

SECTION OF PHYSICAL CHEMISTRY
COMMISSION ON CHEMICAL THERMODYNAMICS*

**RESOLUTION ON PUBLICATION OF
CALORIMETRIC AND THERMODYNAMIC DATA**

In 1953 the 8th Calorimetry Conference adopted a resolution outlining minimum publication standards for the guidance of authors, editors, and referees of calorimetric papers. Because this resolution has helped improve the quality of such papers, the 14th Conference (1959) authorized the preparation of a revised resolution on publication that would be more consistent with the expanded scope of the Conference and the present state of calorimetric science. The revised and expanded resolution that follows was adopted by the 15th Conference at Gatlinburg, Tennessee, 7-10 September, 1960.

INTRODUCTION

This resolution is addressed not only to the specialist in calorimetry and chemical thermodynamics but also to those who determine and publish thermodynamic data as a subordinate part of their research. We urge all who publish thermodynamic data, for whatever purpose determined, to consider the suggestions to follow, so that maximum benefits from their work may be realized. We also recommend this resolution to journal editors and referees as a set of carefully considered criteria for judging the completeness and acceptability of papers reporting calorimetric data.

GENERAL PHILOSOPHY

The very nature of chemical thermodynamics imposes special burdens on the author of a paper reporting the results of calorimetric investigations. Because the body of thermodynamic data is highly interdependent, he must give enough information about his experiments to allow others to appraise the precision and accuracy of his results for proper consolidation with the existing body of data. Further, as accepted values of physical constants change, or as new thermodynamic data for related systems become available, later investigators often can recalculate results based on good calorimetry, however old it may be. For these reasons, an author's first responsibility is to report his results in a form related as closely to experimentally observed quantities as is practical, with enough details of the experiments and

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auxiliary information to characterize the results completely. For the convenience of the reader, the author should interpret and correlate the primary data, as appropriate, and present derived data in a form easy to use. However, derived or secondary data should *never* be published at the cost of omitting the primary data on which they are based.

NECESSARY AUXILIARY INFORMATION

Detailed auxiliary information is required to characterize the results of any definitive thermodynamic study. Applicable items listed in the following paragraphs should always be given either in full or by reference to accessible earlier publications containing full details.

Apparatus and procedures

A complete description of the apparatus and procedures, including details of the reaction container or calorimeter vessel, the controlled environment, and the temperature and time measuring systems; the method of calibration and the sensitivity of measuring instruments such as thermometers, bridges and potentiometers, timing devices, and flow meters; the method of determining the energy equivalent of, or otherwise calibrating, the system; the observational procedure; the method of data reduction; and the precision and accuracy of the results obtained, preferably established by using recognized reference substances such as the Calorimetry Conference samples of n-heptane, benzoic acid, and aluminium oxide for heat capacity or enthalpy measurements, or standard benzoic acid for combustion measurements.

Materials

The source of and/or method of preparing all materials used, including calibration, reference, and auxiliary substances; experimental values for analyses and pertinent physical properties of materials, and criteria of purity; and method of storing samples and preparing them for calorimetric measurements, if important.

Auxiliary data

Atomic or molecular weights; fundamental physical constants; temperature scales; units of energy and relationship between units; and values of thermochemical or thermodynamic data taken from the literature, with sources. The absolute joule or the defined thermochemical calorie equal to 4.184 absolute joules exactly and the International Temperature Scale, with the definition 0° Celsius (International) = 273.15° Kelvin (International), are recommended.

PRESENTATION OF RESULTS

It is not practical to give detailed recommendations for presenting the results of all kinds of thermochemical or thermodynamic investigations. However, the following paragraphs give recommendations for some important kinds of thermodynamic studies and will serve as guides for others.

Thermochemical data

The following experimental data should be included if applicable: Energy equivalent of the calorimetric system; mass of sample and/or mass of product used in determining the amount of reaction; masses of auxiliary substances; corrected temperature increment; total observed energy change; ignition energy; chemical and physical specification of the initial and final states of the reaction; conversion to "standard" concentrations; corrections for side reactions; allowances for energy changes due to flow of gases, stirring, or other effects; allowances for energy from auxiliary substances; reduction to standard states, such as the "Washburn corrections"; temperature of experiments; and final experimental heat of reaction and uncertainty interval, with the chemical reaction to which the result applies.

Thermal data

The following information is considered indispensable for delineating the temperature dependence of thermodynamic properties of non-reacting systems, ascertaining the influence of thermal history on measured properties, and evaluating the precision of the results: A table of experimental values of heat capacity or enthalpy increment; the actual temperature increments used in the measurements when important (e.g., in transition, pre-melting, or anomalous regions), either explicitly or implicitly by chronological presentation of data or by a general statement; indication of values adjusted for curvature or pre-melting; values of the heat and temperature of essentially isothermal phase changes; and an estimate of the accuracy uncertainty of the results. These primary experimental data should be supplemented, but never supplanted, by a tabulation of smoothed values of thermodynamic properties at selected temperatures. Where applicable, such tabulations should include values of the Gibbs free energy function $(F - H_0^0)/T$, enthalpy (heat content) function, $(H - H_0^0)/T$, entropy, S , heat capacity, C_p (or $C_{\text{satd.}}$), and enthalpy, $H - H_0^0$ at 5° intervals from 0° to 50°K , 10° intervals from 50° to 300°K or slightly higher temperatures, and 50° to 100° intervals at higher temperatures, with appropriately smaller intervals in regions of thermal anomaly. Values at the two important reference temperatures, 273.15° and 298.15°K , and at the temperatures of phase changes should be included in the tabulations. Graphical or analytical representation of the results is sometimes worthwhile for the convenience of the reader, but such representations are seldom a satisfactory substitute for tabular presentation of accurate experimental results.

Calculated thermodynamic functions

As the usefulness of calorimetric data is often extended by giving calculated thermodynamic functions based on them, recommendations for presenting this kind of thermodynamic data are included here. The following information, with sources, is needed to characterize the results of statistical thermodynamic calculations: Details of the molecular model used, including bond distances and angles, specification of the exact conformation, moments of inertia or rotational constants, and symmetry number; complete vibrational assignment; parameters used for calculating

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contributions of internal rotation, anharmonicity, centrifugal distortion, *etc.*; citation, usually by reference, of formulae and special tabulations used; comparison with experimental thermodynamic data, when available; and tables of thermodynamic functions at selected temperatures. The functions tabulated should include all of the following: the Gibbs free energy function, $(F^\circ - H_0^\circ)/T$; enthalpy (heat content) function, $(H^\circ - H_0^\circ)/T$; entropy, S° ; heat capacity, C_p° ; and enthalpy, $(H^\circ - H_0^\circ)$. In addition, values of enthalpy of formation, ΔH_f° , the Gibbs free energy of formation, ΔF_f° , and the common logarithm of the equilibrium constant of formation, $\log_{10} K_f$, may be published, if warranted. The values should be reported at temperatures so spaced that no serious loss of accuracy will result by interpolation with a formula equivalent to 5-point Lagrangian interpolation; for example, at 50° intervals to 300°K, 100° intervals to 1500°K, 200° intervals to 2500°K, and 500° intervals at higher temperatures. Values should also be tabulated at the reference temperatures, 273·15° and 298·15°K.

Non-definitive data

This resolution is concerned primarily with the publication of precise and accurate data taken by definitive techniques, but rough measurements are often made for technical purposes and these data occasionally are submitted for publication. As such measurements are sometimes made on materials of undefined composition or by techniques substantially inferior to those accepted as definitive, they clearly do not merit space in scientific journals on the same basis as definitive studies, and the foregoing recommendations do not apply in full. The same is true of calculated thermodynamic functions which are based on unsubstantiated or estimated molecular data and which are not verified by comparison with experimental thermodynamic data. However, even rough data or calculated values *may* be better than empirical estimates and thus have some value, but they are of doubtful significance as a basis for many theoretical deductions or for incorporation in critical tables of scientific data. Therefore, it is recommended that minimum journal space be allotted to such results and that the presentation clearly recognize their lack of reliability. The use of the American Documentation Institute Supplement may be appropriate for the bulk of such data, with the location attested only by a brief Note in a journal.

Note on symbols and terms

The symbols and terms used herein are simply those used by most American chemists, and their use in this report is not to be construed as a recommendation of the Calorimetry Conference. Two differences from European usage are:

- (i) the superscript $^\circ$ is used to designate the thermodynamic standard reference state;
- (ii) the symbol F is defined as $H - TS$.

The I.U.P.A.C. Commission on Physicochemical Symbols and Terminology is expected to make recommendations soon, regarding these matters.

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