\} - \left\{\frac{n_0^2-1}{n_0^2+2}\cdot\frac{1}{d_0}\right\}\left(\frac{100-P}{100}\right)\right]$$

where R is molecular refraction, M is molecular weight of $Nd(ClO_4)_3$, P is % of $Nd(ClO_4)_3$ by weight, n is refractive index of the solution, d is density of the solution, and n_0 and d_0 are the corresponding quantities for water. The molecular refraction shows about a 2% increase from the extrapolated value at infinite dilution to about 7 *N*. The experimental values given are believed to be accurate to 0.3%, which is about the maximum deviation of any single value from a smooth curve drawn through the points. Each value is the mean of several found for slightly different temperatures between 25 and 30°. Part of the increase in refraction may be ascribed to polarization of the solvent molecule. As such polarization is roughly proportional to the charge on the polarizing ion and inversely to its radius, the effect in this case may be expected to be somewhat less than that estimated by Fajans for the case of aluminum sulfate. In any event, it can scarcely be more than a small part of the observed deviation.



Upper curve, 6.63 *N* $Nd(ClO_4)_3$ through 3 mm. layer; lower curve, 0.1989 *N* $Nd(ClO_4)_3$ through 100 mm. layer.

Fig. 4.—Microphotometric curves of the absorption spectrum of neodymium perchlorate.

Increasing concentration brings about quite noticeable changes in the relative intensities of the different absorption bands of neodymium perchlorate. Such changes are apparent from Fig. 4 but the shifts in position at the highest concentration reached are scarcely to be distinguished except under a microscope. There is no question, however, that a shift of most of the bands toward the red has occurred. Figure 5 is an enlarged reproduction of the sharp band at 4272 Å. It will be seen that increased concentration has brought about a shift of approximately 1 Å. toward the red. The shifts of other bands whose positions are less readily measured are of about the same magnitude and in the same direction.

The classical dispersion formula[9] gives for the square of the refractive index

$$n^2 = 1 + \Sigma \frac{N_i e^2 Z_i}{\pi m_i\,(\nu_{oi}^2 - \nu^2)}$$

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[9] Haas, "Atomic Theory," D. Van Nostrand Co., New York, p. 199.

"In this equation different kinds of electrical charges are assumed to exist and they are distinguished by the subscript i; Z_ie is the quantity of electricity in such a charge, m_i its mass, ν_0 the frequency of its characteristic oscillation and N_i the number of these charges in unit volume." This equation shows that a decrease in characteristic frequency will be attended with an increase in refractive index for a given wave length = $\lambda = 1/\nu$. Such is precisely what has been observed in the experiments described here. It must not be taken for granted, however, that this relation always holds, because further work by the writer on the absorption spectrum of other rare earth salts indicates that it is by no means a general law that all bands shift toward the red with increasing concentration.

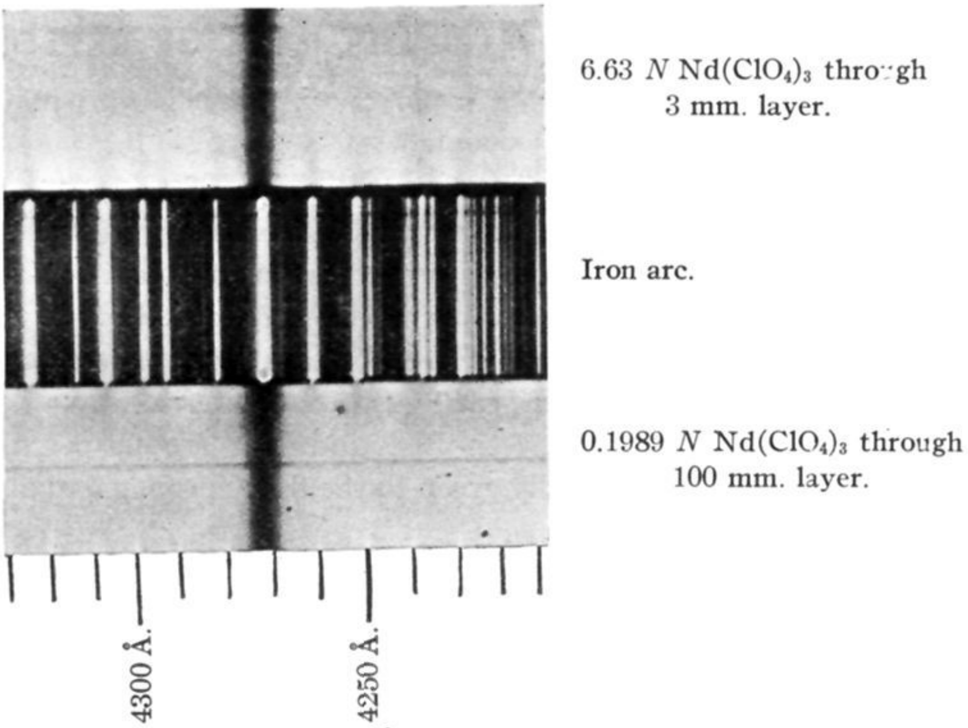

Fig. 5.—The 4272 Å. absorption band of $Nd(ClO_4)_3$.

In terms of the contributions to the subject of Fajans and of Ephraim, it appears that we have here to do with a deformation of the outer electron shells of the rare earth ion. Such deformation seems to be brought about by the approach of the negatively charged perchlorate ion and this deformation appears to be communicated in part at least to the inner electron shell believed to be the source of the characteristic absorption bands.

The writer wishes to thank Professor B. Smith Hopkins, in whose laboratory this work was carried on, for the invaluable advice and encouragement which he has from time to time supplied.

Summary

Deformation of the electron shells of the neodymium ion has been investigated from the standpoints of absorption, volume and refraction

changes. Experimental details are given for the analytical work, for the determination of molecular refraction and for the measurement of absorption bands. In the case of neodymium perchlorate, increasing concentration has been found to be associated with an increase in volume and refraction, and a slight shift toward the red of the absorption bands. Such results agree with deductions from the Clausius–Mosotti theory of dielectrics and are in accordance with recent observations of Fajans and of Ephraim.

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[CONTRIBUTION FROM THE PITTSBURGH EXPERIMENT STATION OF THE U. S. BUREAU OF MINES]

A CHAIN REACTION THEORY OF THE RATE OF EXPLOSION IN DETONATING GAS MIXTURES[1]

BY BERNARD LEWIS[2]

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It is well known that when an explosive gas mixture is ignited at one end of a tube, the initial flame speed, after undergoing a rapid acceleration, acquires a maximum and constant value which does not alter, regardless of the length of the column of gas. Given certain conditions as to temperature, pressure and composition, each gas is characterized by a definite speed of propagation ranging between 1000 and 4000 meters per second. The term detonation wave is usually given to the flame propagated at these velocities.

Theories for the High Rates of Explosions.—Several attempts have been made to account for these high rates of explosions. Berthelot and Vieille[3] compared the speed of a detonation wave to the mean kinetic speed of the molecules in the burned gases. This speed can be readily computed from the temperature attained in the combustion. In many instances the speeds thus calculated differ widely from the experimentally determined velocities of the detonation wave. Dixon[4] likened the speed of the detonation wave in gas mixtures to the velocity of propagation of sound in the same gas at the high temperatures created by the combustion. Although in some cases the velocities calculated agree with those actually found, in others they differ quite widely. It was soon recognized that the "sound-wave theory" was defective and inadequate.[4]

A more satisfactory and hydrodynamical theory was developed independ-

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[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.) Read before the American Chemical Society at Atlanta, Georgia, April, 1930.

[2] Physical Chemist, Pittsburgh Experiment Station, U. S. Bureau of Mines.

[3] Berthelot and Vieille, *Compt. rend.*, **93**, 18, 1881; **94**, 149 (1882).

[4] Dixon, *Trans. Roy. Soc.* (London), **184**, 97 (1893); *J. Chem. Soc.*, **97**, 665 (1910).