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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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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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-