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A Report of IUPAC Commission I.2 on Thermodynamics†

Assignment and presentation of uncertainties of the numerical results of thermodynamic measurements

1. Introduction

In 1972 the IUPAC Commission on Thermodynamics and Thermochemistry published its "Guide to procedures for the publication of thermodynamic data"[1] (hereinafter referred to as the Guide), which sets out in detail the requirements to be met in the detailed description of experiments. In that document, the requirements for reporting the uncertainty of experimental results are given as follows: "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." The purpose of this report is to amplify and, where necessary, to modify this paragraph. It will be assumed that the reader is already familiar with the other recommendations of the Guide.

The recommendations in the Guide ensure that readers will have available sufficient detail to understand the apparatus and method of measurement and to form a judgement on the reliability with which it would be possible to make measurements. The demonstration that the work has been done in a reliable manner should be found in the statement of the uncertainties of the primary results and if this statement is incomplete or ambiguous, much of the value of the work is lost.

In the following, apart from Section 2 on symbols and terminology, no firm recommendations are given because thermodynamic investigations are far too varied to allow brief general statements about presentations of uncertainties to be made. However, it is recommended that experimenters should study relevant parts of this report before giving any expression for the uncertainties pertaining to their numerical results.

It may be objected that to follow the suggestions made in detail will increase the length of papers and the time taken to produce them. The suggestions are, however, intended to produce the minimum amount of detail needed if the work reported is to be of permanent value. All will have had experience of cases where it has not been possible to decide on the relative merits of conflicting data because of insufficient reporting of uncertainties. Thus, years of work may be rendered useless by the failure of the author to present his results fully or perhaps by failure to battle with editors for the essential space.

Finally, it is stressed that although the reporting of uncertainties is important in enabling the reliability of numerical results to be judged, this reporting must be secondary to the presentation of the numerical results themselves.

2. Symbols and terminology

The following symbols are recommended for use in presentation of numerical results.† Short descriptions of their meaning are included. Further discussion can be found in texts on statistical treatment of experimental data.

SINGLE VARIABLE

Measurements are repeated under unchanged conditions. If x denotes an individual variable (a variate, a measurable quantity) then

Symbol	Meaning
x_i	an individual value of x in a series of measurements.
n	number of values in a series.
$\bar{x}$ or $\langle x \rangle$	(arithmetic) mean: $\bar{x} = \sum_i x_i/n$.

Comment: For sufficiently large n, possible values of $\bar{x}$ for hypothetical or actual replicate series will be approximately normally distributed (Gaussian distribution) independent of the distribution of x. If the distribution of x is reasonably symmetrical and not too disperse, a moderate sample size ($n \geqslant 4$) will usually ensure that the distribution of $\bar{x}$ is approximately normal.

d_i	deviation: $d_i = x_i - \bar{x}$.
s, s_x, or $s(x)$	calculated standard deviation of single values of x: $s = \left\{\sum (x_i - \bar{x})^2/(n-1)\right\}^{1/2}$.

Comment: The use of the term "standard error" for this quantity is not recommended.

σ, σ_x, or $\sigma(x)$ limiting value of s for large n.

Comment: The symbol σ should be used only if a sufficiently large number of measurements has been made and analysed to establish the distribution reasonably well.

$s_{\bar{x}}$ or $s(\bar{x})$ calculated standard deviation of the mean of a series: $s_{\bar{x}} = s_x/n^{1/2}$.

Comment: The use of the term "standard error" for this quantity is not recommended.

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† Prepared by the Subcommittee on the assignment and presentation of uncertainties of thermodynamic results: G. Olofsson (Sweden) in the Chair, S. Angus (U.K.), G. T. Armstrong (U.S.A.), and A. N. Kornilov (U.S.S.R.).

† They are in agreement with the Recommendations for the presentation of the results of chemical analysis[2] issued by the Analytical Chemistry Division of IUPAC.

$\sigma_{\bar{x}}$ or $\sigma(\bar{x})$	limiting value of s, that is to say σ, divided by $n^{1/2}$, $\sigma_{\bar{x}} = \sigma/n^{1/2}$. Compare comment under σ_x.

TWO OR MORE VARIABLES

If $x, y, z, \cdots$ denote individual variables and y indicates the dependent variable then

Symbol	Meaning
y_i	individual value of the dependent variable.
y_{calc}	value of the dependent variable calculated from the fit: $y_{\text{calc}} = F(x, z, \cdots)$.
d_i	residual; $d_i = y_i - y_{\text{calc}}$.
s_f	calculated standard deviation of the fit: $s_f = \left\{\sum d_i^2/(n-k)\right\}^{1/2}$.

Comment: The calculated standard deviation s_f represents both the imprecision of the experimental points and deviations due to the inadequacy of the fitting equation to represent correctly the functional relation.

k	number of numerical coefficients in the fitting equation.

Expressions for the calculated standard deviation of parameters obtained from fits of various functions to experimental points can be found in texts dealing with evaluation of experimental results, *e.g.* references 3 to 7.

In the following we shall use the word *result* to mean: numerical value of a physical property. The *primary results* are the values of physical properties derived from the instrument readings after the application of calibration corrections and evaluating equations, *etc.* Further steps, involving for instance reduction to standard-state conditions, may be needed to derive the *final results*.

3. Assignment of uncertainties

CLASSIFICATION OF UNCERTAINTIES

In what follows, the uncertainties associated with numerical results are classified at three fairly clearly defined levels:

A, those uncertainties which can be expressed as standard deviations, which represent the variations of the individual members of the set of primary results. These are usually called random errors;

B, those uncertainties associated with fixed quantities necessary to transform initial readings into results, such as calibration errors, corrections for small variations of conditions from the state in which elements of the apparatus were calibrated, *etc.* These uncertainties are generally statistically tractable, and can be combined with one another and with uncertainties of type A by established procedures. They usually originate as random errors but are constant and thus systematic in the application; and

C, uncertainties which are known to exist or are inferred but for which insufficient information is available for a statistically valid treatment to be used, so that their effect upon the result is dependent on the experience and judgement of the author. They are usually called systematic errors.

When using statistical terms, the degree of unreliability of a numerical value is more naturally described than is the reliability, hence we prefer the use of the words *imprecision* and *inaccuracy*. Random uncertainties as described under A and at least some of those under B contribute to the *imprecision* of a result. The *inaccuracy* constitutes the total uncertainty from all random and non-random contributions.

It is recognized that not all work is carried out to the highest possible accuracy, and so it is not always appropriate for results to be accompanied by the most detailed analysis of uncertainties. However, in every case the existence of these three separate levels of uncertainty must be recognized and each must be dealt with in the original paper.

REPLICATE MEASUREMENTS

Let us begin by considering a simple case: replicate measurements of some property under unchanged conditions. If the recommendations given in reference 1 are followed, then the minimum pieces of information needed to characterize the imprecision of the primary results are the number of determinations, their mean, and their standard deviation;† see paragraph A. These parameters should always be given, and any other statistic, such as the 95 per cent confidence limits, should be included at the authors' discretion. It should be noted that the validity of confidence limits, t-tests, and several other useful statistical devices depend upon the measured values being part of a Gaussian distribution; evidence of conformity to the Gaussian distribution should be given, or if no material evidence is available, the assumption should be stated.

If there are too many primary results for them to be given in full, then the number of results, their mean, and their standard deviation are not only the statement of imprecision, but also the description of the experimental results.‡ It is useful to include some statement which will show whether this compressed description is adequate: for example, is the distribution symmetrical? and are there any results unusually far from the mean? We recommend the use of histograms, which while summarizing a great deal of information very compactly, are useful to critical readers.

The history of previous experiments with the same apparatus and the experimenter's expectation of the uncertainties are valid information for the reader. A statement should be made about the relationship of imprecision found to imprecision

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† It is important to make clear whether the number given is the standard deviation of a single measurement $s(x)$, or the standard deviation of the mean $s(\bar{x})$.

‡ Kornilov and coworkers have discussed the compact representation of thermodynamic results in a series of papers; see *e.g.* references 8 and 9. The "Recommendation by the Scientific Council on Chemical Thermodynamics and Thermochemistry at the USSR Academy of Sciences Concerning the Compact Representation of Experimental Data in the Publication of the Results of Thermochemical and Thermodynamic Studies"(10) summarizes the work. The text of that Recommendation was prepared by A. N. Kornilov, L. B. Stepina, and V. A. Sokolov.

expected. In assessing the imprecision expected the use of pooled standard deviations should be considered; see Appendix 1.

The effect of possible uncertainties in the various corrections made to the primary results should be discussed; see paragraph B. It is reasonable to deal only briefly with those corrections which do not affect the result significantly no matter what reasonable uncertainty may exist. Uncertainties which might arise because the measurements cannot be made under exactly the same conditions should be considered here.

Significant uncertainties that could result from corrections can be combined with the initial primary imprecision by using the "propagation-of-error" formula; if

$$y = \mathrm{F}(x, z, \cdots, w), \tag{1}$$

and the uncertainties in $x, z, \cdots, w$ are $\Delta x, \Delta y, \cdots, \Delta w$, respectively, then the uncertainty Δy in y is given by

$$\Delta y = \{(\partial y/\partial x)^2(\Delta x)^2 + (\partial y/\partial z)^2(\Delta z)^2 + \cdots + (\partial y/\partial w)^2(\Delta w)^2\}^{1/2}, \tag{2}$$

if $x, z, \cdots, w$ are independent. If for $\Delta x, \Delta z, \cdots, \Delta w$ are substituted $\sigma(x), \sigma(z), \cdots, \sigma(w)$ then Δy is $\sigma(y)$: if $s(\bar{x}), s(\bar{z}), \cdots, s(\bar{w})$ are substituted then the resulting Δy is $s(\bar{y})$. A useful discussion of propagation of errors is found in the paper by Ku.(11)

There remain other sources of uncertainty, which are not under the control of the experimenter and which are not linked to the results by any explicit mathematical relation; see paragraph C; a typical example is an uncertainty in the purity (or composition) of the substance (or system) under investigation. Such an uncertainty does not affect the imprecision of the measurement. It affects the certainty with which the measurement can be attributed to a specific system or process.

Possible systematic errors in the experimental method also belong to this category of uncertainties. Estimates of bounds for uncertainties in various steps of the measurement process have to be made and combined to give an estimate of the overall inaccuracy. This estimate should be checked whenever possible by performing measurements using well-characterized reference materials.(13,14) Reference may be made to earlier publications for details about the estimation procedure.

It is usually possible to establish bounds for non-random uncertainties; it is usually difficult to establish the statistical distribution to which such bounds refer. The author may list each of these with his estimate of their possible effects, or if the author feels it important, he may also report his estimate of their total effect on his accuracy. There is no accepted method of handling such combinations and so it is essential that the method chosen by the author be given.

A simple way to handle this combination of non-random uncertainties is as follows. Given that

$$y = \mathrm{F}(x, z, \cdots, w), \tag{3}$$

with estimates of uncertainty $\Delta x, \Delta z, \cdots, \Delta w$, then the corresponding uncertainty in y is

$$\Delta y = |\partial y/\partial x|\Delta x + |\partial y/\partial z|\Delta z + \cdots + |\partial y/\partial w|\Delta w. \tag{4}$$

This will overestimate the size of Δy and can be considered as an estimate of the maximum possible uncertainty. Another method, usually preferable, is to use the propagation-of-error formula to give

$$\Delta y = \{(\partial y/\partial x)^2(\Delta x)^2 + (\partial y/\partial z)^2(\Delta z)^2 + \cdots + (\partial y/\partial w)^2(\Delta w)^2\}^{1/2}. \tag{5}$$

An interesting discussion of this and some other controversial problems in statements of uncertainties is given in a recent paper by Müller.(15)

Both methods require estimates of $(\partial y/\partial x)$, which may be difficult to find, but it should be remembered that we are here dealing with the errors of errors and very crude estimates will suffice.

In the assignment of the uncertainty pertaining to an experimental result the estimation of non-random errors is usually the most difficult as well as the most important part, requiring much effort and ingenuity. What must never be done, however, is to follow a statement of imprecision of the results with an unqualified statement of an undefined overall error. Such a statement simply throws on the reader the responsibility for finding a meaningful statement of error. Useful discussions of this and related problems are given in references 16† and 17.

FUNCTIONAL RELATIONS

When the conditions for replicate experiments differ considerably from measurement to measurement, there is a point when it is necessary to consider these measurements as independent experiments. An example of this class of experiments is measurement of vapour pressure as function of temperature. Frequently the quantity of interest will be dependent on not one but two or more variables. The results are usually evaluated by least-squares fitting of an equation.

Functional relations are of three kinds. In the first kind, which is rare, both the relation and the values of any numerical coefficients are known on sound theoretical grounds. In the second kind the functional relation is known to hold, but the numerical coefficients need to be determined. In the third kind, which is the most common, neither the functional relation nor the numerical values of the coefficients are known. It should be made clear, if least-squares techniques are used, whether the equation is of the second or third kind.

If the correct functional form is known then (ignoring the possibility of error in the theory) the deviations of the experimental points from the fitted equation give an estimate of the total uncertainty in the results since the deviations combine the errors of experiment with the errors of the mathematical process. If the coefficients have physical significance then it is useful to quote the standard deviations of the coefficients. If these are relatively small, differentiation can be done with reasonable confidence, and since the form of the relation is based on theory, extrapolations can be made within the limitations imposed by theory.

Where neither the correct functional form nor the coefficients are known the choice

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† An extensive bibliography on the evaluation of imprecision and accuracy of experimental results will be found in reference 16.

of equation should be explained and the number of adjustable parameters justified (by *e.g.* an F-test).(3,4,6,7,9)

The differences between the observed values of the dependent variable and predicted values obtained by substitution in the fitted equation reflect both the imprecision of the observed values and the inadequacy of the chosen equation to represent the results. The two error components can be separated only if enough replicate measurements have been made to allow independent evaluation of the imprecision.

The dispersion of the fit is usually characterized by the standard deviation of the fit s_f.

The residuals give a minimum estimate of the uncertainty since unexpected effects linked to the independent variables, such as variation of composition with temperature, cannot be taken into account.

It is the responsibility of the author to show that the result of using least-squares techniques produces anything more than an interpolating equation. That the equation is more than an empirical relation between the measured values can be shown by comparing its predictions with other measurements, especially those involving differentiation or extrapolation. If such checks are not made then predictions outside the range covered by measurements, that is, extrapolations, should be made only with great caution. Their reliability cannot be established by statistical methods. Results of differentiations of empirical relations should also be treated cautiously. Particularly if successive differentiations are made, the question should be considered whether the information content of the primary results is good enough to give meaningful higher-order derivatives. The influence on the estimated uncertainty of the form of the model equation should also be taken into consideration. For further discussion of these problems see Appendix 2 and reference 4.

4. Presentation of uncertainties of thermodynamic results

It is not practicable to give detailed recommendations for presenting uncertainties of all types of thermodynamic investigations. The aim should be to give as complete a description as feasible of the uncertainties of presented results bearing in mind that different readers may find different uses for the values and thus may need different types of information about the uncertainties. Various types of uncertainties should be carefully distinguished, preferably using the classification discussed above. Methods used to derive the different categories should be given as well as ways in which uncertainties are combined.

The numerical statement of imprecision rarely merits more than two significant figures. It is the magnitude of the imprecision that should determine the number of significant figures in the reported result.

The following papers contain useful discussions about statements of uncertainties of final results: "Expressions of imprecision, systematic error, and uncertainty associated with a reported value" by Ku,(18) "Expression of the uncertainties of final results" and "Realistic evaluation of the precision and accuracy of instrument-calibration systems" both by Eisenhart.(17,19) Likewise "A code of practice for the detailed statement of accuracy" by Campion, Burns, and Williams(20) is recommended.

In the following sections the presentation of uncertainties of results is discussed for some important kinds of thermochemical, thermophysical, and equilibrium studies. It is convenient to refer to the generalized concept of a thermodynamic measurement and its use to calculate thermodynamic quantities, schematically shown in figure 1.(21)

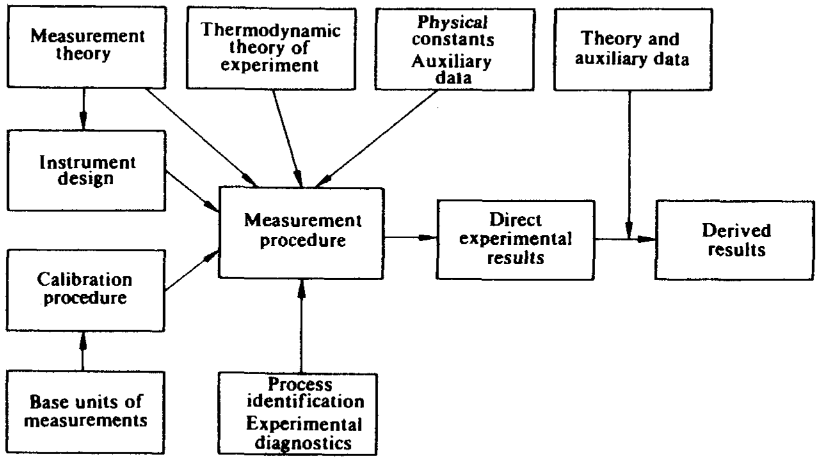

FIGURE 1. Schematic thermodynamic measurement.

Terms entering the design, execution, and interpretation of the experiment are shown as contributions, with arrows pointing to the "measurement procedure" box in the centre. The group of contributions in the upper part of the diagram relate to the design of the experiment: the theoretical thermodynamic and measurement concepts on which the experiment is based, the design and construction of an appropriate apparatus, and the use of appropriate physical constants and auxiliary data.

A second set of contributions relates to the calibration and verification of the measurement devices and the measurement apparatus, by which the measurement is referred to an acceptable set of measurement units. The calibration can include the use of reference materials or processes.

A third and most important contribution is the identification of the process that occurred, and verification and quantification by appropriate diagnostic tests and analyses.

From this assembly of apparatus and concepts are obtained the primary measured results from which can be calculated the direct results. Further mathematical treatment of the results or their use in an appropriate theory, together with additional auxiliary data, leads to final thermodynamic quantities.

The analysis of random and systematic uncertainties should be made with reference to all the contributions indicated in figure 1, and such other contributions as are considered by the experimenter to be of possible significance. These contributions should be considered not only for their possible direct effect on the measurement, but also as these uncertainties might be propagated through the measurement and calculation procedure to the final calculated results. In the measurement some contributions will be suitable for replicate measurements. Others constitute nearly replicate measurements, but with differences from one experiment to another that are easily adjusted to a common set of measurement conditions, at which point they can be treated as replicate measurements. Still a third group of measurements involve systematic shifts of the independent variable (often temperature) over a range of values; and at each condition the corresponding dependent variable is then measured. Finally, there are the quantities that are derived by differentiation, by integration, or by other mathematical manipulation of the experimental results.

To the extent that the component contributions to the experiments are changed from one experiment to another, the random uncertainties in those contributions are included in the random uncertainty of the experimental results. Contributions that are not changed in the experiment and that are treated as constants will have independent standard deviations which might be well known and which should be combined with the experimental standard deviation using equation (2) in order to obtain an overall standard deviation of the result.

THERMOCHEMICAL CALORIMETRIC MEASUREMENTS

The assignment of uncertainties to thermochemical measurements has been discussed by Rossini and Deming,(22) Rossini,(23) and more recently by Olofsson.(24) Although these articles have been written with particular reference to combustion calorimetry they apply to a large extent to other types of calorimetry. In reporting results of calorimetric measurements the following items should be included if applicable.

The imprecision of the primary experimental results normally expressed as the standard deviation of the mean $s(\bar{x})$, should be calculated from the results of a series of repeated measurements. In addition to the mean $\bar{x}$ the number of measurements n should be reported. In case the calibration of the calorimeter system is done in a separate series of measurements, as is usually the case in combustion calorimetry, the imprecision of the energy equivalent should be included as well as its actual value. Pertinent uncertainties in auxiliary materials, auxiliary data, extent of reaction, and influence of side reactions, *etc*., should be given. They can usually be expressed as standard deviations of means or can be construed as such and should be combined with estimates of imprecision of the primary result (including calibration) using relation (2) to give an overall standard deviation of the mean. This will be an estimate of the total imprecision of the final result.

Uncertainty in purity of samples and effects of impurities on measured value(s) may be treated separately or included under "extent of reaction" mentioned above. Possible non-random uncertainties that might affect the results should be given and treated as discussed above.

Reported final values should thus be accompanied by separate statements about their overall imprecision, expressed as the overall standard deviation or a multiple thereof, and by credible bounds to likely systematic errors.

Rossini and Deming(22) and Rossini(23) recommended the use of the "uncertainty interval" to indicate the imprecision of a thermochemical value. It was defined by them as twice the final overall standard deviation of the value. Later the "uncertainty interval" has also been used to indicate the accuracy of reported values. The term "uncertainty interval" has become an ambiguous term which authors should not use without clear specification of its meaning.

Results of measurements of excess enthalpy (of mixing) over a wide composition range are probably best reported in the form of an empirical equation expressing H^{E} as a function of composition, together with a graph or table showing the deviations between measured values and values calculated from the smoothing function. Estimates of imprecision in the form of standard deviations of the individual values and of the fit should be reported. Comments should also be made on the overall accuracy of the calorimetric measurements as estimated from experiments on recommended test systems.(13)

THERMOPHYSICAL CALORIMETRIC MEASUREMENTS

In this section we consider particularly determinations of heat capacities, enthalpies, related quantities such as enthalpies of phase change, and derived quantities such as entropies, that are measured calorimetrically. The assignment of uncertainties in relation to specific types of measurements is discussed in various chapters of McCullough and Scott.(25)

Temperature measurement is an all-pervasive feature of thermophysical calorimetry. It is used, in general, in three ways: (1), to establish the thermodynamic temperature to which the measured property of a material is to be assigned; (2), to measure temperature increments, as in measuring the heat capacity of a material; and (3), to measure small temperature differences in order to measure or control heat flow. In the analysis of the experiment, uncertainties in these three kinds of uses may have quite different effects on the overall uncertainty of the experiment.

The assignment of a temperature to the property depends upon having a calibrated thermometer. The possible uncertainties include: (1), uncertainties inherent in the use of the measuring instruments themselves, such as the measurement of the true resistance of a resistance thermometer; (2), uncertainties in attributing the temperature of the material under test to the temperature indicated by the thermometer; (3), uncertainties in the standardization of the thermometer against fixed points of the international practical temperature scale (IPTS); (4), uncertainties in the faithfulness with which the interpolation formula used for the particular thermometer fits the IPTS between fixed points; and (5), deviations of the IPTS from the thermodynamic temperature.

To find the possible uncertainty in attribution of a thermometer reading to a temperature of a material requires a careful analysis of the experimental arrangement and manner of conduct of the experiment. Only the experimenter is in a position to do this effectively and to make diagnostic tests to verify his analysis, and also to verify the accuracy of his instrumental readings.

The remaining uncertainties depend on how the temperature measuring instrument was calibrated and on the temperature scale used. A standardizing laboratory should make a statement about the uncertainty of calibration of instruments they calibrate; they may not be able to make any statement about the degree of permanence of the calibration, but the author should bear this in mind in his assignment of uncertainties.

Differences between the IPTS and the thermodynamic temperature are discussed by Working Group III of the Consultative Committee for Thermometry (CCT) for the region above 273.15 K.(26–28) Further discussion which includes the region below 273.16 K is given in references 29 and 30.

Descriptions of the errors of interpolation between calibration points are particular to the kind of thermometric device. For thermocouples of various metals such descriptions are given by Powell *et al.*(31) who also give references to information about instabilities. Similar descriptions are given by Riddle *et al.*(32) for platinum-resistance thermometry, by Kostkowski and Lee(33) for optical pyrometry, and by Wise(34) for liquid-in-glass thermometers.

Sources of uncertainties in determining temperature increments involve the precision and accuracy of determining the instrumental reading, the uncertainty in the derivative of the temperature interpolation formula, and the uncertainty in assuming the lower and upper temperatures of the thermometer to be the same as those of the material.

Sources of uncertainties in assessing presence or absence of heat flow because of temperature differences are possibly the most difficult to ascertain. The factors involved here include: (1), whether the thermal sensors are firmly enough stationed on the surfaces of which they are measuring the temperature differences; (2), the proper averaging of the temperatures of the surfaces involved on the basis of a relatively small sampling of surface temperatures; and (3), whether an apparent zero drift rate of the thermometer indicating the temperature of the calorimeter vessel truly reflects zero transfer of work and heat to the vessel.

Hartshorn and McNish(35) discuss in a general way the measurement of electrical energy, its relation to the base units of measurement, and the uncertainties in the measurements. It is clear that with proper care it is possible to make the measurements with inaccuracies that are small compared with other errors in calorimetry. However, not all electrical measurements are made with maximum accuracy, and it is important for the experimenter to identify clearly the inaccuracies in the method of energy measurement used. More important than the energy measurement itself is the proper accounting of the transfer of energy to the test sample itself, and a proper accounting of energy losses and energy transferred to the sample from other sources. As a specific example of a detailed energy accounting problem, Ginnings and West(36) discuss the errors caused by electrical energy dissipation in heater leads.

With respect to specific types of calorimetric measurements, one may find discussions of precision and accuracy relating to high-temperature drop calorimetry by Douglas and King(37) with earlier discussions by Ginnings and Corruccini,(38) Furukawa *et al.*,(39) and Hoch and Johnston.(40) Some particular sources of error in the measurements themselves are: measurement of the temperature of the sample; calibration of the calorimeter; calibration of instruments such as standard cells, potentiometers, thermometer bridges, thermocouples, and pyrometers; the calorimetric measurement itself, including allowance for heat-lack corrections; sample impurities and mass changes; empty-container measurements; and the loss of unmeasured heat by the sample during the drop and in the calorimeter. The calibration uncertainties of some of the instruments mentioned here are part of the error discussed by Hartshorn and McNish.(35)

In drop calorimetry, the results reported for a material are enthalpy increments $\{H(T)-H(T_{\mathrm{ref}})\}$ as a function of temperature T, where T_{ref} is the final temperature of the calorimeter after drop.

The enthalpy increment is measured as the work and heat transferred to the calorimeter. Here, the calibration constant of the calorimeter is important. The upper temperature to which the measurements are referred depends on the accuracy of measurement of the sample temperature, which can be measured directly by a pyrometer or can be inferred from a measurement of furnace temperature. This inference also includes an uncertainty. During the drop some enthalpy losses occur and must be allowed for. The uncertainties in these losses constitute an error in the enthalpy attributed to the sample. Another type of uncertainty associated with this type of measurement is the possible freezing-in of a metastable state of the sample at its final temperature. To the extent that this occurs in a random way it constitutes an imprecision. To the extent that it is repeatable, it constitutes a systematic uncertainty of the measurements. If a means can be found to eliminate this lack of equilibrium this source of uncertainty can be reduced or eliminated.

The resulting measurements of enthalpy increments are used to derive values of heat capacity and entropy. The uncertainty of the heat capacity is difficult to estimate (see derivative quantities in equilibrium measurements). The process of differentiating the enthalpy can cause the relative uncertainty characteristic of the heat capacity to be a factor of 2 or more greater than the relative uncertainty of the enthalpy if the heat capacity itself is changing rapidly with temperature. The uncertainty of the derived entropy is somewhat more definite. It can be calculated from the equation

$$S(T)-S(T_{\mathrm{ref}}) = \{H(T)-H(T_{\mathrm{ref}})\}/T + \int_{T_{\mathrm{ref}}}^{T} [\{H(T)-H(T_{\mathrm{ref}})\}/T^2]\mathrm{d}T. \qquad (6)$$

By substituting the uncertainties of the enthalpy measurements in the second part and integrating graphically, the uncertainty of the entropy can be determined. It is a close approximation to assume the same percentage uncertainty for the entropy increment as for the enthalpy increment.(37)

This example illustrates a common problem of thermophysical calorimetric measurements: the use of measured results to derive quantities related by well-known thermodynamic relations between the functions. Both the derivative functions and the integral functions may be of interest in these or in other measurements. Propagation-of-error formulas, graphical evaluation, or modelled simulation of the effects of uncertainties in the measured values should be used to make estimates of the uncertainties of the results derived in these ways. A discussion of sources of uncertainties and methods of handling them for rapid dynamic calorimetry (millisecond resolution) are given by Cezairliyan and Beckett.(41)

An important resource for improving the reliability of the measured results of calorimetric studies is the use of standard reference materials. These can be used to provide a direct comparison between the measurements obtained in different laboratories. The IUPAC Commission on Physicochemical Measurements and Standards has published(13) a list of recommended reference materials for calorimetric measurements. These include reference materials for heat-capacity measurements and reference materials for enthalpy-of-transition measurements. Citation of a study of a reference material using the same technique is a valuable indication of the accuracy of a reported series of enthalpy measurements, and the use of reference materials in this way is recommended.

UNCERTAINTIES OF NON-CALORIMETRIC THERMOPHYSICAL MEASUREMENTS

In this section we consider what may be defined as non-calorimetric thermophysical measurements, which include (p, V, T) measurements, saturated density measurements, and any other measurements which give information on the (p, V, T) surface of a fluid.

The standard experimental procedure is to make a series of measurements of two of the variables while the third is held constant, repeating the series at further constant values of the third variable. Thus we may speak of measurements along isotherms, or along isochores, or rarely along isobars. Measurements in or at the boundary of the two-phase region may then be described as being made at saturation.

The measurement of pressure is described in detail in several sections of Le Neindre and Vodar(42) and the various corrections necessary to the instrument readings should be reported with an estimate of their imprecision. If any of the corrections are found to be negligible, this should be stated. The most precise measuring device for the range 0.1 MPa to 500 MPa, the piston gauge, has an imprecision proportional to the pressure. Since the piston gauge measures the pressure above that of the atmosphere, and the atmospheric pressure is measured on a standard barometer, usually it is tacitly assumed that the error in the measurement of atmospheric pressure is negligible; however, through use of the principle of propagation of errors, the two may be combined in the following form: $\sigma(p) = (a^2 + b^2p^2)^{1/2}$ where a denotes the standard deviation σ of the barometer reading and b denotes the relative standard deviation σ_r (see Appendix 1) of the piston-gauge measurements.

The measurement of the specific volume of fluid is also discussed in Le Neindre and Vodar.(42) This requires two measurements: of the volume of the container and of the mass of the fluid. The latter may be determined as a difference between two weighings, or by expansion of the fluid to a pressure where its equation of state is known to be accurate. In either case the possible causes of uncertainties are known and can be listed with their values. The volume of the container can also be measured accurately at room temperature and pressure: its variation as the pressure and temperature are changed can only be calculated and is the major source of error. Not only is the calculation necessarily imprecise, but it might also be in error because of the assumptions made, an error which is itself a function of pressure and temperature. Discussion of this problem needs to be detailed, with a clear division between the uncertainties which can be expressed as a standard deviation, and those which might result in a systematic error.

The measurement of the temperature of the fluid is comparatively straightforward, the main problem being caused by the necessarily heavy containers in which the fluid is confined. If the thermometer is outside the container, it is necessary to demonstrate that the temperature recorded by the thermometer is that of the fluid: if this is accomplished by leaving the experimental system for long periods, the question of the stability of the thermostat must be discussed. If the thermometer is inside the container, the effect of pressure on resistance (if a resistance thermometer is used) or on e.m.f. (if a thermocouple is used) must be taken into account, a problem on which there is almost no information.

In past reports, it is usually found that because of the need to cover large areas of the (p, V, T) surface no measurement is repeated a sufficiently large number of times for a reliable estimate of the standard deviation to be made, although in some cases the results given are the mean of a number of readings. The errors which are quoted in these reports, such as "the temperatures are not in error by more than ± 0.01 K", are the result of long experience and as such are to be respected, but they are not statistical in nature. A more informative procedure, which we recommend experimenters to consider, would be to measure each point a small number of times and to treat each group as a small sample drawn from a large population; see Appendix 1. Use can be made of the tables normally associated with control charts for industrial quality control (see, for example, reference 4). In this way the mean range of each sample can be converted into a standard deviation (bearing in mind that it is $\ln p$ not p that is normally distributed). These standard deviations can then be checked by using for instance Bartlett's test(43) if it is desired to discover whether they differ significantly from one another.

OTHER EQUILIBRIUM MEASUREMENTS

In order to discuss thermodynamic results from equilibrium measurements, with respect to the treatment of uncertainties, we refer again to the generalized concept of a thermodynamic experiment and its use to calculate thermodynamic quantities; figure 1. A proper treatment of uncertainties in this experiment requires careful examination of all of these contributions and their propagation through to the final results.

Typical equilibrium measurements are measurements of: vapour pressures in all pressure ranges and by dynamic and static procedures; solubilities; partition coefficients or distribution constants; dissociation constants and other chemical-reaction equilibria; adsorption equilibria; solid-solid phase equilibria; electrode potentials; and other galvanic-cell potentials. Derived quantities closely related to equilibrium measurements include activity coefficients and osmotic coefficients on the one hand, and Gibbs energy changes on the other.

To the extent that replicate measurements result from measurements using the same experimental system, random uncertainties in the parts of the experiment that are varied from experiment to experiment are included in the calculated standard deviation of the mean. Portions of the experiment that are not changed during the experiment and are treated as constants during the experiment will have independent standard deviations which should be combined with the experimental standard deviation in order to obtain an overall standard deviation of the result.

Sources of possible systematic errors will vary from one kind of experimental measurement procedure to another. An extremely important source of potential error is the identification of the process to which the thermodynamic equilibrium quantities are to be assigned. An error here can make the measurements essentially meaningless. It is essential to the valid reporting of measurements that the experimenter make appropriate tests (diagnostics) to demonstrate that the quantity measured indeed belongs to the process to which the value is ascribed. The experimenter is in by far the best position to make confirmatory tests.

When numerical results from an experiment cannot be conveniently replicated exactly, it is often possible to make an approximate replication by taking several measurements under nearly the same conditions and adjusting them to a uniform reference set of conditions using theoretical relations between the variables. Using this procedure it is possible to obtain enough information to estimate the standard deviation.

For the more general case where measurement of a relation between variables is the goal of the experiment, a least-squares analysis of the results is necessary, as is discussed in Section 3.

When derived quantities are obtained from the original measurements by differentiation, restraint is needed in inferring the imprecision or inaccuracy of the derived quantities.

In assessing the propagation of errors in such numerically derived results, the modelling of the derivation process using simulated errors in the input data as described and illustrated by Timini(44) is recommended.

In cases where differentiation must be done, it is suggested (see, for instance, references 45 and 46) that the differentiation be done by numerical treatment of the original measurements rather than of the smoothed results. Numerical differentiation(47) also provides a device for rational selection of the degree of polynomial justified by the experimental results.

A discussion of principal sources of error in e.m.f. measurements in molten salts (as distinguished from more general sources of error related to measurement of temperature, composition, impurities, *etc.*) is given by Braunstein and Braunstein.(48) Takaishi(49) gives a discussion of principal sources of error in measurements of adsorption isotherms and pressure measurements related to adsorption. Whalley(50) gives a discussion of the principal sources of error specifically associated with measurements of the compression of liquids.

Le Neindre and Vodar(51) list among sources of systematic errors in equilibrium measurements: the sensitivity or resolution possible in the measurements; the assumption made in processing the results; possible systematic trends including both those for which corrections are made and those for which no correction is made; uncertainties in auxiliary data taken from other work; and uncertainty in the method of computing.

Le Neindre and Vodar(51) offered rather explicit recommendations for stating the uncertainties of final results; they are commended to the reader.

Appendix 1. Pooled standard deviation

The problem often arises that one wishes to combine several series of measurements performed under similar conditions to get an improved estimate of the imprecision of the process. In case it can be assumed that all the series are of the same precision although their means may differ, the pooled standard deviations s_p from k series of measurements can be calculated(4,5,52) as

$$s_p = [\{(n_1-1)s_1^2+(n_2-1)s_2^2+\cdots(n_k-1)s_k^2\}/(n_1+n_2+\cdots n_k-k)]^{1/2}. \tag{7}$$

The suffices 1, 2, $\cdots$, k refer to the different series of measurements. In this case it is assumed that there exists a single underlying standard deviation σ of which the pooled standard deviation s_p is a better estimate than the individual calculated standard deviations $s_1, s_2, \cdots, s_k$.

For the special case where k sets of duplicate measurements are available, equation (7) reduces to

$$s_p = \left\{\sum_i^k (x_{i1}-x_{i2})^2/2k\right\}^{1/2}. \tag{8}$$

In many cases the imprecision is not constant as assumed above but is proportional to the level of the measured quantity. It can then be reasonable to assume that there is a constant *relative standard deviation* σ_r, or $\sigma_r(x)$, characterizing the imprecision. The *calculated relative standard deviation*† (of single values of x) is denoted s_r or $s_r(x)$ and calculated from the results of a series of measurements as

$$s_r = s(x)/\bar{x} = \{\bar{x}^{-2}\sum(x_i-\bar{x})^2/(n-1)\}^{1/2}. \tag{9}$$

Results from various series of measurements can be combined in the following way to give a pooled relative standard deviation $s_{r,p}$:

$$s_{r,p} = \left[\left\{\sum(n_i-1)s_{r,i}^2\right\}/\sum(n_i-1)\right]^{1/2} = \left[\left\{\sum(n_i-1)s_i^2\bar{x}_i^{-2}\right\}/\sum(n_i-1)\right]^{1/2}. \tag{10}$$

An alternative way of calculating $s_{r,p}$ is given in reference 4:

$$s_{r,p} = \left[\left\{\sum(n_i-1)s_i^2(\ln x)\right\}/\sum(n_i-1)\right\}^{1/2}, \tag{11}$$

that is the calculated standard deviations of ln x are combined. These two ways of calculating the pooled relative standard deviation appear to give equivalent results.(53)

To test whether the various series of measurements that one wants to combine actually are of the same precision, the calculated standard deviations can be

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† The use of the term "coefficient of variation" instead of relative standard deviation is not recommended.(2)

compared. The best known method for such comparisons is the Bartlett test.(43) This method is, however, sensitive to departures from the assumption of Gaussian distribution. A method which does not require this assumption is described in Appendix 6E of reference 4.

Appendix 2. Uncertainties and least-squares techniques

When it is necessary to replace the discrete set of results obtained from an experiment by a continuous function, the method of least squares is almost invariably used and this has implications for the process of assigning uncertainties. We define the least-squares procedure by the following.

For the set of variables y, x_0, x_1, $\cdots$ there are n measured values such as y_i, x_{0i}, x_{1i}, $\cdots$ and it is decided to write a relation:

$$y = f(a_0, a_1, \cdots, a_K; x_0, x_1, \cdots) \tag{12}$$

where $a_0, a_1, \cdots, a_K$ are undetermined numerical constants. If it is assumed that each measurement y_i of y has associated with it a number w_i^{-1} characteristic of the uncertainty, then numerical estimates of the $a_0, a_1, \cdots, a_K$ are found by constructing a variable S, defined by

$$S = \textstyle\sum_i \{w(y-f)\}_i^2, \tag{13}$$

and solving the equations obtained by writing

$$(\partial S/\partial a_j)\tilde{a}_j = 0, \quad (\tilde{a}_j = \text{all } a \text{ except } a_j).$$

If the relations between the a and y are linear, this is the familiar least-squares technique of fitting an equation to a number of experimental points. If the relations between the a and y are non-linear, there is an increase in the difficulty of finding a solution, but the problem is essentially unchanged.

The result is a convenient continuous functional representation of a set of discrete points. If the w_i^{-1} can at each point be identified with $\sigma^2(y_i)$, the y_i all have a Gaussian distribution, and all the $\sigma(x_i)$ are negligible, then the result is an unbiased estimate with a minimum value of S as compared with any other method of evaluating the continuous function from the discrete points. Clearly the result can only be the best estimate if the function is known on *a priori* grounds to be the correct one for the phenomenon studied. If this is so, then the values of the numerical coefficients may have physical significance and their standard deviations are of interest.

The above conditions are those found in textbooks on the standard treatment of the least-squares technique. It is rarely mentioned that there is a further condition: that the relative standard deviation (see Appendix 1) of every variable should be low at every point. If this is so, then even if the other conditions do not hold, the resulting function may be very useful (*e.g.* its second derivatives may be accurate). If this condition does not hold, then even if every other condition is fulfilled, the resulting function may be no more than an interpolating formula and, in particular, the values of $a_0, a_1, \cdots, a_K$ may be cross-correlated and heavily dependent on exactly which results are used in the fit.

To assess the uncertainty of the derived final results one can investigate the sensitivity of the output data for errors in the input data by means of an *experimental perturbational calculation*:(54) one performs the calculations many times with perturbed input data and studies the relation between the changes (perturbations) in the input data and the changes in the output data. The perturbations are preferably generated using random numbers with a distribution function chosen to mimic the distribution of uncertainties in the primary results. It is regrettable that even in the special literature the discussion of the planning and analysis of such numerical experiments is surprisingly meagre.

An alternative method to estimate uncertainties is offered by *interval analysis* using *interval arithmetic*. Here the input data are the primary values plus limits of intervals expressing their uncertainty. The output consists of derived values plus limits of intervals expressing a pessimistic estimate of maximal uncertainty. In reference 55 a computer program for this type of calculation is described. At the present stage of development the use of the method is limited by difficulties in interpreting the meaning of the calculated uncertainty bounds and by the long calculational times needed. However, rapid progress is expected and this method may soon become a useful tool in estimating uncertainties in derived thermodynamic quantities.

Considerable ingenuity is sometimes used to obtain an estimate of w when the standard deviations of the independent variables are not negligible when compared with that of the dependent variable, usually by using the "propagation-of-error" formula. This fails when the independent variables used in the function are themselves compound functions of the measured variables, since the relation between them requires derivatives which are unobtainable. If the relative standard deviations are low, crude estimates of weights are sufficient: if the relative standard deviations are high, no sophistication with weights can turn poor data into good data. An excellent description of a method which works will be found in Haar and Gallagher's study of the thermodynamic data for liquid and gaseous ammonia,(56) and whatever its statistical legitimacy, it is justified by an appeal to the result, which is a (p, V, T) surface fitting the data to within experimental precision and also giving derivatives from which can be calculated other properties such as heat capacities, speed of sound, and Joule—Thomson coefficients which agree with experimentally measured values to within their imprecision.

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