CALORIMETRY

THE seventeenth annual Calorimetry Conference was held during August 22–24 at the University of California, Berkeley. Hosts for the occasion were the Inorganic Materials Research Division of the Lawrence Radiation Laboratory and the College of Chemistry. Local arrangements were made by a committee comprised of Prof. N. E. Phillips (chairman), Prof. R. Hultgren, Dr. D. N. Lyon and Mr. I. Pratt.

In keeping with the traditions of previous conferences, a wide variety of topics pertaining to calorimetry was discussed, including experimental techniques, results and their interpretation. Thirty-seven papers were presented, the principal one of which was that given as the Huffman Memorial Lecture by Prof. E. F. Westrum, jun. (University of Michigan). Prof. Westrum discussed the "Thermodynamics of Globular Molecules" and set out lucidly the problems of understanding the behaviour of the so-called plastic crystals. Thermodynamic measurements on these substances can yield valuable information about transitions, and about rotation of molecules and molecular groups in the solid. Much of the available experimental information has been obtained by Prof. Westrum and his students.

Invited papers were given by M. L. McGlashan (University of Reading), D. Patterson (University of Montreal), A. M. Karo and A. W. Searcy (University of California). Each of these papers served to emphasize a particular part of the programme. For example, McGlashan's discussion of the calorimetric determination of the change of enthalpy of vapours with pressure and Patterson's application of the Prigogine theory to the explanation of heats of mixing of polymer solutions introduced a series of contributions on measurements of heats of mixing, solution and dilution.

Karo described the information about lattice vibrations which is obtainable from thermodynamic properties of crystalline solids and illustrated his

theme by taking examples of alkali halide crystals. In particular, he showed how accurate experimental heat capacities are sufficient to distinguish between several possible ionic models. Papers contributed in related fields dealt with thermodynamic properties of solid yttrium hydrides, transition metal and technetium hexafluorides, palladium hydride, lithium metal, helium and methanes.

High-temperature thermodynamic properties were introduced by Searcy's contribution on the interpretation of the properties of inorganic solid solutions (uranium–oxygen and cerium–oxygen systems), which was coupled with a plea for more experimental measurements. The particular kinds desired were not represented at the Conference; high-temperature studies which were reported had more to do with the measurement of stored energy.

Many other specific topics were touched on, for example, precision bomb calorimetry, which provides accurate and fundamental information on heats of formation and is the very basis of thermo-chemistry; techniques of micro-calorimetry for measuring very small energy changes; improvement of standards of measuring energy and temperature.

Again, in keeping with the practices of previous conferences, no proceedings will be published. The work discussed will in due course appear in regular journals. A report on the Conference would not be complete, however, without mentioning the annual dinner held at Spenger's Fish Grotto in Berkeley. Dr. Nicholas Kurti of the Clarendon Laboratory, Oxford, was the after-dinner speaker and chose as his topic "What's Cooking", a deceptively calorimetric title. Although he did not, as advertised, prove his text, which was the aphorism, "The discovery of a new dish contributes more to the happiness of mankind than the discovery of a star", he kept his audience thoroughly entertained and no one worried unduly.

GAS CHROMATOGRAPHY

AN informal symposium of members of the Gas Chromatography Discussion Group of the Institute of Petroleum was held on September 7 at the Royal College of Advanced Technology, Salford, with Mr. C. S. G. Phillips in the chair. Dr. Ramage, head of the Chemistry Department, welcomed the Group at the College. The first paper was a repeat by Dr. A. J. P. Martin (Abbotsbury Laboratories, Elstree) of his opening address* to the fourth International Symposium on Gas Chromatography (Hamburg, June 1962) entitled "Future Possibilities in Microanalysis". Dr. Martin stated that much could be gained, particularly in the sciences where the amounts of available materials are severely restricted, if the scale of analytical operations were reduced by a factor of 10^6 or greater. It should be possible to design apparatus to weigh 10^{-9} g at room temperature and 10^{-11} g at a few degrees absolute. In gas chromatography he envisaged the possibility of the column effluent being passed over a directly weighed leaf of adsorbent to give a mass integral chromatogram and

* To be published in full in the *Proceedings of the Hamburg Symposium*.

a system of multiple leaves providing fraction collecting facilities. Time-of-flight mass spectrometry and X-ray crystallography could provide the means of identification. As far back as 1946, Engström (*Acta Radiologica*, Stockholm, Suppl. 63; 1946) had used the characteristic absorption of very long X-rays to carry out an analysis on samples of the order 10^{-9} – 10^{-12} g. The main difficulty in the type of pico-chemistry envisaged by Dr. Martin lay in the limitation imposed by the size of our hands. This was exemplified in the 'stone-age' character of the instruments available for handling sizes observable under a simple microscope. Essentially then, smaller hands would be required and ideally these should have similar translatory and sensory facilities as the hands made by nature. Some form of mechanical–pneumatic system used in conjunction with the human hand was the approach suggested. Although at first sight a reduction of about ten to one might not seem difficult to achieve, it should be borne in mind that the aim would be to design a system capable of reproducing itself by the same reduction factor

without modification of the system until, ultimately, a stage was reached when, possibly, single molecules could be examined. At this final stage the energy of the electron microscope would be a disturbing factor as would Brownian movement, hence the need for the final stage to be able to relay back the sense of touch and be able to operate near the absolute zero of temperature. As the scale of operation was reduced the increased surface to volume ratio of the apparatus would give rise to problems associated with the activity of the surface and the grain structure of metals might pose problems in fabrication. The much-reduced size would, however, allow the use of materials prohibitively expensive on present size scales. Surface tension and viscosity effects would also need to be considered.

In concept, if not as yet in size, the adaptation of conventional laboratory balances as detectors to give mass integral chromatograms described by Mr. S. Thorburn (co-authored by Dr. S. C. Bevan, Brunel College, London, W.3) was a natural follow-on to the paper by Dr. Martin. Initially a standard balance had been used at room temperature with the column effluent passing into a liquid absorber, due correction being made for vapour losses. The present version makes use of a commercially available micro-analytical thermo-balance (the oven of which can be used as a column thermostat with a range far in excess of that required by present high-temperature operation) coupled to a recorder. The absorber is glass cloth impregnated with concentrated sulphuric acid, and experience so far shows it to be quite efficient for a wide range of organic compounds. With the present set-up, a 6-10 component sample of 4-5 mg total weight can be quantitatively determined to an accuracy of ± 2 per cent. One limitation of the present design is the susceptibility to variation in gas flow-rate, but with a dynamically symmetrical design of absorber as suggested in the discussion by Dr. Martin a considerable improvement in sensitivity and stability could undoubtedly be obtained.

The desirability of using a sensitive detector giving results directly in terms of mass rather than a property which, by the time it is traced on to a recorder chart, may be some undefined variable function of mass was made apparent in the third paper of the day, "Studies on the Accuracy of Gas-Liquid Chromatography Analysis", presented by Mr. A. F. Williams (Imperial Chemical Industries, Ltd., Nobel Division, Ayrshire). Despite such difficulties, Mr. Williams showed that by concentrating on two types of detector (thermal conductivity cell and flame-ionization) and two types of injection (capillary pipette and micro-syringe) it was possible to decide on conditions to give the accuracy called for on each type of sample and to provide the service required of an analytical department. All the results reported had been obtained using packed columns. With the thermal conductivity cell, sample sizes less than 1 μ l., and mixtures of benzene, toluene and xylenes of widely differing composition it had been found that with nitrogen as carrier gas it was essential to control closely the sample size in order to obtain accurate results; to a lesser degree this also applied to helium. With other types of sample the control of column loading might not be so critical. Thus in contrast to the benzene-toluene-xylene mixture where a micro-syringe was essential, in the case of the methyl-chlorosilanes the sample pipette originally used by James and Martin was satisfactory for sample addition. Calibration on peak height was preferred to

peak areas obtained with an integrator of the servotachometer type. With a flame-ionization detector, results had been obtained for various benzene-toluene-xylene mixtures using splitter technique and direct injection in dilution in carbon bisulphide. Within themselves the repeatability was generally better than ± 2 per cent of the mean, but agreement between results by the two methods was not quite so good. There was an indication that different calibration factors were required for different sample compositions when the splitter technique was used. Dr. J. N. A. Ridyard queried the need to use a splitter or dilution technique with the flame ionization detector. It had been his experience that subject to suitable design of probe and relative position and size of jet, direct injection of samples of weight well in excess of what Mr. Williams had used was possible without loss of linearity. Mr. I. V. Mortimer reported that the results of a study on the quantitative aspects of a thermal conductivity cell were disappointing. A similar study with the flame ionization detector had shown that for concentrations used with capillary columns there was a minimum value for hydrogen flow-rate to the detector below which the response was non-linear and above which it was linear. The exact form of the response curves was variable dependent on the geometry of the jet and collecting electrode to within quite fine limits. The points of view put by the author and contributors to the discussion might well be summarized by saying that quantitative results can best be obtained by knowing both your sample and your detector.

The afternoon session was devoted to the problem of tabulating and reporting retention data. Dr. A. B. Littlewood (University of Durham) had reviewed the literature and attempted to correlate data in terms of specificity of liquid phase. In the simplest case of alkanes in liquid phases of any type, he found that the latter could be put into one order generally independent of whether the V_g value or the slope of the log V_g -carbon number plot (hereafter referred to as a log-plot) was used as the criterion. In both cases values were greatest for an alkane solute-alkane liquid phase interaction. Values obtained for the relative retentions of successive homologues could also be used to put liquid phases into an order, but generally the differences between values for different liquid phases were only significant for the most polar liquids. The V_g value or slope of the log-plot was recommended for giving an order to the weakly selective phases. The results obtained for relative retentions of successive homologues also applied when a polar grouping was introduced into the solute molecule. For the retentions of a variety of solutes with a non-polar liquid phase an approximate correlation could be obtained by plotting $\log V_g$ against $\frac{n^2 - 1}{n^2 + 2} \cdot M$ where n is the refractive index and M the molecular weight of the solute. From the available data and making use of the relative values of successive homologues there was every indication that the retention of solutes in a given non-polar liquid phase could be predicted to within a factor of two. For gradation of polar and non-polar liquid phases to include diverse types of solutes Dr. Littlewood had attempted to construct plots of the type used by Rohrschneider (*Zeitschrift für Analytische Chemie*, 170, 256; 1959; see also *Journal of Chromatography*, 8, 308; 1962) for classifying liquid phases according to selectivity to alkanes, alkenes and alkynes. With such plots it was found possible to predict the

chromatographic behaviour of a liquid-phase sequence such as dibutyl-, diethyl- and dimethyl-formamides. Deviations from a general liquid phase 'polarity order', for example:

paraffin < dinonyl phthalate < dibutyl phthalate < tricresyl phosphate < methoxy polyethylene glycol
350 < 1,2,3-trans (2-cyano ethoxy propane)

could in some cases be ascribed to solute-solvent hydrogen bonding, but there appeared to be no indications of specific aromatic-aromatic interactions.

Dr. J. F. Smith (Natural Rubber Producers' Research Association, Welwyn Garden City) put the case for presenting retentions relative to the *n*-alkanes; either his own R_{x_9} (relative to *n*-nonane) or the retention index system of Kovats was suitable. The relative merits of bracketing the compound to be characterized with *n*-alkanes in one run, or determining the retention of the compound either on its own, or with one *n*-alkane, or bracketed with two *n*-alkanes and then comparing with a separate run of four *n*-alkanes were discussed as was the use of non-linear log-plots when retentions were measured from the point of injection instead of the air-peak. For detectors not responding to air, methane could be used to give the hold-up if the column temperature were greater than 70° C. Dr. P. A. T. Swoboda presented evidence that the same retention index values were obtained by interpolation from retentions measured from the

point of injection as were obtained from retentions measured from the air peak. With the former procedure, however, as Dr. Smith had mentioned, the slope of the log-plots had to be determined from the asymptote. Published V_g values for alkyl nitro- and nitrate compounds (Evered and Pollard, *Journal of Chromatography*, 4, 451; 1960) were used by Dr. Swoboda to illustrate an example of the temperature independence of values of retention index. A written contribution by H. van den Dool and P. de C. Kratz showed that there was good agreement between values of retention index obtained under isothermal and temperature programmed conditions.

Mr. B. A. Knights suggested that in steroid chemistry the gas-liquid analogue (*Nature*, 194, 833;

1962) of the R_M value $\left[\log \left(\frac{1}{R_F} - 1 \right) \right]$ of liquid-liquid systems which could be broken down into contributions from the parent molecule and functional groups should be used to keep the nomenclature in this field as uniform as possible.

In summary, it would appear from the papers and discussion during the afternoon session that once a liquid phase has been characterized in terms of the slope of the log-plot for *n*-alkanes at several temperatures, workers need only report their results relative to one or more *n*-alkanes and the devotees to each system would soon provide a wealth of derived data.

C. G. SCOTT

COASTAL PROCESSES

A SEMINAR on "Coastal Processes" was held at the Department of Geography, University of Cambridge, during June 29-30. Thirty scientists attended the seminar, including geographers, oceanographers, engineers and geologists, most of whom were from the United Kingdom. Those attending from overseas were four engineers from the Dutch Rijkswaterstaat, including J. B. Schijf, director of research, Prof. A. J. Guilcher of Paris and three Australian engineers. Prof. J. A. Steers of Cambridge acted as chairman for the five sessions into which the discussions were divided, namely: (a) wave generation as it affects sediment movement; (b) beach processes, in the surf zone and beyond; (c) beach cycles, annual and long term; (d) equilibrium shapes of coastline in plan; (e) world-wide sediment movement.

Wave generation. For the purposes of studying movement of sediments it was pointed out that only two categories, storm waves and swell, need be considered. The former are still within the fetch while the latter have moved outside it and travel in ever-enlarging circles across the oceans of the world. Waves are seen to be an efficient means of spreading the energy of the wind in given storm areas over the surface of the Earth. Seas, partially or fully enclosed, experience less swell action than coasts bordering the major oceans and, therefore, the beach profiles are significantly different.

Beach processes. The breaking of waves on the beach creates two distinct zones in which sediment is transported: the surf zone and the offshore area beyond the breaker line. Although great turbulence and high velocities exist in the surf zone, more sediment can be transported in the offshore area because of the greater width of action. This width can be miles in some cases, out to depths of 40 fathoms for

10-sec waves and 100 fathoms for 15-sec waves. The difficulties of verifying the theory on this movement were outlined by many speakers.

The action of swell accreting a beach was discussed with emphasis placed on the mass transport¹ of the waves in moving the sediment towards the shore. It was noted how the ripple formation on the sea-bed changes with variations in wave height, period and direction—this disturbed state producing larger rates of sediment transport. The action of storm waves on the steep swell beach profile was seen to be a combination of a hydraulic jump from the backwash occurring at a point on the beach face where the sand is in quasi-suspension due to the excessive ground-water returning to the sea at this point^{2,3}. However, after the material has been forced into an offshore bar the erosion ceases since waves are then dissipated on the bar.

Beach cycles. Storm waves, due to their short duration, are not significant in moving sediment along the coast. Swell, on the other hand, being produced consistently from wind systems, which are repetitive year in and year out, moves material in one particular direction when returning it from the offshore bar to the beach. Any interference with the longshore drift can result in erosion of the offshore area, which then requires more sediment during the next storm sequence before the bar is sufficiently high to protect the beach. Thus, storm waves display the previous erosive action of the swell.

Although most of the discussion related to wave action at a constant sea-level it was noted how tidal fluctuations spread the energy of waves over a greater width of beach profile. The combined action of (a) tidal streams, (b) the salt water wedge and (c) wave propagation into an estuary, causes continuous siltation.