COMMUNICATIONS TO THE EDITOR

THE RATE OF DISSOCIATION OF NITROGEN TETROXIDE

Sir:

Recently Richards and Reid [THIS JOURNAL, **54**, 3014 (1932)] reported that they had obtained a definite value of the velocity constant of the N_2O_4 dissociation, using high-frequency sound waves up to 500 k. c. This value is, of course, calculated from their velocity of sound data by the use of Einstein's theoretical equations, which they felt justified in applying to their measurements since they observed no increase in the absorption coefficient with frequency.

Their observations are not in accord with a series of experiments just completed by the author which are being submitted for publication. Sound velocity measurements at 53.8 k. c. checked with those previously reported by Kistiakowsky and Richards, although high absorption made observation difficult, but above 100 k. c. no evidence of sound transmission could be obtained with the set-up employed, although sound up to 860 k. c. was used. This increasing absorption is in accord with the theoretical predictions of D. G. C. Luck [*Phys. Rev.*, **40**, 440 (1932)], who has extended Einstein's theory to real absorbing dissociating gases. Calculations made by the author from his equations show that velocity constants computed from Einstein's original equations may be as much as 20% too low.

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QUANTUM THEORY OF THE DOUBLE BOND

Sir:

An understanding of the structure of C_2H_4 can be obtained by studying its formation from two CH_2 radicals. Electronic structures of these can be given in terms of molecular orbitals [molecular one-electron orbital wave functions, *cf.* R. S. Mulliken, *Phys. Rev.*, **40**, 55 and **41**, 49 (1932)] similar to the atomic orbitals $1s$, $2s$, $2p$ commonly used in the quantum theory in building up electron configurations to describe the structures of atoms. It can be shown that, in agreement with the chemical evidence, the energy should be a minimum if the two CH_2 come together in the same plane, a maximum if they come together with their planes at right angles. An analogous result holds for other molecules with double bonds.

These results apply to the normal state of such molecules, but for certain excited states, probably including the upper levels of the ordinary ultraviolet absorption bands, it can be shown to be probable that the energy is a maximum for the plane arrangement, a minimum for an ar-

rangement with the planes of the two CR′R″ groups at 90°. Hence after a molecule has absorbed ultraviolet light, its two parts should undergo a spontaneous rotation with respect to each other, which can carry it from *cis* to *trans* or *vice versa*. Olson has already discussed possibilities somewhat similar to this [*Trans. Faraday Soc.*, **27**, 69 (1931)]. Details will be given in an article in the *Physical Review*.

The present quantum theory of the double bond is similar to that of Hückel [*Z. Physik*, **60**, 423 (1930)] but goes farther. As compared with the theory of Pauling and Slater [THIS JOURNAL, **53**, 1367 (1931), and *Phys. Rev.*, **37**, 481 (1931)] it appears to make closer contact with chemical and photochemical facts.

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REACTIONS BETWEEN HYDRIODIC ACID AND HIGHLY INSOLUBLE COMPOUNDS

Sir:

Recently the writer published an account of the action of concentrated hydriodic acid on stannic oxide [THIS JOURNAL, **54**, 3240 (1932)]. Experiments made subsequent to the observations recorded in this paper have demonstrated that this acid reacts readily with numerous other compounds of very low solubility, including many of those not attacked by hydrochloric acid, nitric acid or aqua regia. A number of these reactions are apparently new. Some illustrative examples follow.

The alkaline earth sulfates are attacked and reduced by hot concentrated hydriodic acid with the evolution of hydrogen sulfide, sulfur dioxide or both, and the liberation of iodine, resulting in a solution of the corresponding iodides. Likewise anhydrous chromium sulfate is reduced and dissolved by this acid. Sublimed chromic chloride and bromide are rapidly dissolved by the warm concentrated acid. Lead sulfate and fused lead chromate readily dissolve in the cold concentrated acid. The first is transposed into lead iodide, which then dissolves in the excess acid to form a complex which appears to be iodoplumbous acid. In the case of the chromate the same reaction occurs accompanied by the reduction of the chromium to the tervalent state. The insoluble halides of silver are also transposed and dissolved by the cold concentrated acid, the complex forming in this case being an iodoargentic acid. Certain more complex insoluble compounds such as copper ferrocyanide are readily attacked and dissolved in a series of complicated reactions.

Many of these reactions are not only of interest in themselves but they