

mainly between depths of 50 and 200 metres, symmetrical about the equator and known to occur over most of the width of the Pacific Ocean, while all the adjoining water, above, below, north and south, flows in the opposite direction. Interpretation of previous climates from the study of the stratigraphy of the deep-sea sediments seems to be one of the most popular oceanic studies, and there was a strong plea for samples of older sediments from depths well below the level attainable by coring. Quite shallow bore-holes would give information as valuable as the much discussed deep bore. It might be easier to plot previous positions of the equator from the carbonate content of the sediments than to plot previous positions of the poles from evidence of previous magnetism. Most of the geologists seem to feel that there ought to be a much greater depth of sediments in the ocean.

Discussions on "Boundaries of the Sea" dealt with the effects of land masses and types of coast and sea bottom on the plant and animal populations. The rather special conditions in bays and estuaries were emphasized. The physical papers dealt with the near-shore circulation. One of the most striking papers gave a preliminary survey of the very complex thermal structure in the Straits of Gibraltar obtained with the new towed chain of thermistors. Prof. W. H. Munk's morning lecture on the spectrum of sea-level, from ordinary waves to changes in mean sea-level, was one of the most appreciated by the Congress, and the relevant afternoon discussion dealt with a wide range of contributions about effects of pressure, wind, climate and seismic disturbances. Further afternoons were devoted to the interchange of energy between sea and air, and to proposed methods for predicting surface conditions and changes in currents. There was a very interesting account of observations relating surface slicks to internal waves in a shallow thermocline. The internal waves travelled in the same direction as the surface waves and the slicks also moved slowly in the same direction.

The section on "Cycles of Organic and Inorganic Substances" included discussions of the chemistry of sea water, the occurrence of biologically active substances, including vitamins and trace elements, primary production, nutrient relationships, balance between living and dead organic matter, exchanges between the sea and sediments and between the sea

and atmosphere. C. E. Lucas and J. H. Steele of Aberdeen and L. H. N. Cooper of Plymouth gave morning lectures. There was enough in this section alone to make a conference.

One of the most striking features of the Congress was its evidence of the expanding interest of geologists in the ocean. Biology, for the first time at such a meeting, probably took second place, and except for the new Soviet expeditions it tended to be concentrated in waters not far from shore. The physics of the sea had a good deal to show for the first time, and, not least significant, it could at last be seen to be making observations to check theories.

The morning lectures will be published, and everyone attending the Conference had preprints of abstracts of all the papers contributed to the discussions, a very formidable volume of 1,027 pages. The simultaneous translations provided by the United Nations staff in English, French and Russian were magnificent. We were able to carry on active discussions with Soviet scientists and occasionally listen to them arguing with each other. The facilities of the United Nations building for a large assembly with discussion groups are quite extraordinary. Most of the 1,200 who registered for the Congress seemed to be staying at the Commodore Hotel only a few blocks away, and there was always someone interesting to talk to. The Soviet research ship *Michael Lomonosov*, and five American ships, *Atlantis*, *Chain*, *Crawford*, *Maury* and *Gibbs* were lying at one pier and the French *Calypso* at another. There was a good programme of social events including a particularly agreeable visit to the New York Zoological Park.

One might penetrate deeper into the science at a smaller meeting, but there could be no better way of getting an impressive though perhaps general idea of the increasing interest and advance in all aspects of the subject. For everyone except the organizers it was in fact rather a holiday, and at the same time a most remarkable opportunity for forming new ideas, correcting old ones and thinking what to do next. There can be no doubt that some of the work begun there will be continued in growing friendliness by scientists all over the world. All marine scientists, and especially those privileged to attend, owe a great debt to Dr. Mary Sears and her organizing committee, to all others who helped, and not least to the United Nations.

G. E. R. DEACON

DEVELOPMENTS IN THERMODYNAMICS

A SYMPOSIUM on Thermodynamics was held during August 20-25 at Fritzens-Wattens, near Innsbruck, Austria, under the joint sponsorship of the Deutsche Bunsen Gesellschaft für Physikalische Chemie, and the International Union of Pure and Applied Chemistry, the latter through its Commission on Thermodynamics, the Sub-Commission on Experimental Thermochemistry and the Sub-Commission on Experimental Thermodynamics. The symposium was under the general direction of Prof. K. Schäfer (president of the Deutsche Bunsen Gesellschaft für Physikalische Chemie, and secretary of the Commission on Thermodynamics) with the local arrangements being handled by Prof. E. Cremer, of the University of Innsbruck. Fifty papers were

read, and there were 135 participants, representing seventeen countries, including thirty from North America and twenty from Great Britain.

Experimental Thermochemistry

The first part of the symposium, under the general heading "Experimental Thermochemistry", contained twenty-three papers. Eight of these were studies in bomb-combustion calorimetry. The most novel paper of this group, presented by W. N. Hubbard (Argonne National Laboratory) gave a preliminary account of the successful development of a bomb-calorimeter for combustions in an atmosphere of fluorine gas. The bomb is made of nickel, which is rendered inert to

attack during the combustion process by a careful pre-fluorination treatment, so that the inner surfaces become coated with a stable nickel fluoride film. Combustion experiments of an exploratory character have been made on twenty-five metals and fifteen inorganic compounds, and three-quarters of these immediately appeared to be suitable for accurate calorimetric study.

Two papers described recent studies using the rotating-bomb calorimeter: in this, the bomb is charged before combustion with a suitable solvent, and rotated after combustion to produce a uniform solution of the combustion products in a definite thermodynamic state. The method has been developed over recent years, and has enabled highly accurate combustion data to be obtained for a variety of organic sulphur-containing compounds. D. W. Scott (Bureau of Mines, Bartlesville) described the further application of the technique to organic fluorides and to some organometallic compounds: results obtained on fifteen organic fluorides were presented, and values reported for the heats of formation of lead tetramethyl, lead tetraethyl, and dimanganese decacarbonyl. The application of the method to organic bromides was described by L. Bjellerup (Lund), and the derived heats of formation critically compared with those independently available from heats of bromination. Comparison of the heats of formation from combustion with those from reaction heats measured by Lacher and his associates at Colorado is satisfactory.

The advantages of polythene ampoules over glass ampoules as containers for liquids in combustion calorimeters were discussed by H. Mackle (Belfast); in the discussion, it transpired that several investigators have experimented with plastic ampoules with considerable success, and that polythene and polyesters are suitable materials to use. Three papers reported new combustion studies by conventional 'static-bomb' procedures: J. D. Cox (National Chemical Laboratory, Teddington) presented results on phenol and the three cresols; M. Colomina (Madrid) gave the results of an investigation of five alkylphenylketones and of the three toluic acids; and J. Tjebbes (Lund) reported on the heats of combustion of butanal and five related compounds. In these studies, the error limits were of the order 0.01–0.02 per cent, which is fairly representative of the degree of precision attainable by modern combustion calorimetric techniques in favourable cases. C. T. Mortimer (Keele) reported heat of combustion data on triphenylphosphine, triphenylphosphine oxide, and triethyl phosphate. These compounds can scarcely be described as 'favourable cases' for combustion study, in view of the difficulty of analysing the products of combustion, so that the error limits of only 0.1 per cent reported by Mortimer are encouragingly small, and suggest that further thermochemical studies on organophosphorus compounds of biochemical importance should be rewarding.

Reaction calorimetry (heats of reactions other than combustion) was represented by three papers: E. J. Prosen (National Bureau of Standards, Washington) gave an account of the extensive studies on the thermochemistry of boron hydrides, including the measurement of the heats of thermal decomposition of the boron hydrides into elements, of their heats of hydrolysis, and heats of chlorination. The heat of formation of boron trichloride from elements has also been measured. Reliable values are now available for the heats of formation of the

boron hydrides and of boric acid. Values were derived for the bond-energy terms of various boron bonds, including the tricentric 'bridge bonds' involving boron atoms. The empirical scheme proposed by Prosen was applied to interpret structural features of the more complex hydrides of boron. H. A. Skinner (Manchester) described some thermochemical studies on reactions of diborane, in this case the addition reactions of diborane with olefines to form boron tri-alkyls. These reactions occur rapidly in diglyme solvent at room temperature, and provide a promising route to the heats of formation of the boron tri-alkyls. N. N. Greenwood (Nottingham) described the application of solution calorimetry to the measurement of heats of formation of 1:1 and 1:2 donor-acceptor complexes of gallium trichloride, gallium tribromide, boron trichloride and boron tribromide with various oxygen and nitrogen donors. For a given ligand, the heats of formation of the tribromide complexes are consistently greater than for the corresponding trichlorides, and the heats of reaction of boron trichloride with nitrogen donors are larger than those of gallium trichloride with the same ligands.

Two papers dealt with the thermochemistry of alloys. O. Kubaschewski (National Physical Laboratory, Teddington) reviewed calorimeters suitable for measuring the heat of formation of alloys, with particular reference to calorimeters developed at the National Physical Laboratory for direct measurements on solid alloys formed by heating powdered metal mixtures at high temperatures. A. Schneider (Göttingen) reported directly measured heats of formation of InSb, MgZn₂, MgZn and Mg₂Zn₁₁, and indirectly determined free energies of formation of Fe₂Zr, Al₂Zr, Al₃Zr₂ and Al₃Zr₄.

There were three contributions concerned with the heats of mixing of liquids. In one of these, M. L. McGlashan (Reading) emphasized that measurements on heats of mixing should be carried out under conditions in which the vapour phase is entirely eliminated, and described an ingenious calorimeter for this purpose. Heats of mixing of pairs of compounds from the series Si(CH₃)_{4-n}Cl_n, and from the series C(CH₃)_{4-n}Cl_n were reported, and discussed in terms of the 'quasi-chemical approximation'. Mixing heats in the binary and ternary systems formed from acetic acid, pyridine and a normal paraffin hydrocarbon (hexane, heptane, etc.) were reported by W. Woycicki (Warsaw). W. Wagner (Dresden) described a series of measurements of activity coefficients, heats of mixing and volumes of mixing of the chlorotoluenes in benzene solvent.

Studies of chemical equilibria were the subject of two papers: in one of these, S. Sunner (Lund) described the use of the gas-phase chromatographic technique to analyse the disproportionation reaction $\text{MeSSMe} + \text{EtSSEt} \rightleftharpoons 2\text{MeSSEt}$, at 25° C. and 60° C. A. Pacault (Bordeaux) spoke of a series of equilibrium studies on double decomposition reactions in the solid state between barium sulphate and sodium carbonate and potassium carbonate.

The thermochemistry of tellurium carbonate, tellurium thiocarbonate and barium thiocarbonate, determined from dissociation pressures measured over a temperature range, was described by G. Gattow (Göttingen), and the formation and thermodynamic stability of mixed halides, for example, CuClBr, by R. Perret (Dijon).

I. Wadsö (Lund) described a novel adiabatic calorimeter for the direct measurement of heats of

vaporization at 25° C. suitable for liquids having a vapour pressure of 5–100 mm. mercury at room temperature. The accuracy achieved was of the order of 0.5 per cent.

The accepted value for the heat of dissociation of nitrogen was questioned by G. Glockler (Durham, N.C.), and L. H. Long (Exeter) raised the interesting problem of the relation between bond dissociation energies and valence-state excitation energies, by specific reference to experimental data available on metal-carbon bonds.

This first part of the symposium was summed up by F. D. Rossini (Pittsburgh) and by J. Coops (Amsterdam). Prof. Rossini, reflecting on thirty years of thermochemistry, recalled the stages in its development. First, to design calorimeters of sufficient accuracy; then to prepare compounds of sufficient purity, and now to extend the range of investigation to substances more difficult to prepare, to purify, and to analyse, requiring full use of all the tools of modern analysis.

Physical Constants

The second part of the symposium, arranged by the Commission on Thermodynamics, contained six papers. The first of these, given by F. D. Rossini (Carnegie Institute, Pittsburgh), concerned the present state of knowledge on the fundamental constants of physical chemistry. Five of these have to be determined by experiment; the others are defined by international agreement. In addition, there are auxiliary constants which derive from the fundamental constants. Since 1951, the ice-point of water has become a defined constant, and improved values have become available for the constants, h , c , e , F and N . In 1960, it is proposed to adopt a new scale of atomic weights based on carbon-12 = 12.0000, which will differ from the present chemical scale by 42 p.p.m., and from the present physical scale by 317 p.p.m.

There were three papers on the thermodynamic scale of temperature, and its realization through the international scale, given by Van Dijk (Leyden), H. Moser (Braunschweig) and C. Tingwaldt (Berlin).

In the range 0–90° K., new measurements have been made on the boiling-points of helium and oxygen, with results which differ by only 1/1,000° and 1/100°, respectively, from the older values of 1937 and 1927. The points 4.215° K. and 90.18° K. (relative to the ice-point = 273.15° K.) representing the boiling-point of helium and oxygen may be regarded as in practically complete agreement with the thermodynamic scale. For n -H₂, the most recent measurements of the boiling-point by various investigations gives the mean value 20.379° K. Secondary fixed points in this region are shown in Table 1.

In the range between the two fixed points of the boiling-point of oxygen (–182.97° C.) and the boiling-point of sulphur (440.60° C.), which is spanned in the international scale by measurement

using the platinum resistance thermometer and the three-term formula, the deviations $\Delta T (= T$ (thermodyn.) $- T$ (internat.)) vary from +0.04° at –80° C. to +0.13° at 400° C. In the range from the boiling-point of sulphur to the melting-point of gold, in which the international scale relies on the interpolation formula for the e.m.f. of a platinum/platinum-rhodium element, the deviations ΔT reach as high as 1.7° C. It is suggested on the basis of new measurements that the melting-point of gold is 1,064.76° C. in place of 1,063°, as accepted by the international scale. This is a large change to make, and until more evidence is available it is premature to make the change in the international scale.

A change in the radiation constant from 1.438 to 1.4388, coupled with an increase of 1.76° C. in the defined melting-point of gold, would eliminate the differences between the international and thermodynamic scales above 1,500° K.

The measurement of temperatures above the gold point by optical pyrometry was discussed by C. Tingwaldt, with particular reference to experimental methods of obtaining ideal black-body radiation from a glowing solid. The lateral radiation from a glowing metal is extensively polarized 'non-black' radiation: by allowing radiation from one source to fall at an angle of 45° on to a glowing metal strip, the combined radiation (reflected and emitted) from the strip is unpolarized, black radiation corresponding to the temperature of the glowing source.

There were two papers describing new designs of calorimeter. One of these, by A. R. Meetham (National Physical Laboratory, Teddington) reported on the design and use of an aneroid bomb-calorimeter made of silver, and vacuum-jacketed, for measuring heats of combustion. The heat transfer coefficient of the calorimeter is very much smaller than that of stirred-water calorimeters. The internal volume is 97 ml., and 0.2 gm. benzoic acid on combustion gave a 3.5 deg. C. temperature rise. The standard deviation of individual estimates of the heat of combustion of benzoic acid was less than 1 part in 5,000.

F. E. Wittig (Munich) described the constructional details and operation of a high-temperature calorimeter for thermal studies on metallic alloys.

Phase Changes in Condensed Systems

The third part of the meeting had as its subject "The Thermodynamics of Phase Changes in Condensed Systems", and was sponsored by the Sub-Commission of Experimental Thermodynamics. Introducing the first session, Prof. D. M. Newitt (Imperial College of Science and Technology, London) said that the object of this meeting, and of its predecessor in London in 1957, was to encourage work to fill the gaps in our knowledge of thermodynamic properties, and especially of those of pure substances.

The majority of the speakers discussed the phase transitions of solids. There were two introductory reviews. The first was by J. E. Mayer (Chicago), who gave a lucid account of the thermodynamics of phase changes in terms of the singularities of the Helmholtz free-energy and emphasized how restricted were the types of transition that could be adequately treated by the present developments of statistical mechanics. The second was by J. P. McCullough (Bureau of Mines, Bartlesville), who outlined an empirical division into seven types of the solid-solid transitions of hydrocarbons and of related substances.

Table 1. SECONDARY FIXED POINTS

Gas	Boiling-point (° K.)	Triple-point (° K.)	λ -point (° K.)
Argon	83.81		
Nitrogen	77.35		
Oxygen		54.34	
p -Hydrogen	20.27	18.81	
n -Hydrogen		13.95	
Helium			2.172

A. R. Ubbelohde and his colleagues, Miss E. Rhodes and E. R. Buckle (Imperial College of Science and Technology, London), contributed a group of three papers which discussed the mechanism of melting and freezing. They demonstrated most convincingly that the classical thermodynamic picture of melting as the sharp intersection of two unrelated free-energy curves was inadequate for material composed of complex molecules or ions.

The largest group of papers in this section were detailed studies of particular solid systems. Silver oxide was shown by K. S. Pitzer (Berkeley) to have two anomalous regions in its heat-capacity curve. The first, in the region of 20–40°K., was still without a verified explanation, but the second, 370–470°K., was an annealing of surface and crystal defects. J. G. Aston (Pennsylvania State University) and E. F. Westrum (Michigan) both presented measurements of the heat capacities of systems containing highly symmetrical organic molecules, the *molécules globulaires* of Timmermans. Such systems are of particular interest since the symmetry and 'smoothness' of the molecules allow them to melt with respect to their orientations without disrupting the crystal. This orientation energy and entropy are acquired at one or more transitions below the true melting point. J. E. Spice (Liverpool) reported a detailed study of mixtures of ethylene dichloride and dibromide. The former has long been known to have a broad maximum in its heat-capacity curve at 180° K. On dilution with dibromide the peak moves at first to lower temperatures and becomes less pronounced. The behaviour of the system is, however, complicated by the partial immiscibility of the two solids.

The thermodynamic studies of indane and indene by D. R. Stull (Dow Chemical Co., Michigan) were most notable for the high degree of 'automation' in his calorimeter. This led to many questions regarding the time taken to reach equilibrium in many solid systems.

The magnetic transitions of the divalent salts of manganese, iron, cobalt and nickel were reviewed by J. W. Stout (Chicago). These systems provided unusually elegant examples of the entropy ($R \ln n$) associated with n available electronic states per ion. W. E. Wallace (Pittsburgh) has made a very detailed study by calorimetry and by electrical, magnetic and

X-ray examination of the differences between the α and β phases of tantalum hydride and tantalum deuteride. The results were interpreted in terms of differing amounts of short-range and long-range order in the allocation of the hydrogen atoms to the interstitial sites. G. M. Schwab (Munich) reported a study of the α to β phase change in cobalt.

The last group of papers were those that dealt primarily with liquid phases, or in which the interest was in the application of theories of mixtures to the results. R. Heastie (Queen Mary College, London) had studied the phase equilibria of mixtures of krypton with argon and with xenon. The systems were miscible in both solid and liquid phases at the melting-point and the form of the melting curves provided a test for the lattice theories of solution of Prigogine. Unfortunately, true equilibrium in the solid phases was not always achieved. T. M. Storvick and J. M. Smith (North-Western University, Illinois) have studied the thermodynamic properties of mixtures of hydrocarbons and alcohols in liquid and gaseous phases at temperatures up to the gas-liquid critical points. The deviation of their results from those of purely hydrocarbon mixtures was interpreted in terms of the degree and heat of polymerization of the alcohol molecules. J. S. Rowlinson (Manchester) demonstrated that lower critical solution points are not confined to polar mixtures but are commonly found also in binary hydrocarbon mixtures if the size ratio of the constituent molecules is sufficiently large. This behaviour appears to be the rule for high-polymer solutions, almost all of which separate into two phases above the normal boiling-point of the solvent. Finally, R. I. Munn (Vienna) reported a careful re-examination of the phase-boundary curve near the lower critical solution point of the system water + triethylamine. The curve has an unusual, and unexplained, point of inflexion.

Three papers less easy to classify were given by K. S. Pitzer on "Irreversible Thermodynamics", D. White (Columbus, Ohio) on "*o-p* and Isotope Separations by Preferential Adsorption at Low Temperatures", and by G. Watelle-Marion (Dijon) on a spectrophotometric study of the ionization of a divalent-metal salt.

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OBITUARY

Prof. F. Kögl

PROF. F. KÖGL died on June 6 at Utrecht after an illness of about two years. From 1930 until his death at the early age of sixty-one, he had been professor of organic chemistry and of biochemistry at the State University of Utrecht.

Fritz Kögl was born on September 19, 1897, at Munich. He studied chemistry under such famous teachers as H. Wieland, H. Fischer and A. Windaus and became well known himself at an early age by his studies of natural pigments produced by certain bacteria and fungi. While a *Privatdozent* at Göttingen, he was called to a professorship at Utrecht in 1930 as the successor of Van Romburgh and of Ruzicka. Here he widened his field of activities enormously. Interest in growth phenomena of plants

led to the isolation and characterization of the auxins. He and his co-workers were the first to recognize β -indolylacetic acid as a natural plant-growth hormone. The consequences of this work are well known to all dealing with the theoretical and practical aspects of plant growth. His studies of growth factors for micro-organisms led to the isolation and the partial characterization of biotin.

From normal growth processes Kögl turned his attention around 1939 to the abnormal growth occurring in animal tumours. He developed a daring hypothesis based on a presumed loss of stereospecificity, resulting in the incorporation of D-amino-acids in tumour proteins. Although this theory could not be maintained against experimental evidence, it proved very stimulating for the continued biochemical approach to protein chemistry. During