THE THERMAL CHLORINATION OF METHANE BY A FLOW METHOD

Sir:

We have recently been investigating the thermal (non-catalytic) chlorination of methane by a flow method. The following conclusions as to the kinetics of the reaction may be of interest.

The reaction takes place readily in pyrex glass reaction tubes above about 200° at 1 atm. total pressure. The rate is unaffected if the reaction tube is packed with broken glass, or if the internal surface of the tube is coated with potassium chloride. The reaction is, therefore, homogeneous. The effects of changes in concentration of reactants indicate that it is also bimolecular.

At the lower temperatures (225–300°) the reaction is inhibited by oxygen. Thus at 225° and five minutes' heating, 30% of the chlorine reacts when the reaction mixture consists of 60% methane and 40% chlorine at 1 atm. With 5% of oxygen present there is no measurable reaction. At 300° the suppression by oxygen is still considerable, but at 375°, at which temperature the rate of the unsuppressed reaction is very high, 5% of oxygen has no measurable effect. This effect of oxygen points to a chain mechanism. This is borne out by a discrepancy between the observed reaction rate at any temperature and that calculated by the collision theory of bimolecular gas reactions. About 1000 more molecules react than the theory predicts. A recent study of the photochemical chlorination of methane by Coehn and Cordes [*Z. physik. Chem.*, Abt B, **9**, 1 (1930)] has demonstrated that a chain mechanism applies here also, chains being some 10^4 molecules in length at the maximum.

This work is being extended and will be later reported in full.

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ADSORPTION AND PROMOTER ACTION IN CATALYSIS

Sir:

The results of Elissafoff's experiments [*Z. Electrochem.*, **21**, 352 (1915)] have been quoted by Hugh S. Taylor in his "Treatise upon Physical Chemistry" and also by Rudel and Haring [*Ind. Eng. Chem.*, **22**, 1234–1237 (1930)] as an example of adsorption in catalysis. The first investigator found that copper sulfate in the presence of glass wool decomposed hydrogen peroxide more rapidly than either substance alone, and that the effect was greater than the sum of the individual effects. Since separate experiments showed that a glass powder, of the same composition as the

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