

hooks a, in order to hold the two parts tightly and the tube B is connected with the carbon dioxide generator. The rest of the procedure is as described by Pregl.

2. In this one-piece Pregl's apparatus (Fig. 2) the carbon dioxide is led into the decomposition flask A through the tube D drawn into a capillary and entering the side arm B of the flask. This tube fits tightly at the outer end of the side arm by means of a ground-glass joint C. After the apparatus has been charged through the side arm B, the inside of the latter and the ground joint C are moistened with hydriodic acid and the tube D inserted. Then the rubber tube leading to the carbon dioxide generator is slipped over the end of the glass tube D and over the ground-glass joint. There is no retention of alkyl iodide in the side arm on account of the presence of hydriodic acid.

Numerous methoxyl determinations with either modification 1 or 2 have demonstrated that boiling is smooth, bumping does not occur, accurate results are obtained and almost no attention to the operation is necessary after the initial adjustment of the carbon dioxide stream and the microburner.

CONTRIBUTION FROM THE
LABORATORIES OF THE
ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH
NEW YORK, N. Y.
RECEIVED JULY 16, 1931
PUBLISHED OCTOBER 5, 1931

D. RIGAS RIGAKOS

COMMUNICATIONS TO THE EDITOR

THE STRUCTURE OF THE FERROCYANIDES

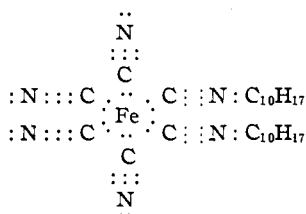
Sir:

A recent contribution by Stephen and Hammerich [*J. prakt. Chem.*, **129**, 285-308 (1931)] on the action of ferrocyanic acid on bicyclic terpenes leads to some interesting conclusions with regard to the structure of the addition compounds.

These investigators have studied the addition of ferrocyanic acid to such compounds as camphene, α -pinene and nopinene, getting compounds corresponding to the formula $(C_{10}H_{17})_2H_2Fe(CN)_6$. Most of the product rearranges on treatment with alkalis but there is a 7% yield of an amine and an alcohol called by the authors isobornylamine and isoborneol. The presence of these two products seems to call for the existence of two forms of the addition product—one completely ionized and the other only partially so.

To obtain isoborneol from the hydrolysis of the α -pinene addition product we may assume complete ionization of the compound $(C_{10}H_{17})_2H_2Fe(CN)_6$, the hydroxyl from water attaching itself to the cation $C_{10}H_{17}$. Potassium formate, ammonia and ferrous hydroxide are the other products.

To obtain isobornylamine, however, we are led to the conclusion that there is some sort of connection between the nitrogen and the $C_{10}H_{17}$ group probably as follows



Tetra-covalent nitrogen is not unique; nevertheless, the experimental evidence presented by these investigators leads to conclusions which may be interesting as applied to the structure of the complex ferrocyanides.

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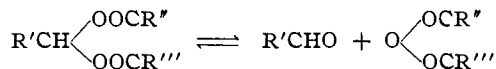
HOWARD W. POST

RECEIVED JULY 24, 1931
PUBLISHED OCTOBER 5, 1931

A NEW SERIES OF HOMOGENEOUS MONOMOLECULAR GAS REACTIONS

Sir:

In the course of a systematic investigation of equilibria and reaction velocities in gaseous and liquid "ester-acid anhydride-aldehyde" systems from points of view outlined elsewhere [Coffin and Maas, *Canadian Journal of Research*, **3**, 526 (1930); **3**, 540 (1930)], a new series of homogeneous monomolecular reactions has been found. Several examples of the gaseous decomposition represented by the general equation



have been found to be monomolecular in accordance with modern ideas regarding the break-up of complicated molecules. In the cases already investigated the reaction is homogeneous and follows the Arrhenius equation. The heats of activation and the absolute temperatures at which the reactions attain a given rate fall in well with the parallelism displayed by known examples of monomolecular change. Experiments are being carried out at present to determine whether or not the rate constant falls off as the pressure is lowered.

As the reaction appears to be particularly well adapted for an investigation of the influence of molecular structure on reaction velocity, the decomposition of as many as possible homologous and isomeric esters is being studied. A description of the experimental method together with the results obtained to date will be published shortly.

It is of interest in connection with the "dreierstoss" theory that in none

of the systems yet investigated does the reverse reaction occur at a measurable velocity. A special search is being made for a measurable equilibrium and a homogeneous bimolecular gas reaction between an aldehyde and an anhydride.

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RECEIVED AUGUST 25, 1931
PUBLISHED OCTOBER 5, 1931

C. C. COFFIN

THE SEPARATION OF THE RARE EARTHS BY FRACTIONAL CRYSTALLIZATION

Sir:

No one working on the fractional crystallization of the rare earths seems to have paid much attention to the differences in the ionic radii. The relative ionic radii in the oxides have been determined by Goldschmidt [Hevesy, "Die Seltenen Erden," Verlag von Julius Springer, Berlin, Germany, p. 111, 1927], and they have been found to differ by several per cent. The usual separations, however, are effected from solution and the ions, both in solution and in the hydrated crystals, are surrounded by water molecules, in most cases, probably, as $\text{La}(\text{H}_2\text{O})_6^{+++}$, $\text{Ce}(\text{H}_2\text{O})_6^{+++}$, etc. The *fractional* differences between these augmented ionic radii are certainly much less than those of the unhydrated ions.

It would be natural to attempt separation from molten salts so as to benefit by the maximum differences in the radii since relative solubilities, etc., are determined here by the radii of the bare ions. However, high temperatures may deprive one of most of the expected advantages, for they tend to smooth over factors associated with small energy differences. (This vague statement might be helped by a more precise example, the elementary law that the smaller the difference in energy between two states of a system in equilibrium the lower must be the temperature to bring about an appreciable concentration of the lower energy state.) Nevertheless, a study of molten salts may prove of value because the unknown thermodynamic magnitudes for the crystals and their molten solutions may not be altogether unfavorable.

On the other hand, one can turn one's attention to those salts crystallizing with so little of the solvent that the positive ion is not screened from the negative ions. The acetates, for example, crystallize ordinarily with only one and one-half molecules of water and hence the acetate ions are directly in contact with the positive ions. Fractional crystallization of the acetates has not appeared very promising in the past, perhaps on account of their high solubilities. Very concentrated solutions do not differ much from crystals, the positive ions are completely "acetated" and their distribution between the liquid solution and the solid solution is almost the

same. A greater difference in the solubilities between the two phases would probably occur if dilute solutions were employed. Crystallization from dilute solution can be brought about by the addition of foreign substances and by the use of low temperatures.

The considerations I have brought forward urge the study of the fractional crystallization of the rare earths, especially their unsolvated ions, at as low a temperature as possible. Perhaps fractionation from alcohol near the freezing point should be attempted first. It may happen at this temperature, if the complete difference in the ionic radii is utilized, that two phases (if the mixture consists of two rare earths) will crystallize out of solution each of which contains one of the rare earths predominantly. Possibly this temperature is not yet low enough. Data alone can give the answer.

CATTOLICA-SAN GIOVANNI
ITALY

SIMON FREED

[Fellow of the John Simon Guggenheim Memorial Foundation]

RECEIVED AUGUST 25, 1931
PUBLISHED OCTOBER 5, 1931

SYNTHETIC CELLULOSE AND TEXTILE FIBERS FROM GLUCOSE

Sir:

A chemical investigation of the structure of the membrane obtained by the action of *Acetobacter xylinum* on glucose has now established the identity of the product as a true cellulose. Hydrolysis with hydrochloric acid and zinc chloride yields glucose quantitatively. Treatment of the triacetate with hydrochloric acid in methyl alcohol solution gives a yield of 94.3% methyl glucoside. The triacetate, after purification, has a rotation of $[\alpha]_D -21.3^\circ$, and is identical in all respects with cotton cellulose triacetate. Methylation of the acetate and hydrolysis of the trimethyl ether yields 2,3,6-trimethylmethylglucoside, the latter on hydrolysis giving the characteristic crystalline 2,3,6-trimethylglucose. A chloroform solution of the triacetate yields a cellulose acetate fiber on dry-spinning identical with cotton cellulose acetate fibers. On hydrolysis of the acetate fibers with alcoholic sodium hydroxide, the regenerated cellulose gives an x-ray diagram which, as found by Dr. George L. Clark, has the typical diffraction pattern of natural cellulose.

Preliminary investigations on similar membranes formed by the action of *Acetobacter xylinum* on fructose, sucrose, mannitol, glycerol and glyceric aldehyde would seem to point to the identity of all of these products with natural cellulose.

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HAROLD HIBBERT
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RECEIVED SEPTEMBER 11, 1931
PUBLISHED OCTOBER 5, 1931

A REVERSIBLE OXIDATION INDICATOR OF HIGH POTENTIAL
ESPECIALLY ADAPTED TO OXIDIMETRIC TITRATIONS

Sir:

We have found that the ferrous-ortho-phenanthroline complex ion discovered by Blau [*Monatsh.*, **19**, 647 (1898)] may be used as a reversible oxidation indicator of high potential and is ideally suited for many oxidimetric titrations. It is of an intense red color, which oxidation to the ferric complex converts to a blue of less intensity. Once formed by reaction of phenanthroline and ferrous sulfate in aqueous solution, the complex is not appreciably decomposed in several hours at room temperature by strong acids, although these do prevent its formation. The ferric complex is resistant to acids and to the action of permanganate, dichromate or ceric ions in acid solution. By electrometric titration with ceric sulfate we have found the indicator system to be of high mobility and perfect reversibility and to have a molar potential of 1.14 volts. It may, therefore, be used for any titration of an active reducing agent with ceric sulfate in the cold. This valuable and extremely stable oxidizing agent has been available for titrations hitherto only by the use of an electrometric end-point or of an indicator of potential not really suited to the titration and susceptible to side reactions and decompositions. We have found that high precision may be attained in the titration of ferrous ion and ceric ion when the amount of indicator used has an oxidation equivalent of 0.01 cc. of 0.1 normal solution. We have furthermore found that a similar precision may be obtained in titrations of ferrous ion and dichromate ion in sulfuric or hydrochloric acid solution, and that the above-named quantity of indicator gives an entirely satisfactory end-point in spite of the color of the chromic and ferric compounds. When titrating dichromate with ferrous salt the color change is instantaneous; in the reverse titration it is necessary to wait for a few seconds after each addition when near the end-point. The standardization of a ferrous sulfate solution against purified potassium dichromate using this indicator agrees excellently with that obtained against sodium oxalate by way of permanganate. The use of this valuable ultimate standard in oxidimetry is thus made simpler than previously possible. The presence of other common metallic ions, including notably mercuric ion, was not found to affect the precision of ferrous-dichromate titrations. The ferrous-dipyridyl complex was found to be a less satisfactory indicator because of its more rapid reaction with acids.

We are continuing the investigation of the application of this and similar compounds to oxidimetric titrations and expect soon to report full details.

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G. H. WALDEN, JR.
LOUIS P. HAMMETT
RAY P. CHAPMAN

RECEIVED SEPTEMBER 12, 1931
PUBLISHED OCTOBER 5, 1931

PRODUCTS OF THE PHOTOCHEMICAL OXIDATION OF ACETYLENE

Sir:

In view of the fact that the mechanism of the photochemical oxidation of acetylene has been discussed recently from a purely theoretical viewpoint [Mecke, *Trans. Faraday Soc.*, **27**, 374 (1931)], it seems worth while to present at this time certain preliminary observations on the products of this reaction.

When a mixture of acetylene and oxygen (saturated with water vapor at room temperature) is exposed (in a flow system) to the complete radiation of a "hot" quartz mercury arc, oxalic acid and a trace of an aldehyde are formed. The presence of oxalic acid was detected by microchemical precipitation of calcium oxalate and of barium oxalate; the crystals of these precipitates had the characteristic appearances of "tiny, highly refractive octahedra" and of "bundles of needles," respectively [Chamot, "Elementary Chemical Microscopy," John Wiley and Sons, Inc., New York, 1921, p. 337]. Additional evidence was obtained by comparing the concentration of acid and of reducing agent (as determined by titration with potassium permanganate) in a solution of the product. The average value for the ratio of the equivalent concentration of acid to that of reducing agents was 1.4. While the departure from the theoretical value of unity may indicate the presence of an acid, such as acetic, which is not readily oxidizable, it is quite possible that it is due entirely to experimental error, since the quantities available for titration were small (usually 1 or 2×10^{-5} equivalents). The aldehyde was detected with Schiff's reagent. Blanks, which were performed by either not exposing the gas mixture to the radiation or by irradiating oxygen-free acetylene, always gave negative results. No attempt was made to analyze for gaseous products.

The mechanism of the oxidation as predicted by Mecke consists essentially of the following steps: (1) electronic excitation of an acetylene molecule by absorption of a photon; (2) direct addition of the excited acetylene molecule to a normal oxygen molecule; (3) rearrangement of the addition product to glyoxal; (4) the decomposition of glyoxal to formaldehyde and carbon monoxide. If the very probable assumption is made that at room temperature glyoxal is more readily oxidized than decomposed, the chief product of the reaction would be oxalic acid, which is in agreement with the experimental results. At higher temperatures, the decomposition would presumably become the more important step, and the products of the photochemical reaction would approach those of the thermal reaction [compare Bodenstein, *Trans. Faraday Soc.* **27**, 386 (1931); also Spence and Kistiakowsky, *THIS JOURNAL*, **52**, 4837 (1930)]. Another possible mechanism of the photochemical reaction would involve the addition of two molecules of oxygen to an excited acetylene molecule with the formation of a double

peroxide. Subsequent rearrangement of the peroxide would yield oxalic acid. This second mechanism was suggested by Professor G. N. Lewis.

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RECEIVED SEPTEMBER 14, 1931
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ROBERT LIVINGSTON

NEW BOOKS

Liebig und die Bittersalz- und Salzsäurefabrik zu Salzhausen (1824-1831). (Liebig and the Magnesium Sulfate and Hydrochloric Acid Factory at Salzhausen.) Edited by Dr. ERNST BERL. Verlag Chemie, G. m. b. H., Corneliustrasse 3, Berlin W 10, Germany, 1931. 65 pp. 17 × 24 cm. Price, M. 3.50.

Justus Liebig was only twenty-one years old when in May, 1824, he was called to a professorship at the University of Giessen. In December of the same year at the request of the Hessian Ministry of Finance he analyzed the waters of the Salzhaus Mineral Springs. On the basis of this analysis Liebig recommended that the mother liquors from these waters after the separation of the sodium chloride be worked up by the government as a source of magnesium sulfate and of hydrochloric acid. This recommendation was adopted and Liebig was commissioned to undertake the development of the process and the erection of the plant. He discharged this task with conspicuous success.

In the present small pamphlet there are reproduced verbatim some twenty reports which Liebig made to the Ministry of Finance during the progress of this work. There is also included a lecture in explanation of them delivered by Dr. Berl at the first annual meeting of the Liebighaus Society in Darmstadt.

It is of interest to point out that it was in the mother liquors from these springs that Liebig found the puzzling substance which he called "sodium hydroiodate" and from which he obtained a substance which he considered to be the chloride of iodine but which he instantly recognized to be bromine when Balard's discovery of that element was announced some months later.

Dr. Berl has already published a notable collection of the letters of Liebig. This present pamphlet makes a valuable supplement to that volume.

ARTHUR B. LAMB

General Chemistry. By H. I. SCHLESINGER, Professor of Chemistry, The University of Chicago. Revised edition. Longmans, Green and Company, 55 Fifth Avenue, New York, 1930. xi + 847 pp. Illustrated. 14.5 × 21 cm. Price, \$4.00.

The second edition of this excellent text has been increased by about two hundred pages: The changes and additions consist "first, in an amplifica-