NATIONAL BUREAU OF STANDARDS REPORT

8546

EUROPEAN TRIP

August 15 to 29 1964

by

E. C. Creitz

U. S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

THE NATIONAL BUREAU OF STANDARDS

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* NBS Group, Joint Institute for Laboratory Astrophysics at the University of Colorado.
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ABSTRACT

The purpose of the trip was to attend the 10th International Symposium on Combustion at Cambridge, England, and to visit two laboratories in Germany where work is being done that is of interest to us.

The strongest overall impression of the Symposium was left from listening to theoretical papers on the mechanisms of combustion. It appears that the combustion of H_2+O_2 is not at all well understood. Since this is probably the simplest flame system, it leaves the understanding of more complicated systems (and ionic reactions in such systems) discouragingly in the future.

Conversations with Drs. Fish and Rumberg on the subject of analysis of combustion products was similarly discouraging except for determination of stable compounds, present in relatively high concentration and in the absence of smoke or soot. The compounds of greatest interest are, of course, those occuring in small concentrations in fires where smoke is present. The recovery of gaseous compounds adsorbed on carbon particles, particularly if the compounds are reactive, presents problems for which no solution is yet known. It appears that no one has attempted the analysis of smokes which consist largely of tar aerosols, where the problems are just as complicated.

European Trip

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I. The Symposium on Combustion

A. Business and Social Aspects

Registration at the 10th Symposium was the largest of any to date - some 800 registrants including about 150 wives, represented eighteen countries and required a symposium budget of some L 12,500. The retiring treasurer reported a total membership of about 2700 in the combustion Institute. The Institute operates on a biannual budget of about $100,000.

The new board of directors, elected at the business meeting consist of:

W. G. Agnew - General Motors Company

W. J. Bennet - Marquardt Corporation

S. L. Bragg - Rolls Royce Ltd.

R. Friedman - Atlantic Research Corporation

N. A. Hall - Commercial Engineering Education

H. C. Hottel - Massachusetts Institute of Technology

W. M. Rohrer - University of Pittsburgh

E. S. Starkman - University of California, Los Angeles

R. S. Levine - North American Aviation

The volume of papers from the 10th Symposium is to be dedicated to Dr. Bernard Lewis. The Sir Alfred Egerton gold medal was presented to Professor Paul Lafittee by Lady Egerton. Professor A. R. Ubbelode presented the Bernard Lewis gold medal to Professor R. G. W. Norrish. The silver medal for the best paper presented at the 9th Symposium was presented to N. M. Howe, C. W. Shipman, and A. Vranos by Professor Glen C. Williams, who characterized one of the students as one of his "grand students."

The 11th Symposium is to be held in 1966 at the University of California at Berkeley.

Extra-curricular Symposium activities included a ladies' program, a garden party, a formal reception, a trip to Woburn Abbey, where the official dinner was held and an organ recital in King's College Chapel.

B. <u>The Technical Program</u>

The 133 technical papers were presented in three concurrent sessions. They were divided, as to technical content as follows:

Flame Chemistry - 13 papers

Detonation - 6 papers on condensed phase and
6 papers on "mostly gas phase."

Discussion on Electrical Properties of Flames - 12 papers.

Discussion on Elementary Combustion Reactions - 24 papers.

Discussion on Aerodynamics in Combustion

1. Free Burning Fires - 8 papers
2. Rocket Instability - 4 papers
3. Low-speed combustion - 5 papers
4. High-speed combustion - 5 papers

Reaction Kinetics - 12 papers

Combustion and Flow - 12 papers

Fire Research - 6 papers

Solid Propellant Combustion Fundamentals - 6 papers

Flame Spectroscopy - 7 papers

General - 7 papers

The first session attended was that on Electrical Properties of Flames. A paper on Ion Sampling from Chemical Plasmas, by G. N. Spokes and B. E. Evans was of interest because it covered the effects of charge accumulation at the inlet orifice (of a dielectric material) of a mass spectrometer. A pulse of ions was generated in a plasma by electrical discharge and the time delay for appearance of ions in the spectrometer was observed. Gas velocities in the order of 2000 to 5000 cm/sec were used through the orifice. Delays as long as 100 seconds were observed. They attribute these delays to the plating-out of ions on the orifice. They observe that 8 to 9 volts will prevent all positive ions from entering an 0.05-inch orifice. Knewstub observed

that they had found that 10 volts is sufficient to "de-cluster" H_3O^+ ions since they observe mass 73 going to mass 55 and then to mass 37. Miller, Aerochem, also observed "de-clustering" of negative ions from flames and additionally observed that most of the negative charge carriers were ions, rather than electrons. Spokes and Evans succeeded in removing some of the delay by making the orifice of a thin dielectric with conductor on each side and the establishment of an electric field between the conductors.

G. Wortburg showed that the maximum ion concentration occurs at the point of maximum heat release in a flat flame at atmospheric pressure. This seems to relate ion production with chemical recombination rather than with dissociation.

A paper on Langmuir probes confirmed our contention that double probes can measure only positive ion concentrations. Proper conditions for the use of single probes are outlined and their accuracy demonstrated. One comment was that collision cross sections for inelastic collisions are somewhat larger than for eleastic collisions.

W. W. Balwanz reported that carbon particles in a flame had no effect on electron concentration, that the diameter of a flame, as measured by electrons, is larger than its optical diameter and that when alumina is added to a supersonic flame the shape of the shock front alters and when it does, the electron distribution follows the gas and not the alumina particles.

Two papers on the acquisition of charges by solid particles in a plasma indicate that the particles may be charged either positively or negatively depending on conditions. In fact, such particles behave as floating probes and aerodynamic effects may be very significant in the removal of the double-layer.

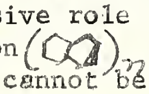
A paper with the very impressive title "On the Effect of Kinetics of Elementary Reactions on Ionization in Stationary and Nonstationary Supersonic Expansion and Compression of Gases" by Miss N. I. Yushchenkova and S. I. Kasterin, is directly applicable to all mass spectroscopic sampling of ions from flames. One may expect that for each gas-dynamic flow there is a limit on the amount of ionization that can exist. It thus appears that ions may disappear simply because of the rate of expansion thru an orifice. The paper applies, of course, only to mass spectrometers where ionization precedes expansion through the orifice.

In the Discussion on Elementary Combustion Reactions, the first paper dealt with gas phase oxidation, at 30°C, of neopentane and other

hydrocarbons. Unexpectedly, the reaction products are formed by direct displacement of two groups (H atoms usually) of the parent hydrocarbon, with the attendant formation of a carbonyl bond, rather than by a free radical mechanism involving extraction of a single group or H atom at a time. While not of direct interest to those working at high temperatures, this information sheds some light on low temperature oxidative processes in organic materials in general.

Many papers in this session, regardless of the system being studied, seemed to depend, in final analysis, on the chemistry of the hydrogen-oxygen system. Most of the studies were made in flow systems which are affected by pressure, composition and temperature gradients, by purity of the reactants and by surface catalysts. A curious fact, in connection with the study of the H_2-O_2 system is that, at flame temperature, pure hydrogen does not dissociate.

In one study it was shown that OH radicals react 2.1 times as fast with CH_4 as with CO and about 70 times as fast with formaldehyde, all work being done in the neighborhood of 500°C. At higher temperatures, the ratio of reaction rates increases, which indicates that the oxidation of CO is the slowest of these processes. Fristrom, et al, show that H and O atoms do not react directly with C_2H_2 or C_2H_4 while OH radicals do. On the other hand, Kaufman gives a very high rate for the destruction of OH radicals by O atoms - something like 1 per less than 10 collisions. Fennimore and Jones showed that the rate of heat evolution in the H_2-O_2 reaction probably depends on the rate of formation of HO_2 radicals.

It was reported that the formation of polyacetylenes play a decisive role in the formation of carbon particles. It was argued that carbon  has more hydrogen present than polyacetylenes, so that they cannot be precursors of carbon.

A study of dissociation and recombination of O_2 showed that, after receiving its dissociation energy, an oxygen molecule exists for a period of time, of the order of a vibrational relaxation time, before dissociating and, if electrons are liberated, it is subsequent to the dissociation. A lot of discussion on ionization processes and the effect of additatives followed this paper. A paper from Aerochem Laboratories on chemiluminescence followed and brought out the fact that electrical discharge through gases produce effects on combustion which are long lasting. This paper showed the existence of both ions and free radicals. The ion CHO^+ was the dominant ion.

Electron attachment in O_2 was observed to be decreased by the addition of CO_2 at 400-600°K, but equilibrium constant values indicate that, at 1000°K, it has little effect at concentrations up to about 1/4 atmosphere. (Phelps & Pack-Westinghouse). Biondi, et al, show that dissociative recombination is the most efficient attachment process for electrons and molecular ions and is responsible for the large recombination rates in afterglows. They found that (a) molecular positive ions must be present to observe large recombination rates, (b) when diatomic ions are present, excited atoms are formed in the recombination process and (c) these excited atoms have kinetic energy of dissociation substantially in excess of thermal energy. Glass (Harvard and Miller)(Aerochem) have observed the ion $C_3H_3^+$. Miller proposes that it is formed according to $CH^* + C_2H_2 \longrightarrow C_3H_3^+ + e$. Miller believes the primary negative ion to be C_2^-.

Van Tiggelen's group report seeing a large number of negative ions from flames, ranging in mass from 16 (O^-) up to mass 63. When Cl_2 is added Cl^- ions replace all other negative ions. Both CO_2^- and CN^- were reported, but Dr. Sugden doubts the probability of their being present because of their high electron affinities. Dr. Knewstub commented that the speed of ions through the inlet orifice must be at least 2.5 cm/sec in order to get the ions through the orifice and that a high sampling rate and resultant cooling favors dissociative attachment of the electrons.

C. Personnalia

In talking with A. V. Phelps of the Physics Department, Westinghouse Electric Corporation, it was learned that Dr. R. E. Fox, who was responsible for the excellent work on electron attachment by SF_6 has become an administrator and is out of laboratory work. Phelps seems to think that probably in flames, as well as in gas discharges, the most important process for the disappearance of electrons is, by far, that of dissociative attachment. In discharges, attachment occurs to positive ions. W. J. Miller, Aero Chem finds dissociative attachment in flames. He thinks that the process usually is

$$e + C_2H_2O^* \longrightarrow C_2^- + H_2O.$$

He also finds O^- and OH^- somewhat downstream from the flame front. Most negative ion concentrations fall off rapidly as the pressure increases, OH^- being the most persistent.

Dr. A. Fish, Imperial College said that they had not been able to determine Br_2 or HBr with the gas chromatograph and had had to go to wet chemical methods. They had not been much interested in bromine compounds, since bromine is not much used in plastics. It was implied that the gas chromatograph was a useful tool but not the complete answer to the analysis of gaseous combustion products.

Dr. T. M. Sugden has left Cambridge University and now works for Shell Oil. From the way he talks, one assumes that he is not working in ionic phenomena at the present.

Dr. J. Lawton, Imperial College, has been working on the effects of electrical fields on flames, in an attempt to improve efficiencies and augment enthalpies by increasing ionization in flames. Power fluxes can be improved, but only at considerable expense for equipment and electrical power.

II. The German Laboratories

A. The State Material Testing Center at Dortmund-Aplerbeck.

This laboratory was established by the State (Westphalia) as an unbiased testing laboratory to make tests for any requester, of all kinds of materials. In general, they do not test structures. The center receives about 25% of its income from the State, the rest coming from charges made for the tests done. The amount of fire testing is rather limited, and seems to be designed to produce results for use in compliance with building codes.

The apparatus for flame spread is similar to that of the British, consisting of a square burner, fed at a specific gas rate, around which is a tall, box-like array of the specimen material. The vertical distance of flame travel and the temperature rise are used in computing a flame spread index.

They are in the process of constructing an enclosure for determining the effects of floor loading of industrial materials, which may have unusual fire properties and may be stored under conditions of unusually high loadings. The enclosure is of sheet iron, on a concrete base, about 15 x 15 x 15 feet, and can be ventilated by air supplied through four large ducts. It was stressed, both here and in Karlsruhe, that there is very little Governmental control over fire hazards in industrial installations.

This laboratory is also doing work in the analysis of combustion products from burning plastics. Their furnace is a conventional zone-refining furnace, in which the sample is placed in a horizontal combustion tube and a small ring-shaped furnace is motor-driven to traverse the combustion tube at a selected constant rate. Air is supplied at one end of the combustion tube and analytical samples are removed from the other end. Smoke from the exit end of the combustion tube is also led to a photoelectric device for measurement of smoke density.

In Dr. Rumberg's opinion, the literature survey of gas analytical methods and results, done by the Underwriters' Laboratories for the Manufacturing Chemists Association, left much to be desired and he has prepared a bibliography augmenting it, a copy of which he gave us.

Dr. Rumberg's analytical methods consist almost entirely of gas chromatographic and wet chemical methods. Some spectroscopic apparatus is available for occasional use, but no mass spectrometer is available. He is very conscious of the difficulty of doing accurate analyses of components which may disolve in liquid aerosols or adsorb on solid particles in smokes, particularly when such solution or adsorption may lead to reaction of some components with others. In his opinion, one must search for each component of the mixture by a separate analytical method before group-analytical methods such as gas chromatography can be trusted. He is probably right, but the prospects for complete analysis of a smoke are discouragingly far in the future.

In connection with smoke density measurements, Dr. Rumberg pointed out that the photocel used should have a spectral response similar to the human eye, or the correlation between visibility and smoke density is meaningless.

Information was obtained from Dr. Rumberg on other laboratories in Germany which are working in fire-related fields.

1. Bundesanstalt für Materialsprufúng
   Berlin-Dahlem
   Unter den Eichen 87

   Attn: Dr. Seekamp

   This institute does work in construction and materials, ignition and chemistry and Dr. Seekamp should be contacted for the names of others in related fields.

2. Amtliche Forschungs-und Materialprufungranstalt für das Baumesen
   Otto-Graf Institute
   7 Stutgart-Volhingen
   Robert-Leicht Str. 209

   Attn: Prof. Egner.

   Specializes in wood and wood construction

3. Schlessig-Holsteinische
   Landesbrandkasse
   Kiel, Germany

   Attn: Dr. Jach

4. Baustaffprüfamt, Hamburg

   Attn: Dipl-Ing. Hertell

5. Deutches Kunstaff Institute
   Darmstadt

   Attn: Dr. Braun

   Pyrolysis of wood and plastics.

6. Institute fur Holzforchung ind
   Holztechnik der Univ. München

   Behavior of wood.

7. Also in Berlin, working in inorganic materials:

   Group 4 Technische Gase
   Feuergefahrliche und Explossive Stoffe

   Attn: Prof. Roenen

B. <u>The Research Center for Fire Protection Technique</u>, at the Technical High School, Karlsruhe.

This center was started by Dr. G. Magnus in the hopes that it might become a Federal fire research laboratory. Since we were there three years ago, hard times have befallen it. Dr. Magnus, who appears to be the only person available with the right proportions of personality and connections has become too busy, with the Manheim Fire Brigade, and his own industrial activity to manage, as well as a technical committee of the V.F.D.B., so that he has not been able to give the Center the requisite amount of time. Competition from State-supported and university laboratories has increased, so that the idea of a Federal center has apparently been dropped. There have been losses of top quality personnel, and the amount of work has decreased,(it is now all contract work for industrial sponsors). Present plans appear to be to make the laboratory a University-(Technische Hochschule) sponsored laboratory, with a professor as its head. No suitable guiding hand has been found and the Hochschule is reluctantly about to confer the title of Professor on Dr. Magnus. Mr. Hinrichs has done all his graduate work but has not been able to get a time assigned for his final examination. His thesis appears to be the only unclassified work done recently.