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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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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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 efficien-