a report

The banquet address on September 19 was given by W. M. Holaday, the Pentagon's guided missile director, who discussed "Free Radicals and the Guided Missile Program". Others shown (from left to right) are Mrs. A. M. Bass, G. Porter, A. M. Bass, Mrs. Holaday, H. P. Broida, Mrs. R. Anderson.

FREE RADICALS RESEARCH SYMPOSIUM

By ***James W. Moyer***

A SYMPOSIUM was held September 18–20, 1957, at the National Bureau of Standards, Washington, D. C., on the Formation and Stabilization of Free Radicals. The title of the meeting reflected the current interest of sponsors' committee representatives, Professor F. O. Rice of the Catholic University of America, Dr. S. N. Foner of the Applied Physics Laboratory of Johns Hopkins University, Professor Roy Anderson of the University of Maryland, and Dr. A. M. Bass of the Bureau of Standards' Free Radicals Research Section, who served as chairman of the Symposium Committee.

Some 21 papers were spread over two and one-half days, permitting ample discussion and exercise/refreshment periods. This schedule also allowed a half day for visits to the Free Radicals Laboratories of the Bureau, where over two dozen researchers from the Bureau and industrial concerns are engaged in a three-year project with the same emphasis as the title of the Symposium.

When the organizing committee met a year ago, it was assumed, on the basis of attendance at the 1956 Free Radicals Symposium at Laval University, Quebec, and also because of the narrowness of scope expressed by the title, that attendance would probably not exceed 250 and, therefore, the 350 capacity of the Bureau's East Lecture Room would be more than adequate.

1957 being the year of the rocket, however, the free radicals researchers in attendance found themselves heavily diluted by industrial and government men who, apparently, were hoping for disclosure of a magical breakthrough in propulsion, partly because the rocketeers are seriously in need of an order of magnitude improvement in fuels, perhaps partly to find justification for entering into or continuing research in this fascinating field, and partly because of publicity given to "freezing" free radicals.

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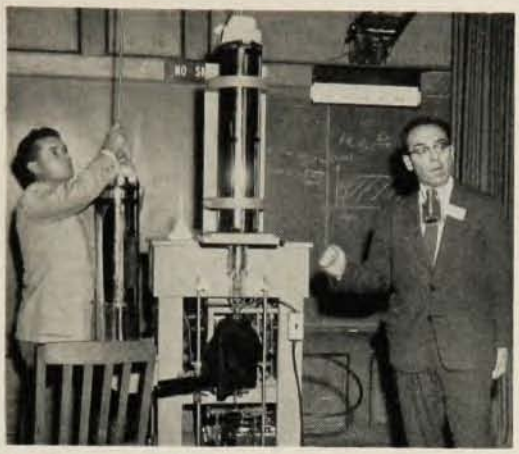
As several of the 21 invited speakers indicated, free radicals have been around for years and their role in many chemical reactions and flames has been studied exhaustively. Under these conditions their lifetimes have usually been so short that it was almost impossible to study their characteristics or to use them for new purposes. The relatively recent advancements in the low-temperature art now make possible the storage of free radicals for a considerable period. How to produce enough free radicals for study, how to store them in appreciable quantities, and how to study their properties, both static and dynamic, forms the research area claiming the attention of most investigators these days.

The program for the first day provided the breadth of approach. After a colorful introduction to the field, "Free Radicals 1900–1957" by Professor Rice, subsequent papers dealt with the statistics of the condensation process (Professor Sidney Golden, Brandeis University), idealized goals for free radicals application to rocket fuels (Dr. George Moe, Aerojet-General), free radicals in biological systems (Dr. Barry Commoner, Washington University, St. Louis), chemical reactions at low temperatures (Dr. Norman Davidson, Caltech; Dr. Robert Ruehrwein, Monsanto Chemical and research guest at the Bureau of Standards, Dr. Gabriel Minkoff, Imperial College and research guest at the Bureau of Standards), and finally a paper on astrophysical free radicals by Professor Bertram Donn of Wayne State University.

The following day was devoted largely to electron paramagnetic resonance studies of the free radicals with the speakers: Professor George Fraenkel, Columbia; Professor Walter Gordy, Duke; Dr. Ralph Livingston, Oak Ridge National Laboratory; Professor Roy Anderson, University of Maryland; Dr. Bernard Smaller, Argonne; and Dr. C. K. Jen, Applied Physics Laboratory. Additional papers by Dr. Samuel Weiss-

C. K. Jen, H. McConnell, and C. M. Herzfeld discuss Dr. Jen's paper on electron spin-resonance studies of stabilized free radicals.

H. P. Broida (at right) assisted by A. K. Stober, preparing to demonstrate the glow emitted by nitrogen discharge products condensed at 4.2°K.



H. Wise and H. P. Broida during an intermission in the symposium program, which was designed to give ample time for discussion.

man, Washington University, St. Louis, on ion free radicals, and formation of free radicals by gamma radiation by Dr. Leo Wall of the Bureau of Standards, rounded out the day.

The final day was devoted to spectroscopy. Infrared, visible, and ultraviolet absorption studies on low-temperature condensates were discussed by Dr. Sidney Leach, University of California, Berkeley, and Dr. Kenneth Harvey, Bureau of Standards. Emission spectroscopy of frozen free radicals was presented by Dr. Maurice Peyron, Bureau of Standards. Dr. Donald Ramsay, National Research Council, Ottawa, discussed the only spectroscopic work in the gas phase. Lastly, Dr. Herbert Broida discussed briefly the scope of the three-year Free Radicals Project at the Bureau of Standards, sponsored by the Defense Department.

BOTH Professor Rice and Dr. Broida attempted demonstrations designed to show the colors of frozen deposits and the light flashes produced by recombination as the deposits are warmed. Neither set of demonstrations came off as planned, but Dr. Broida, at least, must be credited with doing some of his research in public! Professor Rice's demonstration of the historical tellurium mirror attack by methyl radicals was perhaps the most successful.

The reports of several speakers give some indication of how far we are from application of free radicals to the rocket fuel problem. Dr. Moe indicated that the most favorable element hydrogen, containing perhaps 20 molar percent atoms in a stabilized form, might be necessary to yield a substantial gain in specific impulse. Against this requirement we have a theoretical conjecture of an upper limit of order 10% on the simple model considered by Professor Golden, and experimental upper limits for the case of atomic oxygen of order 1% by Dr. Harvey for gas dissociated in a microwave discharge and condensed at 4.2°K, another value of about 11% reported by Dr. Ruehrwein for a similar set of conditions, but derived from a measure of the ozone formed, and about 0.4% (also an ozone determination) for the case of gamma irradiation of oxygen at 77°K reported by Dr. Wall. (The Russian, Shezhetsky, has reported 1% for electron-bombarded frozen oxygen.)

All evidence seems to indicate that free radicals probably can be stabilized only in a dilute form, i.e., that they probably do not exist very long in adjacent positions. Additional support comes from Professor Davidson who believes he has evidence for diffusion of radicals at least a few molecular diameters in an inert solid matrix.

In addition to the experiments on ultraviolet photolysis of oxygen, ozone, and compounds of oxygen and nitrogen in a nitrogen matrix reported by Professor Davidson, Dr. Leach described a similar approach with simultaneous infrared and ultraviolet absorption measurements to be taken on photolyzed styrene and benzene in argon or nitrogen matrices. Professor Davidson was the only one reporting extensive use of liquid hydrogen.

Survey experiments on simple atomic species were reported by Dr. Jen and Dr. Ruehrwein. The APL group has been particularly successful with hydrogen, using electron spin-resonance techniques to measure relaxation times of H atoms in matrices of H_2 and other materials, condensed at liquid helium temperatures. Dr. Ruehrwein reported on his experiments, in collaboration with Dr. J. W. Edwards, also of Monsanto, and Dr. S. Hashman, Callery Chemical Company, of many mixtures involving H_2, O_2, N_2, H_2O, etc., singly and in pairs, passing one or both gases through a microwave discharge before condensing out on a liquid helium trap.

Free radical reactions were deduced from analysis of the gas released on warmup.

The electron paramagnetic resonance (EPR) session opened with a discussion by Professor Fraenkel of the principles and an explanation of the simpler spectra observed in solutions containing free radicals. Professor Gordy related his observations on $Zn(CH_3)_2$, $Hg(CH_3)_2$, and $Hg(C_2H_5)_2$ and argued the case for a nonplanar CH_3 radical in terms of hyperconjugation.

Dr. Livingston discussed gamma irradiation of sulfuric acid at 77°K and the spectra of atomic hydrogen formed. An interesting goniometric application is suggested by his observation of different splitting factors for gamma-irradiated $Ca(OH)_2$ depending on the crystal orientation in the magnetic field. Professor Anderson set the record for total number of organic radicals formed by ultraviolet irradiations at 77°K and investigated by EPR. His presentation must have included almost all of the 100 cases in which he found spin-resonance spectra. Of special interest were those cases in which the spin-resonance spectra altered with time of storage at low temperatures.

On the biochemical side Dr. Smaller's report on gamma irradiation of methane, ethane, propane, etc., led to his discussion of protein systems in which free radicals are being investigated as a possible radiation damage inhibitor. Dr. Commoner showed how EPR techniques have opened up the field for investigation of free radiations in bacteria, yeasts, dried rabbit tissue, and enzyme systems. Ample evidence is available for the stability of free radicals in biological systems. Some work was reported on living cells, algae. Commoner claims to use this technique to distinguish between systems characterized as "molecular" or "semiconductor-type".

Dr. Weissman explored further the application of the EPR method to electron-transfer reactions in hydrocarbons.

For the spectroscopists, Dr. Ramsay gave an account of the elegant, though tedious, work involved in deciding that the NH_2 radical in the ground state (gas phase) was "bent" and that in the excited state is linear.

Dr. Peyron talked about the emission spectra he and Dr. Broida obtained on nitrogen condensed at 4.2°K after passing through a microwave discharge. Some of the glow formerly thought to be due to nitrogen atoms is now attributed to oxygen impurity (atomic in the condensed phase) in the nitrogen. Of interest here also are the shifts and minor changes in band appearances as different gas mixtures are used.

Professor Donn gave interesting speculations concerning the relation between solar outbursts and sudden increases in brightness in comet gases. Free radical reactions contributing excess heat are ascribed to the sudden increase in proton bombardment from the sun. Additional steady ultraviolet or proton radiations may also account for a more satisfactory energy balance for evaporation of comet gases. Another interesting speculation concerned accretion or condensation of interstellar matter at low temperatures including stabilized forms of free radicals. Some laboratory experiments were suggested to explore these "astro-free-radical" ideas.

AMONG the controversial topics discussed between sessions were the crystal structure of solid nitrogen, the excitancy of the imine radical, and the evidence for HO_2. A weighted average of the discussion would indicate that evidence exists for a crystalline nitrogen, even when it appears "glassy", that it is getting increasingly difficult to find support for the existence of a stabilized NH radical, and that the evidence for HO_2 is transitory at best.

One noncontroversial topic was the recognition of the recent advances at the Bureau of Standards in the techniques of experimenting at liquid helium temperatures, particularly with respect to dewar design and refrigerant handling. Satisfactory dewars of glass or metal have been made permitting temperature control and all kinds of observation and instrumentation ports, combined with good storage properties. Emphasis has been placed on ruggedness and economy of fabrication. The overall impressions gained at the meeting were:

1. The "fuels" audience was probably disappointed by the relatively low stabilized free radical concentrations reported so far. Obviously, the time is not ripe for a big development project but a "breakthrough" can always occur and the fuels people are ready to exploit it.

2. The scientists, on the other hand, appear, on the whole, to be reasonably impressed, partly because actual numbers are beginning to come out of experiments, and partly because many new techniques are being applied to the stabilization problem, making research in the field more exciting.

3. Free radicals interest is branching out as evidenced by the surge of inquiries from instrumentation specialists, cryogenics engineers, publishers, and chemical engineers. Increasing attention comes from the biochemical people.

4. The total free radicals research effort is on the upswing. The hope was voiced in many quarters that this will mean fresh approaches and good backing of the most promising. Many research programs have been initiated in the last few months, too recently to produce results. A symposium on the same subject next year might require a whole week!

On Thursday evening, September 19, a cocktail party and banquet were held at the Shoreham Hotel. A large attendance heard a brief talk by Mr. William M. Holaday, Special Assistant for Guided Missiles to the Secretary of Defense. Mr. Holaday spoke in favor of free radicals.

A large part of the work associated with the success of the symposium was borne by Miss Akrevy Pappas of the Bureau's Free Radicals Research Section, who, in addition to making positive arrangements on behalf of those attending, had the unpleasant negative duty of turning down requests for attendance from several hundred the hall could not accommodate.