

CALORIMETRY

By George T. Armstrong

The Eighteenth Calorimetry Conference was held October 16-18, 1963, in Bartlesville, Oklahoma, at the Bureau of Mines Petroleum Research Center. This annual conference provides a gathering place for experimental calorimetrists to exchange views on techniques, to report new developments in thermodynamics and thermochemistry, and to develop cooperative schemes for improving the acquisition and dissemination of thermodynamic data. The eighteenth conference was the first to be held at the home laboratory of its founder and for several years its guiding hand, the late H. M. Huffman. This occasion, together with the fact that the Thermodynamics Laboratory of the Bureau of Mines has recently moved into completely new quarters, made particularly appropriate the subject of the keynote lecture, "Some Legacies of H. M. Huffman to Calorimetry and Thermodynamics". This lecture, given by John P. McCullough (Socony Mobil Oil Co.), a successor of Huffman as director of the laboratory, described the development of a model laboratory and the approach to obtaining a coherent and comprehensive body of thermodynamic data by a coordinated series of experiments of various kinds upon carefully selected classes of compounds. This approach, started by Huffman in those laboratories, and continued by his successors, G. Waddington and J. P. McCullough, and now by D. R. Douslin, has resulted in such outstanding contributions of thermodynamic data that it has become a model of its kind, widely copied and of inestimable influence in its field.

The author, George T. Armstrong of the National Bureau of Standards, served as program chairman for the 18th Calorimetry Conference. Hosts for the meeting were the Bureau of Mines and the Phillips Petroleum company.

The conferees were able to see and be impressed by the completely new laboratories, largely equipped also with new instrumentation for a wide range of thermodynamic measurements, including rotating bomb combustion calorimeters, automatic data logging and computing low-temperature heat-capacity calorimeters, vapor-flow calorimeters, a P-V-T apparatus using gallium as a confining liquid, vapor-pressure apparatus, infrared spectrometry, and purification laboratories.

High-temperature enthalpy measurements have recently presented increasingly great challenges in meeting materials requirements for the space era. In an invited paper, E. D. West (National Bureau of Standards) discussed the problems of making extremely high-temperature enthalpy measurements, and illustrated them by describing a new adiabatic "lift" (as contrasted to "drop") calorimeter for measuring enthalpies to 2500° C. Obtaining valid measurements of any degree of accuracy at these temperatures is a problem, but West has obtained measurements indicating errors as low as 0.1%. To do so he has incorporated automatic photoelectric pyrometry for temperature measurements and furnace temperature control precise to 0.05° C to heat the sample, and a method of making heat measurements with varying amounts of material in the "lifted" capsule. The latter technique gives differential measurements which eliminate some variables which are not easily controlled or measured.

A series of papers on the low-temperature heat capacities of superconductors was introduced by F. J. Morin (North American Aviation Science Center) who showed how it has been possible to map the energy levels of the *f*-band of electrons in a series of transition metals by the measurements of the temperature dependence of the electronic contribution to the heat

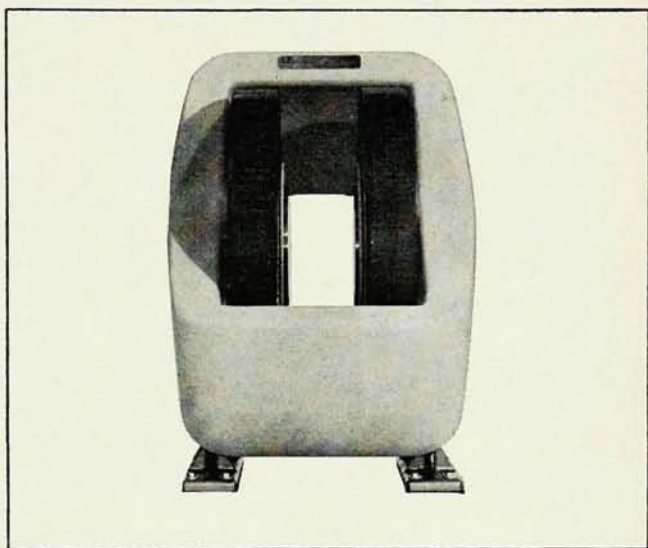
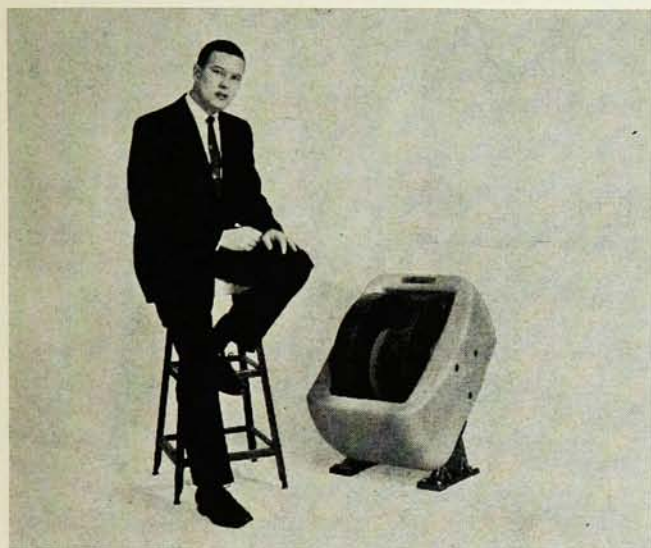
capacities in the elements and inter-metallic compounds of the series. His correlations were remarkably good. The heat capacities of superconductors have contributed much of the essential quantitative information that has led to the elucidation of the nature of superconductivity in recent years. The heat capacities of "hard" superconductors are of particular recent interest because of use of material of this type in high-field solenoids. Papers by E. J. Ryder (Bell Telephone Laboratories) on V_3Si and V_3Si_2 and by B. Serin and G. T. McConville (Rutgers University) on Nb and Nb-Sn alloys added further valuable data on the low-temperature heat capacities of this class of substances.

P. Dean (National Physical Laboratory, England) gave a very graphic and illuminating lecture, in which he was careful to preface his remarks with a statement that he is a mathematician and is really not very much interested in calorimetry. Nevertheless, his analysis of the vibrational-frequency spectrum of linear lattices of light and heavy atoms was followed with careful attention by those in his audience interested in the interpretation of the heat capacities of solids. His method of analysis, utilizing machine computation to work out the tedious arithmetic, allows the variations in the spectrum to be readily followed as changes are permitted in the relative proportions and masses of light and heavy atoms in the lattice. The heat capacity, at least in its broad pattern, is readily derived when the frequency spectrum is fully known.

Of particular interest to calorimetrists is the accuracy of the temperature scale, upon which the validity of most of their measurements must rest. J. L. Riddle (National Bureau of Standards), in an invited paper, discussed the changes in the International Practical Temperature Scale proposed by the Advisory Committee on Thermometry of the International Bureau of Weights and Measures. These changes, currently the subject of intense work in several laboratories, would extend the International Practical Temperature Scale below the oxygen point to the hydrogen triple point, and would extend the platinum resistance thermometer scale upward to 1063°C, as

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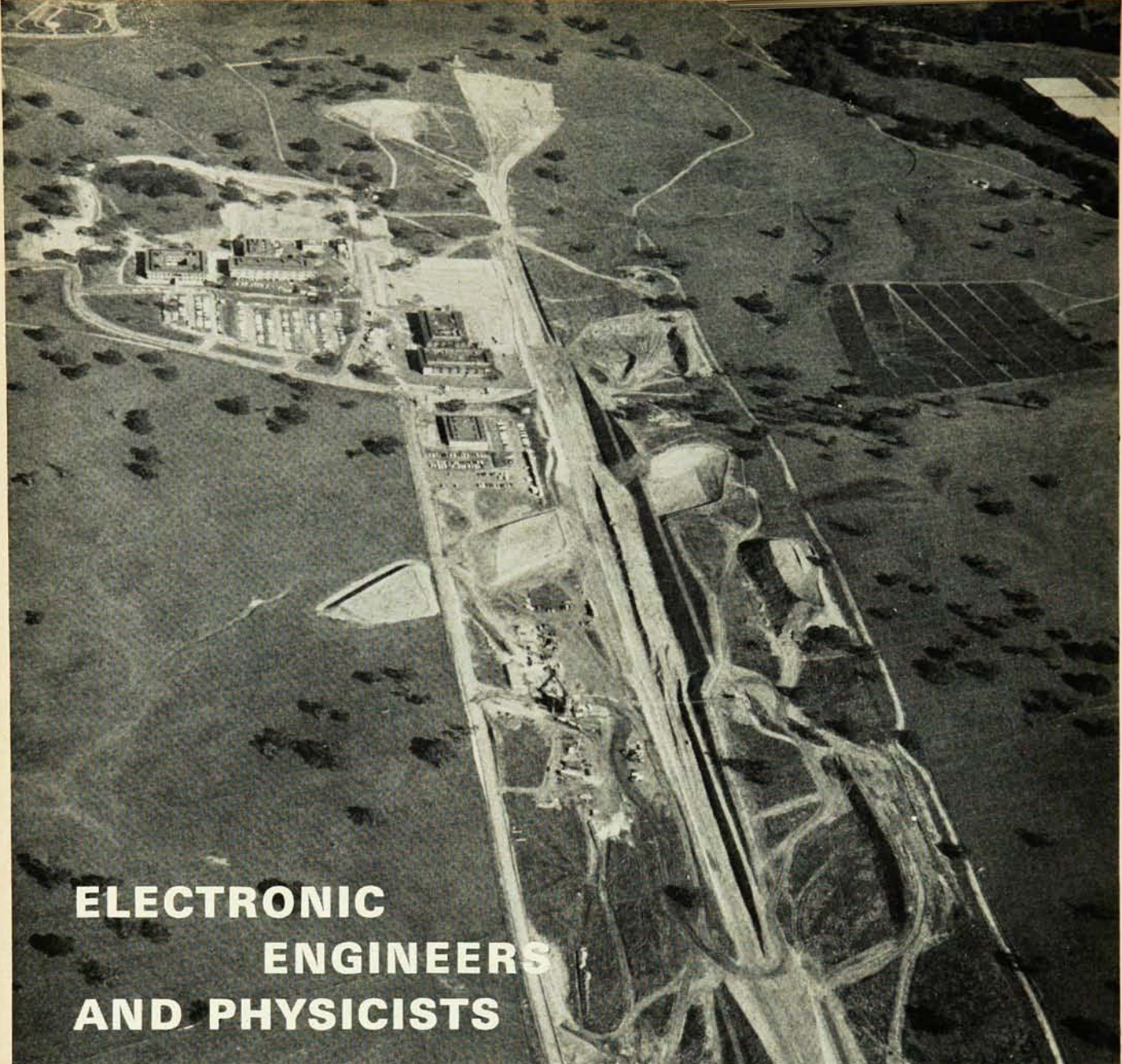
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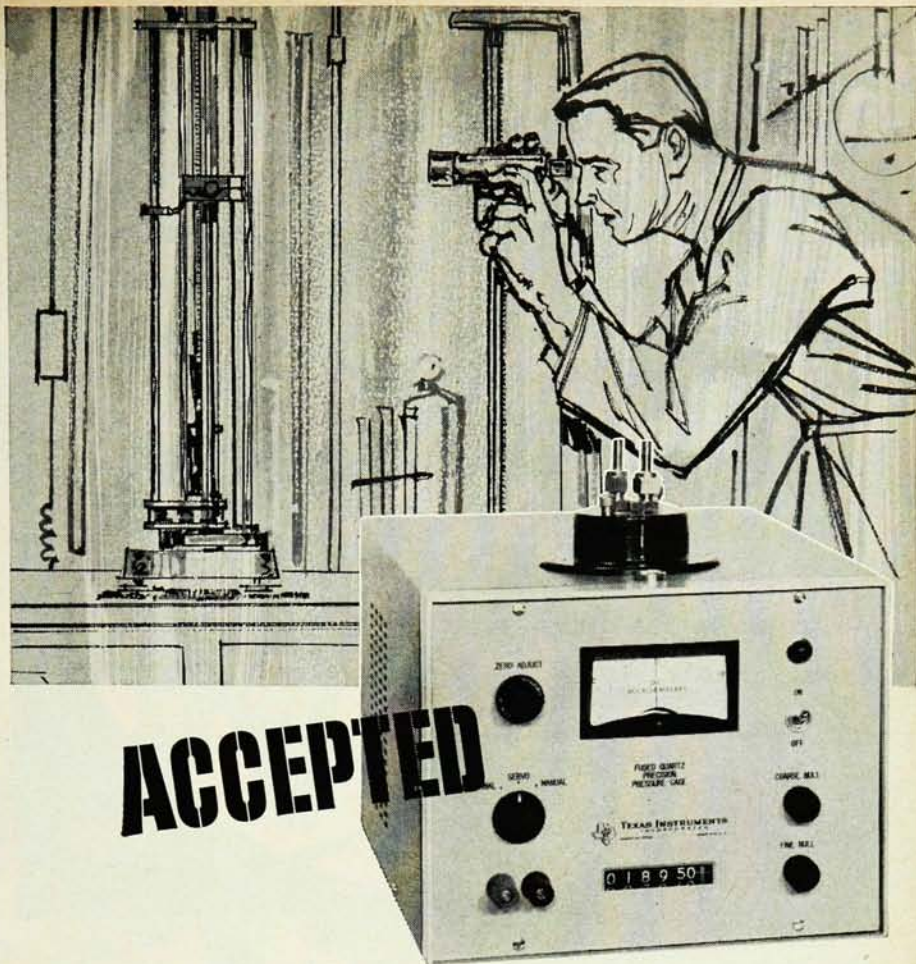
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well as make several minor adjustments of defined fixed points. The object of the change is to create an International Practical Temperature Scale as close to the thermodynamic scale as can be done in the light of current knowledge. The prospect of making these changes within the next few years should stimulate studies to indicate whether or not the proposed changes are consistent with the best thermodynamic data.¹

An illustration of the lack of consistency of the present scales was given by G. T. Furukawa (National Bureau of Standards), who showed consistent deviations in correlations of low-temperature heat-capacity data based on the temperature scales. When the experimental data are analyzed on the basis of the observed resistances of the thermometer instead of converting to temperatures, the deviations are eliminated. The deviations observed are attributed to inconsistencies in the dR/dT of the temperature scales.

In the calorimetry of reacting systems, P. Gross (Fullmer Research Institute, England) illustrated how, with apparatus of utmost simplicity, it is possible to obtain accurate heats of combustion of metals in fluorine or chlorine. He used numerous studies made in his laboratories as examples. The use of fluorine in bomb calorimetry was further illustrated by a report by E. Greenberg, H. A. Porte, and W. N. Hubbard (Argonne National Laboratory) who described studies of the heats of formation of pentafluorides of Nb, Ta, and Ru. W. G. Good, M. Mansson, N. K. Smith, and J. P. McCullough (US Bureau of Mines, Bartlesville) showed that the thermochemistry of boron, long a troublesome element for calorimetrists, can be handled with high precision in a rotating bomb calorimeter. They are able to burn organo-boron compounds completely and form a homogeneous well-characterized final state by converting the boron to fluoroboric acid in aqueous solution.

A principal difficulty which has impeded measurements on the combustion of metals and refractory solids in a bomb calorimeter has been inability



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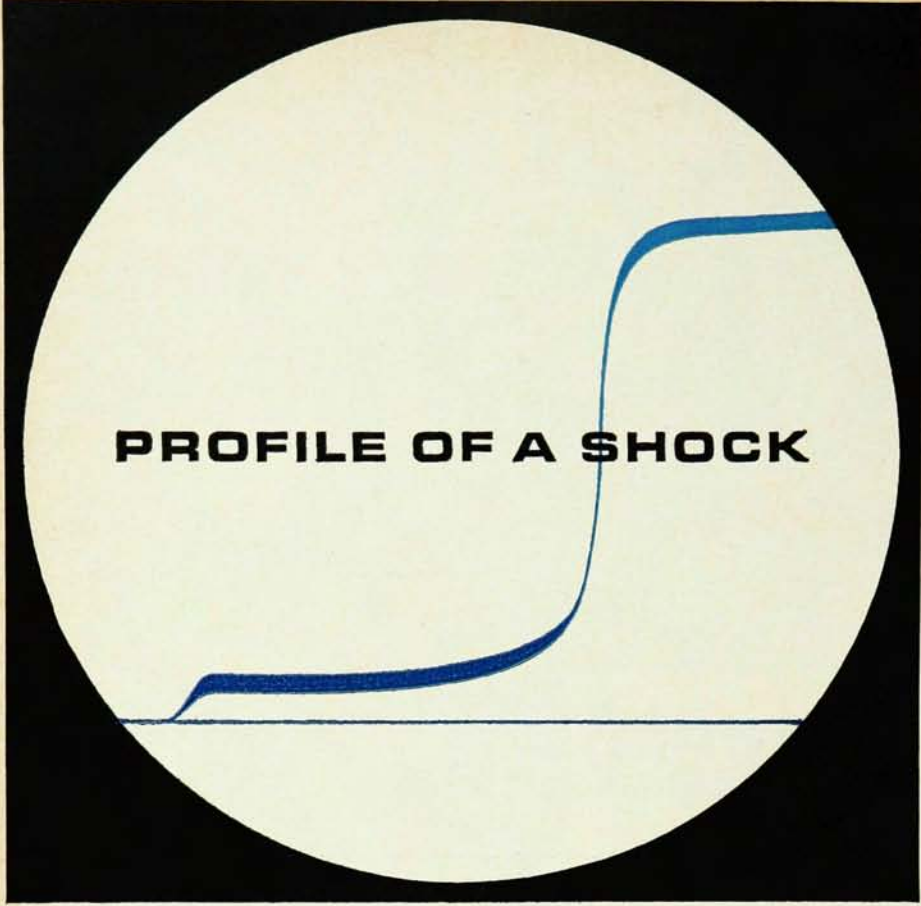
Write for Bulletin S-141.

1. For a description of the proposed revision, see the discussion by F. G. Brickwedde, *Physics Today*, May 1963, p. 24.

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PROFILE OF A SHOCK

This is the shape of a stress-wave due to shock loading a nickel steel specimen. The original trace was recently obtained at Sandia's new \$125,000 compressed gas gun facility where scientists are now studying properties of materials under shock. This facility enables impacting of flat-faced projectiles and specimens at reproducible velocities ranging from 150 to 5700 ft/sec. Furthermore, angular misalignment between impacted surfaces is less than 10^{-3} rad; hence, velocity is imparted to the specimen as a nearly perfect step-function. The two-wave structure above was produced by the impact of a nickel steel projectile traveling at 890 ft/sec. Stress was approximately 26 kbar; observation time, about one microsecond. A quartz gauge technique capable of resolving 10^{-8} sec, developed by Sandia personnel, measured the stress.

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to observe the actual combustion. Slow-motion pictures taken of combustion in a bomb with a window were shown by C. E. Holley, Jr. (Los Alamos Scientific Laboratory). This method, while not in any sense a calorimetric method, gives promise as an auxiliary tool to provide assistance in devising the most suitable conditions for carrying out these heat measurements, which are traditionally very difficult because of the difficulty of obtaining complete and reproducible combustion.

Papers on solution calorimetry were well represented by L. A. K. Staveley (Oxford) and K. W. Dunning (University of Bristol), who presented very ingenious studies of the energies of complex formation of metallic ions in combustion with organic ligands; and by students of Professor Cobble of Purdue University, who reported on precise determinations of specific heats of aqueous salt solutions.

A new topic at the conference was presented in a series of papers dealing with calorimeters for measuring radiation dose. P. Nagl of the International Atomic Energy Agency in Vienna, and E. Schleiger of the US Radiological Defense Laboratory, presented papers in which they described calorimeters for measuring absorbed dose in rads (a rad is 100 ergs/gram); devices of this type have been given increasing attention in the past five years.

It is unfortunately not possible in a report of this kind to mention all the important new contributions that were made. There were altogether 51 papers. The rapid growth of this conference indicates that it is serving a useful purpose in providing a meeting place for calorimetrists to discuss their mutual experimental problems, to learn what others in the field are doing, and to become acquainted with new theoretical and experimental methods of approach.

In order that these goals be effectively met, informal discussion groups were set up one afternoon on the general topics of experimental techniques in enthalpy measurements, experimental techniques in bomb calorimetry, standard reference materials for solution calorimetry, and classification of calorimetric data for publication and retrieval.