glyoxal[6] passed into a solution of cyclohexylmagnesium bromide gave a poor yield of the iso compound, iso-α,β-dicyclohexylethylene glycol, a result in line with the formation of iso-hydrobenzoin by a similar method.[7]

Finally, dodecahydrobenzoin was prepared by the method of Danilow and Venus-Danilowa.[8] This compound was reduced catalytically, and gave an excellent yield of a product which proved to be identical with the previously described compound melting at 194°. Mixed melting point determinations showed no depression.

Hexahydromandelonitrile is a pale yellow, fairly mobile oil, with a faint aromatic odor. It is surprisingly stable and may be distilled under reduced pressure (reported undistillable by Godchot and Frezouls[3]). It is smoothly converted by the Radziscewski[9] method into the amide[3]: b. p. 104° (0.70 mm.), 121° (1.6 mm.), d_{25}^{25} 1.0163, n_D^{25} 1.4716, M_D (n^2) calcd. 38.29, found, 38.19.

Anal. Calcd. for $C_8H_{13}ON$: C, 69.01; H, 9.42. Found: C, 68.68; H, 9.72.

Iso-α-β-dicyclohexylethylene Glycol.—When recrystallized from aqueous alcohol, the compound forms a white, felted mass of slender needles. It is very soluble in absolute alcohol and in most of the usual solvents. Cold, concd. sulfuric acid gives no coloration. The melting point is 153° (corr.).

Anal. Calcd. for $C_{14}H_{26}O_2$: C, 74.27; H, 11.59. Found: C, 74.61; H, 11.64.

[6] Harries and Temme, *Ber.*, **40**, 165 (1907).

[7] Wren and Still, *J. Chem. Soc.*, **103**, 1772 (1913).

[8] Danilow and Venus-Danilowa, *Ber.*, **62**, 2653 (1929).

[9] Method of Rupe and Majewski, *Ber.*, **33**, 3401 (1900).

CONTRIBUTION FROM THE   JOHANNES S. BUCK
EXPERIMENTAL RESEARCH LABORATORIES   WALTER S. IDE
BURROUGHS WELLCOME AND CO.
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COMMUNICATIONS TO THE EDITOR

THE PHOTOCHEMICAL REACTION BETWEEN HYDROGEN PEROXIDE AND HYDROGEN OR CARBON MONOXIDE IN THE GAS PHASE

Sir:

The absorption spectrum of gaseous hydrogen peroxide has been shown by Urey, Dawsey and Rice[1] to be continuous below 3000 Å. Their interpretation of the continuum favored the direct dissociation into OH radicals, namely

$$H_2O_2 \xrightarrow{h\nu} 2OH$$
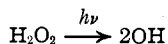
In order to test this point of view the writer carried out experiments to

[1] Urey, Dawsey and F. O. Rice, THIS JOURNAL, **51**, 1376 (1929).

detect the presence of OH radicals by a possible interaction with hydrogen molecules or carbon monoxide.   If the dissociation occurs according to

$$H_2O_2 \xrightarrow{h\nu} H_2O + O$$
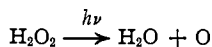
no interaction with hydrogen or carbon monoxide should be observed, because the oxygen atoms would be expected to react with hydrogen peroxide much faster than with hydrogen or carbon monoxide.[2]

The experiments were so carried out that a mixture containing a constant percentage of hydrogen peroxide (about 1%) and the rest hydrogen or carbon monoxide was continuously recirculated in a system at 40°.   The drop in pressure represented the disappearance of hydrogen or carbon monoxide.   Details of the experimental arrangement will be published later.   In the case of carbon monoxide, carbon dioxide could easily be detected in a barium hydroxide solution.   The gases were illuminated with the radiation 2070 Å. and 2530 Å. from a zinc spark.   Blank experiments were made in the dark.

A very decided but slow reaction was measured.   The following table gives a few representative experiments.

TABLE I

Mixture	Partial pressure of H_2O_2 approx. in mm.	Time of illumination, min.	Total pressure Initial	Final	Decrease in pressure per hour in mm.
$H_2O_2 + H_2$	5	70	712.5	709.6	2.5
	5	50	711.1	709.0	2.5
$H_2O_2 + CO$	5	60	706.0	702.0	4.0
	2	60	702.7	700.4	2.3

The results may best be explained on the basis of dissociation of hydrogen peroxide into OH radicals.   These then collide with hydrogen or carbon monoxide and react in the following way with a low efficiency

$$OH + H_2 = H_2O + H \qquad (1)$$
$$OH + CO = CO_2 + H \qquad (2)$$

Both reactions have long been proposed by Bonhoeffer and Haber.[3]

The results as they stand furnish an upper limit of the efficiency of Reactions 1 and 2.   A more exact value will be given elsewhere[4] together with a discussion of its bearing on the much discussed mechanism of the chains in the thermal reaction between hydrogen and oxygen.

COBB CHEMICAL LABORATORY   GUENTHER VON ELBE
UNIVERSITY OF VIRGINIA
UNIVERSITY, VIRGINIA
RECEIVED SEPTEMBER 30, 1931
PUBLISHED FEBRUARY 5, 1932

[2] See Kistiakowsky, THIS JOURNAL, 52, 1868 (1930), and Harteck and Kopsch, Z. physik. Chem., 12B, 327 (1931), for the reaction between O atoms and H_2 or CO.

[3] Bonhoeffer and Haber, Z. physik. Chem., 137A, 263 (1928).   See also Lavin and Jackson, THIS JOURNAL, 53, 383, 3189 (1931), for Reaction 2.

[4] G. von Elbe and Bernard Lewis, THIS JOURNAL, 54, 552 (1932).

THE COMPOSITION OF THE ATOMIC NUCLEUS

Sir:

In recent papers on the atomic nucleus by Harkins,[1] Latimer[2] and Urey[3] various combinations of (1) helium nuclei, (2) additional binding electrons or cementing electron pairs and (3) additional protons and electrons are used to make up the isotopic weight, *i. e.*, the *mass* of the atom. However, it seems that the atomic number, *i. e.*, the *positive charge* on the nucleus, is more significant. If this charge is due to α-particles alone, which are after all the only nuclear fragments of appreciable mass obtained during radioactive decay, it follows that their number in the nucleus is equal to one-half the atomic number, $\alpha = AN/2$, where α is p_4e_2. If the number of protons and electrons corresponding to $AN/2$ α-particles is subtracted from the total number of protons and electrons in the nucleus of any isotope, there remains in *every case an equal number* of protons and electrons. This leads to the conclusion that Harkins' isotopic number must be interpreted as the number of neutrons, *pe*, or a proton and an electron.[4]

The simplest groupings of protons and electrons in the nucleus is therefore as

p_4e_2 or α, helium nuclei or α-particles—the number of which is equal to one-half the atomic number

p_2e or $\alpha_{0.5}$, half α-particles—only one of these occurs in each element with odd atomic number

pe or *n*, neutrons—the number of which is equal to the isotopic number, that is, the proton number minus twice the atomic number. This number ranges from 0 to 54.

With this concept it is also possible to harmonize Latimer's nuclear structure by modifying the number of α-particles to be $AN/2$ and substituting the proper number of neutrons for cementing electron pairs, thereby avoiding the difficulty of ascribing the same number of helium nuclei to different elements, and a different number of helium nuclei to the isotopes of the same element.

Isotopes differ therefore only in the number of neutrons and radioactive decay can be explained as follows

AN or $p - e$		Total no. of p and e	Composition as α and n	Nuclear change during decay
92	U I	$p_{238}e_{146}$	$\alpha_{46}n_{54}$	loss of p_4e_2 or α
90	U X₁	$p_{234}e_{144}$	$\alpha_{45}n_{54}$	loss of e or $2n$ and gain of $\alpha_{0.5}$
91	U X₂	$p_{234}e_{143}$	$\alpha_{45.5}n_{52}$	loss of e or $2n$ and gain of $\alpha_{0.5}$
92	U II	$p_{234}e_{142}$	$\alpha_{46}n_{50}$	loss of p_4e_2 or α
90	Io	$p_{230}e_{140}$	$\alpha_{45}n_{50}$	loss of p_4e_2 or α
88	Ra	$p_{226}e_{138}$	$\alpha_{44}n_{50}$	

and so on

[1] Harkins, *Phys. Rev.*, **38**, 1270 (1931).

[2] Latimer, THIS JOURNAL, **53**, 981 (1931).

[3] Urey, *ibid.*, **53**, 2872 (1931).

[4] Langer and Rosen, *Phys. Rev.*, **37**, 1579 (1931).

This shows that during β-decay a half α-particle is formed from two neutrons, $2pe \longrightarrow p_2e + e;$ inasmuch as two β-decays follow each other in rapid succession, the net result for the nucleus is the formation of an α-particle, $2p_ee \longrightarrow p_4e_2$.

Artificial disintegration could then be explained by the expulsion of neutrons and this would be possible only with Li^7, Be^9, B^{11}, C^{13}, O^{17} and O^{18}, etc., but not with Li,[6] Be,[8] B,[10] etc.

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SAN FRANCISCO, CALIFORNIA
RECEIVED OCTOBER 27, 1931
PUBLISHED FEBRUARY 5, 1932

THE ATOMIC WEIGHTS OF SELENIUM AND OF TELLURIUM

Sir:

The chemically determined values for the atomic weights of selenium and of tellurium have recently been questioned by Aston[1] on the basis of improved measurements with the mass spectrograph.

With the advantage of increased precision in the measurements of relative amounts of the isotopic constituents, Aston reports the following relative percentages: for tellurium, Te_{125} (6.6%), Te_{126} (20.9%), Te_{128} (36.1%) and Te_{130} (36.4%); and for selenium, Se_{74} (0.9%), Se_{76} (9.5%), Se_{77} (8.3%), Se_{78} (24.0%), Se_{80} (48.0%) and Se_{82} (9.3%). Corrected for packing effects and converted to the chemical oxygen scale these figures lead to respective atomic weights 128.03 ± 0.1 and 78.96 ± 0.04. The limits of error are those assigned by Aston. The atomic weights determined by chemical means are, respectively, 127.5 and 79.2.[2] These latter values have stood for over twenty years although subjected to frequent careful redeterminations by different workers.[3] Tellurium, in particular, has received more than usual attention due to its anomalous position with respect to iodine in the older arrangements of the Periodic Table.

Te_{125} is a new discovery. Its discovery, together with the discoveries of Ba_{136} and Sr_{87} also reported by Aston,[1] constitutes confirmation of

[1] Aston, *Proc. Roy. Soc.* (London), A132, 487 (1931).

[2] Table of International Atomic Weights, Report of the Committee on Atomic Weights of the International Union of Chemistry, THIS JOURNAL, 53, 1627 (1931).

[3] Baker and Bennett, *J. Chem. Soc.*, 91, 1849 (1907); Harcourt and Baker, *ibid.*, 99, 1311 (1911); Marckwald and Foizik, *Ber.*, 43, 1710 (1910); Flint, THIS JOURNAL, 34, 1325 (1912); Dudley and Bowers, *ibid.*, 35, 875 (1913); Dennis and Anderson, *ibid.*, 36, 882 (1914); Staehler and Tisch, *Z. anorg. allgem. Chem.*, 98, 1 (1916); Bruylants and Desmet, *Bull. soc. chim. Belg.*, 28, 264 (1919); Bruylants and Michielson, *Bull. sci. acad. roy. Belg.*, [V] 5, 119 (1919); Bruylants and Bytebier, *Bull. Belg. acad.*, 856 (1912); Kusma and Kruhlik, *Trans. Bohemian acad. of Emperor Francis Joseph*, 19, No. 13 (1910); Jannek and J. Meyer, *Z. Electrochem.*, 19, 833 (1913); *ibid.*, 83, 51 (1913); Bruylants and Dondeyne, *Bull. sci. acad. roy. Belg.*, [V] 8, 387 (1922); Bruylants, La Fortuen and Verbruggen, *Bull. soc. chim. Belg.*, 33, 587 (1924 .

definite predictions which were recently made by the writer.[4] The further discoveries by Aston of Ba_{135} and Ba_{137} are also concordant with these predictions. Further predictions of isotopes whose discoveries have not yet been reported include three additional tellurium isotopes, Te_{120}, Te_{122} and Te_{124}, with the possibility of Te_{123} as well, and two additional selenium isotopes, Se_{79} and Se_{81}. It is significant that allowance for these additional isotopes will change Aston's computed values in the directions of the chemical atomic weights, both for selenium and for tellurium.

Small uncertainties which, of course, do exist in the chemical atomic weights preclude the possibility of an exact estimate of the proportions in which these additional isotopes exist. However, we expect that these uncertainties are small compared with the divergences between the chemical and the mass spectrograph values. Hence we can make predictions as to the approximate percentages of these isotopes. These predictions lead to about 8% of Te_{120}, Te_{122}, Te_{124} (and possibly Te_{123}), taken collectively, and to about 9% of Se_{81}. No estimate for the amount of Se_{79} is possible. Failure heretofore to observe the 8% mixture of tellurium isotopes is reasonable since the 6% of Te_{125} alone remained, until now, undiscovered. Proximity to the very abundant Se_{80} (48%) may account for failure to observe both Se_{81} and Se_{79}.

The writer's predictions of these isotopes, as of Te_{125}, Ba_{136} and Sr_{87}, were based on the positions of missing atoms in a "Periodic Table" of atomic nuclei.[4] Independently, Professor H. C. Urey[5] made similar predictions, including isotopes of selenium and of tellurium. The predictions of further missing isotopes can now be extended to include Ce_{141}, Ce_{144}, and Nd_{148}. As a convenient aid in using the "Periodic Table" of isotopes it is useful to observe that the positions at which the various isotopes of a given element may occur occupy a pattern similar to successive knight moves on a chess board.

[4] Johnston, THIS JOURNAL, **53**, 2866 (1931).

[5] Urey, THIS JOURNAL, **53**, 2872 (1931).

DEPARTMENT OF CHEMISTRY   HERRICK L. JOHNSTON
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RECEIVED DECEMBER 10, 1931
PUBLISHED FEBRUARY 5, 1932

PREPARATION OF PINACOLONE

Sir:

Because of the need of large amounts of pinacolone for investigations in progress in this Laboratory, methods for its preparation have been studied. The usual method ["Organic Syntheses," Vol. I, pp. 87, 91] is time consuming.

We find that the addition of a dilute ether solution of tertiary-butyl-

magnesium chloride to an excess of acetyl chloride in ether gives a 40% yield of pinacolone, b. p. 103–106° at 746 mm. pressure.

Somewhat lower yields are obtained with other combinations of tertiary Grignard reagents and acyl halides.

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RECEIVED DECEMBER 26, 1931
PUBLISHED FEBRUARY 5, 1932

DARWIN E. BADERTSCHER
FRANK C. WHITMORE

PREPARATION OF SUBSTITUTED FLUORENONES

Sir:

The appearance of a paper by Langecker [*J. prakt. Chem.*, [2] **132,** 145–52 (1931)] citing certain attempts to prepare 1,8-dinitrofluorenone leads us to call attention to work of a similar nature which has for some time been in progress in this Laboratory. In May, 1927, Moore and Huntress [THIS JOURNAL, **49,** 1324–1334 (1927)] published a synthesis for both 2-nitro- and for 7-nitrophenanthridone. In November of the same year it was further shown [Moore and Huntress, *ibid.*, **49,** 2618–2624 (1927)] that 7-nitrophenanthridone could be prepared in almost quantitative yield by Beckmann rearrangement of 2-nitrofluorenone oxime. In pursuance of the studies of the phenanthridone series begun at that time, the present authors have been engaged since 1927 in attempting to obtain derivatives of fluorenone having substituents in one (or both) of the 1,8 positions. If an unsymmetrically substituted fluorenone oxime of this type could be obtained, it was hoped that stereoisomers might be isolated, and that by joint application of phenanthridone formation and of ring closure reactions involving the substituent and the oximino group, some additional light might be thrown upon the mode of interchange of radicals in the Beckmann rearrangement. Since Langecker's paper indicates its objective as the preparation of 1-substituted fluorenones, and since in dealing with the 2-nitrofluorenone oxime first reported by one of us it gives no evidence that the author was aware of our previous publications on fluorenone derivatives, it seems advisable that we reiterate the continuing interest of this Laboratory in this subject.

Of the few 1- or 1,8-substituted fluorenones on record in the literature (1-bromofluorenone, 1,3-dibromofluorenone, 1-hydroxyfluorenone, 1-aminofluorenone, fluorenone-1,7-dicarboxylic acid, and 1,8-dinitrofluorenone), the alleged "1,8-dinitrofluorenone" of Schmidt and Stützel [*Ann.*, **370,** 22 (1909)] and of Kuhn and Jacob [*Ber.*, **58,** 1440 (1925)] is the only substance prepared by direct substitution. The structure assigned to this material is open to criticism upon several grounds. In the first place the nitrogen content given by Schmidt as 10.40% proves upon recalculation

of Schmidt's own experimental data to be in fact 8.08%, or about half-way between the theoretical value of 6.22% for a mononitrofluorenone and 10.36% for a dinitrofluorenone. In the second place, oxidation of the material yielded an acidic product whose observed melting point and nitrogen analysis suggested that it might be o-nitrobenzoic acid. Despite the proximity of the melting points of o- and of m-nitrobenzoic acids, no other derivatives of this oxidation product were prepared. Assuming for the moment that the product really was o-nitrobenzoic acid, the result accounts for only one of the nitro-substituted nuclei and does not necessarily imply that the same position in the other was involved. The supposed existence of stereoisomeric dinitrobenzidines and dinitrotolidines was based upon negative evidence of this kind. In the third place recent developments have shown that directly contrary to the assumptions prevalent at the time of Schmidt and Stützel's publication there is a strong tendency toward unsymmetrical nitration in the biphenyl series, in the phenanthraquinone series, and in the fluorene series.

In pursuance of our desire to obtain an appropriately substituted fluorenone oxime, we attempted to repeat the work of Schmidt and Stützel. In no case, however, was any material obtained possessing the properties ascribed to "1,8-dinitrofluorenone." In four separate experiments using Schmidt's conditions we obtained instead a 70% yield of 2-nitrofluorenone. The identity of this substance was established in four ways: (1) by analysis for nitrogen; (2) by its melting point and its failure to depress the melting point of a sample of authentic 2-nitrofluorenone; (3) by the identity of its phenylhydrazone with that of authentic 2-nitrofluorenone as shown by comparison and by mixed melting point determinations; and (4) by its reduction to 2-aminofluorenone. We can confirm Langecker, therefore, in stating that nitration of 9-acetylaminofluorene by the method of Schmidt and Stützel gives 2-nitrofluorenone as the only tangible product.

In examining the effect of varying the stated conditions, we have observed that when 9-acetylaminofluorene is treated with concentrated nitric acid (d 1.42) for two hours at 100° there results a mixture from which we have isolated a 30% yield of 2,7-dinitrofluorenone, together with 13% of a new dinitrofluorenone, m. p. 213–4° uncorr. This substance contains 10.57% of nitrogen as compared with the theoretical of 10.60% for a dinitrofluorenone. It depressed the melting points of both 2,7-dinitro- and 2,4-dinitrofluorenones. Its structure is being examined.

The melting point of Langecker's 2-nitrofluorenone oxime is given as 249°. Moore and Huntress [THIS JOURNAL, **49**, 2622 (1927)] obtained a value of 262.5–263.0° uncorr., with decomposition. Since the former material was prepared from the ketone by means of hydroxylamine hydrochloride and barium carbonate in alcohol (i. e., in neutral solution) while our product was prepared from hydroxylamine hydrochloride and an

alcoholic solution of the ketone (*i. e.*, in acid solution), it is possible that the two materials are stereoisomers.   This point will be examined.

Our efforts to prepare fluorenones substituted in positions ortho to the carbonyl group are being continued.

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MASSACHUSETTS INSTITUTE OF TECHNOLOGY   IVAN S. CLIFF
CAMBRIDGE, MASSACHUSETTS
RECEIVED DECEMBER 28, 1931
PUBLISHED FEBRUARY 5, 1932

REACTION OF PHENYLACETONITRILE

Sir:

While investigating the action of sodium on benzyl cyanide, it was found that one mole of phenylacetonitrile dissolved in liquid ammonia reacts almost quantitatively with one mole of sodium to form a salt, presumably sodium phenylacetonitrile, which remains suspended in liquid ammonia.   This when treated with ethyl bromide in liquid ammonia yields phenylethylacetonitrile.

In previous work Rossolymo used sodium hydroxide, Hintikka, sodamide in toluene, Bodroux and Taboury, sodamide in ether, Rising, sodium in ether, Rising and Zee, sodamide in ether, as a means of forming sodium phenylacetonitrile.

It is interesting to note that presumably only one of the hydrogen atoms on the carbon atom, alpha to the cyanide group, can be replaced at one time by sodium in liquid ammonia.   If, after treatment with ethyl bromide to form phenylethylacetonitrile, this latter nitrile is treated with sodium in liquid ammonia, a mole of sodium can be introduced per mole of nitrile.

This procedure can be utilized in the preparation of mono and dialkylated alkyl or aryl cyanides.   It is being investigated further in these laboratories.

DEPARTMENT OF CHEMISTRY   J. A. NIEUWLAND
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NOTRE DAME, INDIANA
RECEIVED DECEMBER 28, 1931
PUBLISHED FEBRUARY 5, 1932

THE CRYSTALLINITY OF OPALS AND THE EXISTENCE OF HIGH-TEMPERATURE CRISTOBALITE AT ROOM TEMPERATURE

Sir:

Opals have thus far been considered as outstanding examples of truly amorphous solids.   The introduction of x-ray methods did not alter this result materially since Lehmann [W. M. Lehmann, *Z. Krist.*, **59**, 455 (1923)] reported that gem opal and ordinary opal give the Debye–Scherrer–Hull diagram of an amorphous solid; however, fire opal gives a faint in-

dication of crystallinity. Later Rinne [F Rinne, *Z. Krist.*, **60,** 55 (1924)] studied several samples of opals by means of x-rays and found them to be amorphous.

The results obtained in this Laboratory are quite different from these previous findings. Thus far fifteen samples of various types of opal have been investigated, all of which show definite crystallinity which is very pronounced in the majority of the cases. Also most of the samples give an identical pattern.

This pattern is of unusual interest since it does not correspond to either low-quartz, low-tridymite or low-cristobalite, which are the only modifications of silica ever definitely established to exist at room temperature. . The pattern, is however, in perfect agreement with the one of high-temperature cristobalite as reported by Wyckoff [R. W. G. Wyckoff, *Am. J. Sci.*, **9,** 448 (1925)., *Z. Krist.*, **62,** 189 (1925)].

Comparison with a picture of the cubic high-temperature form prepared in this Laboratory confirms this identity. The unlikely possibility of a hydrate of similar structure is excluded by the fact that the diagram remains unchanged after heating of the sample for one hour at 1100°.

Two reports have been made suggesting that high temperature cristobalite might persist at room temperature for some time, but according to Sosman [R. B. Sosman, "The Properties of Silica," The Chemical Catalog Co., Inc., New York, 1927, p. 133] these claims, based on optical examination, are of doubtful validity; 200° is the lowest temperature at which high-cristobalite has been observed to exist according to reliable experiments (compare Sosman).

However, we have now provided definite proof of the existence of high-temperature cristobalite at room temperature for an indefinite period of time.

These investigations are being continued and a complete report will appear soon.

DEPARTMENT OF CHEMISTRY   ISADOR LEVIN
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BALTIMORE, MARYLAND
RECEIVED JANUARY 2, 1932
PUBLISHED FEBRUARY 5, 1932

THE STARCH-IODIDE REACTION

Sir:

Remington, McClendon and von Kolnitz have recently reported [THIS JOURNAL, **53,** 1245 (1931)] that they could not confirm Turner's observations as to the reliability and stability of the color produced by the starch-iodide reaction. They state that if the blue solution is read against a blue glass instead of a starch–iodine solution, it will be found that the color is quite sensitive to temperature changes and varies with the time. These

conclusions were drawn apparently from a study of four standard solutions each containing 0.001 mg. of iodine. Their figures show an error of over 100% as read in the colorimeter against their blue glass.

Three years of careful study with the starch–iodide test indicate that the standard solutions prepared as described by Turner are reliable, stable and sufficiently uniform for clinical estimation of small amounts of iodine.

DEPARTMENT OF MEDICAL RESEARCH　　　　　　　R. G. TURNER
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THE ACTION OF HYDRIODIC ACID ON GLYCEROL

Sir:

The following seems reasonably good evidence for the mechanism involved in the formation of allyl iodide in the well-known reaction between glycerol and hydriodic acid.

When $CH_2Br\text{-}CH_2\text{-}CH_2Br$ is treated with zinc or sodium, cyclopropane is formed. However, when $CH_2Br\text{-}CHOH\text{-}CH_2Br$ [Aschan, *Ber.*, **23,** 1833 (1890)] or $CH_2Cl\text{-}CHOH\text{-}CH_2Cl$ is similarly treated [Hübner and Müller, *Ann.*, **159,** 168 (1871); Tornöe, *Ber.*, **24,** 2674 (1891)] allyl alcohol is formed and not cyclopropanol. Strange as it may seem, $CH_2Br\text{-}CHOOR\text{-}CH_2Br$ in absolute ether yields with sodium not cyclopropyl benzoate or acetate but allyl benzoate and allyl acetate, depending, of course, on the nature of the group R. Furthermore, in the action of nitrous acid on cyclopropyl amine, allyl alcohol is formed [Kishner, *Chem. Zentr.*, I, 1704 (1905)] and not cyclopropanol, while in the electrolysis of the potassium salt of cyclopropane monocarboxylic acid, the allyl ester of cyclopropane monocarboxylic acid was obtained [Fichter and Reeb, *Helv. Chim. Acta*, **6,** 454 (1923); Hofer and Moest, *Ann.*, **323,** 284 (1902)] and not the cyclopropyl ester of the cyclopropane monocarboxylic acid. Furthermore, allyl alcohol was obtained from diiodohydrin [Claus, *Ann.* **168,** 28 (1873); Swarts, *Z. Chem.*, 255 (1868)] when that compound was merely allowed to stand. The unstable nature of cyclopropanol offers a clue to the action of hydriodic acid on glycerol. In the light of the foregoing reactions, the following may be postulated

$$H_2COH \atop HCOH \atop H_2COH \quad \xrightarrow{+ \atop HI} \quad {H_2CI \atop HCOH \atop H_2CI} \longrightarrow \overset{H_2C}{\underset{H_2C}{\diagdown}}C\overset{H}{\underset{OH}{\diagup}} \longrightarrow H_2C{=}\overset{H}{\underset{|}{C}}{-}CH_2OH \xrightarrow{HI} H_2C{=}\overset{H}{\underset{|}{C}}{-}CH_2I$$

Spontaneously
decomposes
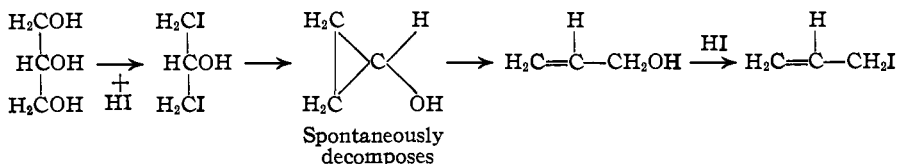
Experiments are under way in this Laboratory to test further the instability of hydroxycyclopropane derivatives.

DEPARTMENT OF CHEMISTRY   LOUIS SATTLER
BROOKLYN COLLEGE
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RECEIVED JANUARY 7, 1932
PUBLISHED FEBRUARY 5, 1932

PYRIMIDINE AZO DERIVATIVES

Sir:

There has just come to our attention the article by Johnson, Baudisch and Hoffman, entitled "Ueber die Bildung von Diazo-uracilanhydrid aus Amino-uracil" ("Concerning the Formation of Diazo-uracilanhydrid from Amino-uracil") in the November, 1931, number of the *Berichte* [*Ber.*, **64,** 2629–2631 (1931)]. Since this article is entitled a "Vorläufige Mitteilung (Preliminary Communication)" and concludes with the sentence "Die Versuche sollen fortgesetzt werden (The experiments are to be continued)," it seems desirable, for the sake of avoiding, so far as may be possible, overlapping of work and duplication of effort, for us to report that prior to the appearance of this article in the *Berichte* we had already completed an investigation of five different types of pyrimidine azo derivatives, and that an article covering this research will appear shortly.

Our studies have included the following groups of reactions: (1) the coupling of aromatic diazonium salts with hydroxypyrimidines; (2) the coupling of diazopyrimidines with aromatic phenols and amines; (3) the coupling of diazopyrimidines with hydroxypyrimidines; (4) the condensation of hydroxypyrimidines with hydrazines, and (5) the condensation of hydrazinopyrimidines with hydroxypyrimidines.

DEPARTMENT OF CHEMISTRY   MARSTON T. BOGERT
COLUMBIA UNIVERSITY   DAVID DAVIDSON
NEW YORK, N. Y.
RECEIVED JANUARY 14, 1932
PUBLISHED FEBRUARY 5, 1932

DILUTE HYDROCHLORIC ACID SOLUTIONS AND THE DEBYE–HÜCKEL THEORY

Sir:

Whether the Debye–Hückel theory is in entire quantitative agreement with the facts even for dilute 1:1 aqueous strong electrolytes at ordinary temperatures is a question which is not yet regarded as closed by all investigators. This is clearly shown in the recent review by Lange and Streeck [*Z. Elektrochem.*, **37,** 698 (1931)]. Davies, in "The Conductivity of Solutions," New York, 1930 and elsewhere has repeatedly expressed the view, supported by some evidence, that in the case of monobasic acids

the limiting value of the ratio of $-\log f$ to $c^{1/2}$ is not 0.5 as required by the theory but something nearer to 0.38.

Since both Davies and Lange and Streeck discuss hydrochloric acid, and conclude that in this case the data are inadequate to decide the question, new evidence on this substance should be particularly welcome. Using the value of $E°$ given by Carmody in his recent paper [THIS JOURNAL, 54, 188 (1932)] a simple calculation yields as values of the ratio of $-\log \gamma$ to $m^{1/2}$: 0.47, 0.45, 0.43, 0.45, 0.47, 0.47 and 0.47 for the seven lowest molalities studied by Carmody, ranging from 0.005 to 0.0003 molal. The mean value 0.46 is slightly lower than the Debye–Hückel value, as has been noted in many other cases, but is not inconsistent with it in view of the experimental uncertainty of the e. m. f. measurements. Carmody's careful investigation certainly lends no support to Davies' views.

DEPARTMENT OF CHEMISTRY   NORRIS F. HALL
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RECEIVED JANUARY 18, 1932
PUBLISHED FEBRUARY 5, 1932

OXYACIDS OF FLUORINE

Sir:

When fluorine is passed into a 50% solution of potassium hydroxide cooled to $-20°$, potassium fluoride separates and the supernatant liquid actively liberates iodine from a solution of potassium iodide. This liquid maintains its oxidizing power for several days at room temperature, even after air has been passed through it for some time, and even after being heated for three hours at 60°. These results seem to preclude the possibility of the oxidation being due to ozone.

To test this point still further, ozone was passed through a cold solution of lithium hydroxide for a considerable time. The liquid showed no oxidizing power. When, however, fluorine was passed into a solution of lithium hydroxide under identical conditions, the resulting liquid was strongly oxidizing, and when this solution was evaporated to dryness on a water-bath and the residue was dissolved in water, the solution still showed strong oxidizing power.

Similarly, a solution of calcium hydroxide was found to be unaffected by ozone, but to have a marked oxidizing action after treatment with fluorine.

These alkaline solutions retained their oxidizing character even after acidification with sulfuric acid, which indicated the presence of an oxyacid of fluorine.

To prepare a solution of the free oxyacids, fluorine was passed into a suspension of calcium carbonate in cold water, and the contents of the

flask was then subjected to distillation. The distillate had an acid reaction and actively oxidized a neutral solution of potassium iodide.

Approximate determinations of the ratio of hydrogen to oxygen in the distillate from three separate distillations gave 1:2.31, 1:2.22 and 1:2.80. These results indicate the presence of fluoric acid (HFO_3) in the distillate; and a greater oxidizing power of the liquid in the reaction flask, before distillation from the calcium carbonate, indicates that a less stable oxyacid of fluorine, probably hypofluorous acid (HFO), is also formed. It may here be added that the distillate contained no trace of chlorine.

When fluorine was passed into a cold solution of cesium carbonate until the salt had been entirely converted into fluorine compounds, the resulting liquid was extremely reactive. It was evaporated to dryness on a waterbath, and a water solution of the residue showed strong oxidizing power. Fractional solution of this residue with successive small amounts of water indicated that the oxidizing power is greatest in the most soluble portions.

This investigation is being carried forward and detailed results will be published later.

DEPARTMENT OF CHEMISTRY   L. M. DENNIS
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ITHACA, NEW YORK
RECEIVED JANUARY 22, 1932
PUBLISHED FEBRUARY 5, 1932

THE THERMAL DISSOCIATION OF NITROUS OXIDE

Sir:

From the known entropies of other triatomic molecules it is possible to determine a value for the entropy of nitrous oxide which is probably correct within a few entropy units. Following the procedure used in a recent article by the author [THIS JOURNAL, **54,** 156 (1932)] the value S°_{298} (N_2O)g = 51.9 E. U. is obtained. This leads to interesting conclusions regarding the thermal dissociation of nitrous oxide into nitrogen molecule and oxygen atom, for the entropy change in this reaction can now be determined, and the change in heat content is known. Thus the free energy change at 298°K. can be found, and by the use of empirical specific heat equations a good estimate of the free energy change at 838°K. can be made and thus of the equilibrium constant $K = p_{N_2} \cdot p_O / p_{N_2O}$. An approximate value such as this is quite sufficient to show that the equilibrium pressure of oxygen atoms is surprisingly high, being of the order of 10^{-4} atm. at this temperature.

At 838°K. the thermal rate of decomposition is low. For the purposes of a calculation to be made in a moment, let us consider simply as an example the thermal rate in a bulb at this temperature containing 190 mm. of N_2O and 10 mm. of N_2. The rate of decomposition is of the order of

10^{18} molecules per cc. per sec. [Hinshelwood and Burk, *Proc. Roy. Soc.* (London), A106, 284 (1924)]. On the other hand, the number of collisions between N_2O molecules and oxygen atoms at the equilibrium concentration under these conditions proves to be of the order of 10^{24} collisions per cc. per sec., and thus the thermal decomposition is very small compared to this. We are thus forced to the conclusion that either the probability of reaction between N_2O and O is very small, or that the rate of thermal dissociation into N_2 and O is very small, never even approximately establishing equilibrium even for low rates of the thermal decomposition. Both statements may, of course, be true. The first is not at all surprising, rather, indeed, probable. However, the second statement, also, may very possibly be true. In this case, in contrast to the case of ozone (see first reference cited above), we are dealing with a molecule made up of the dissociation products O (normal state ^3P) and N_2 (normal state $^1\Sigma$) and this, in addition to all chemical knowledge of the inertness of nitrogen, suggests that the two reactions represented by the equilibrium $N_2O \rightleftarrows N_2 + O$, even at 838°K., are very slow. In the case of the molecule O_3 the situation is different, the constituents being O (normal state ^3P) and O_2 (normal state $^3\Sigma$). It should be noted that, with respect to the dissociation products, the energy content of the two molecules N_2O and O_3 is of the same order of magnitude, namely, about 41,500 calories and 24,000 calories, respectively. The author plans to discuss the above more fully in a later paper.

BUREAU OF CHEMISTRY AND SOILS   OLIVER R. WULF
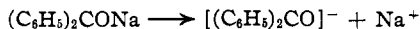U. S. DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C.

THE STRUCTURE OF METAL KETYLS

Sir:

The metal ketyl derived from benzophenone has been found to conduct the electric current in liquid ammonia solution [observations of Mr. Paul B. Bien in this Laboratory] and the results also suggest that this substance is ionized in accordance with the equation

$$(C_6H_5)_2CONa \longrightarrow [(C_6H_5)_2CO]^- + Na^+$$

The anion represents an interesting and unusual type of stable complex for it contains both an *odd* and an *extra* electron. Consequently, a careful study of such substances might be expected to throw some new light on fundamental valence problems.

It has already been shown [Wooster, THIS JOURNAL, 51, 1856 (1929)] that the Schmidlin formula for the metal ketyls is incorrect and that the question of their constitution is still open. Several alternative hypotheses

including those of Schlenk and his co-workers [Schlenk and Weickel, *Ber.*, **44**, 1182 (1911); Schlenk and Thal, *ibid.*, **46**, 2840 (1913)] are now being critically studied.

CHEMICAL LABORATORY OF BROWN UNIVERSITY   CHARLES BUSHNELL WOOSTER
PROVIDENCE, RHODE ISLAND

NEW BOOKS

An Introduction to Chemistry. A Pandemic Text. By JOHN ARREND TIMM, Assistant Professor of Chemistry, Yale University. With a Foreword by John Johnston. McGraw-Hill Book Company, 370 Seventh Avenue, New York, 1930. xviii + 561 pp. 161 figs. 14.5 × 21 cm. Price, $3.50.

Those who are seeking something different in the way of presenting first-year chemistry will be interested in this book. It is an outgrowth of a course given at Yale for those students who desire to broaden their educational horizon by the acquisition not only of some of the pertinent facts of science but an understanding of some of the modern theories of chemistry and physics. It is not intended for those students who plan to take further training in the subject. The author has well stated in his Introduction that "A well-balanced life results from the cultivation of all of its moods. The risks of living too exclusively in any one of them are too great for any but the genius to take. In education none of these moods should be neglected. The student who studies literature and the humanities exclusively, is as ill-cultured as he who cares for science alone." And, further (from the Foreword by John Johnston), "This course endeavors, not to give the student a contemporary command of assorted facts relating to restricted classes of substances, but to correlate, and to explain in simpler terms, some of the chemical and physical phenomena which he encounters every day."

To those orthodox teachers who have always regarded chemistry essentially as a laboratory science, the idea of giving a year's course in introductory chemistry without laboratory work, without the practice of writing equations ("a cruel waste of time"), and without the working of problems, will come somewhat as a jolt. The author is certainly to be commended for his boldness in breaking away from all tradition. In choice of material, its arrangement and method of presentation, the author has thrown aside all that is conventional and, it must be admitted, has produced a book that is both informative and interesting.

The reviewer believes that if the lower seventy-five per cent. of the class of students who will desire to take a "pandemic" course in chemistry could be eliminated this would be a most excellent text. It is difficult for