approximately 1 *N* with respect to sodium hydroxide. Purified acetylene was passed through this solution for eight hours. The hydroxide was then converted to the carbonate by carbon dioxide. In the same manner as above the water was purified and its density determined. This water was found to contain 10.9% of $\mathrm{H}_2^2\mathrm{O}$. A check experiment was run for twelve hours on water containing 12.1% $\mathrm{H}_2^2\mathrm{O}$. (The strength of the alkali was somewhat greater in this experiment than in the previous one.) The concentration of $\mathrm{H}_2^2\mathrm{O}$ was found to be 2.7% at the end of this experiment.

Feeling that an isotopic exchange was occurring too slowly in neutral water, to be detected in the original experiment, acetylene was bubbled through water containing 12.1% $\mathrm{H}_2^2\mathrm{O}$ for thirty-six hours. Again there was no detectable change in the density of the water.

It is evident from these experiments that a remarkable isotopic exchange occurs between acetylene and solutions of $\mathrm{H}_2^2\mathrm{O}$ containing an alkali. If the same exchange occurs in neutral and acid solutions of $\mathrm{H}_2^2\mathrm{O}$ the rate must be extremely slow. These experiments offer additional confirmatory evidence for the acidic nature of acetylene. Further work is in progress on this exchange reaction.

University of Minnesota L. H. Reyerson
Minneapolis, Minn. Samuel Yuster

Received May 22, 1934

THE ELECTRONIC MECHANISM OF INTRAMOLECULAR REARRANGEMENT

Sir:

On page 177 of the "Annual Reports" of the Chemical Society for 1933, it is implied that the work of one of us [Wallis and Moyer, This Journal, **55,** 2598 (1933)] constitutes evidence against the electronic conception of rearrangements [*cf.* Whitmore, *ibid.*, **54,** 3274 (1932)]. We do not agree with this implication; in fact careful reflection will show that the reaction of Wallis and Moyer, in which the optically active amide of a sterically hindered diphenyl derivative (*d*-3,5-dinitro-6-α-naphthylbenzamide) gives an optically active amine (3,5-dinitro-6-α-naphthylaniline), is the strongest existing evidence for the correctness of this modern electronic viewpoint as contrasted with the older ionic mechanisms. The impression that our work is in conflict undoubtedly arises from the too brief statement of the application of the current hypothesis to the Hofmann rearrangement [Whitmore and Homeyer, *ibid.*, **54,** 3435 (1932)]. A fuller statement of this application seems desirable. In the reaction of a base with an N-bromoamide, the bromine appears as a bromide with a complete octet of electrons. Regardless of the mechanism of the process, this change leaves the nitrogen with only six electrons, a condition which necessitates a change to a more stable arrangement. The electronically deficient nitrogen atom attracts an electron pair from the adjacent carbon atom. This transfer requires no special mechanism; certainly the electron pair and its attached group never leave the molecule. Thus, in the reaction of Wallis and Moyer, the ortho position in the diphenyl derivative is not left free at any time and, consequently, there is no opportunity for racemization. The change is thus truly intramolecular.

Princeton, N. J. Everett S. Wallis
State College, Penna. Frank C. Whitmore

Received May 22, 1934

THE POLARITY OF THE NITROGEN TETROXIDE AND NITROGEN DIOXIDE MOLECULES

Sir:

During the course of extended experimental studies of the temperature variation of the dielectric constant and density for equilibrium mixtures of nitrogen tetroxide and nitrogen dioxide there appeared an article by Zahn [*Physik. Z.*, **34,** 461 (1933)] in which there was anticipated that portion of our work which has to do with observations on this system in the vapor phase. As the result of his measurements and calculations, Zahn assigned the electric moment values $\mu = 0.55 \times 10^{-18}$ e. s. u. to nitrogen tetroxide and $\mu = 0.39 \times 10^{-18}$ e. s. u. to nitrogen dioxide. Because earlier and preliminary work of this type with the equilibrium mixture in carbon tetrachloride solution [Fogelberg, Dissertation, University of Wisconsin (1931)] had led to the conclusion that nitrogen tetroxide is non-polar and because our experiments in the vapor phase were nearing the stage where definite conclusions could be drawn from them, it was felt worth while to continue the observations. Work with the vapors between the temperatures 25 and 125° has now progressed to the point where electric moment calculations can be made. Since further observations are impossible for the present, we wish to make brief statement of our conclusions.

The data indicate that the electric moment of nitrogen tetroxide cannot differ greatly from zero. This conclusion is based upon two facts. (1) Within the limits of experimental error the molar polarization of nitrogen tetroxide does not change as the temperature is varied over the interval mentioned above. (2) The value obtained for the molar polarization of this molecule, 16.87 cc., differs but slightly from the polarization, 16.73 cc., which is required by the optical data of Cuthbertson [*Proc. Roy. Soc.* (London), **A89,** 361 (1913)].

Zahn has emphasized that his experimental observations demand a higher moment for the tetroxide as compared to the dioxide. Our data are equally definite in that they require the opposite conclusion. It seems reasonable to expect the polarity of the associated molecule to be smaller than that of the units from which it is formed, especially if the union is through the nitrogen atoms. It may also be mentioned that as far as is known the infra-red spectrum of N_2O_4 can be accounted for if there is assumed a symmetrical molecule where all the atoms lie in a plane [Sutherland, *Proc. Roy. Soc.* (London), **A141,** 342 (1933); see, however, Harris and King, *J. Chem. Phys.*, **2,** 51 (1934)].

The values indicated for the dipole moment of nitrogen dioxide do not differ appreciably from those reported by Zahn. It is a difficulty we are at present unable to explain quantitatively that both sets of data seem to be completely accounted for only if the moment of the dioxide decreases as the temperature is increased. If the moment of a molecule is at all dependent upon temperature it is more natural to expect it to increase with increasing temperature because of an excitation of higher rotational and vibrational states.

The writers hope to be able to present in the near future a more detailed account of these investigations.

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RECEIVED MAY 22, 1934

NEW BOOKS

Handbuch der anorganischen Chemie. (Handbook of Inorganic Chemistry.) Edited by R. ABEGG, FR. AUERBACH and I. KOPPEL. Vol. IV, 3d Division Part III. **Cobalt and its Compounds.** 1st Instalment. Verlag von S. Hirzel, Königstrasse 2, Leipzig C 1, Germany, 1934. 626 pp. 18 × 25.5 cm. Price, M. 58, unbound.

This volume covers the cobalt atom, the atomic weight of cobalt, metallic cobalt, compounds of divalent and trivalent cobalt, the cobaltous ammines, the compounds and alloys of cobalt with the metalloids of groups I-VI and with the metals, and finally the colloid chemistry of cobalt.

The selection, arrangement and presentation of the subject matter are fundamentally the same as in the earlier volumes of this Handbook except perhaps that the great development of physical chemistry has permitted an even more thorough and lucid treatment from this point of view.

The outstanding merit of this Handbook as compared with others in the field, namely, its critical and comprehensible rather than comprehensive presentation, persists undiminished in this latest volume.

The publishers announce that the manuscript of the concluding volume on cobalt, covering the cobaltic ammines, is already completed and that this volume should therefore appear in the near future.

ARTHUR B. LAMB

Sixième Congrès International du Froid, Buenos Aires Août Septembre 1932. Première Commission Internationale (Commission Kamerlingh Onnes) de l'Institut International du Froid. Rapports et Communications Issus du Laboratoire Kamerlingh Onnes. (Review of the Reports and Communications from the Kamerlingh Onnes Laboratory presented at the Sixth International Conference on Refrigeration held at Buenos Aires, August and September, 1932.) Présentés par le Président de la Première Commission, W. H. Keesom. N. V. Boek-en Steendrukkerij Eduard Ijdo, Leiden, Holland, 1932. x + 460 pp. Illustrated. 16 × 24 cm.

The volume of reports and communications is comprised of thirty-six papers from the Kamerlingh Onnes Laboratory dealing with a wide variety of subjects directly and indirectly relating to the realization and maintenance of low temperatures. Many of the papers are progress reports on important problems which the Leiden Laboratory has continued under investigation for many years. Thus further data and information on thermometry at low temperatures are reported with new determinations of the boiling points of oxygen and hydrogen (normal −252.754 and para −252.871). The decision of the Leiden Laboratory not to use the International scale of temperature as interpreted by the electrical resistance thermometer of platinum subject to the specifications of the Paris Convention of