

## LOW-TEMPERATURE CALORIMETRY – QUO VADIS?

E. F. WESTRUM, JR.

*Department of Chemistry, University of Michigan,  
Ann Arbor, Michigan 48109 U.S.A.*

(Received September 21, 1977)

Experimental progress in adiabatic, cryogenic calorimetry is tersely reviewed and contrasted with other techniques for heat capacity determinations in this temperature region—including DSC. Trends and prognostications of important developments including scaling down sample size and use of adjuvant thermometry.

\*This presentation concerns itself primarily with the temperature region about 5 through 350 K which is the normal range of cryogenic calorimetry of most practical concern for chemical thermodynamic purposes. For many substances, this range penetrates sufficiently near absolute zero to include ordering transitions and the reasonably reliable application of the third law of thermodynamics. It is a region over which the techniques have become standardized and the resultant thermal properties have been examined for a variety of substances. The region is broad enough to encompass a wide variety of interesting transitional behavior including order-disorder, Schottky, structural, magnetic, electrical, plastic and “crystalline liquid”, Verwey, Jahn-Teller, metal-insulator, superconductivity, as well as phase and melting phenomenon for typical molecular crystals. This choice does not deny the importance of the “helium” range, nor of the millikelvin range, nor that of higher temperatures; it is simply to be regarded as convenient compass within which to incorporate my review and comments.

Before considering recent innovations and future trends, let us look briefly at the current situation and need for cryogenic calorimetric measurements. Certainly the pre-eminence of heat capacity as a revealing parameter of the energetic spectrum at the molecular and crystalline level is enhanced as the temperature drops below the ambient thermal chaos. At higher temperatures the entropy increment – of an order-disorder transition, for example – becomes an increasingly significant and useful criterion. In modern higher-temperature studies

\*In the oral presentation of this opening plenary lecture, congratulations to Professor J. Pick (President) and to Professor E. Hala of the Czechoslovak Chemical Society and to Dr. Zapletal, Director of the Institute of Inorganic Chemistry for their initiatory success in the creation of the First Czechoslovak Conference on Calorimetry under the auspices of the Czechoslovak Academy of Sciences were followed by expression of pleasure, honor, and appreciation to the Scientific and Organizing Committee for their kindness, hospitality, and generosity. The opportunity to learn directly of Czechoslovakian progress in calorimetry is a welcome step toward better relations between scientists. The graciousness of the Czechoslovak (and other) thermodynamicists in eschewing their native tongues for the common language, English, for the mutual benefit of the foreign guests was also noted.

the practical entropy itself may even become the dominant factor in the Gibbs energy expression ( $G^\circ = H^\circ - TS^\circ$ ) since its contribution is multiplied by the absolute temperature. But after all, it is simply an integral of the heat capacity.

A considered analysis of our need for chemical-thermodynamic functions in meeting the concern of the present world-wide technological problems commonly known as the "energy crisis," suggests the importance of a continuing – or even an enhanced – thrust toward the study of the thermodynamics of important materials in nuclear, geothermal, fossil fuel, and other types of energy sources [1].

Apart from the provision of solutions for "general" scientific and technological problems, the low-temperature calorimeter has proven itself to be an excellent tool for the study of an immense variety of transitions [2]. The above enumeration leaves many unmentioned.

Whether the studies involve phases such as ionic-crystals, metals and alloys, molecular crystals, vitreous (glassy) crystals and liquids, and even the more exotic and less well-explored substances such as charge-transfer complexes, metal salts of organic anions, liquid crystals, etc., they are only fragments from an immense realm of materials whose thermodynamic parameters are largely unknown. Although almost all technological applications – and many scientific ones as well – do indeed depend upon the properties of solutions and mixtures rather than of pure substances, it is nonetheless typical of most endeavors in the calorimetric study of crystalline phases that these substances are aimed at work on "pure" substances. Admittedly, the characterization and the purity of the samples involved leave much to be desired – even in the work of chemists as well as that of physicists – relatively few studies are made on thermophysical properties of liquid solutions and even fewer on the properties of crystalline "solid" solutions [3]. Indeed, the thermophysical study of pure magnetite samples selectively doped with low concentrations of suitable cations on either octahedral or tetrahedral sites has aided the study of the so-called Verwey transition [4, 5].

Despite the fact that fewer practitioners of cryogenic calorimetry exist in the United States at the present time, the need has certainly not diminished [6]. The recent cut-backs in the funding of scientific research, however, have occasioned an increasing concern among scientists as to the economics and to the efficiency of the endeavors to which they are committed.

But even a cursory glance at the literature of thermodynamics over the last few years will convince the reader of a remarkable change. Although the number of "professional" thermodynamicists interested in the solid state is limited to a few hundred individuals the world over, the bulk of solid-state thermodynamic information now comes from the laboratories of a variety of solid-state scientists whose prime interest may be in some other field. Nonetheless, these individuals from time to time do indeed generate thermophysical data. This situation is, however, by no means limited to cryogenic calorimetry but is generally true for other areas of calorimetric and even thermodynamic measurements as well and extends into the biological and geological domains. It emphasizes the importance of guides [7, 8] for the presentation of such data.

In this brief presentation, those areas of cryogenic calorimeter in which the author's research group has been involved have been favored for rather obvious reasons. Yet this inherent subjectivity has been tempered and reinforced by consideration of related endeavors whenever practicable within the limitations of space.

### Cryostats and calorimeters

Although in many areas to be described during this Conference the choice of buying rather than building one's calorimeter may be an option, in cryogenic calorimetry one must depend upon his own ingenuity to provide calorimeter, cryostat, and adjuvant control instrumentation. It should be well appreciated that the design and construction of calorimeters — essential and valuable though they may be — do not excite the scientific community unless these instruments are used to produce scientifically exciting results. To achieve the objectives of advancing the art of cryogenic calorimetry, to recruit proselytes and to ensure production of results, generalizations, and correlations of utility to the scientific community we must convince our fellow scientists in broad areas of chemistry, biology, physics, and engineering that calorimetry is rewarding — that is “pays off”. In some measure this requires greater planning and better organization on the part of experimentalists so that those who devote their interest and skill to the development of calorimetric instrumentation will produce significantly and share in the rewards.

The first decision is really one of “To dunk or not to dunk?” Although earlier calorimeters tended to be contained in “submarines” immersed within a liquid refrigerant bath, we at Ann Arbor have found it exceedingly convenient to operate in an *aneroid* fashion. This provides economy in the use of liquid helium and other refrigerants as well as an apparatus which can be reloaded very quickly and utilized effectively over long periods of time. Slightly more technical skill is required in the manufacture of such a cryostat, but its convenience of operation pays dividends in the prevention of frayed nerves.

The decision which must be made is whether or not one will operate essentially adiabatically or more realistically — “*quasi-adiabatically*”<sup>\*</sup> — or whether one will operate in an isoperibol manner. The latter technique was that pioneered by Nobel prize-winner, Professor Giauque, and advocated by his former student, Professor Stout [9]. The technique has much to recommend it; it is very convenient

\* The term *quasi-adiabatic* is used to indicate the small departures from true adiabaticity which are useful in practice. For example, the slight—but constant— heating effect produced by ohmic heating in the resistance thermometer may be almost exactly counterbalanced by slight cooling provided by controlling the adiabatic shield at a temperature very slightly below that of the calorimeter.

especially at low temperatures where the radiation interchange of heat with the surroundings is quite negligible. It is increasingly, however, the general preference of most other individuals to operate over the chemical-thermodynamic region by adiabatic or quasi-adiabatic calorimetry [10]. This is partly because of the availability of the apparatus which can readily be adapted to the rate, reset, and proportional control circuitry needed to ensure high-quality adiabatic shield control. Measurements on Calorimetry Conference standard materials (*e.g.*, benzoic acid, copper, synthetic sapphire, and *n*-heptane) by several laboratories have demonstrated the reproducibility and the reliability of the adiabatic technique. Its real virtue, however, is most apparent when periods of the order of six or more hours are required for the achievement of equilibrium during melting or transition. Under these conditions, heat exchange between the calorimeter and the surroundings can be minimized as in no other mode. It is, therefore, the preferred mode for the study of transitions where relatively long thermal equilibration times tend to be the rule rather than the exception.

#### *Conventional aneroid adiabatic calorimeters and improvements*

Accurate heat capacity data are typically procured in an instrument depicted in Fig. 1, which is a modern development of a Nernst adiabatic, calorimetric cryostat [10]. This assembly provides a way of maintaining a sample of chemical substance within a calorimeter vessel at any desired temperature under such conditions that no heat is exchanged with the environment except that introduced by an electrical heater during the measurement. The calorimeter vessel is suspended in isolation by a braided silk line and is surrounded by an adiabatic shield. The calorimeter and adiabatic shield may be mechanically brought into direct thermal contact with a refrigerant tank and be thus cooled to the desired operating temperature and again isolated by lowering it. Two chromium-plated copper refrigerant tanks provide thermal sinks. For studies above 90 K, liquid nitrogen is used as refrigerant in both tanks: temperatures as low as 50 K may be achieved by evacuating the lower tank and solidifying the nitrogen. For the range 4 to 50 K, liquid helium is used as refrigerant in the lower tank.

Chromium-plated copper radiation shields not only conserve refrigerants but generate zones of uniform and progressively lower temperatures. Thermal isolation and achievement of adiabatic conditions is facilitated by the high vacuum within the apparatus and the elimination of gas conduction. Thermal conduction along the electrical leads is minimized by firmly anchoring them to the refrigerant tanks and to an "economizer" which serves as a heat exchanger by using the cold effluent helium gas to absorb much of the heat conducted down the leads, and thus conserve liquid helium. The temperature of the lead bundle is tempered by a ring and finally adjusted to the temperature of the calorimeter by the adiabatic shield which is maintained within  $\pm 2$  mK of the calorimeter temperature. Cop-

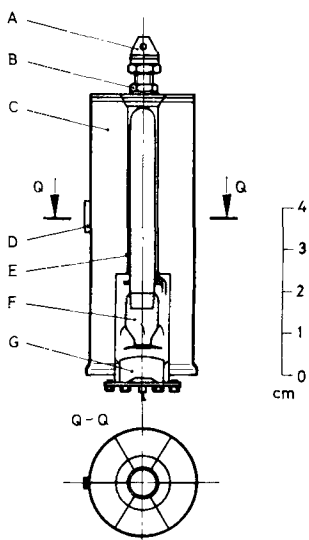


Fig. 1. Intermediate temperature calorimetric thermostat. *A*, guard shield ring; *B*, calorimeter suspension collar; *C*, primary radiation shield; *D*, calorimeter closure assembly; *E*, guard shield; *F*, calorimeter assembly; *G*, thermometer-heater assembly; *H*, thermometer; *I*, thermal equilibration spool; *J*, lead bundle; *K*, adiabatic shield

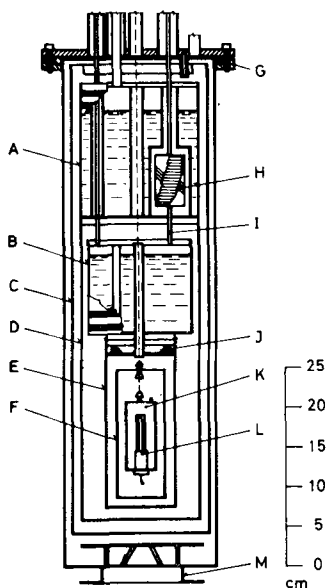


Fig. 2. Cross-sectional diagram of calorimeter for fluid samples. *A*, cone for thermal contact; *B*, demountable valve plug; *C*, vane, sample space; *D*, thermocouple well; *E*, heater sleeve; *F*, platinum-resistance thermometer; *G*, spool to thermally equilibrate leads with calorimeter

per-constantan thermocouples monitor the difference in temperature between calorimeter and shield, between shield and ring, and actuate three separate channels of recording electronic circuitry provided with proportional, rate, and reset control actions for establishment of adiabaticity.

The equilibrium temperature of the sample is determined with a platinum-encapsulated, platinum-resistance thermometer mounted within the calorimeter vessel shown in Fig. 2. As the temperature of the calorimeter is increased by electrical energy input to the heating element installed within the vessel, that of the shield is made to follow it so closely that no unmeasured energy enters or leaves the calorimeter. After the input the new equilibrium temperature is determined. A precision of the order of a few hundredths of a per cent may be obtained over most of the temperature range. Accuracy is assured by ultimately referring all determinations of mass, time, temperature, resistance, and potential to calibrations performed by the National Bureau of Standards and by the measurement of heat-capacity standards provided by the Calorimetry Conference [11].

Useful innovations in the design of calorimeters to permit their use in the exploration of the thermophysical properties of reactive materials include the development of the calorimeters lined with noble metal or even the provision of vitreous borosilicate or vitreous silica cells to contain reactive substances. More massively reinforced calorimeters to withstand higher internal vapor and sublimation pressures may conveniently be made by electroforming metals of high thermal diffusivity on the exterior and interior surfaces of a stainless steel vessel.

Thermometry of higher sensitivity is also clearly a desideratum. Enhanced ability to resolve small thermal anomalies, to delineate the critical constants of second-order transitions or to delimit the breadth of first-order phase changes are only three of the advantages that would accrue. (*Cf.* references 12 and 13 for recent progress.)

#### *Automation (computerization) and data logging*

Automatic, electronic, adiabatic-shield control is now routine practice in most laboratories whether the calorimetry is done by intermittent or by continuous heating techniques. Although circuits employing commercial components such as automatic AC bridges, digital voltmeters, and transistorized digital modules have become rather commonplace, they seem more to serve to lighten the workload of the calorimetrist rather than to enhance his output of useful data. The treatment of the data themselves by digital computers, has become the rule rather than the exception and several programs not only for data evaluation but for curve-fitting, integration, and for testing for the presence of subtle trends in the derived values are widely employed.

After all, science — like haute couture — has its fashions. Automation these days enables you to load your calorimeter, press the button, go to lunch or to Monte Carlo — depending on the duration of the experiment and one's financial

status – and when you do come back to the desk you may pick up the computer output with all the relevant data transposed into a format suitable for printing the table of data and possibly of thermodynamic functions. In most instances, some degree of semi-automatic and semi-manual operation seems to be the preferred solution but an on-line computer may actually be used to operate the calorimeter.

As noted earlier at least partial automation of the operation and data-logging abilities of cryogenic calorimeters are particularly important in the study of transitions in which exceedingly long hysteresis is required for the achievement of thermal equilibration. A computer-linked mode of operation is particularly important in the premonitory region and also in the region following the transition where very interesting thermal effects are often noted. A number of different solutions to this problem have already appeared in the literature.

In our own laboratory a laboratory minicomputer is dedicated to the control operation of three calorimeters in its foreground mode and to evaluate and plot the approach toward equilibrium for manual override where this is a desideratum and to provide calculations, smoothing, and molalling of the data in its background mode.

#### *Scaling down the sample size*

Although in measuring the heat capacity of gold, Geballe and Giauque [14] used several kilograms of this dense and massive metal, and most of us are accustomed to using samples of between 50 and 200 grams when available – we need to think urgently in terms of calorimetry on about the one-gram scale. This implies, of course, determinations of the reliability of the precision and accuracy of our state-of-the-art calorimetry. (It should be pointed out that if suitable heat-capacity measurements can be made on a one-gram sample, this sample might subsequently be expended and burned in 8–10 portions of approximately 100 mg, *e.g.*, in a combustion calorimeter, in order to provide – at least for typical molecular crystals – the complete chemical thermodynamics.) Scaling down beyond this point is not to be excluded although it should be recognized that it may be desirable to have the absolute temperature sensor on the adiabatic shield rather than on the calorimeter and to use a transducer for ascertaining the calorimeter temperature.

#### *Differential scanning calorimetry vis-a-vis equilibrium calorimetry*

Because of their ready availability, speed, and convenience of operation, one finds increasingly scientific and technological data provided by DSC measurements – the present conference is no exception. One also finds continuous heating calorimeters as an intermediate approach. Although the precision of DSC studies is

lower than that of adiabatic cryogenic calorimetry, the former often provides adequate accuracy in values especially above 300 K. But is the use of DSC a solution to the scaling down of sample size referred to earlier?

Long experience with hysteresis in adiabatic calorimetry taught me the limitations of differential-scanning calorimetry – and particularly of such an instrument in the hands of one who has never practiced *equilibrium* calorimetry. I would, therefore, urge that the greatest caution be used particularly in dealing with the thermophysical properties of solids particularly as temperatures below the ambient are achieved. I hope that the day of enhanced development of this instrument will render it even more effective and more reliable. Although accurate data are frequently obtained on the instrument, very often data in error by a factor of two or more are achieved. We have been totally unable, as a consequence of hysteresis, even to detect significant transitions by DSC – known to be present by equilibrium calorimetry – in pure substances due to hysteresis. New DSC's with much slower scan rates should prove efficacious in this respect.

### *Miscellaneous advances*

Only space precludes the inclusion of mention of many other innovations but mention should be made of small sample AC calorimetry [15], AC calorimetry at high pressure [16, 17], measurements on samples of low thermal diffusivity [18], and especially the enhanced sensitivity provided by adjuvant thermometry [19], and by improved adiabaticity [20]. Finally, it may be worth noting that the techniques described here may, in fact – with slight modification – be used to extend this manner of adiabatic calorimetry well above the ambient temperature [21].

\*

\*The author expresses his appreciation to the Chemical Thermodynamics Program, Chemistry Division, National Science Foundation under Contract No. CHE-77-10049 for support of the research endeavors here presented.

### References

1. C. E. HOLLEY, E. F. WESTRUM, JR., L. BREWER, W. HUBBARD, F. D. ROSSINI and C. BECKETT, Eds, Thermodynamics and National Energy Problems, National Academy of Sciences, Washington, D. C., 1975, 438 pp.
2. E. F. WESTRUM, JR., Pure Appl. Chem., 38 (1974) 539.
3. E. F. WESTRUM, JR., In Proceedings of the 1976 Calorimetry Conference, Zakopane, Poland, 1977, 44 pp.
4. J. J. BARTEL and E. F. WESTRUM, JR., J. Chem. Thermodynamics, 8 (1976) 575.
5. J. J. BARTEL and E. F. WESTRUM, JR., J. Chem. Thermodynamics, 8 (1976) 583.
6. C. E. HOLLEY, JR., C. VANDERZEE and E. F. WESTRUM, JR., In Proceedings of the 1977 Calorimetry Conference, Sherbrooke, Quebec, Canada, 1977 (In press).
7. E. F. WESTRUM, JR., Atomic Energy Review, 9 (1972), 869.



8. B. DREYFUS, Ed., CODATA Bulletin, No. 9, CODATA, Paris, France, 1973, 5 pp.
9. J. W. STOUT, In *Experimental Thermodynamics*, Vol. 1, Chap. 6, J. P. McCULLOUGH and D. W. SCOTT, Eds, Butterworths, London 1968, p. 215.
10. E. F. WESTRUM, JR., G. T. FURUKAWA and J. P. McCULLOUGH, In *Experimental Thermodynamics*, Vol. 1, C. P. McCULLOUGH and D. W. SCOTT, Eds., Butterworths, London, 1968, p. 333.
11. D. C. GINNINGS and G. T. FURUKAWA, *J. Amer. Chem. Soc.*, 75 (1953), 522.
12. F. GRØNVOLD, *Pure Appl. Chem.*, 47, (1976), 251.
13. H. E. STANLEY, Ed., In *Cooperative Phenomena Near Phase Transitions, A Bibliography with Selected Readings*, MIT Press, Cambridge, Mass. 1973.
14. T. H. GEBALLE and W. F. GIAUQUE, *J. Amer. Chem. Soc.*, 74, 1952, 2368.
15. J. BATURIC-RUBCIC, B. LEONTIC and J. LUKATELA, *Fizika*, 8 (1976) 45.
16. O. SANDBERG, P. ANDERSSON and G. BACKSTROM, *J. Phys. E*, 10 (1977), 474.
17. J. D. BALOGA and C. W. GARLAND, *Rev. Sci. Inst.*, 48 (1977), 105.
18. J. BATURIC-RUBCIC, D. DUREK and A. RUBCIC, *J. Phys. E.*, 10 (1977) 373.
19. S. SEKI, cited by Y. TAKAHASHI, *Pure Appl. Chem.*, 47 (1976) 323.
20. J. KLEINCLAUSS, R. MAINARD and H. FOUSSE, *J. Phys. E*, 10 (1977) 485.
21. J. T. S. ANDREWS, P. A. NORTON and E. F. WESTRUM, JR., *J. Chem. Thermodynamics* 10 (1978) (In press).

RÉSUMÉ — Brève mise au point sur les progrès réalisés dans le domaine expérimental en calorimétrie adiabatique à basses températures et comparaison de cette méthode avec les autres techniques de mesure de la chaleur spécifique dans ce domaine de températures — y compris la technique DSC. On donne les tendances et les prévisions sur les développements importants concernant la diminution de la taille de l'échantillon et l'utilisation de la thermométrie comme méthode auxiliaire.

ZUSAMMENFASSUNG — Die experimentelle Entwicklung auf dem Gebiete der adiabatischen kryogenen Kalorimetrie wird kurz zusammengefaßt und anderen Techniken zur Bestimmung der Wärmekapazität in diesem Temperaturbereich — einschließlich DSC — gegenübergestellt. Trends und Prognosen werden hinsichtlich der wichtigen Entwicklungsrichtungen einschließlich Herabsetzung der Probengröße und Anwendung der Thermometrie als Aushilfe, gegeben.

Резюме — Сжато рассмотрен экспериментальный прогресс в адиабатической, криогенной калориметрии по сравнению с другими методами, включая и ДСК, определения теплоемкости в этой температурной области. Рассмотрены тенденции и прогноз дальнейших развитий, включая понижение размера образца и использование усиливающей термометрии.