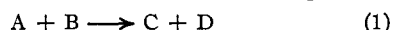# COMMUNICATIONS TO THE EDITOR

## RELATIONS INVOLVED IN THE DISINTEGRATION OF ATOMS BY "NON-CAPTURE" COLLISIONS

Sir:

A large number of the atomic disintegrations produced by the collision of nuclei at high relative velocities are known to be of the type represented by a chemical change in which two molecules change into two others. Thus the equation

$$A + B \longrightarrow C + D \tag{1}$$

represents what occurs in a disintegrative synthesis or disintegration by capture, in which the nucleus AB may be formed as an evanescent intermediate stage.

In a pure disintegration "by non-capture" of the projectile A, which merely supplies energy, the reaction is

$$B \longrightarrow C + D \tag{2}$$
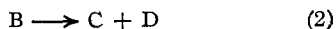
That "disintegrations by non-capture" occur has been assumed by Chadwick, Gamov, Feather and others.[1] However, the only evidence for this which is of any apparent value is that related to the use of the neutron as the projectile, so we have made a specific study of this case, and have developed equations which represent the mechanics of the collision process which is involved. The equations are general, and apply to collisions between any nuclear particles.
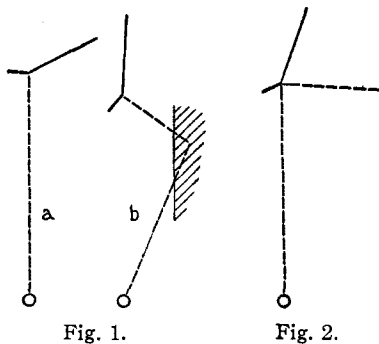
Fig. 1.   Fig. 2.

Figure 1 illustrates the disintegration of a nucleus (B) by a projectile which is captured. In (a) this projectile comes in a straight line from the source. In (b) it is first deflected by a nucleus in adjacent material.

Figure 2 illustrates the disintegration by a projectile which is not captured. The equations given below refer to Fig. 2.

Equation (3) gives the velocity of the projectile immediately before the collision occurs and is moderately accurate for velocities below $1/3$ that of light.

$$V_A = \frac{M^2 + 2m_A(E_C + E_D + E_m)}{2m_A M \cos \alpha} \tag{3}$$

or

$$V_A = \frac{M}{2m_A \cos \alpha} + \frac{(E_C + E_D + E_m)}{M \cos \alpha} \tag{3'}$$

v_A and m_A = speed and mass of projectile, before the collision
v' = speed of projectile after collision
M = magnitude of resultant momentum of C and D
E_C and E_D = their kinetic energies
E_m = energy corresponding to increase of mass in the reaction, or $E_m = c^2 \Delta m$
α = angle between V_A and direction of M

It is assumed that a γ-ray is not emitted. However, an approximate solution may be obtained if the term $E\gamma$ is added to the quantity between the parentheses, since the momentum of the γ-ray is, in general, negligible.

The relativity equation, similar in form to (3), may be written:

$$v_A = \frac{c(w^2 - K^2) + 2k_A cK}{2k_A w \cos \alpha} \tag{4}$$

in which $k \equiv 1/\sqrt{1 - (v^2/c^2)}$,

$$k_A - k_A' \equiv K \text{ and } \frac{k_A V_A}{c} - \frac{k_A' V_A'}{c} \equiv w$$

and c is the velocity of light, will be discussed in a more complete paper. Of twenty-eight disintegrations[2] of the nitrogen nucleus by bombardment with neutrons, nine were found to be due to neutrons which were scattered either by the disintegration process ("non-capture") (Fig. 2), or earlier (Fig. 1b). The important relations which emerge are: (A) If these nine are calculated to occur by capture, then the distribution curve which relates the number of disintegrations to the velocity of the neutrons is found to be the same as for the disintegrations by capture. (B) If, however, the assumption is made that the neutron was not captured, then the values for the velocity of the neutron are found to exceed that for the fastest known neutron by 50% or more. Since such high velocities are altogether improb-

(1) Chadwick and Gamov. *Nature*, **126**, 54 (1930); Chadwick, Constable and Pollard, *Proc. Roy. Soc.* (London), **A130**, 463 (1930); Feather, *ibid.*, **A136**, 709 (1933).

(2) W. D. Harkins, D. M. Gans and H. W. Newson. *Phys. Rev.*, **44**, 529 (1933).

able, it seems that these disintegrations are not of this type.

Taken together, (A) and (B) seem to indicate that these disintegrations actually occur by capture, and that non-capture disintegrations are absent.

The evidence is extremely weak for non-capture disintegration by α-particles or by protons and is shown above to be invalid for neutrons, the only projectile for which the evidence had apparent strength, due to a neglect of the mechanics involved. Thus there seems to be no basis for the idea that any nucleus whatever has been disintegrated by a process in which the projectile was not captured. Obviously this does not prove that such disintegrations cannot be discovered in the future.

UNIVERSITY OF CHICAGO   WILLIAM D. HARKINS
CHICAGO, ILLINOIS   DAVID M. GANS
          RECEIVED MARCH 26, 1934

PREPARATION OF CYSTINEHYDANTOIN
Sir:

Using the method advocated by Dakin [J. Biol. Chem., 8, 25 (1910)] for the preparation of tyrosinehydantoin, cystinehydantoin has been prepared in practically quantitative yields and of a high order of purity. Two grams of cystine is suspended in 10 cc. of boiling water and 1.5 g. of potassium cyanate is added. The solution is then acidified with 25 cc. of 10% hydrochloric acid and heated with a reflux condenser for thirty minutes. The cystinehydantoin separates in diamond-shaped plates; yield 2.2 g., 91%. *Anal.* Calcd. for $C_8H_{10}N_4S_2O_4$: N, 19.17; S, 22.09. Found: N, 19.30; S, 21.96. It begins to decompose at 310° and has no definite melting point. It is insoluble in ordinary organic solvents, insoluble cold and slightly soluble in hot water. Alkalies dissolve the hydantoin with decomposition. Using the loosely bound sulfur procedure of Sullivan and Smith [U. S. Pub. Health Repts., 43, 1334 (1928)] it forms lead sulfide in twenty seconds.

Cystinehydantoin gives a negative Sullivan cystine reaction. The nitroprusside reaction for a disulfide, using sodium cyanide as the reducing agent, is positive. The Okuda [J. Biochem. (Tokyo), 5, 201 (1925)] method gives the theoretical cystine equivalent. The Folin–Marenzi [J. Biol. Chem., 83, 103 (1929)] cystine method gives the same amount of color with the hydantoin

as the equivalent weight of cystine. As in the case of cystine [Folin–Looney, ibid., 51, 421 (1922)] sodium cyanide will inhibit the color production. In all the colorimetric work a solution containing 24.2 mg. of the hydantoin in 100 cc. of a 0.1 N hydrochloric acid equivalent to a 200 parts per million cystine solution was used.

CHEMO-MEDICAL RESEARCH INSTITUTE
GEORGETOWN UNIVERSITY,
WASHINGTON, D. C.   WALTER C. HESS
          RECEIVED MARCH 26, 1934

OPTICAL ROTATION AND ATOMIC DIMENSION
Sir:

It has been established in the writer's previous investigations on this subject [fifth article, THIS JOURNAL, 47, 1285 (1925), and the ninth article, Bureau of Standards Journal of Research, 7, 573 (1931)] that certain halogen derivatives may be divided into two classes. Those compounds which constitute the first class have the halogen directly attached to an asymmetric carbon atom and differ only in having one halogen replaced by another. For these substances the *specific rotations* have the ratio 41:17:21, which agrees closely with the ratio 41:16:21 for the differences in atomic diameter of the respective neutral atoms. Those in the other class have the halogens attached indirectly (by a chain of atoms) to the asymmetric carbon. For these substances the *molecular rotations* have a ratio which likewise agrees with the ratio of the diameters of the respective neutral atoms. All the investigated compounds were carbohydrate derivatives which contain several asymmetric carbon atoms, so it was found desirable to prepare the halogen derivatives of two active amyl alcohols, 2-methylbutanol (1) and methylpropylcarbinol, for testing the above regularities, as these compounds are simple in structure and contain only one asymmetric carbon atom. The halogen derivatives of one of these alcohols, the negative rotating 2-methylbutanol (1) (in which the halogen is indirectly attached to the asymmetric carbon), have now been prepared in pure condition. The rotational values obtained are:

	$[\alpha]_D^{20}$ Specific rotation	$[M]_D^{20}$ Molecular rotation
1-Fluoro-2-methylbutane	−8.87	− 799.1
1-Chloro-2-methylbutane	+1.68	+ 179.0
1-Bromo-2-methylbutane	+4.04	+ 610.1
1-Iodo-2-methylbutane	+5.68	+1124.7

The chlorine, bromine and iodine derivatives were prepared by the action of hydrogen halides on the pure active negative rotating 2-methylbutanol (1), whereas the negative rotating fluorine derivative was prepared from the bromine derivative by the action of silver fluoride, as will be described in detail later. The similar procedure used for preparing the chlorine, bromine and iodine derivatives makes it very probable that these derivatives are of the same form whether or not a Walden inversion is involved in their preparation. It is immaterial for our present purpose whether this form fits into any particular scheme of classification as a d-form or as an l-form. In the case of the fluorine derivative, however, it is not certain whether the *negative* rotating form must be classified with the other halogen derivatives, which are positive rotating (Possibility I), or whether the *positive* rotating one must be taken (Possibility II). If we test both possibilities in regard to the above stated atomic dimension relationship we obtain, using the molecular rotations, for the ratio Cl-F, Br-Cl and I-Br for the first possibility, 41:18.1:21.6. This agrees very well with the ratio for the respective atomic diameters. For the second possibility no regularity is obtainable if the fluorine derivative is included. This will be observed from the rotations given above which show first a decrease and then an increase in value. Further work will be done in connection with the conclusion that the negative rotating fluorine derivative is of the same form as the positive rotating chlorine, bromine and iodine derivatives.

Further, it is obvious from these data that the ratio for the differences in weight (Guye's hypothesis) does not fit in both possibilities, as theory would require for Cl-F, Br-Cl and I-Br the ratio 16.5:44.4:47.0. This differs greatly from the observed ratios. The results of an investigation of the halogen derivatives of methylpropylcarbinol will be given in the near future. This will be of interest in connection with the present subject as the possibility exists that the relationship which involves the specific rotations is due to the arrangement of the asymmetric carbons in a ring.

BUREAU OF STANDARDS   D. H. BRAUNS
WASHINGTON, D. C.
RECEIVED APRIL 14, 1934

THE BIOLOGICAL SEPARATION OF HEAVY WATER

Sir:

Eyring and Sherman [*J. Chem. Physics*, **1**, 345 (1933)] have pointed out that reactions in biological processes may fractionate the isotopes of hydrogen. In view of this, we considered that the concentrations of heavy water in the urine and in the milk of the same animal might possibly be different from each other and from that of normal water.

We have compared, by the method of the temperature of floating equilibrium [Richards and Harris, THIS JOURNAL, **38**, 1000 (1916)], the specific gravities at 24.50° of water prepared from cow's milk and from urine, with that of pure tap water. The samples of water were obtained by distilling a liquid fraction from four liters of milk, of urine and of the control water, until the dry residue of solids was left. The liquid fractions, including some volatile organic material which had been carried over during the first distillations, were distilled successively from acid and alkaline permanganate, leaving in each case approximately the same volume as residue at the end of each distillation. After six distillations, the distillates were refluxed for twenty-four hours in the presence of alkaline permanganate and finally distilled carefully through a block-tin condenser fitted with a specially constructed spray trap.

The temperature of the thermostat could be controlled to within ±0.001°. The movement of the thin-walled glass float, 6.24 ml., was observed with a reading telescope. The correction to the temperature of floating equilibrium due to changing barometric pressure was determined by artificially adjusting the pressure over a sample of water containing the float and Beckmann thermometer. This was found to be −0.001° per cm. change in pressure.

The temperatures of floating equilibrium in water from milk, tap water and urine were identical to within a maximum deviation of ±0.001°. The pressure corrections to the temperatures were negligible, as the maximum variation in atmospheric pressure during the measurements was 0.74 cm. From these results it can be concluded definitely that the isotopic concentration of deuterium in the samples of water obtained from the liquid fraction of milk and urine does not differ from that of normal water.

We appreciate the fact that the isotopic composition of the total hydrogen in milk and in urine may not be identical, as a considerable portion of the hydrogen was left in the first organic

residues. To examine this point further, we contemplate performing complete combustions of these products.

We are glad to acknowledge our indebtedness to Dr. J. F. Snell for the facilities of these laboratories and to Dr. Darol K. Froman for his kind assistance.

DEPARTMENT OF CHEMISTRY   W. W. STEWART
MACDONALD COLLEGE   R. HOLCOMB
McGILL UNIVERSITY, CANADA
          RECEIVED APRIL 21, 1934

THE HEAT CAPACITIES OF CRYSTALLINE, GLASSY AND UNDERCOOLED LIQUID GLUCOSE

Sir:

The heat capacities of glucose in the crystalline α-form (Pfanstiehl Chemical Co.) and in the undercooled glassy and liquid condition have been measured with a "radiation" calorimeter, described previously by Thomas and Parks [J. Phys. Chem., 35, 2091 (1931)]. The specific heats thereby obtained, expressed in calories per gram, are represented graphically by Curves 1, 2 and 3 in the accompanying figure. Curve 1 is for the α crystals and conforms closely to the linear equation $C_p = 0.270 + 0.00092t$. These crystals decomposed slightly when heated slowly up to the melting point. A measurement of their heat of fusion gave 41.7 cal./g. at about 141°. Curve 2 was obtained on heating undercooled liquid glucose, at the rate of about 10° per hour, from the condition of a hard, brittle glass to that of a highly viscous liquid ($\eta = 10^8$ poises at 48.5°). It shows a large maximum or "hump" between 28 and 38°. Conversely, Curve 3 was obtained while this glucose sample was similarly cooling from 45 to 10° and in this case no hump appears, although the total energy changes represented under Curves 2 and 3 are approximately the same. Similar curves have been found with B_2O_3 glass.

In an earlier investigation Parks, Huffman and Cattoir [J. Phys. Chem., 32, 1366 (1928)] have measured the heat capacities of glassy and liquid glucose from −180 to +70°. Curve 4 represents their results within the temperature range of the present study. They used an aneroid calorimeter and the Nernst method, which involved the introduction of discontinuous increments of energy sufficient to raise the temperature at the rate of about 3° per hour. No hump appears in this curve but there is a 60% rise in the heat capacity between 5 and 15°.

The marked differences between Curves 2 and 4 are due to two factors: (1) the use of different samples of glucose glass, with perhaps a few tenths of one per cent. of water (as an impurity) in the material with Curve 4, and (2) the employment of very different methods in heating these samples in this transition range within which the hard glass is transformed into a pasty liquid.
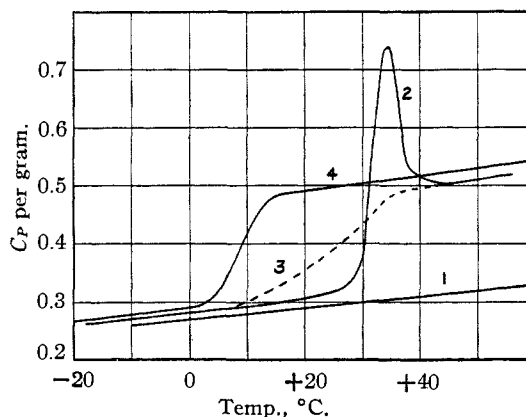

Fig. 1.

In our judgment the second factor is the more important, at least in determining the shape of the curves. In the case of Curve 4 the temperature interval from 5 to 40° was traversed discontinuously in a period of over forty-eight hours; with Curve 2 it was traversed by a continuous heating process within four hours. Curve 4 undoubtedly represents a much closer approach to a true equilibrium condition, although probably no process carried on with a glassy material within finite time can be regarded as involving complete equilibrium. Above 40° the 4% difference between Curves 2 and 4 should probably be attributed to experimental errors, as each method at this temperature may have involved absolute systematic errors of 2 or 3%.

DEPARTMENT OF CHEMISTRY   GEORGE S. PARKS
STANFORD UNIVERSITY   S. BENSON THOMAS
STANFORD UNIVERSITY, CALIF.
          RECEIVED APRIL 24, 1934

SEPARATION OF DEXTRO AND INACTIVE LUPANINES

Sir:

No convenient method has been reported for separating the mixture of optically isomeric alkaloids derived from Lupinus albus. Soldaini [Arch. Pharm., 231 321, (1893)], and Davis

[*ibid.*, **235**, 200 (1897)] accomplished the separation by fractional crystallization of the hydrochlorides. A simpler procedure has now been developed.

The mixed alkaloids extracted from white lupine seeds were freed from residual solvent and impurities by vacuum distillation. Both forms distil at the same temperature, 220–226° at 12 mm. The distillate had n_D^{34} 1.5400; $[\alpha]_D^{25}$ 32.02 in alcohol (indicating 38% of *d*-lupanine). It solidified on standing, softened at 40°, became fluid at 67° and was completely melted at 81°; 105 g. was extracted with four 75-cc. portions of warm petroleum ether [Soldaini, *op. cit.*, states that *dl*-lupanine is insoluble in this solvent]. The undissolved material was dissolved in warm acetone and on cooling the solution deposited 20 g. of rhombic prisms, m. p. 98°, $[\alpha]_D$ 1.14° at 27° in alcohol. These were recrystallized from acetone and yielded optically inactive colorless prisms of *dl*-lupanine, m. p. 98°. Further crops were obtained from the mother liquors. The last mother liquor contained much *d*-lupanine which was recovered by the method used for the petroleum ether soluble fraction.

The petroleum ether solution was cooled and then deposited 7.5 g. of long needles melting above 90°. The solution was evaporated and left 31 g. of sirupy base that gradually crystallized; in water $[\alpha]_D^{25}$ 56.86° (indicating 67.4% of *d*-lupanine). The *d*-base was purified by adapting the method of Ingersoll [This Journal, **47**, 1168 (1925)], which has been used successfully by Clemo, Raper and Tenniswood [*J. Chem. Soc.*, 429 (1931)] to resolve *dl*-lupanine: 24.3 g. of the mixed alkaloids in 25 cc. of acetone was added to a mixture of 23 g. of *d*-camphorsulfonic acid and 25 cc. of acetone. Heat was evolved and the whole went into solution. On cooling a good yield of crystals was obtained which when recrystallized from acetone yielded 23.5 g. of *d*-lupanine camphorsulfonate, m. p. 116–8°, $[\alpha]_D^{29}$ 44.76° (4.184 g. in acetone). The whole was dissolved in 35 cc. of water, and 7.7 g. of potassium iodide (1 mole) was added. Small needle crystals of the hydriodide were formed immediately, m. p. 183–184°, $[\alpha]_D^{25}$ 43.31° (5.084 g. in water). These dissolved in water, made alkaline with sodium hydroxide and extracted with chloroform yielded *d*-lupanine as a sirup that slowly crystallized. It distilled between 190 and 195° at 3 mm. The fluid distillate had n_D^{24} 1.5444 and,

in alcohol, $[\alpha]_D^{25}$ 84.35°, $l = 2$, $c = 4.776$, $a = 7.782°$.

Bureau of Animal Industry　　　James Fitton Couch
Washington, D. C.
Received April 30, 1934

THE DEHYDROGENATION OF GITOGENIN

Sir:

The authors have recently studied the dehydrogenation of sarsasapogenin with selenium, a report of which is now in press [*Journal of Biological Chemistry*]. The reaction has yielded a low boiling fraction from which a semicarbazone was obtained which melted at 143–144° and analyzed as the derivative of a ketone $C_8H_{16}O$. This melting point does not agree with that (152°) reported for the same material by Ruzicka and van Veen [*Z. physiol. Chem.*, **184**, 69 (1929)] who concluded that it is the derivative of methyl isohexyl ketone. Through the kindness of Prof. I. M. Heilbron, we have obtained a sample of the semicarbazone of methyl isohexyl ketone (m. p. 152°) which, when mixed with our semicarbazone, melted at 130–133° after preliminary softening. The identity of this ketone is under further investigation. In addition, from the higher boiling fractions a crystalline hydrocarbon mixture was obtained which yielded after repeated fractionation by the triangle scheme an apparently homogeneous hydrocarbon of melting point 123.5–124°. This at once suggested identity with methyl-cyclopentanophenanthrene (Diels' hydrocarbon, $C_{18}H_{16}$). This conclusion was strengthened by the preparation of the trinitrobenzene and trinitrotoluene addition products.

We have since made a parallel study of the dehydrogenation of the digitalis sapogenin, gitogenin, with similar results. From the low boiling fraction of the reaction mixture the same semicarbazone was obtained which melted at 144.5–145°. In addition, a crystalline hydrocarbon resulted which after extensive fractionation gave a substance which melted at 123.5–124° and showed no depression when mixed with Diels' hydrocarbon. For confirmation of identity a study of its derivatives is in progress.

It would appear, therefore, in so far as the formation of Diels' hydrocarbon, $C_{18}H_{16}$, may be considered a characteristic of the sterol ring system, that sarsasapogenin and the digitalis sapogenins as well as the cardiac aglucones are alicyclic

derivatives of a cyclopentenophenanthrene ring system like the sterols and the bile acids.

FROM THE LABORATORIES OF   WALTER A. JACOBS
THE ROCKEFELLER INSTITUTE   JAMES C. E. SIMPSON
FOR MEDICAL RESEARCH   Commonwealth Fund Fellow
NEW YORK CITY

THE PEROXIDE EFFECT IN THE ADDITION OF REAGENTS TO UNSATURATED COMPOUNDS

Sir:

On the basis of a study of the addition of hydrogen bromide to pentene-1 and heptene-1 in glacial acetic acid, hexane and water, Sherrill, Mayer and Walter [THIS JOURNAL, 56, 926 (1934)] conclude that the solvent is the dominant factor governing the direction of addition, and that the peroxide effect is insignificant or non-existent. They ignore the work of Kharasch, McNab and Mayo on the addition of hydrogen bromide to vinyl chloride, allyl and vinyl bromides and reject their work on the addition of hydrogen bromide to propylene on the ground that the small quantities of materials employed furnish yields which are "not very significant" [Kharasch and Mayo, THIS JOURNAL, 55, 2468 (1933); Kharasch, McNab and Mayo, *ibid.*, 55, 2521 (1933); 55, 2131 (1933)].

We have now repeated our earlier study of the addition of hydrogen bromide to propylene using larger quantities of reagents. Identification of the products was made by boiling points, refractive indices and the preparation of mercury derivatives. Using 1.4 mol (85 g.) of hydrogen bromide, 1 mol (31.5 g.) of propylene and 2 g. of ascaridole as peroxide or antioxidant we obtained, working at $-80°$, both without a solvent and using glacial acetic acid, an 80% yield of 100% n-propyl bromide, b. p. 70–71°, n_D^{20} 1.4340, and with a mercury derivative melting at 137.2°. With carbon tetrachloride as a solvent an 18% yield was obtained. Similar experiments using 2 g. of diphenylamine as peroxide or antioxidant gave, with no solvent, or glacial acetic acid or carbon tetrachloride, respectively, 61, 65 and 44% yields of 100% isopropyl bromide, b. p. 59–60°, n_D^{20} 1.4250 (± 0.0001) and a mercury derivative melting at 92.6°. These results confirm our earlier observations and conclusions in every detail.

We would also point out that recently published work on butene-1 and isobutylene [Kharasch and Hinckley, Jr., THIS JOURNAL, 56, 1212,

1243 (1934)] and unpublished work on the addition of hydrogen bromide to pentene-1 are also completely in accord with our earlier observations. Finally, in view of the possibility of interpreting the work of Whitmore and Homeyer [*ibid.*, 55, 4555 (1933)] as in disagreement with our observations, we would say that Professor Whitmore in a private communication assures us that he has confirmed our recent findings as to the effects of peroxides and antioxidants in the addition of hydrogen bromide to 4,4-dimethylpentene-1 [Kharasch, Hannum and Gladstone, *ibid.*, 56, 244 (1934)]. Professor Whitmore has generously withheld publication of his note in order to accord us priority.

JONES CHEMICAL LABORATORY   M. S. KHARASCH
UNIVERSITY OF CHICAGO   M. C. McNAB
CHICAGO, ILLINOIS

THE ACTION OF THE GRIGNARD REAGENT ON α,β-UNSATURATED ALDEHYDES

Sir:

Up to the present time the reaction of the Grignard reagent with α,β-unsaturated aldehydes has been considered as taking place solely through the carbonyl group, *e. g.*, 1,2-addition. It has now been found that t-butylmagnesium chloride reacts with crotonic aldehyde yielding both 1,2- and 1,4-addition products in about equal amount (about 25%). Moreover, preliminary experiments with ethyl-, propyl- and isopropylmagnesium bromides and crotonic aldehyde indicate that here, too, some 1,4-addition takes place though to a very much less extent.

The aldehyde, $C_8H_{16}O$, semicarbazone: m. p. 166°, arising from t-butylmagnesium chloride and crotonic aldehyde was easily oxidized by Tollens' solution to an acid, $C_8H_{16}O_2$, amide: m. p. 163–4°. Bromination of this acid by the Hell, Volhard and Zelinsky method followed by treatment with methyl alcohol led to an α-bromo ester, $C_9H_{17}O_2Br$, which when heated with diethylaniline yielded an α,β-unsaturated ester, $C_9H_{16}O_2$. Ozonolysis of this ester produced pinacolone identified as the semicarbazone: m. p. 155°. The original aldehyde was therefore β,γ,γ-trimethylvaleric aldehyde.

THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CONTRIBUTION No. 111
CAMBRIDGE, MASS.   PHILIP G. STEVENS

CHRONOMETRIC CATALYTIC METHOD FOR THE DETERMINATION OF MICRO QUANTITIES OF IODINE

Sir:

We have found that very small amounts of iodine as iodide can be detected and determined by making use of the catalytic effect of the element on the reaction between arsenious acid and ceric sulfate in sulfuric acid solution

$$As^{3+} + 2Ce^{4+} \longrightarrow As^{5+} + 2Ce^{3+}$$
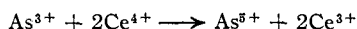
In the absence of iodide this reaction proceeds with extreme slowness [cf. Browning and Cutler, Z. anorg. allgem Chem., 22, 303 (1900); other literature references having a bearing on this matter will be considered in a detailed account of the method]. Traces of iodide increase the speed of the reaction enormously, the rate being directly proportional, or nearly so, to the iodide concentration, other factors being constant. Thus, if 1 ml. of potassium iodide solution containing 5 microgram of iodine is added to a mixture of 2 ml. of 0.1 N arsenious acid, 1 ml. of 0.1 N ceric ammonium sulfate, and 1 ml. of 6 N sulfuric acid, the reaction between ceric ions and arsenious acid is found to be complete in 0.9 to 1.0 min. (25°) as indicated by the disappearance of the yellow color of ceric cerium; with 2.5 microgram of iodine the time required for the reduction of the ceric cerium is 1.8 min. under the same conditions; with 1 microgram, 4.5 min., etc. In the absence of iodine the reaction requires 36 hours or more for completion. It is thus possible to determine the amount of iodide added by noting the time required for the yellow color due to ceric ions to disappear, since the time is inversely proportional to the amount of iodine present. The end-point of the reaction can be determined more precisely by using o-phenanthroline ferrous sulfate as indicator; the solution then assumes a pink color when the ceric cerium has been reduced, whereas the indicator is practically colorless in the presence of a slight excess of ceric cerium. Alkali chlorides and bromides, and other salts also, have a relatively slight effect, and by a special procedure it is possible to determine iodine in quantities ranging from 0.01 to 1 microgram in a dilution of 1:10⁷ in the presence of 10⁵ times as much chloride or bromide with an accuracy of about 20%.

The test is quite specific for iodine, since osmium and presumably ruthenium, are the only other elements showing similar behavior [cf. Gleu,

Z. anal. Chem., 95, 305 (1933)]. Micro quantities of osmium can be determined in the same way as iodine.

SCHOOL OF CHEMISTRY   E. B. SANDELL
UNIVERSITY OF MINNESOTA   I. M. KOLTHOFF
MINNEAPOLIS, MINNESOTA
          RECEIVED MAY 21, 1934

AN ISOTOPIC EXCHANGE BETWEEN H_2^2O AND $C_2H_2^1$

Sir:

Preliminary to the preparation of $C_2H_2^2$ it was decided that a study of the possible isotopic exchange between acetylene and water was essential to the proper set up of a purification system. The weakly acidic character of acetylene has been demonstrated by several investigators,[1] as for example in the formation of metallic acetylides. Billitzer[2] claims to have evidence for an acetylenic anion. Accordingly we passed tank acetylene through a purification train as recommended by McIntosh[3] and then through water containing a high concentration of H_2^2O. In the first experiment acetylene was bubbled for three hours at a rate of 3.5 liters per hour through about 3 cc. of water containing 18.5% of H_2^2O. In order to minimize evaporation the bubble tube was immersed in an ice-bath and any vapor escaping was frozen out in a trap immersed in a salt–ice bath. The acetylene was swept out of the system by purified air in the first experiments and nitrogen was later substituted with no detectable change in results. The water in the trap and bubbler was combined and doubly distilled before the density determination. No detectable change in density was observed.

A similar experiment was carried out using 3 cc. of 18.5% solution of H_2^2O to which was added sufficient anhydrous phosphorus pentoxide to make approximately a 1 N solution of phosphoric acid. After passing acetylene through this solution for five hours sufficient sodium oxide was added to more than neutralize the acid and excess alkalinity was removed by carbon dioxide. After the elimination of the gases the water was again doubly distilled and its density determined. Again there was no detectable change in composition.

To 3.5 cc. of 18.5% solution of H_2^2O, enough sodium oxide was added to make the solution

(1) Keiser, Am. Chem. J., 14, 285–290 (1892); 15, 535–539 (1893); Jones and Allen, Chem. News, 74, 18–19 (1896); Bredig and Usoff, Z. Elektrochem., 3, 116–117 (1896).
(2) Billitzer, Monatsh, 23, 489–501 (1902); 23, 502–511 (1902).
(3) McIntosh, J. Phys. Chem., 11, 306 (1907).

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_2^2O. A check experiment was run for twelve hours on water containing 12.1% H_2^2O. (The strength of the alkali was somewhat greater in this experiment than in the previous one.) The concentration of H_2^2O 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_2^2O 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_2^2O containing an alkali. If the same exchange occurs in neutral and acid solutions of H_2^2O 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 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-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 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.

PRINCETON, N. J.   EVERETT S. WALLIS
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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.

DEPARTMENT OF CHEMISTRY   J. W. WILLIAMS
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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