THE SPECIFIC NATURE OF ENERGY EXCHANGE IN UNIMOLECULAR REACTIONS

Sir:

Since the energy of activation in unimolecular reactions is undoubtedly obtained by collision, the velocity constants fall off at low pressures. It is well known that certain inert gases will prevent this falling off by furnishing the necessary collisions. The specific nature of this effect is, however, very remarkable. In general, hydrogen and the products of the reaction are effective, while other inert gases are usually ineffective. Rice has recently discussed the question from the point of view of quantum mechanics [O. K. Rice, *Chem. Reviews*, **10**, 125 (1932)].

In the past most of the inert gases employed have been of comparatively simple structure. It seems desirable to obtain information regarding the behavior of gases which are as complicated as the reactant, and which resemble the reactant as much as possible. The series of ether decompositions investigated by Hinshelwood and his co-workers are ideal for the purpose. Accordingly an investigation has been undertaken on the rate of decomposition of mixtures of aliphatic ethers. Mixtures of dimethyl and diethyl ether have already been investigated. These ethers decompose in an almost identical way, and have a pronounced resemblance in physical properties, and in the manner in which the velocity constants fall off with diminishing pressure. Each might therefore be expected to show a high efficiency in activating the molecules of the other.

The surprising result has been obtained that the two gases have absolutely no activating effect on each other. A mixture of the two (at pressures where the falling-off is large) decomposes at a rate which is exactly the mean of those of its components (within an experimental error of about three per cent.). This appears to be the most pronounced example of the specificity of energy transfer which has yet been observed.

The decomposition of mixtures of methyl ethyl ether with both diethyl and dimethyl ether is being investigated. A full account of the work will appear later.

PHYSICAL CHEMISTRY LABORATORY
MCGILL UNIVERSITY
MONTREAL, CANADA
E. W. R. STEACIE

RECEIVED MARCH 7, 1932
PUBLISHED APRIL 6, 1932

THE PREPARATION OF AN OPTICALLY ACTIVE TRIARYLCARBINOL

Sir:

A survey of the chemical literature shows that many primary and secondary alcohols containing an asymmetric carbon atom have been successfully resolved. However, all previous attempts to resolve asymmetrically substituted tertiary alcohols have failed. In an article published