Meetings

Thermal Analysis

Thermal analysis may be defined as the study of the properties of a sample under dynamic temperature conditions. The two principal techniques under this heading are thermogravimetric analysis (TGA) and differential thermal analysis (DTA). Thermogravimetric analysis involves continuous recording of weight as a function of increasing temperature. In differential thermal analysis the heat or enthalpic changes associated with physical or chemical changes are recorded as a function of temperature or time as the substance is heated at a uniform rate; this measurement is accomplished by continuously comparing the sample temperature with that of the reference material. The difference in temperature is recorded as a function of furnace temperature.

An international symposium on thermal analysis was held at the Northern Polytechnic, London, England, 13–14 April 1965, and was attended by 323 delegates from 12 countries. The main lectures dealt with the broader aspects of thermal analysis, while details of application and technique were covered in contributed papers.

The main theme which arose from all the discussions was that, as with all instrumental techniques, unless great care is exercised in the interpretation of results, erroneous conclusions may be obtained. The various sources of error in these techniques were emphasized by many speakers. M. Harmelin (C.N.R.S., France) discussed the causes of error in thermogravimetry. She drew attention to the way in which, for example, changes in sample size, crucible shape and material, atmosphere, heating rate, and other factors may influence the result. She also pointed out the need for applying a correction to compensate for the change of crucible buoyancy with temperature. P. D. Garn (University of Akron, Ohio) discussed atmosphere effects in differential thermal and thermogravimetric analysis, and demonstrated that resolution of overlapping reactions may in many cases be improved by using self-generated atmospheres at sub- and supra-atmospheric pressures. He described apparatus to accomplish such resolution in both thermogravimetric and differential thermal analysis. Examples were cited of the examination of barium chloride dihydrate by differential thermal analysis. The first step involves loss of approximately one molecule of water.

$$BaCl_2 \cdot 2H_2O \rightarrow BaCl_2 \cdot H_2O + H_2O$$
$$BaCl_2 \cdot H_2O \rightarrow BaCl_2 + H_2O$$

Under pressures of greater than 4 atmospheres of self-generated water vapor the loss of the second molecule of water occurs in two steps, which have yet to be described.

Garn further discussed the effect of sample size, and showed that with larger sample sizes the diffusion of volatile matter through the sample became an important factor. Harmelin also took up this point and showed that reaction gradients are set up within large samples. This point was still further emphasized by other speakers. F. and J. Paulik, J. Sestak, and D. A. Smith described various types of sample holders for thermogravimetric analysis which would allow easy escape of volatile material; for example, a thin layer of sample on a wide flat dish.

The increase of resolution with decrease of sample size was noted by Mazieres (University of Paris), who described his semimicro- and microapparatus for differential thermal analysis; it accommodates samples as small as a few micrograms and resolves peaks separated by less than 1°C.

The two principal techniques of thermal analysis are complementary. When they are carried out in different apparatuses the comparison of results must be done carefully, bearing in mind the different environmental and experimental conditions. L. Erdey (Technical University, Budapest) described the construction and application of the Derivatograph which overcomes this problem and in which simultaneous DTA and TGA can be carried out on the same sample. F. and J. Paulik also discussed the applications of this instrument.

Another point emphasized throughout the symposium was that TGA and DTA data must be corroborated and must always be complemented by data obtained by other methods, for example, x-ray crystallography, spectroscopy, and macroscopic bench pyrolysis. W. W. Wendlandt, in a lecture entitled "Miscellaneous thermal methods," discussed many of the ancillary thermal techniques. For example, in DTA it is at first difficult to separate those peaks associated with chemical reaction and involving loss of volatile material from those associated with other chemical reactions and phase changes. He described gas evolution analysis (GEA) in which an inert gas stream passed over the sample and then through a gas chromatography detector which records the evolution of gas. Further aids involve actually analyzing the gas evolved and, when GEA indicates evolution of gas, sampling for gas chromatographic or mass spectroscopic analysis. Wendlandt also described the new variation in differential thermal analysis—differential scanning calorimetry. Instead of measuring a differential temperature, the sample temperature is maintained the same as that of the reference material by supplying heat to either the sample or reference material. The heat supplied is then recorded as a function of temperature.

G. Guiochon (Ecole Polytechnique, Paris) discussed the derivation of kinetic data from thermogravimetric data. J. Sestak (Czechoslovak Academy of Sciences) reviewed the published literature on methods of obtaining kinetic data, and showed that the application of all these methods to a few selected systems rendered similar results.

The applications of thermal analysis to inorganic compounds and to organic materials, including polymers, demonstrate the wide range of such analysis. For example, in the study of polymers, differential thermal analysis may be used to "fingerprint" individual polymers, to obtain information on the structure of the polymer from a study of the physical transitions, and to investigate the chemical decomposition of polymers. The application of thermogravimetric analysis is limited to those chemical reactions in which change of weight occurs. Many examples were discussed which showed how thermogravimetric analysis gave information on the temperature stability of polymers, and, by virtue of having a continuous weight recording, showed up intermediates in the decomposition of inorganic compounds. If the nature of the volatile material evolved was known, the formula of the intermediate could be calculated.

The techniques of thermogravimetric and differential thermal analysis have been known for over 50 years but it is only recently that there has been a rapid increase of interest and a widening of its range of application. These recent developments depend upon advances in instrumentation; such advances were reflected in the Apparatus Exhibition, which was arranged in conjunction with the symposium and in which 16 manufacturers were represented.

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Air-Sea Interface

The dynamic interaction between the ocean and atmosphere is a determining factor in designing structures for use at the air-sea interface. Environmental influences acting upon interface structures, and the design of interface structures (in particular, high-speed sailcraft, seagoing aircraft, and the Mohole platform) were discussed at a conference held in Miami, Florida, 22–25 November 1964. Oceanographers, meteorologists, marine and aeronautical engineers, and naval architects attended.

In discussions on the wind field above the air-sea interface, Roll stressed the need for definitive wind measurements. The difficulty of interpreting model experiments was emphasized by Hasselmann, who suggested that wind-wave flumes be designed in such a way that initial conditions can be varied. St. Denis argued that much time and effort would be saved if field experiments were preceded by laboratory experiments with models.

Measurements of Reynolds stress made from Argus Island Tower were described by De Leonibus. The readings of an eddy fluxmeter were compared directly with velocity correlations. The resulting drag coefficient increases slowly with wind speed, although a wide scatter is evident.

The relation between wind stress and the wave spectrum was discussed by Kraus. He emphasized the high wind velocities present immediately above the interface and discussed the drift of monomolecular films at the surface.

Woodcock described some visual observations of Langmuir cells. These cells are held responsible for the weed lines which sometimes develop parallel to the wind. Woodcock's observations show that ballasted bottles also align themselves parallel to the wind. It is likely that the cells extend to the bottom of the mixed layer.

A field study to determine the growth parameters for the initial generation of 17-meter wind waves was described by Snyder. A four-component accelerometer array was towed downwind starting from a windward shore. The resulting growth curves are consistent with Hasselmann's energy equation, but the instability parameter is almost an order of magnitude larger than predicted by Miles.

Review of the history and design of ocean-going catamarans was presented by Choy. The ocean-going catamaran differs from the day-sailing catamaran in its ability to ride a seaway. The bows are built high to prevent tripping, and the underbody profile is somewhat convex. If properly designed the ocean-going catamaran will attain a speed-length ratio of 4 (compared to a ratio of 1.35 for a conventional hull). The day-sailing catamaran is designed to cut through waves rather than ride over them. Hubbard showed several movies of an 18-foot catamaran which competed in the Little America's Cup race. He discussed the inadequacies of tank testing of catamarans and described a tank in which models are towed from the center of effort of their sail plan.

A new type of sailing vessel, the aerohydrofoil, was described by Smith. The aerohydrofoil is theoretically capable of high speeds and small angles of attack. Present models, however, have poor directional stability and require at least four independent controls.

Lill gave a brief description of the Mohole platform, and St. Denis discussed the design of the riser system for this platform. Objections were raised by Spilhaus, who felt that a submerged platform would eliminate many of the problems associated with a surface platform, and by Hasselmann, who, challenging the engineering practice of designing for the catastrophic event, suggested that a statistical approach would be simpler and more to the point.

Turning to the subject of aircraft at the air-sea interface, Griffing reviewed the history of seagoing aircraft and presented sketches of several craft currently in the design stage. He emphasized the need for aircraft capable of taking off and landing routinely at sea. Another aspect of this problem was discussed by Lehnert who described the loss of performance of a gas turbine engine as a result of the ingestion of salt water near the water surface.

The conference closed with a brief exposition by Roll of a shallow-water wave-attenuation study, a summary by Griffing of ground-effects machines (hovercraft), a description by Kraus of a taut-wire spar buoy, and a description by Koczy of a 135-foot power catamaran designed for the Institute of Marine Science.

It was generally agreed that there is still much to be learned about the dynamic interaction between the ocean, atmosphere, and structures at the air-sea interface. The shape of the wind profile above the ocean surface needs to be investigated carefully and extensively. The physical basis for the wind generation of ocean waves is not completely understood. The forces acting on interface structures and the response to these forces need to be investigated in detail. Only then can the design of interface structures become less of an art and more of a science.

The conference was worthwhile in that it brought together for the first time marine scientists, engineers, and architects, and helped to acquaint these groups with one another's problems. Except for several brief discussions of design procedure, however, there was little direct exchange between scientist and engineer. Several important questions concerning the mechanics of interface structures were not discussed: the specification of the forces acting