benzylmagnesium chloride and mercuric chloride leads to a mixture of mercury dibenzyl and benzylmercuric chloride. Since sodium stannite will convert benzylmercuric chloride to mercury dibenzyl, it is suggested that the product of the Grignard reaction be treated with sodium stannite. This procedure would not only eliminate the difficulty of separating the two mercury compounds, but would increase the yield of the desired mercury dibenzyl.

COMMUNICATIONS TO THE EDITOR

THE RELATION BETWEEN THE ACTIVITY OF THE WATER AND THE POTENTIALS OF THE GLASS ELECTRODE

Sir:

In the differential thermodynamic equation recently used to explain the potentials of the glass electrode [M. Dole, THIS JOURNAL, **53**, 4260 (1931)] the correction for possible transference of solvent [see P. B. Taylor, *J. Phys. Chem.*, **31**, 1480 (1927)] was purposely omitted for two reasons. In the first place it was not certain that water could be carried through the glass by ions on the passage of an electrical current, and in the second place the activity of the water was maintained in the actual experiments nearly the same and constant on both sides of the glass membrane; hence if there had been any transfer of water, there would have been no increase or decrease in the free energy of the water as it passed through the glass from one solution to the other and consequently no contribution to the total e. m. f. due to this effect. MacInnes and Belcher [THIS JOURNAL, **53**, 3315 (1931)] have shown that water may be drawn out of the glass, and there have also been recently published [G. Buchböck, *Z. physik. Chem.*, Abt. A, **156**, 232–236 (1931); D. A. MacInnes and D. Belcher, THIS JOURNAL, **53**, 3315 (1931)] data of experiments performed under conditions in which the activity of the water was not maintained constant, but was reduced by the addition of concentrated acids. The observed potentials did not agree with those of the hydrogen–platinum electrode, the resulting error being negative in sign in contrast to the errors of the glass electrode in alkaline solutions which are positive in sign [Dole, *loc. cit.*]. Considering a possible transfer of water, the equation for the glass electrode in acid solutions (where only hydrogen ions are assumed to carry the current across the boundary) becomes

$$E_1 = \frac{RT}{F} \ln \frac{a'_H}{a''_H} + S \frac{RT}{F} \ln \frac{a'_{H_2O}}{a''_{H_2O}} \qquad (1)$$

In this equation a_H is the hydrogen ion activity, S is the number of moles of water carried across the boundary by one mole of hydrogen ions and a_{H_2O} is the activity of the water. If the glass electrode acted as a perfect hydrogen electrode, the equation would be

$$E_2 = \frac{RT}{F} \ln \frac{a'_H}{a''_H} \tag{2}$$

Subtracting E_2 from E_1, an equation for the error of the glass electrode in acid solutions is obtained, namely

$$\Delta E = E_1 - E_2 = S \frac{RT}{F} \ln \frac{a'_{H_2O}}{a''_{H_2O}} \tag{3}$$

If the activity of the water is decreased in solution ($'$), the error will be negative, as is actually observed (Ref. 4). In order to test equation (3) further experiments have been carried out in alcoholic solutions and in acid solutions of various salts; they will be fully described in a paper to be submitted shortly for publication. At this time it should be emphasized that this apparent connection between the activity of the water and the proper functioning of the glass electrode must be considered by those who are using or hope to use the glass electrode for determining the P_H in non-aqueous solutions.

CHEMICAL LABORATORY   MALCOLM DOLE
NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS

THE CATALYTIC INFLUENCE OF DRIED CELLULOSE ON THE HYDROLYSIS OF SUCROSE

Sir:

The writers have found that the rate of hydrolysis of sucrose in aqueous solution is subject to a many-fold increase in the presence of dried cellulose fiber at elevated temperatures.

The cellulose fiber which was used as a catalyst in these studies was prepared from the purest quantitative filter paper (Whatman number 43). The paper was disintegrated to a pulp by boiling with distilled water. This treatment was repeated five times with fresh supplies of water. The pulp was pressed into a cake on a Büchner funnel and dried in air at atmospheric pressure at 130–135° for eighteen hours. The fiber was pulled apart with tweezers into a fluffy mass. It was reheated at the same temperature for several hours, and placed in a desiccator over a fresh charge of Dehydrite. Ash determinations on this fiber showed no more than 0.10% of non-volatile matter.

The hydrolysis of the sucrose was brought about by heating a 10% solution of the sugar at 80–85° in a thermostat for several hours. The increase in the rate of hydrolysis of the sucrose was studied originally by the quantitative determination of the ratio between the amount of reducing sugar formed in the control solution (containing no cellulose) and the amount formed in the solution containing cellulose. In later experiments the effect was studied by comparison of the specific rotation of the unhydrolyzed (unheated) sugar solution with that of the control solution, and that of the solution containing cellulose, respectively.

In a typical determination of the relative amounts of reducing sugar formed in the catalyzed and uncatalyzed hydrolysis of sucrose, the controls showed less than 0.01% of reducing sugar, whereas the cellulose catalyzed solutions showed $0.1 \pm 0.02\%$ of reducing sugar. This corresponds to a ten-fold difference. A one hundred and thirty-fold difference was observed in an hydrolysis carried out at 96–98°.

The writers are at present investigating the catalytic properties of dried cellulose fiber for the purpose of determining: (1) the conditions best suited to the activation of cellulose fiber; (2) the relationship (if any) between the structure of disaccharides and the effectiveness of dried cellulose fiber in promoting their hydrolysis; (3) the nature of the effect herein described.

A full account of this investigation will be submitted shortly to THIS JOURNAL.

DEPARTMENT OF CHEMISTRY UNIVERSITY OF NEBRASKA LINCOLN, NEBRASKA

MARY L. MORSE
W. E. CRAIG

THEBAINONE

Sir:

The investigations of Clemens Schöpf have shown that the ketone originally called thebainone, resulting from reduction of thebaine with stannous chloride in concentrated hydrochloric acid, contains a new structural skeleton, differing from that present in the starting material. The ketone has been renamed metathebainone. In a recent publication [Schöpf and Hirsch, *Ann.*, **489**, 224 (1931)] the isolation of the true thebainone from the mother liquors of metathebainone preparation is described. In a footnote the statement is made that the true thebainone is undoubtedly different from the "sulfur-free ketone" obtained by Pschorr in 1910 by hydrolysis of β-ethylthiocodide.

In the course of studies which we have been conducting in the thiocodide series we have prepared a quantity of the "sulfur-free ketone" and find it to

be identical in every respect with Schöpf's true thebainone. A sample of the latter, generously supplied by Professor Schöpf, showed no depression in melting point with the "sulfur-free ketone." Schöpf's base shows $[\alpha]_D^{26}$ −45.7°, while Pschorr's shows $[\alpha]_D^{28}$ −46.4°, −46.9° in 95% alcohol. Schöpf bases his statement that the two ketones are different upon discrepancies in the melting points of the methiodide and hydriodide, and the fact that Pschorr's hydriodide is hydrated. The methiodide which we obtain from Schöpf's thebainone sample melts at 250–251°. that from the "sulfur-free ketone" at 251°. When the hydriodide of Schöpf's thebainone is crystallized from a large amount of water, it separates hydrated, and shows two melting points, 163–165° and 257–260°, like the "sulfur-free ketone" hydriodide, whose melting point it does not depress.

The structure of Pschorr's "sulfur-free ketone" is thus settled, and another case of supposed isomerism in the thebainone series eliminated. The true thebainone is obtained in nearly quantitative yield by the hydrolysis of β-ethylthiocodide, which constitutes a very convenient preparative method.

COBB CHEMICAL LABORATORY   LYNDON F. SMALL
UNIVERSITY OF VIRGINIA   DAVID E. MORRIS
UNIVERSITY, VIRGINIA
RECEIVED MARCH 17, 1932
PUBLISHED MAY 7, 1932

THE HEAT OF DISSOCIATION OF THE SODIUM MOLECULE

Sir:

The original determination of the heat of dissociation of Na_2 from the band spectrum indicated a value of about 1 volt (= 23,000 cal.). If this were the case saturated sodium vapor should show an abnormal density at all pressures. Rodebush and Walters [THIS JOURNAL, **52,** 2654 (1930)] found this to be true but the abnormality is small and the value of the heat of dissociation calculated from their best results is 0.79 volt (= 18,200 cal.).

Lewis [*Z. Physik*, **69,** 786 (1931)] calculated the heat of dissociation from a vapor density determination by a molecular ray method and obtained the value 0.73 volt (= 16,900 cal.). Recently Nusbaum and Loomis [*Phys. Rev.*, **39,** 179 (1932)] have carried out an accurate analysis of the vibrational bands and find the heat of dissociation to be 0.76 volt (= 17,500 cal.) with an uncertainty of 0.02 volt. It seems quite certain that 0.76 volt is the lower limit and that the true value is in the interval of 0.76–0.78 volt.

CHEMISTRY DEPARTMENT   W. H. RODEBUSH
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URBANA, ILLINOIS
RECEIVED MARCH 28, 1932
PUBLISHED MAY 7, 1932
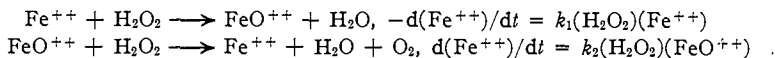
FERRYL ION, A COMPOUND OF TETRAVALENT IRON

Sir:

Several independent kinetic investigations in this Laboratory have furnished evidence that a compound of tetravalent iron, FeO^{++}, is formed as an intermediate. The results are in agreement with the theory that

$$2Fe^{+++} + H_2O = Fe^{++} + FeO^{++} + 2H^+$$
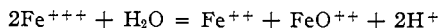
is a reversible and fairly rapid reaction. The equilibrium constant has the form $K = (Fe^{++})(FeO^{++})(H^+)^2/(Fe^{+++})^2$.

If H_2O_2 reacts with both Fe^{++} and "ferryl ion" but not directly with Fe^{+++}

$$Fe^{++} + H_2O_2 \longrightarrow FeO^{++} + H_2O, \quad -d(Fe^{++})/dt = k_1(H_2O_2)(Fe^{++})$$
$$FeO^{++} + H_2O_2 \longrightarrow Fe^{++} + H_2O + O_2, \quad d(Fe^{++})/dt = k_2(H_2O_2)(FeO^{++})$$

then a steady state will be reached in which $(FeO^{++})/(Fe^{++}) = k_1/k_2 = $ a constant, and the above equilibrium is maintained. The rate of catalytic decomposition of H_2O_2, $-d(H_2O_2)/dt$, is then equal to

$$2k_1(Fe^{++})(H_2O_2) = 2(\sqrt{Kk_1k_2})(H_2O_2)(Fe^{+++})/(H^+) = k(H_2O_2)(Fe^{+++})/(H^+)$$

This rate law was determined by von Bertalan in 1920 and has been confirmed in this Laboratory [Bray, *Chem. Rev.*, **10**, 171 (1932), $k = 0.125$ (not 125) at 40°]. The proposed mechanism explains also the decomposition of H_2O_2 during the very rapid oxidation of Fe^{++} to Fe^{+++}.

If in the reduction of Fe^{+++} by a stannous salt Sn^{++} reacts with FeO^{++} but not with Fe^{+++}, and the equilibrium between 2, 3 and 4-valent iron is established relatively rapidly, the rate law will be $-d(Sn^{++})/dt = k'(Sn^{++})(Fe^{+++})^2/(Fe^{++})(H^+)^2$. This has now been established as a limiting law in solutions in which the only negative ion is ClO_4^-. Also, by raising the temperature and lowering the concentration of Fe^{++}, another limiting condition has been found where the rate is independent of the concentration of Sn^{++}, and the indicated rate-determining reaction is $2Fe(OH)^{++} \longrightarrow Fe^{++} + FeO^{++} + H_2O$.

Other investigators have already observed and studied the retarding effect of ferrous salts during the reduction of ferric salts by hydroxylamine and by iodide. The results of Mitchell [*J. Chem. Soc.*, 336 (1926)] with hydroxylamine and Fe^{+++}, published in 1926, are in accord with the ferryl ion mechanism. In the case of the reactions of iodide with ferric salt and with ferricyanide, Wagner [*Z. physik. Chem.*, **113**, 271 (1924)] in 1924 postulated the formation of I_2^- as an intermediate. There seems, however, to be no supporting evidence for the existence of this compound.

In order to obtain more information about the reaction between Fe^{++} and I^-, Bray and Hershey are studying the reverse reaction between Fe^{++} and I_2. The first experiments, in the presence of AgI, AgBr and Br^-, *i. e.*, at very low concentrations of I^-, are in agreement with the rate law, $-d(I_2)/dt = k''(Fe^{++})(I_2)/(I^-)(H^+)$. This result and the analogy with

other reactions of iodine in aqueous solution have led to the conclusion that the rate-determining reaction is $Fe^{++} + HIO \longrightarrow FeO^{++} + H^+ + I^-$.

Additional experiments have been planned which, it is hoped, will furnish further information about the properties of ferryl ion.

DEPARTMENT OF CHEMISTRY   WILLIAM C. BRAY
UNIVERSITY OF CALIFORNIA   M. H. GORIN
BERKELEY, CALIFORNIA
RECEIVED MARCH 28, 1932
PUBLISHED MAY 7, 1932

THE EXISTENCE OF NEUTRONS IN THE ATOMIC NUCLEUS

Sir:

In my article on the Arrangement of Protons and Electrons in the Atomic Nucleus [THIS JOURNAL, **53**, 981 (1931)] the discussion was limited to nuclei in which the numbers of protons and electrons are multiples of four and two, respectively. These atoms are by far the most abundant and in terms of the proposed coupling pattern represent the highest symmetry attainable. Although it is not yet possible to make a definite extension to the other nuclear series, it is of interest to discuss the problem briefly in reference to recent investigations.

It appears significant that the next most abundant nuclear type is that which resembles the symmetrical or $4n$ proton type most closely and may be derived from it by the removal of a single proton. This series, *i. e.*, with $4n-1$ protons, follows very closely the $4n$ series: the first and second "extra electron pair" enter at the corresponding atomic numbers. All other nuclei, *i. e.*, those with $4n-2$ and $4n-3$ protons and those with uneven numbers of electrons constitute but a fraction of one per cent. of the atoms of the earth's crust and appear in general to owe their instability to the presence of incomplete or unsaturated groups. More information about nuclear spins and a knowledge of the coupling rules in these cases are necessary before definite conclusions can be drawn regarding these structures. At present we can only discuss certain possibilities.

As an illustration we may consider carbon 13. In the accompanying figure, this nucleus is pictured in the same symbols formerly employed, a proton, or the direction of the proton spin vector, by a bar and an electron pair by a ball. The structure is the same as that of carbon 12 plus one proton and one electron (half ball). Of course we do not know where the extra proton is coupled but we do know that such a bond of two protons and one electron as suggested in the figure (two bars and the half ball) is stable from the existence of the hydrogen isotope [Urey, Brickwedde and Murphy, *Phys. Rev.*, **39**, 154 (1932)] of mass 2. Beryllium 9 must also contain such a group and when it captures a high speed alpha particle to form carbon 13 it is not difficult to imagine that occasionally the loosely bound

proton and electron are detached and emitted as a neutron leaving carbon 12, as postulated by Chadwick [*Nature*, **129,** 312 (1932)].

The essential point may be stated in this way. In the proposed structure alpha particles and neutrons do not exist as such in any nucleus, merely protons and electrons coupled in a certain definite pattern. When these couplings are broken, alpha particles and electrons in pairs are normally formed as in the radioactive series. However, it should also be possible to break the bonds in such a way as to give neutrons, mass one or two, hydrogen, mass one or two, helium mass 5, etc., and it is to be expected that such particles would be formed more readily from nuclei containing unsymmetrical or unsaturated groups.

DEPARTMENT OF CHEMISTRY   WENDELL M. LATIMER
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA

ROTENONE. XXI. THE STRUCTURE OF ISOROTENONE, β-DIHYDROROTENONE AND DEHYDROROTENOL

Sir:

In a recent publication [S. Takei, S. Miyajima and M. Ōno, *Bul. Inst. Phys. and Chem. Research* (Tokyo), **11,** 1–4, Feb. 1932] Takei and his associates proposed a formula for rotenone which differs from the one (I) proposed by us [F. B. LaForge and H. L. Haller, THIS JOURNAL, **54,** 810 (1932)] only in the point of attachment of the isopropenyl side chain on the substituted dihydrocoumarone ring as indicated in formula II.


I   II
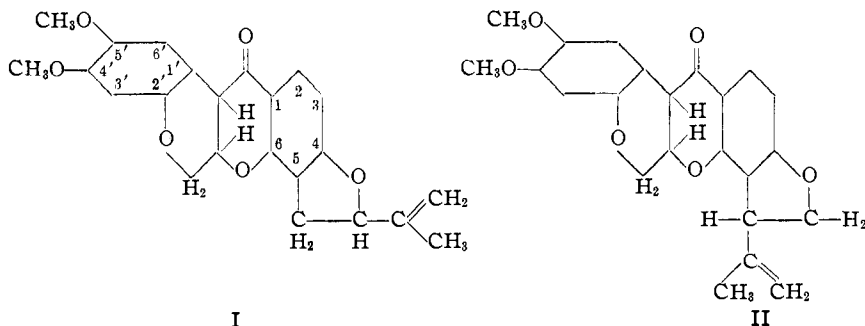
The formula of Takei takes no account of the loss of optical activity by cleavage of the oxygen bridge with the resultant formation of the phenolic hydroxyl in position 4 by hydrogenation of tubaic acid and the analogous formation of tetrahydro derivatives from other rotenone derivatives. Moreover, the mechanism suggested by us is strongly supported by analogy with that of certain codeine derivatives, which is referred to in a previous article [H. L. Haller and F. B. LaForge, THIS JOURNAL, **54,** 1988 (1932)].

Both these results are to be expected from the groupings present in formula I but would not be possible according to Takei's formula II.

As the complete formula for rotenone is now known, it is possible to propose a formula for isorotenone [S. Takei, *Biochem. Z.*, **157**, 1 (1925); *Ber.*, **61**, 1003 (1928)] and for β-dihydrorotenone. [H. L. Haller, THIS JOURNAL, **53**, 733 (1931)]. However, a modification of the structure proposed for dehydrorotenol [H. L. Haller and F. B. LaForge, THIS JOURNAL, **53**, 2271 (1931); F. B. LaForge, H. L. Haller, and L. E. Smith, THIS JOURNAL, **53**, 4403 (1931)] is necessary.

It has been shown that rotenone and isorotenone differ from each other in the position of a double bond. Therefore, structure III, which accounts for all the facts, is proposed for isorotenone.
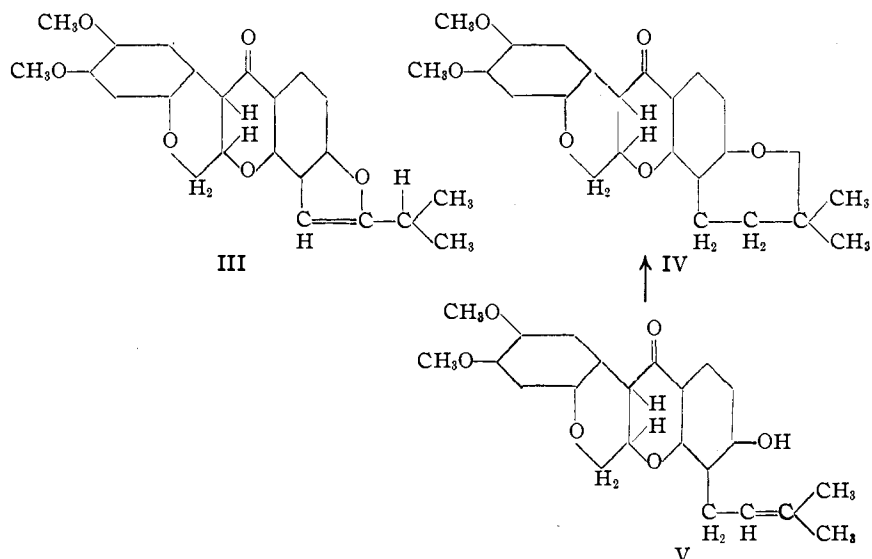

β-Dihydrorotenone (IV), an isomer of dihydrorotenone, which gives many of the typical reactions of dihydrorotenone, is obtained when rotenonic acid (V) is dissolved in a solution of acetic and sulfuric acids. The formation of β-dihydrorotenone is in a measure analogous to the formation of a saturated lactone by the isomerization of an unsaturated acid.

Dehydrorotenol, which is obtained on mild oxidation of rotenol, is colorless, unlike all other dehydro derivatives of the rotenone series, which are yellow. It also differs from these in that it can be reconverted into rotenol by reduction.

Dehydrorotenol, like rotenol, can be hydrogenated to a tetrahydro derivative which is alkali soluble but which differs from the tetrahydrorotenol (dihydrorotenolic acid) in that it is not cleaved by alkaline hydrogen peroxide. Rotenol possesses a free hydroxyl group in the tubaic acid half of the

molecule, and this free hydroxyl group is essential for the cleavage of the carbonyl group with alkaline hydrogen peroxide. It follows therefore that this group is not present in dehydrorotenol. Rotenol gives a color test with ferric chloride, whereas dehydrorotenol does not. Thus it follows that the hydrogen atom of the free hydroxyl group is involved in the formation of dehydrorotenol. If the original ether linkage in rotenone was reformed in the formation of dehydrorotenol from rotenol, dehydrodihydrorotenolic acid and *dl*-dihydrorotenonic acid [H. L. Haller and F. B. LaForge, THIS JOURNAL, **53**, 3426 (1931)] should be identical as the asymmetric center I [*ibid.*, p. 3427] is racemized in the formation of rotenol. Besides, dehydrorotenol does not react with iodine and alcoholic potassium acetate to lose two hydrogen atoms and to form dehydrodihydrorotenone. It is possible, therefore, that the structure for dehydrorotenol is either VI or VII.

The product obtained from dehydrodihydrorotenolic acid and acetic anhydride, which was thought to be a mixed anhydride [H. L. Haller and F. B. LaForge, THIS JOURNAL, **53**, 2271 (1931)], is in fact a true acetyl derivative, the hydroxyl group in the 4 position having been acetylated.

VI   VII
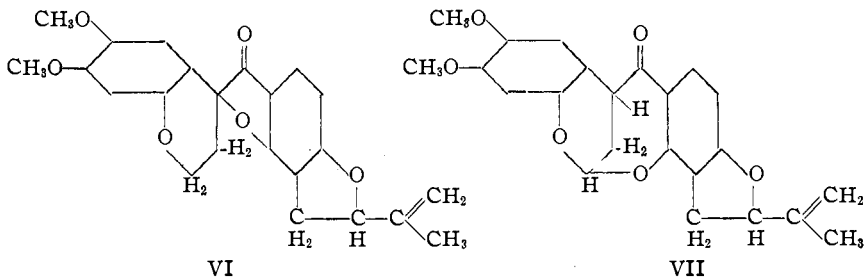
INSECTICIDE DIVISION   H. L. HALLER
BUREAU OF CHEMISTRY AND SOILS
WASHINGTON, D. C.
RECEIVED APRIL 4, 1932
PUBLISHED MAY 7, 1932

THE RELATION BETWEEN THE DISSOLUTION OF METALS IN ACIDS AND THE ELECTROLYTIC EVOLUTION OF HYDROGEN

Sir:

The finding of Brönsted and Kane [THIS JOURNAL, **53**, 3624 (1931)] that the velocity of the reaction of sodium amalgam with aqueous solutions is proportional to a fractional power of the concentration of sodium in the amalgam suggests strongly that the rate of hydrogen evolution on a sodium amalgam surface is essentially the same as on a mercury surface polarized electrically to a potential equal to that established by the sodium–sodium ion equilibrium. From the precise and definitive work of Bowden [*Trans.*

Faraday Soc., **24,** 473 (1928)] we know that the coefficient n in the Tafel polarization equation

$$E = \frac{RT}{nF} \ln I + \text{constant}$$

is 0.5 on mercury surfaces at current densities below about 10^{-4} amp. per sq. cm., and changes discontinuously at higher current densities to 0.27. Since

$$E = \frac{RT}{F} \ln \frac{a_{Na^+}}{a_{Na}} + E_0$$

and since current is proportional to reaction velocity, the above hypothesis indicates such a fractional order of reaction as was found.

$$v \propto \frac{[Na]^n}{[Na^+]^n}$$

This assumes, of course, that these amalgams are so dilute that there is approximate proportionality between activity and concentration of the sodium.

It also follows that the reaction velocity should vary inversely as the same fractional power of the sodium-ion activity. While Brönsted and Kane seem not to have expected any such effect, and report no quantitative results on the effect of sodium ion, they do report that addition of sodium chloride decreases the reaction velocity.

It should therefore be possible to apply to the amalgam reaction all of the electrochemical evidence that the reaction $H^+ + e \rightleftharpoons H$ is reversible and very rapid compared with the process of formation of H_2 from the atomic hydrogen or its alloy with the metal. In particular it is extremely difficult to understand the saturation effects observed in the electrochemical oxidation of hydrogen to hydrogen ion [see Hammett, THIS JOURNAL, **46,** 7 (1924)] on the basis of any other mechanism.

The contrary conclusion of Brönsted and Kane that the first step in the formation of molecular hydrogen from hydrogen ion is the rate-determining one depends upon their observation of a direct effect of the concentration of the reacting acid upon the velocity. This would be strong evidence if it could be proved that diffusion was not a factor in the determination of the reaction velocity in their experiments and in those of Kilpatrick and Rushton [*J. Phys. Chem.*, **34,** 2180 (1930)]. Certainly Bowden showed that the electrolytic evolution of hydrogen on mercury is determined by hydrogen-ion concentration and is subject to no generalized acid effects when the reaction velocity is so low that diffusion is not a significant factor.

DEPARTMENT OF CHEMISTRY   LOUIS P. HAMMETT
COLUMBIA UNIVERSITY   ARTHUR E. LORCH
NEW YORK, N. Y.

THE ELECTROMOTIVE FORCE OF CELLS CONTAINING DILUTE HYDROCHLORIC ACID

Sir:

In a recent paper Carmody [THIS JOURNAL, **54**, 188 (1932)] has published the results of some very accurate measurements of the e. m. f. of cells containing dilute solutions of hydrochloric acid. Mainly owing to the use of silica vessels these results differ from those of Linhart [THIS JOURNAL, **41**, 1175 (1919)] and of Nonhebel [*Phil. Mag.* [7] **2**, 1085 (1926)] but it can be shown that the results of these earlier workers are not incompatible with those of Carmody.

It has been suggested elsewhere [*J. Phys. Chem.*, **31**, 1647 (1927)] that the conductivity data for strong acids and bases in dilute solution can be corrected for the effect of impurities by the equation

$$\Lambda = \Lambda_0 - bc^{1/2} - k/c$$

where b is a constant calculable from Onsager's theory or determinable experimentally and k is a measure of the amount of acid removed by the
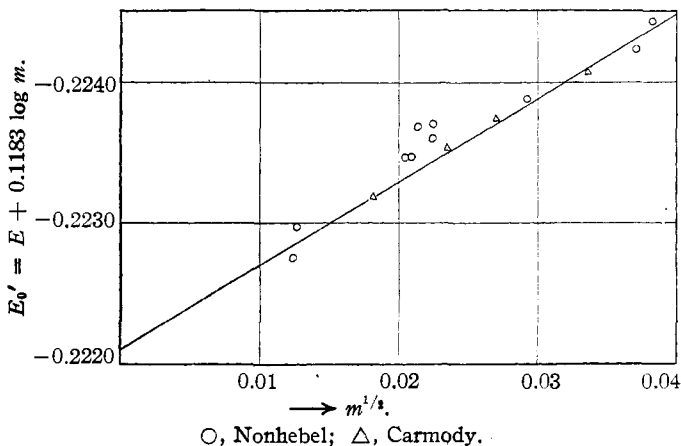

O, Nonhebel; △, Carmody.

Fig. 1.

impurities which either have dissolved from the glass or were originally present in the water. By the courtesy of Sir Harold Hartley, F.R.S., I have been able to avail myself of some measurements by Marshall on the conductivity of dilute solutions of hydrochloric acid in cells of similar glass and water of comparable conductivity to those employed by Nonhebel. Using the above equation, I have calculated from these data that Nonhebel's results are about 0.0010 volt high at 0.0001 molal and 0.0001 volt high at 0.001 molal. Even Carmody's results require a slight correction which can be calculated from the recent conductivity data of Jeffery and Vogel [*J. Chem. Soc.*, 400 (1932)], who employed silica cells and water of

about the same conductivity as that used by Carmody: the correction lowers Carmody's most dilute point by 0.00012 volt.

The corrected data are plotted in the accompanying diagram and the straight line is drawn with the slope required by the limiting equation of Debye and Hückel. It is evident that the agreement is satisfactory and that the most probable value of E_0 is 0.2221 volt, which is the value previously adopted by Randall and Young [THIS JOURNAL, **50**, 989 (1928)].

THE UNIVERSITY   W. F. KENRICK WYNNE-JONES
READING, ENGLAND
RECEIVED APRIL 13, 1932
PUBLISHED MAY 7, 1932

THE ESTIMATION OF IRON IN SOLUTIONS CONTAINING BOTH BIVALENT IRON AND TRIVALENT TITANIUM

Sir:

It is known that sulfuric acid solutions of ferrous sulfate undergo oxidation but very slowly at room temperatures.[1] Thus, Baskerville and Stevenson[2] found that upon passing air for twelve hours through a sulfuric acid solution of Mohr's salt, there resulted but 0.0001 g. of Fe^{+++} out of a total of approximately 0.71 g. of Fe^{++}.

Furthermore, titanous sulfate solutions of ordinary acidity are extremely unstable in air. Thus, while reduction of titanium in the Jones reductor proceeds quantitatively to the trivalent condition, the deoxidized substance is usually collected under a protective solution, such as ferric sulfate, whereby the titanium is immediately converted to the quadrivalent state with the formation of an equivalent amount of the more stable ferrous sulfate.[3]

These facts, namely, the stability of acidified ferrous sulfate solutions and the instability of acidified titanous sulfate solutions toward atmospheric oxidation, suggested the possibility of estimating Fe^{++} in the presence of Ti^{+++} by subjecting the solution containing these ions to an air-bubbling process. It was hoped that in the time required to effect the complete oxidation of the Ti^{+++} the amount of Fe^{++} oxidized would be negligible, so that titration of the aerated solution with standard potassium permanganate would give a value corresponding to the iron alone.

This hope has indeed been realized and we have found that results obtained by the method outlined above are in good agreement with those obtained by the well-known method of Gooch and Newton,[4] wherein the Ti^{+++} is oxidized by bismuth trioxide, which does not affect the Fe^{++}, the metallic bismuth thus precipitated and excess bismuth oxide removed by

[1] McBain, *J. Phys. Chem.*, **5**, 623 (1901).

[2] Baskerville and Stevenson, THIS JOURNAL, **33**, 1104 (1911).

[3] Lundell and Knowles, *ibid.*, **45**, 2620 (1923); *Ind. Eng. Chem.*, **16**, 723 (1924).

[4] Gooch and Newton, *Am. J. Sci.*, **23**, 365 (1907); Newton, *ibid.*, **25**, 343 (1908).

filtration, and the filtrate, containing the Fe^{++}, titrated with standard permanganate in the usual manner.

Lundell and Knowles[5] have shown that sulfuric acid solutions of uranous sulfate, like ferrous sulfate, exhibit marked stability toward air oxidation, and we hope to employ our differential oxidation procedure in the evaluation of uranium in solutions containing U^{++++} and Ti^{+++}.[6] Other determinations, involving similar combinations, suggest themselves as possibilities in the further application of this method.

In the course of this work, a technique has been developed for the preparation of very pure solutions of titanic sulfate and titanous sulfate.

We expect to publish a complete account of this work in the near future.

[5] Lundell and Knowles, THIS JOURNAL, **47**, 2637 (1925).

[6] *Cf.* Newton and Hughes, *ibid.*, **37**, 1711 (1915).

[7] J. T. Baker Chemical Company Fellow in Analytical Chemistry, 1930–1931.

DEPARTMENT OF CHEMISTRY
THE JOHNS HOPKINS UNIVERSITY
BALTIMORE, MARYLAND
RECEIVED APRIL 20, 1932
PUBLISHED MAY 7, 1932

WILLIAM M. THORNTON, JR.
REUBEN ROSEMAN[7]
SAMUEL I. KATZOFF

PENTAVALENT BORON

Sir:

A compound of boron has been prepared which has the formula BR_3Na_2 in which R is the α-naphthyl group. This compound seems to be of a type not heretofore known and to be of particular interest from the standpoint of valence theory.
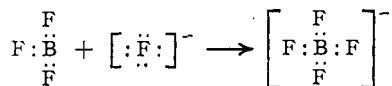
The compound has been prepared by treating tri-α-naphthyl boron in ether solution with 40% sodium amalgam in the absence of air and water.[1] The solution turns first yellow and finally black as the reaction progresses. Upon hydrolyzing the ether solution and titrating with acid the number of mols of sodium was found to be twice (1.97–1.98) the number of mols of the tri-α-naphthylboron originally introduced into the solution. The compound was then prepared in crystalline form from a mixture of ethyl ether and petroleum ether. It is nearly black in color, somewhat resembling iodine in appearance. This material was analyzed for sodium and boron. A second crop of crystals was obtained from the mother liquor. This had the same appearance and gave the same analysis. The analyses indicated one molecule of ether of crystallization, which was removed quantitatively by evacuating and heating to 175°. The first analysis given below is for the first crop of crystals, the second for the crop

[1] A solution of this compound was undoubtedly first obtained by Krause and Nobbe [*Ber.*, **63**, 934 (1930)] but inasmuch as they did not analyze their product they naturally assumed that it was a monosodium addition compound as in the case of triphenylboron.

from the mother liquor before heating and the third for this same material after heating to remove ether.

Anal. Calcd. for $C_{30}H_{21}BNa_2$: Na, 10.50; B, 2.47. Found: Na, 10.59; B, 2.49. Calcd. for $C_{34}H_{31}OBNa_2$: Na, 8.98; B, 2.11. Found: Na, 8.92; B, 2.15. Calcd. for $C_{30}H_{21}BNa_2$: Na, 10.50; B, 2.47. Found: Na, 10.53; B, 2.40.

Compounds of boron showing a valence of more than three are of course known, such as KBF_4. In such cases an octet is completed by four co-valent bonds thus

$$F:\overset{\overset{F}{\cdot\cdot}}{\underset{\underset{F}{\cdot\cdot}}{B}} + \left[:\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}:\right]^- \longrightarrow \left[F:\overset{\overset{F}{\cdot\cdot}}{\underset{\underset{F}{\cdot\cdot}}{B}}:F\right]^-$$

No compound has been reported, however, in which the boron completes its octet by taking two electrons from different atoms to give ionic linkages. Thus no compound is known of the formula Na_2BF_3. It now appears that in case the three fluorine atoms are replaced by three naphthyl groups, then the boron atom can complete its octet by taking two electrons from two sodium atoms. How these sodium atoms are held is a question to be decided by further experiment. This work is being continued.

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THE ACTIVATOR OF CATALASE[1]

Sir:

The activation of glandular proteinase (cathepsin) by glutathione[2] and other —SH compounds points to a connection between enzymic hydrolysis and the sulfur oxidation–reduction system of Hopkins. A connection of the sulfur system to enzymic oxidation is also indicated, however, by our findings that the catalase activity (of pig's or lamb's liver) is increased by S–S derivatives, namely, cystine, insulin and oxidized glutathione. In liver juice, which contains sulfhydryl derivatives, the catalase may therefore be activated by all manner of oxidizing agents, such as iodine, ferric iron, oxygen and hydrogen peroxide, so that in the usual preparations of catalase the enzyme will be found completely active.

The natural activator which occurs in the liver press juice is not cystine, since in larger amounts this again inhibits the catalase action, but in view of the quantity of glutathione present in liver, it may be that the natural activator is, in part at least, composed of oxidized glutathione.

Since the presence of –SH derivatives accelerates proteolysis, and that of S–S derivatives, the decomposition of hydrogen peroxide, it would there-

[1] Food Research Division Contribution No. 145.
[2] *Naturwissenschaften*, **18**, 645 (1930).

fore seem that the state of the S–S – SH equilibrium determines whether the cell at the moment functions proteolytically or oxidatively.

NEW BOOKS

Matière et Atomes. (Matter and Atoms.) By A. BERTHOUD, Professor of Physical Chemistry at the University of Neuchâtel. Second edition. G. Doin et Cie, 8 Place de l'Odéon, Paris, France, 1932. 324 pp. 28 figs. 11.5 × 18 cm. Price, 26 fr.

This is a revised and enlarged second edition of "New Conceptions of Matter and the Atom." The earlier book has been conscientiously revised and brought up to date. The present chapters include: Historical Introduction, Classical Theories of Light and of Electrons, Theory of Relativity and Mass, x-Rays and Atomic Numbers, Radioactivity and Isotopes, Rutherford Atom and Transmutation, Bohr Atom and Quantum Theory, Complex Atoms, x-Rays and Chemical Affinity, Wave Mechanics.

The style is clear and readable throughout and the selection of material judicious. The book is addressed to "a wide circle of cultivated readers," and the plan is to present selected facts, intelligently grouped, and then to state the conclusions drawn from them. The names of Prout and Proust are frequently confused.

NORRIS F. HALL

Gmelins Handbuch der anorganischen Chemie. (Gmelin's Handbook of Inorganic Chemistry.) Edited by R. J. MEYER. Eighth edition. System-Number 7. **Bromine.** Issued by the Deutsche Chemische Gesellschaft. Verlag Chemie G. m. b. H., Corneliusstrasse 3, Berlin W 10, Germany, 1932. xxi + 342 pp. 17 × 25 cm. Price, to subscribers, M. 56; singly, M. 49.

This volume presents the chemistry of bromine itself and of its compounds with those elements of smaller System-Numbers (1–6): namely, chlorine, fluorine, nitrogen, oxygen, hydrogen and the inert gases. The relevant literature has been covered up to August 1, 1931.

The great extension of our knowledge of this element, since the previous edition, particularly as regards its physico-chemical properties and those of its compounds, is most impressive. Attention should also be called to the section on the history of our knowledge of this element and on its economics.

The present volume is a worthy addition to this invaluable encyclopedia of inorganic chemistry.

ARTHUR B. LAMB