A Guide to Procedures for the Publication of Thermodynamic Data[1]

At the 1971 Washington, D.C. meeting of the IUPAC Commission on Thermodynamics and Thermochemistry it was resolved that the following guide should be given the widest publicity to aid in the resolution of some current problems in scientific communication and in the hope that it might stimulate similar action by other organizations concerned with specialized fields of science.

This guide was previously ratified by the All-Union Calorimetry Conference (U.S.S.R.), The Calorimetry Conference (U.S.A.), the Experimental Thermodynamics Conference (U.K.), the Society of Calorimetry and Thermal Analysis (Japan), and the Société Francais des Termiciens (France).

In 1953, the 8th (U.S.A.) Calorimetry Conference adopted a resolution providing guidance on minimum publication standards in calorimetry. This resulted in an improvement in the quality of publication, and so led the Calorimetry Conference to revise, extend, and publish its recommendations in 1960 *(1)*. A second revision was authorized in 1970, and it was intended that this new version should be submitted to various calorimetry and related conferences *(2)*, and to the International Union of Pure and Applied Chemistry for suggestions and ratification.

This has been done with the approval of Commission I.2 of IUPAC and the agreed text is hereby presented in accordance with the terms of the resolution cited at the head of this document. The Commission itself has also prescribed recommendations on the publication of thermochemical studies as early as 1934 *(3)*, as has the scientific council on chemical thermodynamics of IONKh of the U.S.S.R. Academy of Sciences *(4)*.

1. Introduction

This guide is addressed not only to specialists in calorimetry or in the various aspects of thermodynamics but also to all those who measure and publish thermodynamic quantities as incidental aspects of their research endeavors. We would urge all who ever publish thermodynamic values for whatever purpose to follow these suggestions so that maximum benefit from their studies will be realized. Journal editors and referees should note that this document embodies a set of consistent carefully considered criteria for judging the completeness and acceptability of papers reporting thermodynamic quantities. The ultimate needs of the compiler and correlator of such data have been considered also.

2. Essential Information

The highly interdependent nature of thermodynamic quantities imposes special obligations upon the author of papers reporting the results of thermodynamic investigation. He must give enough information about his experiment to allow readers to appraise the precision and accuracy of his results so they may be properly consolidated within the existing body of data in the literature. Further, as accepted values of physical constants change or as new thermodynamic quantities for related systems become available, subsequent investigators often can recalculate results if it is clear that they are based on good experiments for which adequate information is presented, however old they may be. For these reasons, an author's prime responsibility is to report his results in a form related as closely to experimentally observed quantities as is practical, with enough experimental details and auxiliary information to characterize the results adequately and to allow critical assessment of the accuracy claimed. For the convenience of the reader, the author may interpret and correlate the primary results as appropriate and present derived results in a form easy to utilize. However, such derived (or secondary) results *never* should be published at the cost of omitting the primary results on which they are based. Reference may be made to accessible earlier publications for some details.

In addition to the presentation of the data themselves, estimates of the precision indices and probable accuracy of the data should be given by the authors. The various sources of uncertainty should be rigorously described with clear separation of measurement imprecisions, numerical analysis deviations, and possible systematic biases. The methods and assumptions for the statistical analyses should be indicated. Possible sources and magnitudes of systematic errors should be identified and enumerated.

Because temperature scales are of such great significance for all thermodynamic measurements the considerations and conversions cited by Rossini *(5)* and others should be observed. For accurately measured temperatures depending on an International Practical Temperature Scale, the scale used in calibration of the temperature-measuring instrument(s) (e.g., "IPTS-48 as amended in 1960") and the scale to which the specified temperature values refer (sometimes these two scales are different, e.g. the latter might be IPTS-68) should be stated.

In instances where requisite primary results are too extensive or for other reasons do not merit journal publication in full, the use of auxiliary publication services may be appropriate *(6)*. A footnote in the publication indicates how the reader may obtain the additional data.

Apparatus and procedures. A description of the apparatus including details of the reaction container or calorimeter vessel, the controlled environment, and measuring systems such as those for time, temperature, and pressure; the design of calibration heaters and heater lead placement; precautions as to shielding or isolation of calibration circuits; the method of calibration and the sensitivity of the instruments used in these measuring systems such as thermometers, bridges, and potentiometers, flowmeters, weighing devices should be given. The history of a particular apparatus which is used in a continuing series of researches should be maintained and documented as to modifications, improvements, etc., to the end that should corrections be made necessary by subsequent recalibrations or by revelation of systematic errors or bias, such corrections can be applied to all affected data either by the author or by compilers or reviewers. Information establishing the heat capacity of the calorimeter or the energy equivalent (preferably with traceability to a calibrating or standardizing laboratory), together with details of the observational procedures, the methods of evaluating the corrected temperature increment, methods of analysis of results, and the precision of the measurements should be given. The reliability of the results should be established by the use of recognized

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reference substances such as the samples likely to be recommended by the IUPAC Sub-commission on Standard Calibration Materials *(7)*, those provided by the National Bureau of Standards (U.S.A.) *(8)*, or by VNIIM (U.S.S.R.) *(9)*, those authorized by the Calorimetry Conference for thermophysical or thermochemical measurements *(10)*, or those systems generally recognized as standard for mixtures, e.g. the solubility of oxygen in water at 101.325 kPa and 298.15 K for gas solubility *(11)*, hexane + cyclohexane for enthalpy changes on mixing *(12)*, and benzene + cyclohexane for volume changes on mixing *(13)*. Determination of the same quantity by two or more independent methods is often an advisable alternative method for detection of systematic error.

Materials. The source of and/or method of preparation for all materials used, including calibration, reference, and auxiliary substances; experimental values for analyses and pertinent physical properties of materials, the criteria of characterization and purity, as well as the method, temperature, time interval, etc., of storing samples and preparing them for measurements should be stated whenever this is important. The density used in reduction of weighing to mass, and special procedures such as for dealing with partially filled ampoules, should be specified. For studies made on solutions, the source, preparation, and quality of the *solvent* should always be included, as should information as to dissolved gases (CO_2, air, etc.) whenever these impurities may be of influence on the results. For all thermochemical studies, the methods and results of all analytical investigations on the initial and/or final system should be presented, including tests for incomplete reaction, side reactions, evaporation losses of components from mixtures, corrosion of apparatus, etc. These considerations as well as possible dialysis of compounds prior to actual reaction, buffers employed, etc., may be especially important in biothermodynamic studies.

Symbols, terminology, units. Authors are encouraged to follow as closely as possible the recommendations of the International System of Units (SI) *(14)*, and the symbols and nomenclature approved by IUPAC *(15)*. In particular, authors are urged (a) to use the recommended name for each physical quantity and the preferred symbol, (b) to use the internationally accepted symbols for units, (c) to use SI units, and (d) to adhere, particularly in the labels of columns or rows in tables and in the labels of the axes of graphs, to the implications of the convention: physical quantity = number × unit; for example by the use of $S/\mathrm{J\ K^{-1}\ mol^{-1}}$ as a label for a series of numbers rather than "S" (with or without a statement somewhere as to what the units are), or "S, J/K mol", or "S(J/K mol)", and (e) to use functional expressions such as $S^\circ(\mathrm{H_2O,\ g,\ 298.15\ K})$ rather than expressions like $S_{298,\mathrm{H_2O}}^{\circ,g}$. (Those authors who elect to use non-SI units should define them in terms of SI units. This might be done, for example, by means of such a footnote as: "Throughout this paper $\mathrm{cal_{th}}$ = 4.184 J, Torr = (101.325/760) kPa, and Å = 0.1 nm.")

Mode of presentation of results. Although a table giving the appropriate independent and dependent variables is often the best form of presentation in that it permits recovery of the primary results, circumstances arise where especially for a great many determinations the same end may be achieved, for example, by the presentation of an equation representing the temperature dependence of the measured quantity and a *deviation* plot showing the individual points. This procedure saves space, promotes clarity, and in many instances can be sensitive enough to permit full recovery of individual results without a table.

Occasionally, as in combustion calorimetry, each set of replicate measurements can be acceptably recorded as only the mean value, the magnitude and definition of its precision index, and the number of individual measurements made. For the precision indices on thermochemical data, the conventions suggested by Rossini *(16)* are recommended.

Occasionally, tabulations of high-temperature thermodynamic functions are given by empirical equations which, instead of being in pre-determined form and number of disposable parameters, are derived to fit the enthalpy, vapor-pressure, or other data within their precision at every temperature of measurement. This not only provides ready analytic interpolation, differentiation, or integration (as by a computer), but can save the journal space of longer-than-abbreviated tables when this is an issue. It is obviously not expedient, of course, when the given property function shows major lack of monotonic behavior. Graphical and analytical representation of the primary results or secondary results are occasionally worthwhile for the convenience of the reader, but are not generally a satisfactory substitute for tabular presentation of accurate experimental results. Extensive tabulations of secondary values (e.g. smoothed values at rounded temperatures) should be so designed with values reported at temperatures (or pressures, etc.) so spaced that no serious loss of accuracy will result by using an interpolation formula equivalent to five-place Lagrangian interpolation *(17)*. In particular, a sufficient number of digits should be retained to make such interpolation feasible.

It is not practicable to give detailed recommendations for presenting the results of all types of thermodynamic investigations. However, the following paragraphs do provide recommendations for some important kinds of thermochemical, thermophysical, and equilibrium studies and will serve as guides for related areas.

3. *Presentation of Thermochemical Calorimetric Data*

Reaction calorimetry. The following experimental quantities 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 (or if appropriate initial and final temperatures plus heat exchange adjustment), total observed energy change, ignition energy, chemical and physical specification of the initial and final states of the reaction, conversion to "standard" concentrations, correction for side reactions, reduction to standard states (e.g., the "Washburn corrections"), temperature of experiments, final experimental energy (or enthalpy) of reaction and uncertainty interval (with the chemical reaction to which the result applies precisely specified). Derived values such as standard enthalpy and standard Gibbs energy of formation may be provided for the convenience of the reader. Detailed discussion of procedures is available *(18, 19)*.

Solution calorimetry. Although most of the considerations and literature of the previous paragraph apply, additional material to be included would involve the specification of the temperature of the measurements, appropriately specified concentrations of all reactants, solvent, supporting electrolyte, ionic strength, the precise reaction occurring, etc. Thermochemical studies on solutions should present primary and derived results in sufficient detail that the actual calorimetric process is clearly discernible. Dilution corrections to standard states should describe any approximations for unmixing (e.g., Young's rule) *(20)* or approximations as to the relative apparent enthalpy of uncharged solutes such as NH_3, CO_2, etc. in the solution. Investigators of thermochemical properties of solutions are urged to ascertain densities of their solutions to facilitate theoretical comparison.

4. Presentation of Thermophysical Calorimetric Data

The following information is important for delineating the temperature dependence of the thermodynamic (thermophysical) properties of non-reacting systems and ascertaining the influence of thermal history on measured properties and evaluating the reliability of the results: a table of experimental values of heat capacity or enthalpy increment values including the actual temperature increments used in the measurements (if important as e.g., in transition, pre-melting, or anomalous regions), the chronological sequence of measurements where the thermal history may be significant either implicitly by chronological presentation or by a general statement), values of the energy (or enthalpy) increments and temperatures of essentially isothermal phase changes, and the reliability of the data indicated by an estimated uncertainty. These primary experimental results may be supplemented, but never supplanted, by a tabulation of smoothed values of thermodynamic properties at selected temperatures for the convenience of the reader. Where applicable, such tabulations should include values of the appropriate heat capacity, the standard entropy $S°$, the standard enthalpy increment $\{H°(T) - H°(0)\}$, and the standard "Gibbs energy function" $\{G°(T) - H°(0)\}/T$ *(21)*. Frequently these have been tabulated at 5 K intervals from 0 to 50 K, at 10 K intervals from 50 to 300 K or slightly higher temperatures, at 100 K intervals at higher temperatures, and at the temperatures of phase transitions. Such details need not be given for all substances but are desiderata for important compounds. Use of auxiliary publication services as mentioned above may be more appropriate as repositories for such tabulations. Certainly values at the two important reference temperatures, 273.15 and 298.15 K, should be included in the tabulations. Definitive information on procedures is available *(22)*.

5. Presentation of Calculated Thermophysical Functions

Because the usefulness of calorimetric data is extended if calculated thermodynamic functions based upon them are provided, recommendations for the presentation of such calculated values are incorporated here. The following information with appropriate 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, symmetry number, complete vibrational assignments, parameters used for calculating contributions of internal rotation, rotational isomerism, anharmonicity, centrifugal distortion, etc., the citation (usually by reference) of formulas and special tabulations used, and comparison with experimental thermodynamic data. The functions tabulated should include those indicated in previous sections except that the heat capacity should be $C°_V$ or $C°_p$ and in addition, values of the standard enthalpy of formation $\Delta_f H°$, standard Gibbs energy of formation $\Delta_f G°$, and the common logarithm of the standard equilibrium constant of formation $\log_{10} K°_f$, may be published if warranted. The criterion suggested above for the spacing of values is recommended; this corresponds, for example, to 50 K intervals to 300 K, 100 K intervals to 2000 K, 200 K intervals to 3000 K, and 500 K intervals at higher temperatures. Again the values should be given also at the reference temperatures, 273.15 and 298.15 K.

For purposes of smoothness, interpolation, and internal consistency, one (but seldom more than one) more digit may be retained than is justified by the absolute accuracy. For calculations on small rigid molecules, involving anharmonicity, centrifugal stretching, rotation-vibration interaction, Fermi resonance, isotopic composition, and any other significant effect, functions may be reported to three decimal digits, e.g.:

$$12.345\ \mathrm{cal_{th}\ K^{-1}\ mol^{-1}}\ \text{or}\ 51.651\ \mathrm{J\ K^{-1}\ mol^{-1}}.$$

For more approximate calculations, but with agreement with calorimetric values of $C°_p$ and $S°$ obtained by empirical anharmonicity corrections or other semi-empirical procedure, two decimal digits are appropriate. For calculations to the rigid-rotator, harmonic-oscillator, independent-internal-rotator approximation, only a single decimal digit should be retained. For even more approximate calculations (based on non-definitive calorimetric data, rough incremental calculations, etc.) the single decimal digit should be printed as a subscript, e.g.:

$$12._3\ \mathrm{cal_{th}\ K^{-1}\ mol^{-1}}\ \text{or}\ 51._7\ \mathrm{J\ K^{-1}\ mol^{-1}}.$$

6. Presentation of *p, V, T* Data

Full disclosure should be made of the use and calibration of the pressure gauge including buoyancy, local gravitational acceleration, fluid heads, pressure reference standards, and pressure point in the sample. Volumetric measurements should be referred to a calibration standard as, for example, the density of mercury or water, and the effects from combined pressure and temperature should be described. Also, volumetric data presented in terms of mass or amount of substance should include the values assumed for atomic weights as well as a statement of the corrections applied for impurity in the sample.

Here also, the importance of the presentation of primary results should be observed. Primary results are not the instrument readings but the values of physical properties derived from these instrument readings after the application of all calibration corrections, and evaluating equations, etc. These experimental values should be reported in full, together with a brief discussion of the application of various corrections and adjustments. The steps necessary to transform experimental values into final results should be made clear. Particularly, methods of smoothing results and of numerical differentiation or integration should be given as well as the sequence in which they are used. The final results should be accompanied by a statement regarding the magnitude of the difference between the smoothed and the unsmoothed results. Care should be taken to indicate clearly any results of other workers which are included in the preparation of a composite table. The base for tabulating entropy or Gibbs energy of a compressed fluid should be defined in one of the following ways:

$$\{S(p, T, \text{real}) - S(p, T, \text{ideal})\}\ \text{or}\ \{S(V, T, \text{real}) - S(V, T, \text{ideal})\}.$$

When results are presented in tabular form, the spacing of data should be sufficiently close to permit accurate mapping of the *p, V, T* surface. Consistency tests for anomalous trends should be applied whenever possible.

A related guideline *(23)* for the specialized communication of results may be of interest.

The results of thermophysical measurements leading to Joule-Thomson coefficients or $(\partial H/\partial p)_T$ should include adequate descriptions of apparatus, procedures, calibrations, and comparison measurements, as well as procedures for analysis of results.

Since more accurate characterization of the pressure scale to increasingly high values is now possible *(24)*, authors should be scrupulous in indicating the pressure scale involved.

7. Presentation of Other Equilibrium Measurements

Included in this category are such diverse measurements as vapor pressures, either by equilibrium or effusion techniques; studies of solubility, distribution, dissociation, adsorption, or other chemical equilibria, by whatever techniques are applicable; electrochemical measurements, etc. Such measurements provide information leading to the standard Gibbs energy increment $\Delta_r G°$ for a reaction, but care is needed before associating this value with a *particular* reaction. Here again, details of apparatus, calibration, and experimental procedures should be clearly presented, together with preparations of materials, analytical procedures, and any special procedures applicable to the problem. Evidence as to attainment of equilibrium should be given. Primary results, as defined in connection with p, V, T data, should be reported in full, together with results and methods for reduction of results to standard conditions, including any auxiliary information or equations, such as those from the Debye-Hückel theory of electrolytes. The chosen standard state should be clearly defined, and the final results, such as $\Delta_r G°$, $\log_{10} K$, or $\log_{10} p$, should be accompanied by an explicit description or statement of the related reaction, process, or change in state. The presentation should include a discussion of errors, and estimates of other factors including instrumental and analytical limitations, effects of non-attainment of equilibrium, side reactions, non-ideality correction, etc., to the end that the precision indices for $\Delta_r G°$ of reaction include such contributions.

Definitive studies on activity or osmotic coefficients should likewise present clear descriptions of apparatus, materials, experimental, and computational procedures, together with sufficient primary results to permit verification of derived results. A forthcoming book will discuss procedures in the areas of equilibrium measurement *(25)*. In reporting adsorption studies, the mass of adsorbent used as well as the duration of the experiment are important.

8. Non-definitive Data

Although this resolution is concerned primarily with precise and accurate measurements taken by definitive techniques on well-characterized samples it is recognized that survey measurements are often made for technical and/or analytical purposes and the results are submitted for publication. Such results may be of doubtful significance as a basis for theoretical deductions or for incorporation in critical tables of scientific data. Therefore, the foregoing recommendations do not fully apply and presentation of a brief note summarizing the most important values and heralding a more detailed documentary presentation may be appropriate. However, in differential-scanning calorimetric measurements, for example, the characterization of the solid phases before and after the experiment, the composition and pressure of the gas phase, the heating rate, the arrangement of the sample in the cell, the extent of base-line drift during the thermal effect and the way it is taken into account, should all be noted. Additional recommendations for presentation of thermal analysis data have been cited *(26)*.

References

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(2) The All-Union Calorimetry Conference (U.S.S.R.), The Calorimetry Conference (U.S.A.), The Experimental Thermodynamics Conference (U.K.), The Society of Calorimetry and Thermal Analysis (Japan), La Section de Calorimétrie de la Société Francaise des Termiciens, The International Conference on Calorimetry & Thermodynamics (meeting in Maine), and the Colloque International de Thermochimie (meeting in Marseilles).

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(5) Rossini, F. D. *J. Chem. Thermodynamics* **1970, 2, 447**.

(6) For example, National Auxiliary Publications Service of the American Society for Information Science, c/o CCM Information Corp., 909 3rd Ave., New York, New York 10022, U.S.A.

(7) IUPAC Subcommission on Standard Calibration Materials; personal communications.

(8) U.S. National Bureau of Standards, Office of Standard Reference Materials, Washington, D.C. 20234, U.S.A. *E.g.*, NBS Standard Reference Material 720 (Sapphire heat capacity standard), benzoic acid combustion standard 39i, =736 trishydroxymethylaminomethane (THAM) for aqueous solution calorimetry.

(9) Vsesoyuzny Nauchno-Issledovatel'skiĭ Institutt Metrologiĭ (All-Union Scientific Research Institute for Metrology).

(10) Calorimetry Conference standards such as *n*-heptane, benzoic acid, synthetic sapphire (aluminum oxide), and copper for heat capacity and/or enthalpy measurements.

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(15) A convenient source for this is: *Manual of Symbols and Terminology for Physiochemical Quantities and Units*, M. L. McGlashan; editor. *Pure and Applied Chemistry* **1970,** 21, 3.

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(21) The names 'Gibbs energy function', and 'enthalpy function' for $\{H°(T) - H°(0)\}/T$, have been widely used. They are presently being reconsidered by IUPAC and other international scientific unions.

(22) *Experimental Thermodynamics*, Vol. 1. J. P. McCullough and D. W. Scott; editors. Butterworths: London, **1969**.

(23) "A.S.M.E. Resolution on Communication of Experimental Data" *Mechanical Engineering* **1958**, 80, 147.

(24) *Accurate Characterization of the High Pressure Environment.* N.B.S. Special Publication 326. U.S. Government Printing Office: Washington, D.C., U.S.A. **1971**, especially pp. 1–3, 313–340.

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