chlorodioxanes described by Butler and Cretcher and have confirmed their findings. In addition, we have obtained several new derivatives. The dichlorodioxane reacts with the Grignard reagent to produce disubstituted dioxanes. As an example, 2,3-diphenyldioxane (m. p. 49°) was prepared and its structure established. This reaction should be a general method of preparing the homologs of dioxane. We are now extending it to the symmetrical tetrachlorodioxanes. Catechol reacts with dichlorodioxane to give a derivative similar to 1,4,5,8-naphthodioxane [Böeseken, Tellegen and Henriquez, *Rec. trav. chim.*, **50**, 909 (1931)]. Only one isomer could be isolated. The evidence is inconclusive regarding the *cis–trans* isomers which Böeseken reported in this class of compounds. We expect to submit evidence in the near future on this point.

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RECEIVED JULY 14, 1932
PUBLISHED SEPTEMBER 5, 1932

THE DECOMPOSITION OF DIETHYL ETHER AT LOW PRESSURES

Sir:

We have made experiments on the decomposition of diethyl ether at 525° with initial pressures ranging from about 0.15 mm. to 200 mm. and at 462° with initial pressures ranging from about 0.8 mm. to 450 mm. These experiments have been made in a Pyrex vessel immersed in a salt-bath the temperature of which can be controlled within 0.1°, using ether which had been dried over sodium and purified by distillation in vacuum. Runs have also been made with a bulb packed with Pyrex tubing in order to test the homogeneity of the reaction. At the lower pressures it is necessary to correct the runs with packed bulbs for gas, probably water vapor, which is continuously distilled out of the apparatus, whether the ether is there or not; when this is done it appears that the reaction is homogeneous throughout the pressure ranges reported. The results have been compared with the results previously obtained by Hinshelwood [*Proc. Roy. Soc.* (London), **A114,** 84 (1927)] in the more limited range of pressures in which he worked. Our rates at 525° are somewhat faster, corresponding to a difference in the absolute temperature scale of about 7°; our activation energy is about 60,000 calories compared to Hinshelwood's 53,000; the cause of these discrepancies is not clear. It will be seen that this means that we agree, roughly, with Hinshelwood, and with Steacie [*J. Phys. Chem.*, **36,** 1562 (1932)] at the lower temperature.

When we plot the logarithm of the rate constant against the logarithm of the pressure, we get a curve which does not fall off nearly as fast in the lower pressure region as one would expect on the basis of the usual theory.

In fact, it appears to have a very slight concave upward curvature. This suggests, though we cannot be quite certain, that it is approaching a second unimolecular region at low pressures, a possibility previously discussed by one of us [*Z. physik. Chem.*, **B7**, 226 (1930)]. The temperature coefficient appears to be slightly greater at the lower pressures. We hope to be able to give a more thorough discussion of these phenomena at a later time, when the experimental results will also be presented in full.

It may be well to note that we have verified the effect of hydrogen in increasing the reaction rate. It appears to have the same effect within the limit of error—which is rather large in the presence of excess hydrogen— at the two temperatures, a point which is of some importance in connection with the question of whether hydrogen is really an inert gas, or whether its effect is due to reaction with the ether. We see no reason at present to believe that it is not inert, as far as the decomposition of the ether is concerned—it may, of course, react with the products of the decomposition.

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PUBLISHED SEPTEMBER 5, 1932

ACTIVITY COEFFICIENTS OF BARIUM CHLORIDE

Sir:

In a communication from the Laboratory of Yale University [Harned and Nims, THIS JOURNAL, **54**, 423 (1932)], it was presented that the evidence obtained indicates a maximum in the activity coefficient–temperature curve for sodium chloride. Direct confirmation of this phenomenon was lacking, however.

Studies in progress at this Laboratory on the activity coefficients of barium chloride from electromotive force data at different temperatures indicate that this phenomenon certainly exists for barium chloride.

Electromotive forces have been measured very satisfactorily using barium amalgam cells of special construction. Activity coefficients calculated from the data at 0 and 45° coincide fairly closely while those at 25° are appreciably higher for the same concentration.

With complete electromotive force data the heats of dilution may be calculated. When experimental work has been completed the data will be submitted for publication.

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RECEIVED JULY 23, 1932
PUBLISHED SEPTEMBER 5, 1932