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NEW PRINCIPLES OF CALORIMETRIC DESIGN*

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ABSTRACT

A brief outline of the historical development of calorimetric instrumentation shows that temperature-measurement- and shielding techniques have been substantially improved and modern electronic methods of data-processing and data-acquisition have been successfully applied to calorimetry during the last decades, but the calorimeter itself has nearly been left unchanged. The limitations of classical calorimetry will be discussed and an information-theoretical approach to calorimetry given. Some of the more important results of a general theory of calorimetry will be stated and used to derive new features of design for a modern calorimeter. Experimental results of thermodynamic measurements with such an instrument disclose large discrepancies between precision calorimetric data in the literature, systematic errors ranging from about 0.1% to as much as 0.4%.

INTRODUCTION

The title of this paper is likely to divide the readers into two groups: The experienced calorimetrists, knowing that new principles in calorimetry are very unlikely because of fundamental reasons, and the scientists, interested in the capabilities of calorimetry and hoping to read about new, perhaps easier or even more accurate methods. The author hopes to be able to present at least some useful information to both groups of readers by starting with a discussion of old principles of calorimetric design.

At the very beginning of calorimetry stands the ice-calorimeter first constructed by Joseph Black, a chemist in Edinburgh, more than 200 years ago. Although the ice-calorimeter is a strikingly simple and powerful instrument, it has nearly been abandoned in modern calorimetric work. It is important, however, to stress that the failure of ice-calorimetry and phase-change calorimetry in general is only a failure of the particular instrumental realizations, but not of the idea itself. The idea of a direct measurement of a definite quantity of heat by a corresponding change of the energy of the calorimeter can be much better realized by an electrical compensation method.

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Such methods have been tried for nearly 50 years with moderate success only. The accuracy and precision of classical calorimetry (anisothermal and adiabatic) have never been either excelled or reached. The latter has nearly been left unchanged in principle despite an enormous improvement in temperature-measurement- and shielding-techniques and modern methods of electronic control and data-treatment, although many advances have been achieved at extreme conditions (very low and very high temperatures, small samples etc.).

LIMITATIONS OF CLASSICAL CALORIMETRY

The failure of compensated calorimetry and the stagnation of classical calorimetry can be shown as consequences of natural limitations. Universality and speed, precision and accuracy, two pairs of ideas fundamentally important in modern instrumentation suffer from an a priori impossibility to be joined in calorimetry. The first pair has been realized in differential thermal analysis (DTA) or in differential scanning calorimetry (DSC), the second in classical calorimetry. The current trend in calorimetry goes again in the first direction of universality and speed, neglecting precision and accuracy. What is the reason for this unlucky gap between the two pairs of requirements? The indirect measurement of heat through measurement of a temperature change in the sample cannot be universal because the sample itself is part of the instrument and its thermal properties have a large influence on the calibration constant. Every kind of process to be investigated calls for a special design of the instrument and it cannot be fast, since temperature equalization in a large volume is slow. But it can be made precise and accurate*, if the adequate temperature-measurement- and shielding-techniques are provided.

A direct measurement of heat by substituting electrical energy, however, can be made both universal and fast, precise and accurate, when the following requirements are fulfilled:

(1) The calorimeter is a black box with an interior part where a sample in a cell can be introduced, with all accessory parts to start, control and measure the process under investigation and means for a rapid thermal equilibration (sample system).

(2) Sample system and calorimeter are of such construction, that the heat ΔQ evolved or absorbed by the process is completely and rapidly exchanged with the calorimeter and is considered as input signal to the black box.

(3) The black box has an output signal ΔX and a transfer function very near to: $\Delta X = \Delta Q$.

(4) Any exchange of heat of the calorimeter with other bodies (surroundings) is considered as disturbing input to the black box and must be suppressed below noise level.

Such a calorimeter is clearly universal since every type of sample system for a

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*Only in cases where the specific heat of the sample changes slowly with the process.

variety of investigations can be inserted. It can be called a modular calorimeter. The temperature of the sample can be set or programmed as a function of time and fast measurements can be made by achieving good thermal equilibration in the cell and between cell and calorimeter. Accuracy and precision will follow as a direct consequence of obeying points (3) and (4). Such an approach to calorimetry, however, is beyond the possibilities of the classical theory of calorimetry, a theory limited to classical calorimetric designs and moreover limited by a number of assumptions to make a theoretical treatment of a calorimeter possible. Among the numerous efforts to establish a more powerful and modern theory of calorimetry, there are three papers[1–3] giving a very similar theoretical treatment of calorimetry to the one discussed here.

INFORMATION-THEORETICAL APPROACH TO CALORIMETRY

Forgetting all about calorimetric design principles, a general calorimeter will be treated as a black box for the transfer of thermodynamic signals, to be more specific, a thermal system is defined as a material macroscopic system with well-defined boundary. The input signals are power signals with defined spacial distribution $q(x)$, called input functions and the output signals are mean temperatures $e(t)$ measured over defined regions of the system with spatial weights called output functions $Q(x)$. The heat exchange with the surroundings through the boundary can be accounted for as disturbing input signal with input function $\sigma(x)$. The thermal structure of the system is given by the thermal conductivity and the specific heat per unit volume $\lambda(x)$ and $c(x)$ in every point x of the system as well as by the heat-transfer coefficients $\alpha(x)$ on the boundary. In case of constant thermal structure and fixed input and output functions $q(x)$, $\sigma(x)$ and $Q(x)$, the thermal system is linear. The input–output relations can then be given in terms of convolution integrals over the weight functions $r(t)$ of the system in the time domain, or in terms of products with the transfer

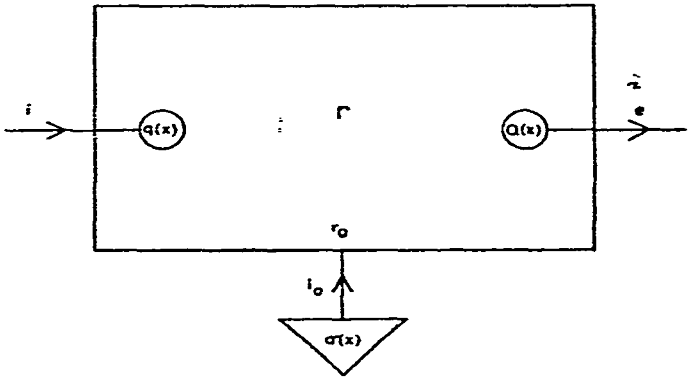

Fig. 1. Passive linear thermal system:

$$e(t) = (r * i)(t) + (r_0 * i_0)(t) \quad \text{and} \quad e(\omega) = r(\omega)\cdot i(\omega) + r_0(\omega)\cdot i_0(\omega).$$

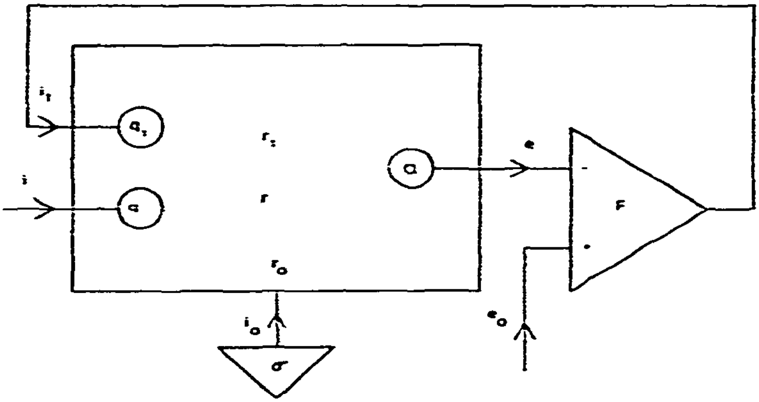

Fig. 2. Active linear thermal system:

$$-i_1(\omega) = \{1+r_1(\omega)F(\omega)\}^{-1}\{r(\omega)F(\omega)i(\omega)-F(\omega)e_0(\omega)+r_0(\omega)F(\omega)i_0(\omega)\}.$$

functions $r(\omega)$ of the system in the frequency domain. Figure 1 shows schematically the main features of such a passive linear thermal system. Active linear thermal systems can be obtained by combining a linear thermal system with linear amplifiers in such a way as to obtain thermal control-loops (Fig. 2). The theory of general linear thermal systems has been worked out in detail[4] and the analytical structure of the transfer functions has been obtained by transformations and formal solutions of the basic heat-conduction equations. The general case of varying thermal structure and changes in the input and output functions, which often occur in real calorimeters, has also been treated. The most important results of this theory applicable to all types of calorimeters can be stated in the following single equation:

$$\Delta Q = C\{\Delta T+\eta+\eta_2\} \tag{1}$$

RESULTS OF NEW THEORY OF CALORIMETRY

When eqn (1) is applied to classical calorimetry—ΔQ is the integral quantity of heat to be measured, C is the heat equivalent of the calorimeter, ΔT the measured temperature rise and η the calculated temperature loss—the basic classical equation of calorimetry is obtained but with an additional term η_2. η_2 is a second-order temperature correction term arising mainly from thermal lags in the calorimeter, changes of the jacket temperature and secondary processes in the calorimeter. This correction term has not been reported in the literature, except in a very thorough and complete paper[5] on lag errors, in which the existence of such a term can be anticipated. Close investigation of the explicit structure of η_2 enables a complete discussion of all calorimetric methods with the following results:

In anisothermal and adiabatic calorimeters, precise measurements call for a very good temperature equalization in the calorimeter and in the jacket, with use of a thick air gap with a very thin convection shield or a vacuum gap in between. Much precaution must be taken to make all accessory parts as small and as near the calorimeter temperature as possible. Much attention must be paid to the system of covers in order to prevent evaporation and adsorption errors and other effects caused by leads and rods. The calorimeter must be completely jacketed and heat-flow along rods and wires must be prevented.

The use of the adiabatic control does not improve precision, it is even likely to lessen it and its advantages are indirect ones: Measurements over a long period or a large temperature interval become possible, but at considerable cost of precision. Secondary disturbing processes and non-linearities will appear. These findings are not new and have been pointed out first by White[6]. His keen judgment on the belief in the adiabatic method culminated in his expression: "The Calorimetric Fallacy". Unfortunately this fallacy still seems to be alive today and there are only very modest signs of its disclosure in the near future.

When eqn (1) is applied to the heat-flow and isothermal methods, the term:

$$\Delta X = C\eta \tag{2}$$

is dominant in isothermal experiments. The term η_2 then becomes much larger than in anisothermal calorimeters. The contributions to η_2 from the jacket can be made small by using a complete jacket with a very good thermostat. But there is no remedy against lag errors and errors from secondary processes, unless the compensation method is used. An analysis of compensated calorimeters leads directly to the new design principles.

PRINCIPLE OF MODERN ISOTHERMAL CALORIMETER

Three major points must be obeyed in a modern compensated calorimeter:

(1) An excellent jacket thermostat must be used.

(2) The geometry of the sensing and heating elements in the compensating loop is very critical.

(3) The compensating circuit must be of excellent quality, of sufficiently low drift and the band-width of the temperature acquisition must be correctly limited.

The thermostat lessens contributions to η_2 from the surroundings and a correctly designed compensation lessens lag errors and errors from secondary processes. It also lessens systematic errors. It has in fact been shown[4] that by properly obeying points (1)–(3), a compensated calorimeter can be constructed accurately to 0.01% and with a precision limited only by the small quantity corresponding to the uncertainty in the temperature of the sample. The principle of such a construction is shown in Fig. 3. A complete elimination of the effects from the surroundings calls for a multiple jacket control. The jacket is controlled at about ambient temperature T_1 with a jacket controller and heat transfer to the surroundings is done by some cooling facility. For maximum precision, the jacket should be wrapped with a material of low thermal conductivity and care should be taken to prevent large temperature gradients in the jacket. A precision of 10^{-2} °C of the jacket controller is sufficient. The

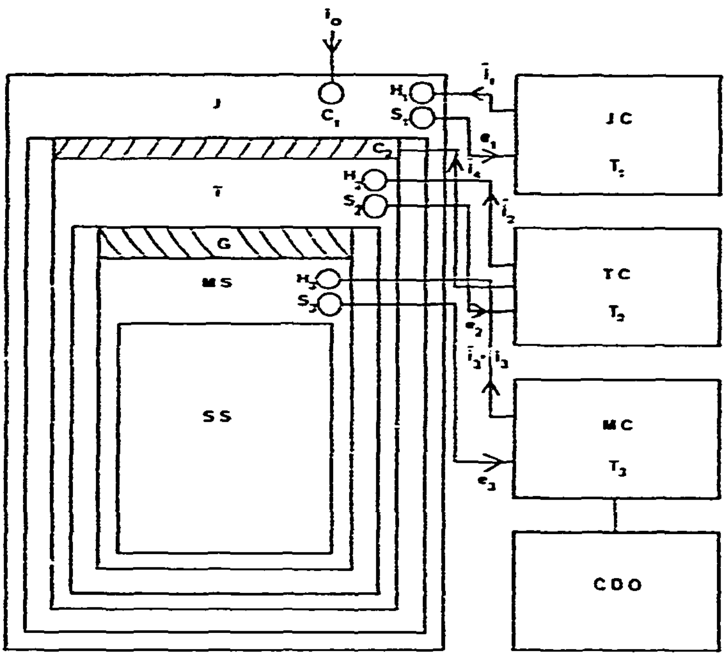

Fig. 3. Principle of modern calorimeter. Calorimeter: J = Jacket; T = thermostat; MS = measurement system; SS = sample system. Electronic controls: JC = Jacket control; TC = thermostat control; MC = measurement control; CDO = counter, display and output.

jacket completely surrounds the thermostat, which contains the measurement system. The thermostat consists of a jacket with high thermal conductivity (e.g., copper) and the control is performed electronically with a temperature sensor S_2 and an electrical heater H_2. The setting temperature T_2 is variable in an interval $T_l \leq T_2 \leq T_u$ and when its lower limit T_l is near T_1 or below, cooling must be provided. This is done with the element C_2, either electrically with a peltier element or conventionally with liquids. The control of C_2 is such that the thermostat control is in an optimum working range at every temperature of the interval. If the geometry of the sensing and heating elements S_2 and H_2 is suitably chosen, the inside of the thermostat is at constant and nearly homogeneous temperature. A precision of 10^{-5}°C can be obtained. The measurement system completely surrounds the sample system, i.e. the cell with the sample containing all the accessory parts to control the process under investigation. The measurement system is a sort of second thermostat, but with exactly defined conditions of heat-flow to the surrounding thermostat. The thermal conductance G between measurement system and thermostat must be very well defined, because changes of G affect the stability of the baseline. Compensation is most conveniently done with an electrical heater, but circulating fluids can also be used. Of major importance is a complete or nearly complete compensation of the heat input, such that the thermostat is nearly unaffected. It is very unsatisfactory to use peltier elements or other heat-pumping devices like element H_3. The sensing element S_3 is conveniently chosen as differential temperature sensor measuring the difference between the nearly uniform temperatures of the measurement system and the thermostat. If the setting of the measurement control is fixed at:

$$e_{03} = \Delta T = T_3 - T_2$$

the total rate of heat input to H_3 is (in the absence of reactions):

$$f_3 + i_3 = G\Delta T$$

independent of the setting of the thermostat T_2. The sample temperature is then given by $T = T_2 + \Delta T$ and the thermostat setting can be calibrated directly by the sample temperature T. The baseline of the output signal, $-f_3$, can be shifted over the whole range: $0 \leq -f_3 \leq G\Delta T$ of the instrument by use of the input i_3. Maximum precision and accuracy are obtained by using a digital measurement control. If the energy to H_3 is supplied in pulses with an accurately constant energy content, power and energy measurement is merely a matter of counting. When the geometry of the heating and sensing elements is suitably chosen, systematic errors can easily be made less than 0.1%. In a carefully constructed calorimeter, kinetic work becomes possible up to rates not higher than about $10^{-1}\,s^{-1}$. Apart from a constant factor very near to one, the signal measured is just the power: $i(t) = \dot{Q}(t)$ given from the sample to the calorimeter. For higher rates, the still linear relation:

$$-f_3(t) = (\pi^* i)(t), \quad \text{with} \quad \int_0^\infty \pi(t)\,\mathrm{d}t = 1$$

may be used. The detailed conditions to be obeyed in the construction of such calorimeters have been carefully studied elsewhere[4].

In order to obtain a universal and fast, precise and accurate direct energy measuring instrument, point (2) of Limitations to classical calorimetry must be fulfilled. The sample system consists of a sample container (cell), all the accessory parts to start, control and measure the process under investigation and a system of covers: cell cover, thermostat cover and jacket cover. It must be easily removable from the calorimeter, very good thermal contact between the corresponding parts of the sample system and the calorimeter is essential and it should be possible to use several sample systems with the same calorimeter. Such a system can be called modular. In constructing a satisfactory sample system, the following points must be obeyed:

(1) The cell must be sealed vapor-tight.

(2) All elements such as stirrer, heater, syringe, etc. must be entirely located in the cell.

(3) The cell cover (in good thermal contact with the cell) must be attached to the thermostat cover with a thermally low conducting material.

(4) All connections from the outside to the cell (stirrer rod, piston rod, heater leads, etc.) must be thermally anchored to the thermostat cover and if possible also to the jacket cover.

EXPERIMENTAL RESULTS

The instrument constructed to test the new design principles and the exact experimental procedure have been described in detail elsewhere[4]. To test the instrument, the neutralization reaction of tris(hydroxymethyl)-aminomethane (Tris) with HCl has been chosen. A number of baseline experiments and electrical calibrations showed that secondary processes. A test with dry nitrogen before and after every experiment was made to make sure that no evaporation and absorption errors were present. A precision of ±100 mJ (90% confidence interval) could be obtained in every single experiment of about 200 J and 200 s duration. The systematic error could be estimated from a series of measurements with a different cell and its sign could be determined. The heater lead error could be held as low as 50 ppm. The total electric calibration error was certainly within 100 ppm. The result obtained for the reaction:

$$\text{Tris} + \text{H}^+ \rightarrow \text{TrisH}^+$$

at $T = 25\,^\circ\text{C}$ in aqueous solution is $-47381\ \text{J mol}^{-1} \leq \Delta H \leq -47311\ \text{J mol}^{-1}$*, referring to the following initial and final conditions:

State	*Initial*	*Final*
c(Tris)	0.057 mol kg^{-1}	0.05 mol kg^{-1}
c(HCl)	0	0.0625 mol kg^{-1}

COMPARISON WITH PUBLISHED WORK

Table 1 shows different results for the same reaction under different conditions obtained by various workers. The first two results have been obtained electrochemically. The large discrepancies between the data indicate that the ionic strength, I, has a significant influence. The heats of dilution of the final systems should be measured to reduce the data, but this is impossible with ordinary instruments and still very difficult with a microcalorimeter. Fortunately the data given in the paper of Datta et al.[8] can be used to reduce all the results to the standard state $I = 0$. The result of this calculation is given in Table 2. Although this calculation is somewhat uncertain in the absolute value of the corrected result, it is rather accurate as to the differences between the results of different workers. Although the author obtained much lower absolute values in a first calculation[4], the differences are about the same as in this refined calculation.

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*The interval given is a 90% confidence interval, the systematic error included.

TABLE 1

REACTION ENTHALPY $\Delta H(I)$ AND IONIC STRENGTH, I, OF THE REACTION $\mathrm{Tris}+\mathrm{H}^+ \rightarrow \mathrm{TrisH}^+$ AT $T=25$°C IN AQUEOUS SOLUTION MEASURED BY DIFFERENT AUTHORS

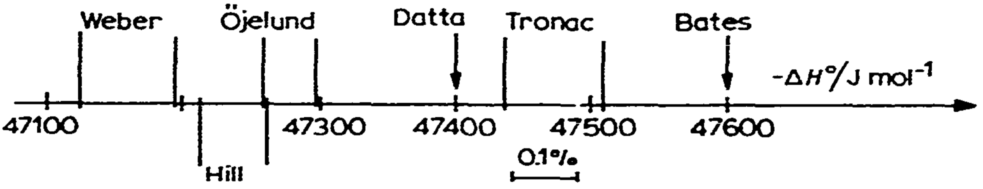
Reference	$-\Delta H(I)/\mathrm{J\ mol^{-1}}$	$I/\mathrm{mol\ kg^{-1}}$
7	47600	0
8	47400	0
9	47480±17	0.07
10	47500±10	0.1
11	47530±40	0.015
4	47346±35	0.0625

TABLE 2

RESULTS OF TABLE 1 EXTRAPOLATED TO $I=0$ BY USE OF THE ACTIVITY COEFFICIENTS GIVEN IN REF. 8

No ionization correction has been applied; with ionization correction the value becomes 36 J mol^{-1} less.

Reference	$-\Delta H^\circ/\mathrm{J\ mol^{-1}}$
7	47600
8	47400
9	47279±20
10	47237±25
11	47476±40
4	47159±35



CONCLUSIONS

Table 2 shows that the non-calorimetric values of $-\Delta H^\circ$ are certainly high. The calorimetric results are spread over nearly ½%. Since the random errors of the results are rather small, the differences must be systematic errors. Of the four calorimetric works, systematic errors have been investigated in only one case. These seem to range from about 0.1% to about 0.4%. In a typical run with a 100-ml calorimeter, the energy measured in this reaction is of the order of 300 J, so the absolute systematic error ranges from about 300 mJ to 1 J. It looks as if systematic errors in calorimetry have been neglected in the past.

REFERENCES

1 G. M. Laville, *C. R. Acad. Sci.*, 240 (1955) 1060.
2 E. D. West and K. L. Churney, *J. Appl. Phys.*, 41 (1970) 2705.
3 F. H. Verhoff, *Anal. Chem.*, 43 (1971) 183.
4 H. Weber, *Isothermal Calorimetry for Thermodynamic and Kinetic Measurement*, Series XII, Vol. 5, European University Papers, Herbert Lang, Bern, 1973.
5 W. P. White, *Phys. Rev.*, 31 (1910) 565.
6 W. P. White, *The Modern Calorimeter*, Chemical Catalog Company, New York, 1928.
7 R. G. Bates and H. B. Hetzer, *J. Phys. Chem.*, 65 (1961) 667.
8 S. P. Datta, A. K. Grzyboroski and B. A. Weston *J. Chem. Soc.*, 792 (1963).
9 G. Öjelund and I. Wadsö, *Acta Chem. Scand.*, 22 (1968) 2691.
10 J. O. Hill, G. Ojelund and I. Wadsö, *J. Chem. Thermodyn.*, 1 (1969) 111.
11 Tronac Model 450, Calorimeter Instruction Manual, Tronac Inc., Orem, Utah, U.S.A.