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STANDARDS IN ISOTHERMAL MICROCALORIMETRY

(IUPAC Technical Report)

Prepared for publication by
INGEMAR WADSÖ^{1,‡} AND ROBERT N. GOLDBERG²

¹Physical Chemistry 1, Chemical Center, University of Lund, P.O. Box 124, S-221 00 Lund, Sweden;

²Biotechnology Division, National Institute of Standards and Technology,
Gaithersburg, MD 20899, USA

*Membership of the Commission during preparation of this report (1998–2001) was as follows:

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Chairman: I. Wadsö (Sweden); **Members:** A. E. Beezer (UK); R. N. Goldberg (USA); G. Olofsson (Sweden); K. Murphy (USA); J. Rouquerol (France); J. Sipowska (USA).

[‡]Corresponding author

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Standards in isothermal microcalorimetry

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Abstract: The main calorimetric principles used in isothermal microcalorimetry are briefly discussed. Different chemical calibration and test reactions are discussed, with a focus on reactions suitable for ambient conditions: reactions initiated by mixing of liquids (including titration microcalorimetry), dissolution of solid compounds and of slightly soluble gases, a photochemical process, and thermal power signals released over an extended period of time. Guidelines on the use of standardized chemical test and calibration reactions in isothermal microcalorimetry are presented. A standardized terminology in reporting characteristics of isothermal microcalorimeters is proposed.

1. INTRODUCTION

The term “isothermal microcalorimeter” is commonly used for calorimeters designed for use in the microwatt range, under essentially isothermal conditions. The word “isothermal” is in this connection normally not used in a strict sense, but is merely an indication that the temperature of the calorimeter is constant or very nearly so within narrow tolerances.

Isothermal microcalorimetric techniques have been much improved during the past decades, and several types of instruments are commercially available. Application areas include, for example, ligand binding studies, dissolution and sorption measurements, estimation of the stability of chemical substances and technical products, and measurements of metabolic reactions in living cellular systems.

Essentially, all physical and chemical processes and reactions are accompanied by the absorption or release of heat, and calorimeters are therefore used in a broad range of applications. However, as calorimetric measurements are nonspecific, this property can make calorimetric results subject to systematic errors from evaporation, condensation, adsorption, corrosion, friction, and various spurious chemical or biological reactions. Another important source of systematic error is the calibration itself. As may be expected, the smaller the measured heat or thermal power, the more systematic errors tend to be difficult to control.

Most isothermal microcalorimeters are calibrated by the release of heat in an electrical heater positioned in the calorimetric vessel or in its close proximity. However, in some cases it is difficult to conduct electrical calibration experiments, which will closely mimic the heat flow pattern of the process or reaction under investigation. This can lead to a significant error in the calibration value and, in some cases, the use of some chemical calibration would therefore be preferable. Regardless which calibration technique is used, it is often desirable to quantitatively control the overall performance of an instrument by use of a suitable test reaction. Simple and reliable test reactions are also very suitable for the training of experimenters. In order to allow a close comparison between results from chemical calibrations or test experiments and results from a calorimetric investigation, it is important to have many different chemical calibration and test reactions available.

In this report, guidelines are presented on the use of standardized chemical test and calibration reactions suitable for use in different areas of isothermal microcalorimetry. The focus is on reactions suitable for use under ambient conditions. Further, a standardized terminology in describing the characteristics of isothermal microcalorimeters is proposed. “Nanocalorimeters”, usually indicating calorimeters with a detection limit approaching the nanowatt range, are in this report not distinguished from “microcalorimeters”.

2. MAIN CALORIMETRIC PRINCIPLES

When a calorimeter is calibrated, the calorimetric signal is standardized by release of an accurately known heat, q , or thermal power, $P = dq/dt$. The result of a calibration experiment is usually expressed in terms of a calibration constant, ϵ , valid for the instrument under some specified conditions. The physical meaning of the calibration constant depends on the measurement principle employed. In the next few paragraphs, the main calorimetric principles used in isothermal microcalorimetry will be briefly reviewed: the adiabatic, the heat conduction, and the power compensation principle. Most isothermal microcalorimeters are designed as twin instruments, and it is thus a differential signal that is measured.

2.1 Adiabatic calorimeters

In an ideal adiabatic calorimeter there is no heat exchange between the calorimetric vessel and its surroundings. This implies that the temperature of the calorimetric vessel, which is the measured quantity, will increase (exothermic reactions) or decrease (endothermic reactions) during the measurement. Calorimeters used for studies of reactions of short duration are often of a semi-adiabatic (quasi-adiabatic, isoperibol) type. When such calorimeters are used in accurate work, a correction must be applied for the heat exchange with the surroundings, for example, see refs. 1 and 2.

The quantity of heat evolved or absorbed in an adiabatic calorimetric experiment is, in the ideal case, equal to the product between the temperature change, ΔT , and the heat capacity of the calorimetric vessel (including its contents), C ,

$$q = C \Delta T. \quad (1)$$

In practice, there will normally be some heat transfer between the vessel and the surroundings, and a "practical" heat capacity value, the calibration constant, is determined in a calibration experiment,

$$q = \epsilon_a \Delta T, \quad (2)$$

where ϵ_a is the calibration constant (sometimes referred to as the "energy equivalent"). A change in the heat capacity of the content of the calorimetric vessel (following, for example, injection of a sample) will thus lead to a change in the calibration value. The thermal power is

$$P = \epsilon_a dT/dt. \quad (3)$$

In a strict sense, experiments with adiabatic calorimeters cannot be conducted isothermally, but the temperature change in a microcalorimetric experiment is usually small, typically $<10^{-3}$ K, and the reaction can in practice be considered isothermal. However, a microcalorimeter may be used as a "macrocalorimeter", in which case ΔT may be in the order of 0.5 K or larger and cannot be neglected in accurate work. The issue of the assignment of the reaction temperature has been discussed by Sturtevant [1]. In the case where the calibration of the calorimeter has been performed on the final reaction system, the measured enthalpy change refers to the initial temperature of the calorimeter. In the case where the calibration of the calorimeter has been performed on the initial reaction system, the measured enthalpy change refers to the final temperature of the calorimeter.

2.2 Heat conduction calorimeters

Most microcalorimeters in current use are of the heat conduction type. In such instruments, heat is allowed to flow between the reaction vessel and a surrounding body (usually a comparatively large metal block) serving as a heat sink. The temperature of the heat sink is kept essentially constant. For an exothermic reaction, heat will flow from the reaction vessel to the heat sink; for an endothermic reaction, heat will flow in the opposite direction. The heat transfer normally takes place through a ther-

mopile that is located between the vessel and the heat sink. If no significant thermal gradients exist in the vessel, the Tian equation [1,3–5] will hold:

$$P = \varepsilon_c [U + \tau (dU/dt)], \quad (4)$$

Here, ε_c is the calibration constant, U the measured potential difference across the thermopile, and τ the time constant. A more complex expression should be used in cases where gradients in the reaction vessel are significant [3,4].

Under steady-state conditions, for example, during the release of a constant electrical calibration current, eq. 4 simplifies to

$$P = \varepsilon_c U. \quad (5)$$

The heat released in the calorimetric vessel is obtained by integration of eqs. 4 or 5, leading to the simple expression

$$q = \varepsilon_c \int_{t_1}^{t_2} U dt, \quad (6)$$

provided that the initial and final potentials are the same (normally the baseline value); t_1 and t_2 are, respectively, times in the fore- and after-periods.

The time constant is in the ideal case equal to the quotient between the heat capacity of the system (usually the reaction vessel and its contents, a vessel holder, and half of the thermopile wall) and the heat conductance of the thermopile. The heat capacity of the system is therefore a key parameter for heat conduction calorimeters used in kinetic measurements. However, in contrast to the case for an adiabatic calorimeter, ε_c does not depend on the heat capacity of the system. Ideally, ε_c is equal to the ratio between the thermal conductance associated with the thermopile and the Seebeck coefficient for the thermocouple material, for example, see refs. 3–5. Thus, ε_c is normally not influenced by heat capacity changes caused by injection of small samples into the reaction vessel and is the same for calibrations carried out before and after the reaction has taken place. This is a real advantage in that a calibration experiment does not have to be performed for each measurement.

2.3 Power compensation calorimeters

In a power compensation calorimeter, the thermal power from an exothermic process is balanced by a cooling power, typically by using the Peltier effect. For endothermic reactions, compensation is achieved by reversing the Peltier effect current or by release of electrical energy in a calibration heater. Thus, measurements in a power compensation calorimeter are conducted under essentially isothermal conditions.

In a special kind of power compensation microcalorimeter [6], the temperature is allowed to increase at a constant rate, as in a DSC but very slowly. The thermal power from a measured process is, in that case, compensated for by a change of the electrical heating power.

3. CALIBRATION AND TEST REACTIONS

Electrical calibration techniques are precise and convenient, and the measurement of electrical power and energy can easily be made with a higher accuracy than needed in practical calorimetric experiments in chemistry or biology. However, an electrical calibration heater may give rise to significantly different temperature distributions in the reaction vessel or cause a different heat flow pattern compared with that caused by the reaction under investigation. The calorimetric sensor (for temperature or heat flow) may thus react differently for the same heat quantity or the same thermal power released in an electrical calibration experiment and in a practical measurement. This can lead to significant systematic errors influenced by factors such as the calorimetric principle employed, a nonideal design of the vessel or the electrical heater, the position of the heater, the thermal conductivity of the vessel material, stirring efficiency, etc. For flow or perfusion vessels, the problems can be very different from those in a stirred

batch vessel [7]. Calibration errors can be more serious for microcalorimeters than for instruments where larger heat quantities or thermal powers are measured. Further, for practical reasons the design of microcalorimeters is frequently less ideal than that of "macrocalorimeters". It is felt that the quality of results in isothermal microcalorimetry would improve if some types of instruments were calibrated by use of chemical reactions and not by electrical calibration methods. However, the present guidelines have not been prepared with the intention generally to discourage the use of electrical calibration methods in isothermal microcalorimetry. Standardized test reactions should be used much more frequently than at present in connection with all kinds of microcalorimetric measurements.

Isothermal microcalorimeters are used in many types of thermodynamic investigations leading to values for different well-defined thermodynamic properties. The most important property is, in this connection, the enthalpy change, ΔH . When the enthalpy change is determined as a function of temperature the change in heat capacity can be derived, i.e., $\Delta C_p = d\Delta H/dT$. Determination of ΔT in adiabatic type instruments will lead to values for the heat capacity, eq. 1. For a heat conduction calorimeter, the heat capacity can be determined from the cooling curve following a steady-state electrical heating experiment [3,4]. Titration calorimetry, an important technique in isothermal microcalorimetry, can lead to the simultaneous determination of both the molar enthalpy change and the equilibrium constant, and thus also to values for the standard molar Gibbs energy change and the standard molar entropy change [6,8,9]. Isothermal microcalorimeters are often suitable for the direct determination of thermal power or the rate of heat evolution, including the determination of rate constants and reaction orders for moderately fast to very slow reactions [10–12]. Therefore, it is important to have available different test reactions for which such thermodynamic and kinetic properties are well known, but this does not preclude the usefulness of test and calibration materials (samples) for which the chemical reaction has not been identified.

Any reaction that can be conducted in a calorimeter under standardized conditions and has sufficiently well-known thermochemical properties, can be used as a calibration or a test reaction. It is important that such reactions will reach a wide acceptance. Therefore, chemicals used in most of the recommended calibration and test reactions should be readily available in a quality that does not require extensive purification and analysis. Where possible, expensive, hazardous, and unstable materials should be avoided.

Chemical substances and reaction systems recommended as reference materials for use in physical chemistry, including calorimetry, were reported in the IUPAC monograph edited by Marsh [13]. More recently, an extensive review of reference materials for calorimetry and thermal analysis was prepared under the auspices of ICTAC (R. Sabbah, editor) [14]. Several of the systems discussed in this review are primarily intended for different types of macrocalorimetry, but several are also of direct interest in isothermal microcalorimetry. Several chemical systems have specifically been proposed for use in isothermal microcalorimetry, in particular with respect to studies of aqueous solutions [7,15].

In the next section, some chemical calibration and test reactions are discussed with reference to their use in microcalorimetry. Most isothermal microcalorimetric measurements are conducted by using commercial instruments and are mainly made at ambient or slightly increased temperatures. A large fraction of them are conducted on aqueous systems. The main attention in the next section is therefore directed toward those areas.

4. SOME CHEMICAL CALIBRATION AND TEST REACTIONS

4.1 Reactions initiated by mixing of liquids

4.1.1 Aqueous dissolution and dilution of propan-1-ol in water

Propan-1-ol is readily available in pure form and is a stable and noncorrosive compound. The enthalpy of solution of propan-1-ol in water is well known for the temperature range 283 to 348 K [7]. Thus, the dissolution of propan-1-ol can serve as a convenient and safe calibration and test reaction for experi-

ments where small volumes of liquid are injected into a larger volume of solvent. In microcalorimetric experiments, the final molality of a solute is usually low. Propan-1-ol molalities $m \leq 0.017 \text{ mol}\cdot\text{kg}^{-1}$ (mass fraction $w \leq 0.001$) can be considered as infinitely dilute. Extrapolation to infinitely dilute solution is needed if the final molalities are higher [16]. Table 1 contains values of $\Delta_{\text{sol}}H_{\text{m}}^{\infty}$ for the temperature range 288.15 to 348.15 K. A fit to the results given in Table 1 is

$$\Delta_{\text{sol}}H_{\text{m}}^{\infty}/(\text{kJ}\cdot\text{mol}^{-1}) = -15.7484 + 0.237901 (T/\text{K} - 273.15) - 5.7674 \cdot 10^{-4} (T/\text{K} - 273.15)^2. \quad (7)$$

It should be noted that $\Delta_{\text{sol}}C_{p,m}^{\infty}$ for the dissolution reaction is high. This can be an advantage if the user wants to test the ability to measure this quantity.

Table 1 Enthalpy of solution of propan-1-ol in water at infinite dilution, $\Delta_{\text{sol}}H_{\text{m}}^{\infty}$ [7].

T/K	$\Delta_{\text{sol}}H_{\text{m}}^{\infty}/(\text{kJ}\cdot\text{mol}^{-1})$
288.15	-12.31 ± 0.02
298.15	-10.16 ± 0.02
308.15	-8.13 ± 0.03
318.15	-6.21 ± 0.03
348.15	-1.15 ± 0.02

For microcalorimetric experiments conducted at ambient temperatures, the heat evolved in the dissolution of propan-1-ol is often inconveniently large. In such cases, the dilution of aqueous propan-1-ol solution can be more useful, and it has been proposed as a suitable standard reaction [7]. Enthalpies of dilution have been reported [17,18] for aqueous propan-1-ol over the temperature range 284 K to 218 K and for molalities $m < 2 \text{ mol}\cdot\text{kg}^{-1}$. These molar enthalpies of dilution can be expressed according to the McMillan–Mayer theory [18] using the equation

$$\Delta_{\text{dil}}H_{\text{m}}(m_i \rightarrow m_f) = h_{\text{xx}}(m_f - m_i) + h_{\text{xxx}}(m_f - m_i)^2. \quad (8)$$

Here, m_i and m_f are, respectively, the initial and final molalities; and h_{xx} and h_{xxx} are virial (interaction) coefficients for the enthalpy. At $T = 298.15 \text{ K}$ the values of these quantities are $h_{\text{xx}} = (558 \pm 9) \text{ J}\cdot\text{kg}\cdot\text{mol}^{-2}$ and $h_{\text{xxx}} = (158 \pm 8) \text{ J}\cdot\text{kg}^2\cdot\text{mol}^{-3}$. Thus, for the dilution of a propan-1-ol solution (mass fraction $w = 0.1000$ or $m = 1.849 \text{ mol}\cdot\text{kg}^{-1}$) to an infinitely dilute solution at 298.15 K, $\Delta_{\text{dil}}H_{\text{m}} = -(1572 \pm 44) \text{ J}\cdot\text{mol}^{-1}$. For use as a calibration and test reaction, the results reported in refs. 7 and 16 can be stated as: $\Delta_{\text{dil}}H = (2.57 \pm 0.02) \text{ mJ}$ for the dilution of 1 mg of an aqueous propan-1-ol solution ($w = 0.1000$), provided that the mass fraction of propanol ≤ 0.0014 in the final solution.

4.1.2 Dilution of aqueous sucrose solutions

The enthalpy of dilution $\Delta_{\text{dil}}H_{\text{m}}$ of aqueous sucrose solutions, extensively studied mainly by Gucker and coworkers [19], is well known over a wide range of molalities and temperatures [7,13,14], and has been used for tests of microcalorimeters where two liquids are mixed. Concentrated sucrose solutions ($w = 0.15$ to 0.25) are quite viscous and can be difficult to mix with water, especially in flow calorimeters without stirring. This dilution is therefore particularly useful in tests of mixing efficiency. Values of $\Delta_{\text{dil}}H_{\text{m}}$ can be calculated with eqs. 9–11 [7].

$$\Delta_{\text{dil}}H_{\text{m}} = A(m_2 - m_1) - B(m_2^2 - m_1^2), \quad (9)$$

where m_1 and m_2 are the initial and final molalities, respectively, of the sucrose solution. (In ref. 7 the symbols for molalities (m_2, m_1) were erroneously given in the reverse order.) The temperature dependencies of the parameters A and B in eq. 8 are given by

$$A/(\text{J}\cdot\text{kg}\cdot\text{mol}^{-2}) = -834.95 + 4.719 (T/\text{K}), \quad (10)$$

$$B/(\text{J}\cdot\text{kg}^2\cdot\text{mol}^{-3}) = -389.12 + 2.7362 (T/\text{K}) - 4.4690 \cdot 10^{-3} (T/\text{K})^2. \quad (11)$$

Values of $\Delta_{\text{dil}}H_{\text{m}}$ calculated by use of eqs. 9–11 are judged to be accurate to about $\pm 1\%$ for the temperature range 293 to 313 K and for m_1 and m_2 in the ranges (0.1 to 2.0) mol·kg⁻¹ and (0.01 to 0.2) mol·kg⁻¹, respectively.

4.1.3 Dilution of aqueous urea solutions

Dilution of aqueous urea solutions, giving endothermic enthalpy changes, has been used in test experiments of different types of isothermal microcalorimeters [7]. Since aqueous urea solutions are not stable, it is important that freshly prepared samples be used in the measurements. Equations summarizing enthalpy values, determined mainly by Gucker *et al.* [20], are given in refs. 13 and 14.

4.1.4 Dissolution of slightly soluble liquids

Benzene has been used as a test substance for the dissolution of slightly soluble liquids in water [7]. However, the use of benzene as a reference material has been criticized owing to its health hazard, and toluene has been proposed as a substitute [21]. Normally, it can be assumed that a solution of toluene in water is infinitely dilute. A calorimetric value for the dissolution reaction at 298.15 K is $\Delta_{\text{sol}}H_{\text{m}}^{\infty} = (1.73 \pm 0.04)$ kJ·mol⁻¹ [22]. The temperature coefficient is high, as for all hydrophobic solutes in water, $\Delta_{\text{sol}}C_{p,m}^{\infty} = (263 \pm 13)$ J·mol⁻¹·K⁻¹ (288 to 308 K). $\Delta_{\text{sol}}H_{\text{m}}^{\infty}$ is zero at 291.6 K [22].

Some other liquid compounds with low solubilities in water may serve as test materials for dissolution reactions, for example octan-1-ol and several esters for which calorimetric $\Delta_{\text{sol}}H_{\text{m}}^{\infty}$ and $\Delta_{\text{sol}}C_{p,m}^{\infty}$ values have been determined [17,23]. No suitable test reaction can at present be proposed for dissolution of slightly soluble liquids in organic solvents.

4.1.5 Mixing of organic liquids

Four organic mixtures have served as test systems of macrocalorimeters used for measurements of the enthalpies of mixing [13,14]: (cyclohexane + hexane) for endothermic mixing, (1,4-dioxane + tetrachloromethane) for exothermic mixing, (methanol + water) and (ethanol + water) for both endo- and exothermic mixing. All four mixtures could serve well as test systems of microcalorimeters, but the use of dioxane, tetrachloromethane, and methanol have been discouraged for safety and health reasons. Taking this into account singles out (ethanol + water) as the best test system. Accurate data are available, over a wide range of temperatures (298 to 548 K) and pressures (0.4 to 15 MPa) [14,24–27]. The values of $\Delta_{\text{mix}}H$ vary from exothermic at 298 K to endothermic at temperatures above 333 K. Enthalpies are strongly dependent on the concentrations and therefore provide an excellent test for mixing efficiency (*cf.* section 5.6) in continuous flow mixing calorimetry.

4.1.6 (Acid + base) reactions

Aqueous (acid + base) reactions have been used extensively in macro solution calorimetry as calibration and test reactions. In microcalorimetry it is common to use the reaction between dilute hydrochloric acid (or some other strong acid, readily available at standardized molalities) and a large excess of dilute sodium hydroxide solution. Recommended values for protonation of hydroxyl ions at 298.15 K and infinite dilution are $\Delta H_{\text{m}}^{\infty} = -55.81$ kJ·mol⁻¹ and $\Delta C_{p,m}^{\infty} = 224$ J·mol⁻¹·K⁻¹ [28]. Experimental values should normally be corrected empirically for enthalpy of dilution of the comparatively concentrated injected solution. Neutralization of amine buffer solutions, in particular of “tris” [tris(hydroxymethyl)aminomethane], have also been used as a test reaction [29].

Neutralization reactions can be convenient to use as test and calibration standards. However, some problems that often will disqualify them should be pointed out. In experiments where one reaction component is mixed with a large excess of the other component, the reaction may go to completion even if the mixing efficiency in the calorimetric vessel is very poor. Thus, a neutralization test or calibration

reaction can give a correct value even if the calorimeter, because of inferior mixing properties, will give false results in other types of measurements, for example, in titration experiments [7].

Contamination with CO_2 can influence results significantly, in particular when a reaction is conducted in very dilute hydroxide solution. The two $\text{p}K_{\text{a}}$ values for carbonic acid are 6.35 and 10.33 at 298.15 K, and both protonation steps have low enthalpies, $\Delta H_{\text{m}}^{\infty} = -9.15$ and $-14.70 \text{ kJ}\cdot\text{mol}^{-1}$, respectively [30], as compared with the value for protonation of hydroxyl ions, $\Delta H_{\text{m}} = -55.81 \text{ kJ}\cdot\text{mol}^{-1}$ [28]. In order to minimize the extent of reaction between acid and carbonic acid ions, the solutions should be freshly prepared from CO_2 -free water and be protected from uptake of CO_2 during the experiments.

In many types of microcalorimetric experiments (e.g., titration, dissolution, and dilution experiments) small volumes are injected into the reaction vessel (typically a few μl into a few ml). The concentration of an injected acid solution in a neutralization experiment may therefore be comparatively high, for example, $0.1 \text{ mol}\cdot\text{dm}^{-3}$. Injection tubes made from "acid-proof" stainless steel, can be corroded by an HCl solution of that concentration. Nitric acid solution is less corrosive towards stainless steel.

With calorimetric vessels made from glass or metal there can be significant heat effects from the absorption of ions [31], which thus may provide serious complications in the use of neutralization reactions in test and calibration experiments (*cf.* the proposed use of dissolution and dilution reactions for the nonionic compounds propanol and sucrose, above).

4.1.7 Sucrose hydrolysis

The hydrolysis of sucrose to form (D-glucose + D-fructose) in dilute aqueous solution is a well-defined reaction that has been studied by three different calorimetric techniques. An adiabatic macrocalorimeter has been used in the study [32] of the acid-catalyzed hydrolysis with the result $\Delta H_{\text{m}}(298.15 \text{ K}) = -(14.91 \pm 0.12) \text{ kJ}\cdot\text{mol}^{-1}$. In another study [33] that used isothermal heat conduction microcalorimeters and the enzyme invertase (β -fructofuranosidase, EC 3.2.1.26) to catalyze the reaction in $0.1 \text{ mol}\cdot\text{dm}^{-3}$ sodium acetate buffer at $\text{pH} = 5.65$, the result was $\Delta H_{\text{m}}(298.15 \text{ K}) = -(15.00 \pm 0.07) \text{ kJ}\cdot\text{mol}^{-1}$. From calorimetric measurements performed as a function of temperature, the result $\Delta C_{p,m} = (57 \pm 14) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ (298 to 316 K) was also obtained [33]. Additional confirmation of these results has come from use of an isothermal titration calorimeter that was used [34] in a study of the enzyme-catalyzed reaction. Here, the result was $\Delta H_{\text{m}}(298.15 \text{ K}) = -(14.80 \pm 0.20) \text{ kJ}\cdot\text{mol}^{-1}$. The agreement of these studies, together with the ready availability of high purity sucrose (cr), leads one to consider this to be a useful test reaction for isothermal reaction microcalorimetry: $\Delta H_{\text{m}}(298.15 \text{ K}) = -(14.95 \pm 0.1) \text{ kJ}\cdot\text{mol}^{-1}$.

4.1.8 Titration microcalorimetry

Two ligand-binding reactions have been used as test reactions in titration microcalorimetry (for the simultaneous determination of enthalpy change and equilibrium constant, K_{c} , on a concentration basis): the binding reactions between Ba^{2+} and the macrocyclic compound 18-crown-6 (1,4,7,10,13,26-hexaoxacyclooctadecane) and between 2'-CMP (cytidine 2'-monophosphate) and bovine pancreatic ribonuclease A (RNaseA). Both reactions are conducted in aqueous solution and are 1:1 binding reactions. No test reactions have been proposed for more complex binding models or for reactions in organic solvents.

The binding of Ba^{2+} (BaCl_2 solution) to 18-crown-6 forms a convenient and reliable test reaction involving inexpensive and stable compounds that are easily available in sufficiently pure form. The values for ΔH_{m} and K_{c} are of a magnitude suitable for calculation of precise results. A small correction should normally be applied for the enthalpy of dilution of the injected barium salt solution. No significant variation in the derived thermodynamic quantities was observed when the concentration c for the crown ether in the vessel was varied from 0.001 to 0.01 $\text{mol}\cdot\text{dm}^{-3}$ or for a variation in $c(\text{BaCl}_2)$ in the injection syringe from 0.01 to 0.1 $\text{mol}\cdot\text{dm}^{-3}$ [7]. Values tentatively recommended for the thermodynamic quantities at 298.15 K are: $\Delta H_{\text{m}} = -(31.42 \pm 0.20) \text{ kJ}\cdot\text{mol}^{-1}$, $K_{\text{c}}/(\text{mol}\cdot\text{dm}^{-3}) = (5.90 \pm 0.20) \cdot 10^3$, and $\Delta C_{p,m} = 126 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ (288 to 310 K) [7], *cf.* [35].

The binding of 2'-CMP to RNaseA has been studied calorimetrically at different values for pH, ionic strength, temperature, and RNaseA concentration [6,8,36,37]. It is important to note that the

derived thermodynamic properties are highly dependent on all these variables, which makes this a somewhat questionable choice for a test reaction. It is proposed that the standard test reaction be performed at high salt concentration because the enthalpy change is less sensitive to protein concentration under these conditions [8]. Proposed standard conditions are: [potassium acetate ($c = 0.2 \text{ mol}\cdot\text{dm}^{-3}$) + potassium chloride ($c = 0.2 \text{ mol}\cdot\text{dm}^{-3}$) + RnaseA ($c = 0.175 \text{ mol}\cdot\text{dm}^{-3}$)] at pH = 5.5. Values tentatively recommended at 298.15 K [8] are: $\Delta H_{\text{m}} = -(50 \pm 3) \text{ kJ}\cdot\text{mol}^{-1}$; $K_{\text{c}}/(\text{mol}\cdot\text{dm}^{-3}) = (1.20 \pm 0.05) \cdot 10^5$. Given the variation in the current results in the literature, a value of $\Delta C_{p,m}$ is not yet established.

4.2 Dissolution of solid compounds

Accurate dissolution measurements of solid compounds is an area of increasing interest, in particular in the pharmaceutical industry where it frequently is of importance to characterize samples with respect to their (content of different) polymorphic forms [38,39].

4.2.1 Dissolution of potassium chloride in water

The dissolution of potassium chloride into water has been used extensively as a test and calibration reaction in macro solution calorimetry [13,14] and has also found use on the microcalorimetric level. A value for the enthalpy of solution of KCl(cr) into 500 H₂O (molality $m = 0.111 \text{ mol}\cdot\text{kg}^{-1}$) has been certified [40] by the National Bureau of Standards (NBS, now the National Institute of Standards and Technology) for their Standard Reference Material 1655, $\Delta_{\text{sol}}H_{\text{m}}(298.15 \text{ K}) = (17.584 \pm 0.017) \text{ kJ}\cdot\text{mol}^{-1}$ based on the very careful measurements done by Kilday [41] with an adiabatic calorimeter. The NBS certificate also gives $\Delta_{\text{sol}}C_{p,m} = -(154.8 \pm 6.4) \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ for the temperature range 293 to 301 K. The certificate recommends that the measurement be done at $m = 0.111 \text{ mol}\cdot\text{kg}^{-1}$. Following this procedure avoids uncertainties due to possible inaccuracies in values of the relative apparent molar enthalpy [42].

It has been noted that the scatter in results from apparently careful dissolution measurements at different laboratories has been larger than expected. It had been inferred [43] that the most reliable and consistent results are obtained when the samples have been dried at temperatures $>600 \text{ K}$ before use. However, from a more recent examination of the published data it was concluded that “the heat treatment recommended by the NIST certificate appears, at this point, to have a higher probability of corrupting the sample than improving the accuracy of the measurement” [42].

4.2.2 Dissolution of solid amines in aqueous acid solutions

The dissolution of “tris” [tris(hydroxymethyl)aminomethane] in $0.1 \text{ mol}\cdot\text{dm}^{-3}$ hydrochloric acid has been extensively used as a test reaction in macrocalorimetry [13,14]. However, microcalorimetric vessels are often constructed from steel, which may be corroded by the acid solution. To a much lesser extent, 4-aminopyridine [14] has been used as a test substance, but in this case the solid sample of the amine is reacted with an excess of aqueous perchloric acid, which is much less corrosive toward steel than hydrochloric acid solution.

4.2.3 Dissolution of slightly soluble solids

The dissolution of adenine in water has found some use as a test substance for slightly soluble solids. A carefully determined calorimetric value is $\Delta_{\text{sol}}H_{\text{m}}^{\infty}(298.15 \text{ K}) = (33.5 \pm 1.0) \text{ kJ}\cdot\text{mol}^{-1}$ [44].

4.3 Dissolution of slightly soluble gases

The enthalpy of dissolution of oxygen in water is well known for the temperature range 288 to 308 K, and this reaction has proved to be suitable in calibrations and tests of gas dissolution microcalorimeters. For this reaction, $\Delta_{\text{sol}}H_{\text{m}}^{\infty} = -(12.01 \pm 0.01) \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta_{\text{sol}}C_{p,m}^{\infty} = 196 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ at 298.15 K [7].

4.4 Sorption reactions

Sorption reactions [i.e., adsorption or absorption of gases (vapors) and solutes onto solids] are of fundamental importance in thermochemistry, and several special microcalorimeters have been designed for such experiments. Sorption reactions, in particular sorption of water vapor, has recently become one of the most important practical application areas for microcalorimetry, for example, in the pharmaceutical industry. Unfortunately, at present there appears to be no well-defined material available, which can be recommended as a standard for testing or for calibration.

4.5 Photocalorimetry

The photoreduction of potassium ferrioxalate [potassium tris(oxalato)ferrate(III)] ($c = 0.15 \text{ mol}\cdot\text{dm}^{-3}$) in aqueous sulfuric acid solution ($c = 0.05 \text{ mol}\cdot\text{dm}^{-3}$) is used as an actinometer in general photochemistry (the "Hatchard–Parker actinometer", see IUPAC recommendations [45]), and has also been employed as a test reaction in photomicrocalorimetry, $\Delta H_{\text{m}} = -(52.6 \pm 0.8) \text{ kJ}\cdot\text{mol}^{-1}$ [46]. It should be observed that calorimetric vessels made from stainless steel could be corroded by the sulfuric acid, leading to the formation of iron ions that will interfere with the chemical analysis needed in connection with this reaction.

4.6 Vaporization and sublimation reactions

There exist very few accurate calorimetric data of enthalpies of sublimation at ambient temperatures. Hardly any microcalorimetric work is currently conducted on sublimation reactions—there appears to be a need for further instrument developments in this area. However, there are several compounds with low vapor pressures, for which accurate enthalpies of sublimation or vaporization are accurately known, over a wide temperature range. For recommendations of reference materials in this field see refs. 13 and 14.

4.7 Thermal power signals released during extended periods of time

4.7.1 Hydrolysis of triacetin in imidazole-acetic acid buffers

It is often desirable to have available a chemical test and/or calibration reaction that releases a predictable thermal power over an extended period of time, for example, in cell biological experiments. The hydrolysis of triacetin in aqueous imidazole-acetic acid buffers has proved to be a useful test and calibration reaction for batch and flow microcalorimeters [7]. Five different mixtures releasing heat at well-defined, nearly constant rates in the range (10 to 100) μW have been described [7], see Tables 2 and 3 and eq. 12. Triacetin is added to the buffer solution immediately before use. The uncertainty of

Table 2 Composition of five test solutions for the triacetin hydrolysis reaction. Buffer solutions are prepared by adding acetic acid and triacetin to a solution containing 27.23 g of imidazole in 100 g of water [7]. The masses m of acetic acid and triacetin added to the solution are given in this table.

Test solution	$m(\text{acetic acid})/\text{g}$	$m(\text{triacetin})/\text{g}$
A	10.00	10.000
B	16.00	5.000
C	18.00	3.600
D	20.00	3.600
E	24.00	3.600

Table 3 Triacetin reaction mixtures and values for the constants in eq. 12.

Test solution	<i>T</i> /K	<i>a</i> / (10 ⁻⁶ ·W·g ⁻¹)	<i>b</i> / (10 ⁻¹⁰ ·W·g ⁻¹ ·s ⁻¹)	<i>c</i> / (10 ⁻¹⁶ ·W·g ⁻¹ ·s ⁻²)
A	298.15	34.32	-0.62	1.2
A	310.15	90.66	-3.63	8.1
B	298.15	13.35	-0.26	1.0
B	310.15	35.35	-1.16	2.3
C	310.15	21.80	-0.79	3.5
D	298.15	5.19	-0.08	0.4
D	310.15	16.00	-0.45	1.1
E	310.15	7.25	-0.16	0.5

the predicted thermal power *P* for time periods of 20 h is claimed to be ±1%. A reaction mixture can be stored in a freezer with a small and predictable decline of its thermal power value. The thermal power vs. time curve for any of the reaction mixtures, at a given temperature, can be described by the empirical equation

$$P = a + bt + ct^2 \quad (12)$$

where *P* is the thermal power (W), *t* is the time (s), and *a*, *b*, and *c* are constants given in Table 3.

The kinetics of the triacetin-imidazole hydrolysis reaction has recently been investigated using isothermal microcalorimetry, and molar enthalpies and rate constants have been determined at 298.15 K [10,11]. A series of inter- and intralaboratory tests have also been conducted on this reaction [47].

4.7.2 Radioactive probes

Radioactive probes, hermetically sealed in metal ampoules, can be very convenient and accurate in some test and calibration experiments. However, the trade, transfer, and possession of such probes is restricted, and it is not likely that they will be widely used.

5. TERMINOLOGY FOR REPORTING CHARACTERISTICS OF ISOTHERMAL MICROCALORIMETERS

It is important that a well-defined and generally understood terminology is used when an instrument is described in lectures, scientific papers, and in the printed material from commercial producers. Where possible, IUPAC terminology should be applied [48,49]. Below follows a brief discussion of some key characteristics, which normally should be included in the description of an isothermal microcalorimeter.

5.1 General

The calorimetric principle employed should always be reported when a calorimeter is described. The physical description of the instrument, including materials used in vessels, injection devices, etc., should be reported in adequate details. The useful temperature range of the instrument and the temperature stability (short term and long term) of the surroundings should be reported. The time constant(s) of the calorimeter should be reported, in particular for heat conduction calorimeters. All numerical data should be given in SI units (calorie, inch, etc. are not acceptable).

5.2 Repeatability

“Repeatability” (earlier the term “precision” was used) is a measure of the scatter in a series of observations or results about a mean value and is expressed in terms of the standard deviation (standard devi-

ation of the mean, relative standard deviation) [48–50]. When characteristics of calorimeters are reported, it is common that values for the “repeatability” refer to a series of electrical calibration experiments. Such values can be useful to report, but it should be observed that results of electrical calibration experiments are often more precise than those from chemical experiments performed with the same instrument. “Repeatability” determined with chemical test experiments will therefore give a more realistic characterization of the instrument. Significantly different relative repeatability values can be obtained for different test reactions using the same instrument. It can therefore be valuable to characterize the repeatability by different types of test reactions.

5.3 Uncertainty

“Uncertainty” (earlier the term “accuracy” was used) is a quantity referring to differences between the mean of a set of results or an individual result and the value that is accepted as the true or correct value for the quantity measured [48]. The uncertainty in the result of a series of measurements is often evaluated by combining values for repeatability and estimated systematic errors. However, it is often difficult to make such estimates, in particular when small heats or thermal powers are measured. The uncertainty of a microcalorimetric measurement is therefore normally best characterized by comparison between results obtained for standard test reactions, of a similar nature as the studied reaction, and corresponding recommended values.

5.4 Limit of detection and sensitivity

In calorimetry, the term “limit of detection” is the smallest heat quantity (q_{lim}) or thermal power (P_{lim}) that can be determined with a reasonable certainty, in a practical experiment conducted under specified conditions. The term “sensitivity” (S) is often misused to denote “limit of detection”, a practice that is discouraged [48,49]. In general, “sensitivity” is defined as the slope of an analytical calibration curve [48,49], and in the present context the sensitivity is thus equal to the inverse of the calibration constant, $S = \varepsilon^{-1}$.

IUPAC recommendations for determination of limit of detection (referring to techniques in analytical chemistry [48,49]) are not directly applicable in isothermal microcalorimetry. It is recommended that q_{lim} and P_{lim} be taken as equal to the values for repeatability determined for these quantities, using a suitable standard chemical test reaction. Values for the limit of detection derived from a series of electrical calibration experiments are also useful to report, but such values are normally significantly lower than those determined using more realistic chemical test reactions.

5.5 Baseline

The baseline of a calorimeter is defined as the value recorded for the calorimetric signal when no thermal power is evolved in the reaction vessel, except for a constant or predictable power from stirring, etc. Small, nearly constant contributions from corrosion, oxidation or other background chemical reactions that give a nearly constant thermal power, can also be part of the baseline value.

We may distinguish between different types of deviation from a constant baseline value. “Noise” is a short time (normally <1 min) random fluctuation of the baseline value, often due to effects from the electronic system. It is often adequate to give an estimate of the noise from the bandwidth of the calorimetric signal. If the noise is irregular, one may sample the baseline values (e.g., each second) and make a least square fit to a straight line over a short period of time (e.g., 5 min). The noise level may be defined as \pm (twice) the standard deviation of the fit. The “baseline drift” is a random or nonrandom change in the baseline value over a specified period of time. A “long-term drift” (e.g. over 24 h) can often be approximated to a straight line and evaluated by a least squares treatment. The “baseline fluctuation”, during the specified observation period, is defined as the difference between the experimental

baseline and the constructed straight line. The “baseline deviation” over a specified time period, is derived by combination of values for drift and fluctuation.

It is not uncommon that the baseline signal will show a “shift” associated with the practical operation of an instrument, for example, when an insertion reaction vessel is introduced into its measurement position or when a valve or an injection device is used. Such baseline shifts can be large compared with the baseline deviation during a measurement period, and baseline shifts can thus cause significant systematic errors when low thermal power values are determined, for example, in the study of slow degradation reactions of technical materials or for small samples of living cellular systems. Such shifts, evaluated by relevant blank experiments should be reported.

5.6 Mixing time, mixing efficiency

A calorimetric batch vessel is often fitted with an injection device, or with other means to achieve mixing between fluids. It is then important to report the time needed to obtain a uniform concentration of the components in the reaction vessel under specified experimental conditions (different stirring rates, etc.). The calorimetric signal observed following the initiation of a fast reaction in a batch calorimetric vessel can be used to monitor the mixing reaction, if this is slow compared with the time constant for the instrument. It is often useful to conduct mixing experiments as “bench experiments” using a transparent dummy vessel with the same geometry as the real calorimetric vessel. An estimate of the mixing time can be obtained visually after injection of some colored solution.

The “mixing efficiency” in a continuous flow mixing vessel must be expressed in different terms compared with those for a batch vessel. In a flow mixing vessel it is important that the mixing is completed well before the mixture reaches the exit of the vessel. It is recommended that such vessels are characterized by performing standard mixing reactions, easy as well as nontrivial ones such as the dilution of aqueous solutions of sucrose with water (4.1.2).

6. CONCLUSION

Currently, isothermal microcalorimetric measurements are mainly conducted at ambient or slightly increased temperatures, and a large fraction of the measurements are conducted on aqueous solutions. This is reflected by the fact that most calibration and test reactions proposed here are primarily intended for use under such conditions. Clearly, there is a need for standard reactions conducted at higher temperatures, on solid materials (some of the most important practical applications are on solid materials), and for reactions conducted in organic liquids (presenting special problems owing to evaporation effects and possible interaction with seals, etc.). As noted earlier, there is a serious lack of standard material suitable for calibration and test reactions in connection with all kinds of sorption measurements.

Thermodynamic data given in this document are believed to be accurate within the stated uncertainty limits. However, it is desirable that many of the values be verified and improved by further measurements, where possible using different calorimetric techniques.

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