A SYMPOSIUM ON GASEOUS COMBUSTION[1]

INTRODUCTION TO THE SYMPOSIUM. THE DEVELOPMENT OF COMBUSTION RESEARCH AND THE PRESENT OUTLOOK[2]

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Nine years ago the Division of Gas and Fuel Chemistry of the American Chemical Society, jointly with the Division of Petroleum Chemistry, sponsored a symposium which was essentially on gaseous combustion.[4] The present symposium reflects the progress in combustion research made since then. Three divisions may be distinguished in this research. One includes the chemistry and kinetics of slow and explosive oxidation reactions. Another is the propagation of flame with the establishment of boundaries between burnt and unburnt gases. A third consists of a study of the state of the burnt gas, that is, the establishment of thermodynamic equilibrium and temperature gradients. In a number of technical problems such as are presented by internal-combustion engines, problems in more than one of these divisions occur.

The time limitations that are unavoidably placed on the present large program and other circumstances have prevented the inclusion of contributions from many active investigators both here and abroad. It is regretted that it was not possible to obtain a representative group of contributions in the exceedingly important and active field of catalytic com-

[1] This symposium was held by the Division of Gas and Fuel Chemistry, with the coöperation of the Divisions of Industrial and Engineering Chemistry, Petroleum Chemistry, and Physical and Inorganic Chemistry, at the Ninety-fourth Meeting of the American Chemical Society, Rochester, New York, September 9-10, 1937.

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[4] This symposium was held at the Seventy-sixth Meeting of the American Chemical Society, held at Swampscott, Massachusetts, September 10-14, 1937. The papers of this symposium were published in Industrial and Engineering Chemistry, Vol. 20, pp. 998-1057 (1928).

bustion. The problem of the diffusion flame was ably treated at the earlier symposium, and it has been omitted from this one since little could be added at this time that would contribute to a further understanding of the subject. The subject of the detonation wave, which in the main is a physical problem in hydrodynamics, has also been omitted, since it had already reached an advanced stage of theoretical development. Some more recent discoveries in this field, such as the discontinuous progress of the detonation wave and the spinning detonation in which a spiral track is described by the wave front, merit further study. It does not appear that problems of technical interest are involved.

Certain fundamental lines of development are indicated by the present accomplishments in the various divisions of the symposium. Ultimately, it is desired to understand fully the intricate chemistry and kinetics of the oxidation of combustibles. In the case of hydrogen we are probably not very far from this realization. This can also soon be said of carbon monoxide. The reactions of hydrocarbons are much more complicated. There is a well-founded suspicion that the key to the chemistry and kinetics of hydrocarbon oxidation lies in the formation and decomposition of peroxidic substances. The subject of the complicated and extremely important heterogeneous reactions of hydrocarbons is a field of study in itself. It can be stated with some assurance that there is hardly a case of slow oxidation or of the establishment of a critical condition leading to ignition, as, for example, in engine knock, that does not involve surface reactions of some kind. The function of the interface between gas and fuel droplets as the possible initiator of ignition in the Diesel engine should not be overlooked and deserves study. Thus, the oxidation of organic substances offers challenging problems to the kineticist. Such studies should stimulate research and technical development in many directions, possibly much more than we can foresee now.

There are a number of problems encountered that are of such extreme complexity that a rational and immediate scientific solution seems to be quite impossible. Sometimes they are of such practical importance that something has to be done about it, despite the impossibility of a quantitative scientific analysis of the problem or even of the guiding principles that are involved. A perplexing problem of this sort is that of fuel rating. Nevertheless, one must admire the practical progress that has been made in this work. It is in the nature of the problem that the methods of rating fuels developed thus far are not entirely satisfactory, and that their shortcomings become more pronounced as the limits of tolerance in fuel specifications narrow. If active investigators in this field were asked today whether they could improve on the principles of present fuel rating practice, the answer would probably be in the negative. They would protest that they have not even an assured qualitative knowledge of the processes that occur between the fuel, the air, and the surface in the engine; much less could they give a quantitative estimate of the likelihood of knock in the Otto engine or of the length of the preignition period in the Diesel engine. There is, however, nothing to suggest that the problems are insoluble.

Among other problems of great complexity are those of ignition by a local source such as a spark and of the propagation of flame. In the approach to both problems the older idea that only the transfer of heat need be considered the decisive element must now give way to the inclusion of the migration of chain carriers and the various kinetic aspects of chain development. There will be presented in this symposium pertinent experiments pointing to the rôle of chain carriers, and also a first attempt at a mathematical analysis of the dual problem of heat flow and diffusion of chain carriers. In safety practice the specification of an admissible spark would be materially aided by a deeper understanding of the action of the spark on a combustible mixture. A similar situation exists with respect to the problem of flame propagation which entails limits of inflammability, the latter being of utmost practical importance in hazardous industrial operations.

Whether mine and other explosions can be effectively inhibited by some means such as the addition of small amounts of substances acting as negative catalysts to the reaction chain development, remains to be answered in the future. However, there is no question but that present knowledge can materially aid in the elimination of thousands of explosion hazards that today lurk below and above ground all over the country.

A much clearer description of the state of the burnt gas that emerges from the flame can now be given than was possible ten years ago. The essential tool to study the burnt gas has been provided by band spectroscopy, in the form of accurate data of energy contents (specific heats) and equilibrium constants. It has become possible to establish order in this field, which has admittedly been in a confused state ever since it was first touched upon by Bunsen. It has been shown that the flame effects a potent transformation of the combustible mixture to practically thermodynamic equilibrium, leaving no room for large hidden sources of energy in the form of latent heat. There are, however, certain problems that should be studied further, such as the anomalous effects that appear as a time-dependence of specific heats and the study of flames of very rich mixtures of organic combustibles where complicated and partly unknown dissociation equilibria exist.

No doubt we all shall learn and profit from the present gathering. It is hoped that the impetus given by the work presented will stimulate further research along both experimental and theoretical lines.