sugar produces the nitriles of the two stereoisomeric monocarboxylic acids containing an additional carbon atom in the molecule. These nitriles can be hydrolyzed subsequently to the corresponding acids by an excess of hot alkali and the well-known Kiliani synthesis is then complete. We believe that the more convenient modifications used by us since 1926 to carry out these important reactions may be of general interest and therefore we describe as an example the preparation of the α- and β-glucoheptonic lactones from glucose.

Five liters of a filtered aqueous solution containing 200 g. of anhydrous calcium chloride (3.6 equivalents) and 163 g. of sodium cyanide (3.3 moles) was used to dissolve 540 g. of anhydrous glucose (3.0 moles).[4] The temperature of the solution rose from 20 to 33° within an hour and after two hours 94% of the theoretical amount of ammonia could be expelled from a sample by distillation. Thus the formation of the glucoheptonic nitriles and their hydrolysis to α- and β-calcium glucoheptonate and ammonia is quite rapid. The reaction was complete within twenty-two hours at ordinary temperature. Calcium hydroxide (222 g., 3 moles) was then dissolved in the solution and in a short while the basic calcium salts of the two glucoheptonic acids precipitated and were filtered off, washed with cold lime water until the filtrate showed only a faint chloride test, and decomposed with oxalic or sulfuric acid in the usual way. By concentrating the solution a yield of 42% of α-glucoheptonic lactone was crystallized, and a yield of 11% of the crystalline lactone of the beta acid was obtained from the residue through the brucine salt.[5] By working up mother liquors these yields were increased to 58 and 21%, respectively.

This preparative method has been applied by various workers associated with us to the conversion of xylose to gulonic lactone, lactose to a corresponding 13 carbon acid, and to the preparation of the gluco-octonic lactones. It seems to be generally the case that the basic calcium and barium salts of the monobasic sugar acids are only sparingly soluble. In the case of mannose, barium chloride was used in place of calcium chloride and the neutral barium salt of α-mannoheptonic acid, which is of low solubility and crystallizes well, could be obtained directly from the reaction mixture. It will be observed that sodium cyanide is used in the preparations in place of hydrocyanic acid, an alteration which is markedly convenient in large scale work. The preparation of α-glucoheptonic lactone from glucose is now so readily performed that it might well be used in college instruction.

The work was carried out during 1926–8 in the National Bureau of Standards and subsequently in the National Institute of Health.

WASHINGTON, D. C.

RECEIVED MARCH 12, 1934

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[4] One may prefer to use calcium cyanide in place of the two salts, if it is available.

[5] E. Fischer, *Ann. Chem.*, **270**, 64 (1892).

COMMUNICATIONS TO THE EDITOR

THE AMPHOTERIC CHARACTER OF SILVER HYDROXIDE

Sir:

A recent paper by H. L. Johnston, F. Cuta and A. B. Garrett on this subject [THIS JOURNAL, **55**, 2311 (1933)] agrees satisfactorily with the conclusions reached by E. Laue in a paper "Ueber den amphoteren Charakter des Silberhydroxyds" [*Z. anorg. allgem. Chem.*, **165**, 325 (1927)] which escaped the attention of these authors. In this paper it was pointed out that silver hydroxide is amphoteric and that the solubility product of argentic acid is about 2×10^{-18}.

Johnston, Cuta and Garrett's value 2.22×10^{-4} mole per liter for the solubility of silver hydroxide in neutral solution at 25° is not in agreement, however, with my figure of 1.36×10^{-4}, which I believe to be correct within 5%. This discrepancy would be easily understood if the water employed by Johnston and his co-workers had contained the usual equilibrium amount of carbon dioxide and had had in consequence a conductivity of 2×10^{-6} mho or more [methods for the calculation of such carbon dioxide corrections, E. Laue, *Z. anorg. allgem. Chem.*, **165**, 305 (1927)]. However, Dr. Johnston informs me that the water was of extreme purity, in which case this explanation becomes impossible. Further work on this problem is clearly necessary.

E. LAUE

RECEIVED MARCH 2, 1934

THE SOLUBILITY OF Ag_2O IN WATER AND IN ALKALI

Sir:

We regret that Dr. Laue's paper [*Z. anorg. allgem. Chem.*, **165**, 325 (1927)] was accidentally overlooked, especially since his measurements in strong alkali are roughly in agreement with our own and caused him to draw the same conclusion as ourselves respecting the existence of amphoteric properties in silver hydroxide.

We would point out that Dr. Laue's values deviate from ours not only in pure water, but to a somewhat less extent throughout the entire range of alkalinity. For this reason the agreement of his value for the activity product of the ions of argentic acid 1.96×10^{-18} with the value which may be calculated from our dissociation constant for this acid $a_{\mathrm{AgO}^-} a_{\mathrm{H}^+} = K_{\mathrm{A}} a_{\mathrm{AgOH}} = K_{\mathrm{A}} m_{\mathrm{AgOH}} = 7.9 \times 10^{-13} \times 2.5 \times 10^{-6} = 1.97 \times 10^{-18}$ must be considered as fortuitous.

After a careful study of Dr. Laue's paper we still believe that our values are nearer to the true solubilities of silver oxide in the various solutions which we have measured.

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THE CZECHOSLOVAKIAN
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F. CUTA

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A. B. GARRETT

RECEIVED FEBRUARY 5, 1934

PREPARATION OF CRYSTALLINE β-*d*-ALLOSE

Sir:

Levene and Jacobs [*Ber.*, **43**, 3141 (1910)] prepared sirupy *d*-allose and *d*-altrose from *d*-ribose obtained from yeast nucleic acid but were unable to obtain the sugars in crystalline form. Austin and Humoller [THIS JOURNAL, **55,** 2167 (1933)] have recently prepared crystalline β-*l*-allose from synthetic *l*-ribose. We have now prepared crystalline β-*d*-allose from *d*-ribose obtained from nucleic acid.

Application of the cyanohydrin reaction to 50 g. of purified *d*-ribose gave 25.5 g. of crude calcium *d*-altronate and 27.8 g. of crude *d*-allonic lactone. The latter after several recrystallizations was reduced with sodium amalgam. After converting the unchanged allonic lactone to the sodium salt and removing both the sodium sulfate and sodium allonate with alcohol, the *d*-allose crystallized from the alcoholic solution in good yield. The crude product was dissolved in a little water by warming, about three volumes of hot methyl alcohol was added, and the solution filtered through a little carbon. The sugar was allowed to crystallize, and was then filtered and washed with absolute ethyl alcohol. The *d*-allose thus purified gave a melting point (uncorrected) of 128–128.5°. *Rotation:* 1.338 g. in 25 ml. in a 2-decimeter tube at 20.1° gave the following specific rotations: 2 min. after solution, $[\alpha]_{\mathrm{D}}^{20.1}$ 0.58°; 4 min., 2.10°; 10 min., 3.26°; 20 min., 6.03°; 40 min., 9.57°; 120 min., 14.12°; 20 hrs. (constant), 14.41°. Since this sugar is the less dextrorotatory form of a sugar in the *d*-series, according to the nomenclature of Hudson [THIS JOURNAL, **31,** 66 (1909)] it is to be designated as the β-form. It is the eighth of the sixteen possible aldohexoses to be reported in the crystalline state.

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FRANCIS P. PHELPS
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RECEIVED MARCH 30, 1934

THE FORMATION OF CHLORINE HEPTOXIDE ON ILLUMINATION OF MIXTURES OF CHLORINE AND OZONE

Sir:

In a recent communication [THIS JOURNAL, **56,** 364 (1934)] we reported that when mixtures of chlorine and ozone are illuminated with blue light the observed pressure change is not sufficient to account for the amount of oxygen formed. At that time the discrepancy was attributed to the formation of chlorine trioxide which condensed on the walls of the reaction vessel. Further experiments, however, have shown that the discrepancy was much greater than could be accounted for in that manner alone. We have found it possible to isolate from these reaction mixtures a drop of colorless liquid which has been identified as Cl_2O_7. The identification consisted of measuring the vapor pressure of the substance over the range 213–268°K. and comparing the data with those obtained by Goodeve and Powney [*J. Chem. Soc.*, 2078 (1932)]. The agreement was excellent. In addition we have the qualitative observations that the melting point is below 190°K., and that the liquid dissolves slowly in water to give an acid solution which does not react with sulfurous acid (indicating perchlorate rather than lower valences of chlorine). The amount of this oxide produced in a given reaction mixture seems to be proportional to the initial ozone pressure and to increase somewhat with the chlorine pressure; it is only slightly dependent on temperature between 20 and 30°. It is obvious that the formation of these oxides, Cl_2O_7 and ClO_3, invalidates any interpretation of the behavior of chlorine and ozone mixtures which assumes that the pressure change measures the oxygen formed.

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RECEIVED APRIL 12, 1934

CHAINS IN THE ACETALDEHYDE DECOMPOSITION

Sir:

A recent paper by F. O. Rice and Herzfeld [THIS JOURNAL, **56,** 284 (1934)] gives an explanation of the kinetics of the homogeneous thermal decomposition of certain organic compounds on the basis of chain mechanisms, involving in some cases very long chains. In many cases this theory comes into direct conflict with the generally accepted explanation [L. S. Kassel, "The Kinetics of Homogeneous Gas Reactions," Chapter V] of these reactions as unimolecular decompositions "falling off" at low pressures. In fact, most supposed examples of the latter theory, such as the ethers and azo compounds, must now be regarded as under suspicion of being due to chain mechanisms.

There is a simple test, applicable in many cases, for the existence of such chains. One step in these chains will nearly always be the reaction of a methyl radical with the molecule of the substance, and the activation energy for this must be lower than that for the primary decomposition into free radicals. Hence if we introduce free methyl radicals from some extraneous source into an organic vapor at a temperature somewhat below that at which it ordinarily decomposes, a chain decomposition should be set up. Thus, these decompositions should be induced at an abnormally low temperature by mixing our compound with another that decomposes at this lower temperature to give methyl radicals.

We have tried this experiment with a mixture of acetaldehyde and azomethane. Decomposition is actually induced in the aldehyde; a few per cent. of azomethane is sufficient to cause complete decomposition of the aldehyde at 300°, at which temperature the aldehyde alone is quite inert. Chain lengths, calculated from rate measurements, are found of the order of 30. The rate of the reaction is found, within the accuracy of our few preliminary experiments, to be proportional to the first power of the aldehyde pressure and to the square root of the pressure of the azomethane, just as the chain theory predicts.

Our result strongly confirms the above explanation of the decomposition of pure acetaldehyde as a chain reaction, but this is not yet definitely proved since there may be some other faster reaction superimposed upon the chain reaction at higher temperatures. We expect, however, by further experiments with azomethane–aldehyde mixtures to establish this point by getting the activation energies of the chain steps. These experiments may also throw light on the question of whether the azomethane decomposition is a chain reaction.

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RECEIVED APRIL 16, 1934

THE LOW PRESSURE EXPLOSION LIMITS OF DEUTERIUM AND OXYGEN

Sir:

We have compared the explosion limits of deuterium–oxygen and hydrogen–oxygen mixtures at low pressures at 500° and 520° in potassium chloride-coated Pyrex according to our original technique [THIS JOURNAL, **55,** 3227 (1933)]. Deuterium was generated by electrolysis of pure heavy water; in some cases additional care was taken to purify it by diffusion through palladium. Tank hydrogen was used in alternate experiments. From Fig. 1 and Fig. 2 it is seen that the deuterium curve is much broader. At high pressures where there is no appreciable deactivation at the wall of the vessel, the negative reciprocal slope of the explosion limit curve represents the relative deactivation efficiencies ZH_2/ZO_2 and ZD_2/ZO_2 in the chain-breaking processes $X + O_2 + M$, where X is the chain-carrier and M is H_2, D_2 or O_2. Experimentally these values are 3.1 and 2.1, respectively; whence $ZH_2/ZD_2 = 1.5$. This value compares favorably with the value $ZH_2/ZD_2 = \sqrt{\mu D_2/\mu H_2} = \sqrt{4/2} = 1.4$, roughly calculated from the simple theory of three-body collision frequency [Grant and Hinshelwood, *Proc. Roy. Soc.* (London), **A141**, 29 (1933)], assuming equal collision diameters for H_2 and D_2. For according to this, the ratio ZH_2/ZD_2 is a function only of the reduced masses, μ, of the respective complexes $(X + O_2 + H_2)$ and $(X + O_2 + D_2)$; and the reduced masses are approximately the masses of H_2 and D_2 when $X + O_2$ is large compared with H_2 and D_2. The whole of the observed change due to deuterium, therefore, can be accounted for on the basis of relative deactivating efficiencies. This leads to the observation that any additional changes, due to the substitution of deuterium for hydrogen, in the relative rates of chain branching and chain breaking process controlling the explosion limit, must cancel one another. It is unlikely that this would be the case if D and H or D_2 and H_2 were the chain carriers.

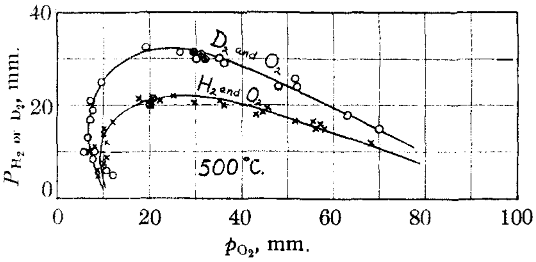

Fig. 1.—Explosion limits at 500°: ×, hydrogen and oxygen; ○, deuterium and oxygen; ☒, hydrogen diffused through palladium; ◉, deuterium diffused through palladium.

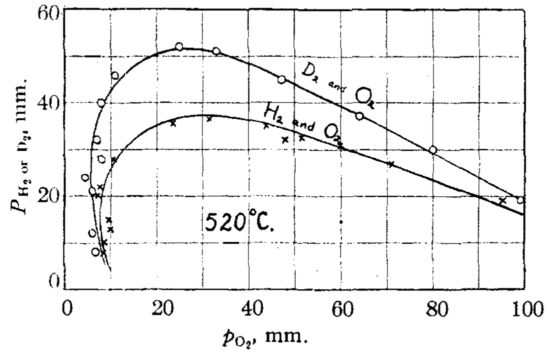

Fig. 2.—Explosion limits at 520°: ×, hydrogen and oxygen; ○, deuterium and oxygen.

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RECEIVED APRIL 17, 1934

THE PREPARATION OF HYDROGEN COMPOUNDS OF SILICON

Sir:

In our studies on the kinetics of the catalytic decomposition of the hydrogen compounds of some of the fourth and fifth group elements it became necessary to prepare rather large quantities of silane, SiH_4. Being acquainted with the very favorable results obtained in the preparation of the germanes in liquid ammonia [Kraus and Carney, THIS JOURNAL, **56**, 765 (1934)], it was thought advisable to follow the same procedure in an attempt to prepare some of the silicon compounds, since the former were obtained in unusually high yields, three to four times as great as those found in the aqueous method [Dennis, Corey and Moore, *ibid.*, **46**, 657 (1924)].

Magnesium silicide, prepared by the direct combination of the elements, was dropped into a solution of ammonium bromide in liquid ammonia. A reaction was noticed to proceed immediately with the liberation of considerable quantities of gases, which upon examination were found to consist chiefly of hydrogen, silane and disilane, and of small amounts of trisilane. To date approximately 30 liters of these silanes have been prepared by this method, with yields ranging from 65 to 80% based on the silicon used in the preparation of the magnesium silicide. The yield obtained here is about three times as great as that found by Stock and co-workers [Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, New York, 1933, p. 21], who employed the analogous aqueous method.

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RECEIVED APRIL 18, 1934