

amalgam dropping into an air-free 0.1 *N* potassium chloride solution which was 0.04 *M* with respect to cadmium sulfate. The potential of the dropping electrode, referred to the saturated calomel electrode,  $E_{d.e.}$ , is plotted on the abscissa, and the corresponding current in microamperes on the ordinate. The horizontal line marks the rest point (zero current) of the recording galvanometer. The section of the curve above the galvanometer zero line (positive current) corresponds to the discharge of cadmium ions into the amalgam,  $Cd^{++} + 2e + Hg \rightarrow Cd(Hg)$ . The section of the curve below the galvanometer zero line (negative current) is due to the anodic dissolution of cadmium from the amalgam,  $Cd(Hg) \rightarrow Cd^{++} + 2e + Hg$ . The anodic section of the curve exhibits a prominent maximum, exactly similar to the maxima frequently obtained in the reduction of metal ions at the dropping mercury electrode, which is followed by a well-defined diffusion current whose magnitude is proportional to the amalgam concentration.

The curve in Fig. 2 was obtained in a similar way, except that 0.1 ml. of a 0.1% solution of sodium methyl red was added to 10 ml. of the solution. The addition of the methyl red completely eliminated the anodic maximum, and produced a very well-defined wave with a constant diffusion current. This effect of methyl red shows that the anodic maximum, like the common cathodic maxima,<sup>2</sup> is caused by phenomena on the solution side, and not the amalgam side, of the amalgam-solution interface.

The characteristics of these anodic c. v. curves with dropping amalgam electrodes are being further investigated, and a more detailed report will be submitted in the near future.

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JAMES J. LINGANE

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#### KINETICS OF HYDROCARBON DECOMPOSITION

Sir:

I have to thank you for your courteous permission to call attention to the fact that, in his recent review of the Kinetics of Hydrocarbon Decomposition [*Chem. Rev.*, **22**, 311 (1938)] Professor Steacie has completely mis-stated our results and conclusions. We show that when one experiments with equilibrium mixtures of ethane, ethy-

lene, and hydrogen, instead of with the pure hydrocarbons, the effect of the changes represented by the equation



is eliminated. Professor Steacie's statement is exactly the opposite to this. Following the pyrolytic changes by means of exact analyses, which are not "unchecked," it is then found that the rates of disappearance of 2-carbon hydrocarbon is represented by the equation

$$-d(\text{2-carbon hydrocarbon})/dt = K(C_2H_6)(C_2H_4)$$

This conclusion results from nearly a hundred experiments with equilibrium mixtures, and can hardly be a matter of chance. The conclusion is that the time-determining step is a process involving one molecule of each of the hydrocarbons.

Our experiments do, indeed, differ from those of others, but because we alone work with equilibrium mixtures, and also take account of the fact that the formation of benzenoid condensation products is of importance equal to that of the formation of methane. This latter point has been generally ignored. In these experiments, contrary to Professor Steacie's statement, we observe no induction period, and the  $x/t$  graphs show no breaks. Initial temperature lag is of no importance, or is easily corrected for.

With pure ethane the rates of formation of methane and condensation products are self-accelerated, a fact which supports the conclusion which we draw from our experiments on the equilibrium mixtures. The rates of formation of these products are, however, somewhat faster than the rates calculated from the experiments with equilibrium mixtures, and the graphs show breaks, but not till a long time after the start, so that they cannot be accounted for by initial time lag. We cannot explain these phenomena, a fact which is hardly remarkable, considering the present position of our knowledge of chemical kinetics.

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#### NATURE AND PARTIAL SYNTHESIS OF THE CHICK ANTIDERMATITIS FACTOR

Sir:

The preparation of highly active concentrates of the chick antidermatitis factor has been de-