

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 H<sub>2</sub>O. A check experiment was run for twelve hours on water containing 12.1% H<sub>2</sub>O. (The strength of the alkali was somewhat greater in this experiment than in the previous one.) The concentration of H<sub>2</sub>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% H<sub>2</sub>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 H<sub>2</sub>O containing an alkali. If the same exchange occurs in neutral and acid solutions of H<sub>2</sub>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.

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RECEIVED MAY 22, 1934

#### THE ELECTRONIC MECHANISM OF INTRA-MOLECULAR 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- $\alpha$ -naphthylbenzamide) gives an optically active amine (3,5-dinitro-6- $\alpha$ -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 re-

arrangement [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.

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#### 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.