Meetings

Chemical Thermodynamics Discussed at Symposium Held near Innsbruck, Austria

A symposium on chemical thermodynamics was held 20–25 August at Fritzens-Wattens, near Innsbruck, Austria, under the joint sponsorship of the Deutsche Bunsen Gesellschaft für Physikalische Chemie and the International Union for Pure and Applied Chemistry, the latter through its Commission on Chemical Thermodynamics, its Subcommission on Experimental Thermochemistry, and its Subcommission on Experimental Thermodynamics. The symposium was under the general direction of K. Schäfer (president of the Deutsche Bunsen Gesellschaft für Physikalische Chemie and secretary of the Commission on Chemical Thermodynamics), and the local arrangements were handled by E. Cremer of the University of Innsbruck. Fifty papers were read, and there were 135 participants representing 17 countries; 30 were from North America.

Thermochemistry

In the first part of the symposium, on "Experimental Thermochemistry," 23 papers were presented. 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 impervious to attack during the combustion process by a careful prefluorination treatment so that the inner surfaces become coated with a stable nickel fluoride film. Combustion experiments of an exploratory character have been made on 25 metals and 15 inorganic compounds, and three-quarters of these appeared to be immediately suitable for accurate calorimetric study.

Two papers described recent studies in which the rotating-bomb calorimeter is used. 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 the last few years and has made it possible to obtain highly accurate combustion data for a variety of organic sulfur-containing compounds. D. W. Scott (Bureau of Mines, Bartlesville, Okla.) described the further application of the technique to organic fluorides and to some organometallic compounds. The results obtained on 15 organic fluorides were presented, and values were 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, Sweden), and the derived heats of formation were critically compared with those independently available from heats of bromination. The values for heats of formation from combustion compare satisfactorily with those from reaction heats measured by Lacher and his associates at the University of Colorado.

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 developed that several investigators have experimented with plastic ampoules with considerable success, and that Polythene and polyesters are suitable materials. Three papers reported new combustion studies by conventional "static-bomb" procedures: J. D. Cox (National Chemical Laboratory, Teddington) presented results on phenol and 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 limits of error were of the order of 0.01 to 0.02 percent; this is fairly representative of the degree of precision attainable by modern combustion calorimetric techniques in favorable cases. C. T. Mortimer (University College of North Staffordshire, Keele) reported heat of combustion data on triphenylphosphine, triphenylphosphine oxide, and triethyl phosphate. These compounds can hardly be described as "favorable cases" for combustion study, in view of the difficulty of analyzing the products of combustion, so the limit of error of only 0.1 percent reported by Mortimer is encouragingly small and suggests 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 (Washington, D.C.) gave an account of the extensive studies at the National Bureau of Standards on the thermochemistry of boron hydrides, in which measurements have been made of the heats of thermal decomposition of the boron hydrides into elements, of their heats of hydrolysis, and of their heats of chlorination. The heat of formation of BCl_3 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 (University of Manchester) also described some thermochemical studies on reactions of diborane—in this case the addition reactions of diborane with olefines to form boron trialkyls. These reactions occur rapidly in Diglyme solvent at room temperature and provide a promising route to determination of the heats of formation of the boron trialkyls. N. N. Greenwood (University of Nottingham) described the application of solution calorimetry to the measurement of heats of formation of 1:1 and 1:2 donor-acceptor complexes of $GaCl_3$, $GaBr_3$, BCl_3, and BBr_3 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 formation of BCl_3 with nitrogen donors are larger than those of $GaCl_3$ with the same ligands.

Two papers dealt with the thermochemistry of alloys. O. Kubaschewski (National Physics Laboratory, Teddington) reviewed calorimeters suitable for measuring the formation heats of alloys, with particular reference to calorimeters developed at the National Physics Laboratory for direct measurments on solid alloys formed by heating powdered metal mixtures at high temperatures. A. Schneider (Göttingen) reported directly measured heats of formation of InSb, $MgZn_2$, MgZn, and Mg_2Zn_{11}, and indirectly determined free energies of formation of Fe_2Zr, Al_2Zr, Al_3Zr_2, and Al_3Zr_4.

There were three contributions concerned with the heats of mixing of liquids. In one of these, M. L. McGlashan (Reading University) emphasized that measurements of heats of mixing should be carried out under conditions in which the vapor phase is entirely eliminated;

he described an ingenious calorimeter for this purpose. Heats of mixing of pairs of compounds from the series $SiCH_3)_{4-n}Cl_n$ and from the series $C(CH_3)_{4-n}Cl_n$ 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, and so on) 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 analyze the disproportion reaction $MeSSMe + EtSSEt \rightleftharpoons 2MeSSEt$, at 25° and 60°C. A. Pacault (Bordeaux) spoke of a series of equilibrium studies on double decomposition reactions in the solid state between $BaSO_4$ and Na_2CO_3 and K_2CO_3.

The thermochemistry of Tl_2CO_3, Tl_2CS_3, and $BaCS_3$, 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) were discussed 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 vapor pressure of from 5 to 100 mm-Hg at room temperature. The accuracy achieved was of the order of 0.5 percent.

The accepted value for the heat of dissociation of N_2 was questioned by G. Glockler (Durham, N.C.) and L. H. Long (Exeter University) 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). Rossini, reflecting on 30 years of thermochemistry, recalled the stages of development in this field: first, design of calorimeters of sufficient accuracy; second, preparation of compounds of sufficient purity; and now, extension of the range of investigation to substances more difficult to prepare, to purify, and to analyze, through the use of all the tools of modern analysis.

Chemical Thermodynamics

In the second part of the symposium, arranged by the Commission on Chemical Thermodynamics, six papers were presented. The first of these, given by Rossini, 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. It is proposed that, in 1960, a new scale of atomic weights based on $C^{12} = 12.0000$ be adopted; this differs from the present chemical scale by 42 parts per million, and from the present physical scale by 317 parts per million.

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

In the range 0° to 90°K, new measurements have been made on the boiling points of helium and oxygen, with results which differ by only 0.001° and 0.01°, respectively, from the older values of 1937 and 1927. The values 4.215° and 90.18°K (relative to an ice point of 273.15°K) for the boiling points of helium and oxygen may be regarded as in practically complete agreement with the thermodynamic scale. For n-H_2, the most recent measurements of the boiling point by various investigations give the mean value 20.379°K. For secondary fixed points in this region there are: argon, boiling point 83.81°K; nitrogen, boiling point 77.35°K; oxygen, triple point, 54.34°K; p-hydrogen, boiling point 20.27°K; n-hydrogen, triple point, 13.95°K; p-hydrogen, triple point 13.81°K; helium, λ-point, 2.172°K.

In the range between the two fixed points of the boiling point of oxygen (−182.97°C) and the boiling point of sulfur (440.60°C), which is spanned in the international scale by measurements based on the platinum resistance thermometer, the deviations ΔT ($= T_{\text{thermodyn.}} - T_{\text{internat.}}$) vary from + 0.04° at −80° to <0.01° between 0 and 100° to + 0.13° at 400°C. In the range from the boiling point of sulfur to the melting point of gold, in which the international scale relies on the interpolation formula for the electromotive force of a Pt/Pt-Rh element, the deviations ΔT are as high as 1.7°C. It is suggested on the basis of new measurements that the melting point of gold is 1064.76°C rather than 1063°, as accepted in the international scale. This is a large change, and until more evidence is available, it is too soon 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 the thermodynamic scales above 1500°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° onto 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.

Two papers were presented in which calorimeters of new design were described. One of these, by A. R. Meetham (National Physics 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 of benzoic acid on combustion gave a temperature rise of 3.5°C. The standard deviation of individual estimates of the heat of combustion of benzoic acid was less than 1 part in 5000.

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, on "The Thermodynamics of Phase Changes in Condensed System," was sponsored by the subcommission on experimental thermodynamics. Introducing the first session, D. M. Newitt (Imperial College, 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 in our knowledge of pure substances.

Most 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 pointed out how restricted are the types of transition that can be adequately treated by the present developments in 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.

A. R. Ubbelohde and his colleagues E. Rhodes and E. R. Buckle (Imperial

College, London) contributed a group of three papers on 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 is 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, at 20° to 40°K, is still without a verified explanation, but the second, at 370° to 470°K, is 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 *molecules 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 orientational energy and entropy is 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 behavior 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.) were most notable for the high degree of "automation" in the calorimeter. This led to many questions from an audience very conscious of the time it takes 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 Ta_2H and Ta_2D. 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 was that which dealt primarily with liquid phases, or in which interest centered 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 (Northwestern University) 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 for purely hydrocarbon mixtures was interpreted in terms of the degree and heat of polymerization of the alcohol molecules. J. S. Rowlinson (University of 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 behavior 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 reexamination of the phase boundary curve near the lower critical solution point of the system water and triethylamine. The curve has an unusual, and unexplained, point of inflection.

Three papers less easy to classify were those by K. S. Pitzer (Berkeley) on irreversible thermodynamics, by 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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Forthcoming Events

January

28–30. Mathematical Assoc. of America, 43rd annual. Chicago, Ill. (H. M. Gehman, Univ. of Buffalo, Buffalo 14, N.Y.)

28–30. Western Soc. for Clinical Research, 13th annual, Carmel-by-the-Sea, Calif. (W. N. Valentine, Western Soc. for Clinical Research, Univ. of California Medical Center, Dept. of Medicine, Los Angeles 24.)

29–30. American Group Psychotherapy Assoc., Inc., 17th annual conf., New York, N.Y. (American Group Psychotherapy Assoc., Inc., 1790 Broadway, New York 19.)

29–30. Host Influence on Parasite Physiology, New Brunswick, N.J. (L. A. Stauber, Rutgers Univ., New Brunswick.)

31–5. American Inst. of Electrical Engineers, New York, N.Y. (N. S. Hibshman, AIEE, 33 W. 39 St., New York 18.)

31–7. Pan American Cong. of Ophthalmology, 6th, Caracas, Venezuela. (J. W. McKinney, 921 Exchange Bldg., Memphis, Tenn.)

February

1–4. American Soc. of Heating, Refrigerating and Air Conditioning Engineers, semi-annual, Dallas, Tex. (Miss J. I. Szabo, ASHRACE, 234 Fifth Ave., New York 1.)

1–4. Instrument-Automation Conf., Houston, Tex. (Director, Technical and Educational Services, Instrument Soc. of America, 313 Sixth Ave., Pittsburgh 22, Pa.)

1–5. American Inst. of Electrical Engineers, winter general, New York, N.Y. (N. S. Hibshman, AIEE, 33 W. 39 St., New York 18.)

1–5. Clinical Cong. of Abdominal Surgeons, Miami Beach, Fla. (CCAS, 633 Main St., Melrose 76, Mass.)

2–4. Haemopoiesis—Cell Production and Its Regulation, Ciba Foundation symp. (by invitation only), London, England. (G. E. W. Wolstenholme, Ciba Foundation, 41 Portland Pl., London, W.1, England.)

2–4. Society of the Plastics Industry (Reinforced Plastics Div.), Chicago, Ill. (W. C. Bird, SPI, 250 Park Ave., New York 17.)

3–5. Military Electronics, IRE winter conv., Los Angeles, Calif. (G. B. Knoob, Motorola, Inc., Military Electronics Div., 1741 Ivar Ave., Hollywood 28, Calif.)

3–6. American College of Radiology, New Orleans, La. (W. C. Stronach, 20 N. Wacker Dr., Chicago 6.)

3–6. Parathyroid Research, symp., Houston, Tex. (R. V. Talmage, Dept. of Biology, Rice Inst., Houston.)

4–6. American Soc. for Metals, San Francisco, Calif. (R. Huggins, ASM, Stanford Univ., Stanford, Calif.)

4–6. Congress on Administration, 3rd annual, Chicago, Ill. (R. E. Brown, American College of Hospital Administrators, 840 N. Lake Shore Drive, Chicago 11.)

5. Parenteral Drug Assoc., New York, N.Y. (H. E. Boyden, PDA, 4865 Stenton Ave., Philadelphia 44, Pa.)

7–9. Congress on Medical Education and Licensure, Chicago, Ill. (CMEH, AMA, 535 N. Dearborn St., Chicago 10.)

7–10. Radioactive Isotopes in Clinical Medicine and Research, 4th intern. symp., Bad Gastein, Austria. (R. Höfer, 2nd Medical Univ. Clinic, 13 Garnisongasse, Vienna 1X, Austria.)

10–11. Gas Cooled Reactor, symp., Philadelphia, Pa. (F. L. Jackson, Franklin Inst., Philadelphia, Pa.)

10–12. American Acad. of Occupational Medicine, Williamsburg, Va. (L. B. Shone, Bureau of Medicine and Surgery, Navy Dept., Washington 25.)

10–12. Solid States Circuit Conf., Philadelphia, Pa. (T. R. Finch, Bell Telephone Laboratories, Murray Hill, N.J.)

10–13. National Assoc. for Research in Science Teaching, 33rd annual, Chicago, Ill. (C. M. Pruitt, Univ. of Tampa, Tampa, Fla.)

(See issue of 18 December for comprehensive list)