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.

RESEARCH LABORATORY OF INORGANIC CHEMISTRY   CHARLES E. TEETER, JR.
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASSACHUSETTS

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.

RYERSON PHYSICAL LABORATORY   ROBERT S. MULLIKEN
UNIVERSITY OF CHICAGO
CHICAGO, ILLINOIS
RECEIVED AUGUST 6, 1932
PUBLISHED OCTOBER 5, 1932

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

hold some promise of useful analytical application in the separation and identification of members of the group of highly insoluble compounds. The writer hopes to have the privilege of publishing a more detailed account of these reactions at some future date.

DEPARTMENT OF CHEMISTRY   EARLE R. CALEY
PRINCETON UNIVERSITY
PRINCETON. NEW JERSEY
RECEIVED AUGUST 17, 1932
PUBLISHED OCTOBER 5, 1932

GERMICIDAL ACTIVITY OF ALKYL SULFUR ETHERS

Sir:

A problem interesting various investigators during recent years in the field of antiseptics has been the effect on the activity of phenol germicides of variations in substituting groups. Johnson and Lane [THIS JOURNAL, **43,** 348 (1921)], and Dohme, Cox and Miller [*ibid.*, **48,** 1688 (1926)] pointed out that alkyl resorcinols become progressively more active as the length of an alkyl side chain increases. Hilbert and Johnson [THIS JOURNAL, **51,** 1534 (1929)] showed that the activity of the three hydroxy diphenyl sulfides increased in the order: ortho, meta, para. The authors [*ibid.*, **54,** 1195 (1932)] discussed the effect of alkyl chains substituted into the phenol nucleus, stating that position isomerism is of slight importance but that variations in the chain are of greatest importance.

It seemed of interest to compare certain sulfur containing phenols with those previously studied. Methyl, ethyl, *n*-propyl, *n*-butyl, *n*-amyl, *n*-hexyl, isopropyl, isobutyl, isoamyl and benzyl thio ethers of phenol of the general formula RSC_6H_4OH have been prepared.

As in the case of the alkylresorcinols, alkyl phenols and alkyl ethers of hydroquinone [Ref. 4 and Klarmann, Gatyas and Shternov, THIS JOURNAL, **54,** 298 (1932)], the germicidal activity of these alkyl sulfur ethers increases with increase in the size of the alkyl group. They show, however, a higher activity for a given alkyl group and reach the maximum with the amyl derivative. An increase in the temperature at which the bacteriological examination is made raises this maximum to higher members of the series. The iso-alkyl ethers have lower phenol coefficients than the corresponding normal alkyl derivatives.

The O-ethers of thiophenol are probably much less active than the corresponding S-ethers of phenol.

A complete report of this work will be published in the near future.

CHEMICAL LABORATORIES   ELLIS MILLER
SHARP AND DOHME   R. R. READ
PHILADELPHIA, PA.
RECEIVED AUGUST 18, 1932
PUBLISHED OCTOBER 5, 1932

THE CONCENTRATION AT WHICH HEATS OF DILUTION ARE MEASURED IN THE CALORIMETRIC METHOD

Sir:

In a series of excellent experimental papers, E. Lange and A. L. Robinson and their collaborators [for a summary of their work to 1931, see E. Lange and A. L. Robinson, *Chem. Rev.*, **9**, 89 (1931)] have greatly improved the precision with which heats of dilution can be measured and have recorded results at much higher dilution than previous investigators. Unfortunately, their method of standardizing their data to the reference state of infinite dilution is open to a misunderstanding in respect to the concentration for which the heat of dilution has been actually measured which appears to be quite widespread.

They dilute a volume of solution at a given initial concentration with a measured amount of water to a readily computed final concentration and measure the heat evolved in the process. Thus

$$\frac{NaCl + n_1 H_2O}{0.01 \, m} + xH_2O = \frac{NaCl + (n_1 + x) H_2O}{0.0005 \, m}$$

$$\Delta H = \bar{L}_2 (0.0005 \, m) + (n_1 + x) \bar{L}_1 - \bar{L}_2 (0.01 \, m) - n_1 \bar{L}_1 (0.01)$$

These so called intermediate changes in heat content when calculated to one mole of salt are designated in Lange's notation as $V_{(c \text{ initial } c \text{ final})}$. Each dilution experiment thus gives two points on a curve, the initial and final concentrations. When a region of concentration is reached where these ΔH values become proportional to $\sqrt{c}$ (c = moles/liter), an extrapolation is made to $c = 0$ whereby these intermediate heats of dilution are interpreted as integral heats of dilution by addition of the quantity of V_c obtained by graphical extrapolation.

$$\frac{NaCl + n_1 H_2O}{0.0005 \, m} + (\infty - n_1) H_2O = \frac{NaCl + \infty H_2O}{m = 0}$$

$$\Delta H = -\bar{L}_2 (0.0005 \, m) - n_1 \bar{L}_1 (0.0005) = V_c \text{ (Lange's notation)}$$

Lange and Robinson represent their results by curves in which the values for both the initial and final concentrations are plotted, thereby giving the impression that measurements of the heat of dilution have actually been made for the lower concentration. In fact, in their conclusions they state that the integral heats of dilution have been measured over a range which includes the lower concentration limits. [See, for example E. Lange and A. L. Robinson, THIS JOURNAL, **52**, 4218 (1930); H. Hammerschmid and A. L. Robinson, *ibid.*, **54**, 3120 (1932)]. That the measured values should refer only to the initial concentration and not to the final or any intermediate concentration is obvious when we recognize that, had the authors been able to measure the heat evolved by the addition of an infinite volume of water, all of the plotted points corresponding to the final concentrations would have vanished. All the data recorded in

their final tables, in the two papers referred to, below 0.0125 m (0.00625 m in the case of sodium bromide) should be designated as extrapolated and not as interpolated values. Although the values which they record for the final concentrations are very likely correct, it is, nevertheless, desirable to point out that they do not constitute measured values, but involve the acceptance of the validity of the Debye–Hückel theory. This theory is without doubt the best to employ at the present time, yet there have been examples in which specific individual characteristics have been obscured by its use at concentrations which, at the time, were thought to be sufficiently dilute for application.

DEPARTMENT OF CHEMISTRY   V. K. LA MER
COLUMBIA UNIVERSITY   I. A. COWPERTHWAITE
NEW YORK, NEW YORK
RECEIVED AUGUST 23, 1932
PUBLISHED OCTOBER 5, 1932

THE OXYGEN VALENCE ANGLE AND THE STRUCTURE OF GLUCOSE AND RELATED COMPOUNDS

Sir:

During the last ten years an extensive series of investigations has been carried out on the synthesis and structure of various oxygen-bridged ring compounds from the point of view of elucidating the structure and properties of glucose and polysaccharides. During the progress of this work, it has become more and more evident that the assignment of the same tetrahedral angle to both the oxygen and carbon atoms is incorrect and that many of the anomalies found in the study of carbohydrate chemistry are due to the lack of recognition of this factor.

In the case of furanose and pyranose ring forms of the sugars this point has also been stressed by Haworth, Cox and other workers.

During the last three years a careful study has been made on the electric moments of ethylene oxide, propylene oxide, trimethylene oxide, tetrahydrofuran (tetramethylene oxide) and tetrahydropyran (pentamethylene oxide), and the oxygen valence angles calculated in each case. These have been determined as follows.

OXYGEN VALENCE ANGLES IN CYCLIC ETHERS

Compound	Moment ($\times 10^{18}$)	Oxygen valence angle
Ethylene oxide	1.88	77°
Propylene oxide	1.88	65°[a]
		77°
Trimethylene oxide	2.01	102°
Tetrahydrofuran	1.71[a]	105°
		ca. 100°[a]
Tetrahydropyran	1.87	88°

[a] Smyth and Walls, THIS JOURNAL, **54**, 3230 (1932).

The "normal" oxygen valence angle has been determined from these measurements as $90 \pm 5°$. This value is the first experimental confirmation, by electric moment measurements, of the same angle suggested by the quantum mechanical considerations of Pauling. From these results it can be definitely shown that the pyranose ring of carbohydrates and related polysaccharides represents a "strainless" puckered ring system in which the carbon valence linkages are tetrahedral while the oxygen valence angle is approximately 90°. The pyranose ring has therefore a di-planar structure with all the carbon atoms in one plane and the oxygen atom in a different plane from the carbon atoms. On the other hand, the furanose ring structure of similar compounds represents a strained flat ring in which both the carbon and oxygen valence angles are distorted. The relative instability of furanose as compared with pyranose rings thus finds a satisfactory explanation. A full account of this work will be published in the near future.

DIVISION OF INDUSTRIAL AND CELLULOSE CHEMISTRY   HAROLD HIBBERT
MCGILL UNIVERSITY   J. STANLEY ALLEN
MONTREAL, CANADA
RECEIVED SEPTEMBER 22, 1932
PUBLISHED OCTOBER 5, 1932

NICKEL BY THE RANEY PROCESS AS A CATALYST OF HYDROGENATION

Sir:

There is now available (Murray Raney, Chattanooga, Tennessee, U. S. Patent 1,628,190, May 19, 1927) a pure nickel catalyst which under some circumstances is preferable to the "nickel on kieselguhr" type of catalyst [Covert, Connor and Adkins, THIS JOURNAL, **54,** 1651 (1932)]. The Raney catalyst is prepared by alloying equal parts of nickel and aluminum and then dissolving out the latter with aqueous sodium hydroxide. Both the alloy and the metallic nickel suspended in water are commercially available. The latter is satisfactory for many hydrogenations but a more active catalyst may be prepared from the alloy by the following procedure. Three hundred grams of the finely ground nickel–aluminum alloy was added slowly (two or three hours) to a solution of 300 g. of sodium hydroxide (80%) in 1200 ml. of distilled water, contained in a 4-liter beaker surrounded by ice. The mixture was then heated on a hot-plate for four hours with occasional stirring at 115–120°. A further 400 ml. of a 19% solution of sodium hydroxide was added and the mixture kept at 115–120° for about three hours or until bubbles of hydrogen were no longer evolved, after which it was diluted to a volume of three liters. The clear solution of sodium aluminate was decanted, and the nickel washed by decantation six times, and then alternately by suspension and by washing on a Buchner filter with distilled water until the filtrate was neutral to litmus. The nickel was then washed three times with 95% ethanol and kept under

ethanol in glass-stoppered bottles. (Nickel prepared by this process is so reactive that it deoxygenated nitrobenzene, o- and p-nitrobenzene and p-nitrophenol with 38 to 50% yields of azo- and azoxybenzenes, when mixed with the nitro compounds in an open beaker.)

The outstanding characteristic of the Raney catalyst is its activity at low temperatures and pressures. For example, with a supported nickel catalyst, acetone did not undergo hydrogenation in any considerable amount much below 100°, while with the Raney catalyst, complete hydrogenation was obtained after 11.2 hours at 23° and 2 to 3 atmospheres' pressure. Similar hydrogenations were obtained with mesityl oxide and acetoacetic ester. Complete hydrogenations at room temperature but at 110 atmospheres' pressure were obtained with benzaldehyde, acetaldehyde, cinnamaldehyde, azobenzene and benzyl cyanide. In the case of all of these compounds hydrogenation proceeded to completion at pressures and (or) temperatures below those at which the supported catalyst was sufficiently active for the satisfactory hydrogenation of these compounds. Both catalysts are active against certain alkenes such as styrene at 23° and 2–5 atmospheres. The hydrogenation of aldol, furfural and the diethyl furfural acetal also proceeded at temperatures somewhat lower than have been observed with the supported catalyst. In the case of benzene, toluene, acetophenone, benzyl alcohol, ethyl benzoate, diethyl phthalate and pyridine the Raney catalyst was not active at markedly lower temperatures and pressures than was the supported catalyst. (The ratio of nickel to organic compound in the experiments referred to in this paragraph was in most instances approximately 1 to 15.)

A precise comparison of the activity of the Raney catalyst with the supported catalyst is impossible not only because they may show their optimum activity for a given compound in quite different temperature ranges but because there is no ratio of catalyst to hydrogen acceptor which would be fair to both catalysts. For example, 8 g. (occupying a volume of 4 ml.) of Raney catalyst was required for the hydrogenation at 23° of 74 ml. of acetone within 11.2 hours. An equivalent amount of nickel on the supported catalyst would have necessitated using 80 g. or *300 ml.* of the supported catalyst with *74 ml.* of acetone! If the Raney catalyst had been used in the same proportion as was nickel on kieselguhr (0.2 g. for 74 ml. of acetone), it would have been quite ineffective. The ratio of surface to weight of nickel is of course much higher for the supported than for the Raney catalyst so that comparisons of activities on the basis of weight of nickel in the catalyst are unduly unfavorable to the Raney catalyst.

LABORATORY OF ORGANIC CHEMISTRY   LLOYD W. COVERT
UNIVERSITY OF WISCONSIN   HOMER ADKINS
MADISON, WISCONSIN