LABTERMO: METHODOLOGIES FOR THE CALCULATION OF THE CORRECTED TEMPERATURE RISE IN ISOPERIBOL CALORIMETRY

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In isoperibol temperature-rise calorimetry, different approaches can lead to the corrected temperature rise. The description of the methodology, as well as an improvement in the approach to the accurate numerical calculation of the corrected temperature rise in isoperibol calorimetry, based on the comparison between the exponential functional description of the initial and final periods and an independent third order polynomial fitting, is presented. The latter is focused on the strategy of minimizing the result dependency on the definition of the main period of the reaction. Furthermore, the dedicated software application Labtermo is introduced.

Keywords: *calorimetry, corrected temperature rise, extrapolation method, heat exchange corrections, isoperibol calorimetry, Labtermo, Regnault–Pfaundler method, true temperature rise*

Introduction

Isoperibol temperature-rise calorimeters are those in which the temperature of the calorimeter varies during the course of the experiment but the temperature of the environment remains constant. Procedures for the calculation of the corrections for energy exchange between an ideal isoperibol calorimeter and its surroundings through heat exchange, with a constant stirring power, a constant thermal modulus and a constant energy equivalent, have been described by several authors [1–12]. Cases in which stirring power changes due to rotations of the calorimetric bomb (or analogous problems in solution-reaction calorimetry) have been analyzed by Wadsö [2] and Gunn [6]. Oetting [5] proposed and described a procedure to calculate the true temperature rise of an isoperibol calorimeter using only the after-period of the obtained experimental values; this procedure was especially developed for drop calorimeters. A complementary treatment was presented by Vanderzee [9] where some additional perturbations for the calculation of the true energy exchange (changes in the energy equivalent, steady or constant parasitic processes or non-linear parasitic processes) were taken into account. King and Grover [10] as well as West and Churney [11] described and analyzed the application of a two-body model in isoperibol calorimetry in which the calorimeter is represented by two thermally connected regions, one surrounding the other and exchanging heat with the constant temperature environment. Hansen *et al.* [12] presented a method of calculating the heat loss corrections for small isoperibol-calorimeter reaction vessels.

The exact calculation of the corrected temperature rise in isoperibol calorimetry is one of the key factors for accuracy in high precision calorimetry. An isoperibol temperature-rise calorimeter is designed to have a big and constant thermal resistance to the surroundings and an insignificant thermal gradient inside the calorimetric vessel. The calorimetric vessel and its surroundings, at constant temperature, could be considered as a system where the physical heat exchange model is simplified to allow a more accurate calculation of the corrected temperature rise (the real temperature rise in the calorimeter if the process would occur under perfect adiabatic conditions, without any extraneous thermal effects).

In this work, an ideal isoperibol temperature-rise calorimeter will be considered; it will be focused on the description of the different methodologies and on the improvements of the numerical calculations of the corrected temperature rise, based on a fitting procedure, in order to decrease the dependency of the numerical calculation from an exact definition of the interval for the main period.

Calculation of the corrected temperature rise

In isoperibol temperature-rise calorimetry, a temperature (T)–time (t) curve is usually divided into three periods as shown in Fig. 1. In the main period (t_b to t_c),
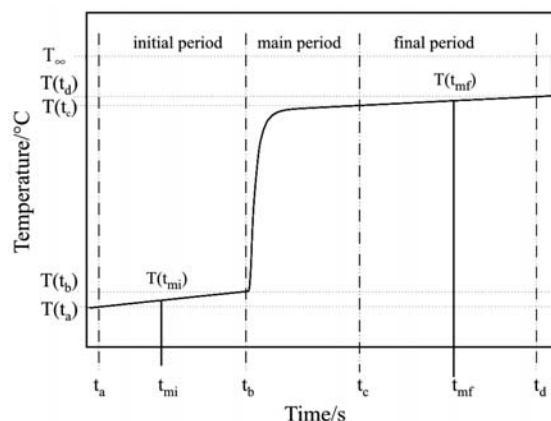
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Fig. 1 Schematic representation of a typical temperature–time curve in isoperibol temperature-rise calorimetry

the chemical or physical process under investigation occurs; the initial (t_a to t_b) and final (t_c to t_d) periods are ideally governed by the energy exchange between the calorimetric system and its surroundings only. The rate of change of temperature during the initial and final periods can be described by a single body-model having a geometrically uniform but time-dependent temperature; it is exchanging heat with an environment at a uniform, constant temperature. A two-body model should be considered in systems with significant internal thermal gradients. Considering the simplest single body-model, the rate of change of temperature during the initial and final periods can be assumed to be described by Newton's law of heat transfer,

$$dT/dt = u + k(T_J - T) \qquad (1)$$

where u – rate of change of temperature due to all constant thermal effects, like stirring, evaporation, self-heating of the temperature sensor, etc., T – temperature, t – time, T_J – effective jacket temperature and k – thermal leakage modulus (overall heat-transfer coefficient to the surroundings divided by the total heat equivalent of the calorimeter).

In isoperibol calorimetric systems, the thermal leakage modulus is usually small (a high total heat capacity and a small overall thermal conductivity to the surroundings).

Considering the Eq. (1) for the description of the rate of temperature change, term u represents the rate of change of temperature due to all constant thermal effects and can be derived from the condition of a pseudo thermal equilibrium, in which the heat exchange flow balance is reached, and where $dT/dt = 0$:

$$u = k(T_\infty - T_J) \qquad (2)$$

where T_∞ is the convergence temperature when the heat flow from the calorimetric vessel to the surroundings equals the heat flow due to all constant thermal effects inside the vessel. The substitution of u, in Eq. (1), yields

$$dT/dt = k(T_\infty - T_J) + k(T_J - T) \qquad (3)$$

or

$$dT/dt = k(T_\infty - T) \qquad (4)$$

Assuming u, k and T_J being constant, a condition which is nearly maintained for calibrations and experiments at similar conditions, the analytical integration of Eq. (4) gives an exponential function that describes the temperature in the calorimetric vessel, $T(t)$, as a function of the time, t, considering an initial point, (T_i, t_i),

$$T(t) = T_\infty - (T_\infty - T_i)\exp[-k(t - t_i)] \qquad (5)$$

Considering both the rate of change of temperature in the mean time of the initial period, t_{mi}, and final period, t_{mf},

$$(dT/dt)t_{mi} = u + k(T_J - T t_{mi}) \qquad (6)$$

$$(dT/dt)t_{mf} = u + k(T_J - T t_{mf}) \qquad (7)$$

the value of the thermal leakage modulus, the cooling constant k, could be derived from Eqs (6) and (7).

$$k = \frac{(dT/dt)_{t_{mi}} - (dT/dt)_{t_{mf}}}{T_{t_{mf}} - T_{t_{mi}}} \qquad (8)$$

The equilibrium temperature, T_∞, is, after all, derived from Eq. (4) using the derivative at any point of the initial or final periods, t_z.

$$T_\infty = \frac{(dT/dt)_{t_z}}{k} + T_{t_z} \qquad (9)$$

In order to minimize the interpolation errors of the derivative, $(dT/dt)_{t_z}$, and temperature, T_{t_z}, the time, t_z, is chosen as the mean time of the initial or final periods, t_{mi} or t_{mf}.

The corrected temperature rise, ΔT_{ad}, occurring during the main period, can be calculated as:

$$\Delta T_{ad} = T_{t_c} - T_{t_b} - \Delta T_{exc} \qquad (10)$$

where T_{t_c} and T_{t_b} are the temperatures at the end (t_c) and the beginning (t_b) of the main period, respectively, and ΔT_{exc} corresponds to the temperature change (during the main period) which occurs due to the heat exchange and due to the constant thermal power within the calorimeter. ΔT_{exc} can be calculated by integration of Eq. (4) over the time interval t_b to t_c, provided that, according to the previous assumption, u, k and T_J remain constant during the calorimetric experiment.

$$\Delta T_{exc} = \int_{t_b}^{t_c} (dT/dt)dt = k\int_{t_b}^{t_c} (T_\infty - T)dt \qquad (11)$$

$$\Delta T_{ad} = T_{t_c} - T_{t_b} - k\int_{t_b}^{t_c} (T_\infty - T)dt \qquad (12)$$

Calculation methodologies

Definition of the time intervals

The calculation of the corrected temperature rise is based on Eq. (12). To derive this equation, it was assumed that t_b and t_c are congruent with the true main period interval. The previous assumption is in many cases the main source for errors in the calculation of ΔT_{ad}, due to the difficulty to define if the power effect due to the process in the calorimeter has ceased, and, as a consequence, when the calorimeter reaches a pseudo steady state in the final period.

The choice of time t_b is not problematic, as it is usually well known when the process starts; the problem arises with the fixing of the end time of the main period, t_c. The time t_c should be taken as soon as possible, with the guaranty, that the temperature–time evolution is already following Eq. (1). A premature choice of the time t_c is a known problem in high precision solution–reaction calorimetry; it becomes even more critical in small calorimeters with small heat capacities and large cooling constants [12, 13].

If the time t_c is headily chosen, the following consequences arise:

- wrong fitting of the exponential function which is used to describe the initial and final periods;
- systematical deviations in the initial and final temperatures of the main period;
- introduction of errors in the calculation of the T–t derivative, dT/dt, in the value of the thermal leakage modulus, k, and in the convergence temperature, T_∞.

Fitting equations

The exponential function (Eq. (5)) describes the temperature in the calorimeter vessel, $T(t)$, as a function of the time t, assuming a simple one-body heat transfer model. In most cases, the exponential description is closely approximated by quadratic equations, which are, in numerical terms, easier to deal with. It is still common practice to fit the initial and final periods to straight lines, especially when the exponent, $[-k(t-t_i)]$, is small, or in the case of low quality of the temperature–time data. Due to the symmetry, the derivative obtained from the fit of linear or quadratic equations at the mean of the fitting period is very close to the derivative obtained at the same point from the Eq. (5). It can be analytically proven [14] that, in a series of equally time spaced data, a least square fitting of a linear or quadratic function to any series of data gives exactly the same derivative at the middle point of the interval. Linear or quadratic fittings show an equal accuracy but the use of a cubic polynomial fitting results in a significant increase in the accuracy of the interpolation of the temperature–time derivative, even when the mean time is considered.

Calculation procedures

In isoperibol calorimetry, the corrected temperature rise, ΔT_{ad}, is usually calculated following the procedures known as the Regnault–Pfaundler method (integration method) [1] or by the extrapolation method in several variations [1, 2].

The Regnault–Pfaundler method can essentially be described as the calculation of ΔT_{ad} using a numerical solution of Eq. (12), including the numerical integration of the temperature change during the main period which occurs due to heat exchange, and the calculation of k and T_∞, from Eqs (8) and (9), respectively.

The results obtained by the Regnault–Pfaundler method are highly dependent on the k value. The calculation of k from experimental data is very critical when the change in dT/dt, between the initial and final period, is very small (experiments with a small ΔT_{ad}). The definition of the main period is also very crucial as it defines the time interval for the numerical integration of the temperature change due to the heat exchange to the surroundings and due to the constant thermal power within the calorimeter.

The extrapolation method, as described by Challoner *et al*. [15], is based on the extrapolation of the temperature rise from the fitted exponential function, Eq. (5), for the initial and final periods, T_i and T_f. This extrapolation is done at the time t_x, where the temperature-time integration of the fitted equation, T_i and T_f from t_a to t_x and from t_x to t_d, respectively, equals the overall temperature–time integration of the experimental curve as represented by the following equation:

$$\int_{t_a}^{t_d} T(t)dt = \int_{t_a}^{t_x} T_i(t)dt + \int_{t_x}^{t_d} T_f(t)dt \qquad (13)$$

This is equivalent to the schematic representation on Fig. 2a, where the temperature–time lines (A, B) are extrapolated to a common point in time, (t_x). The time (t_x) is selected in a manner which ascertains that the two shaded areas in the graph are equal. The corrected temperature rise, ΔT_{ad}, is calculated from the final and initial temperatures at the time t_x.

$$\Delta T_{ad} = T_f(t_x) - T_i(t_x) \qquad (14)$$

Numerical procedures

In order to minimize errors due to an unintentionally premature choice of the end time of the main period t_c, the following procedure is proposed:

- Fitting of independent polynomial equations to the initial and final periods:

In the presented procedure we will consider the fitting to a third-order polynom, with the initial period, t_a to t_b
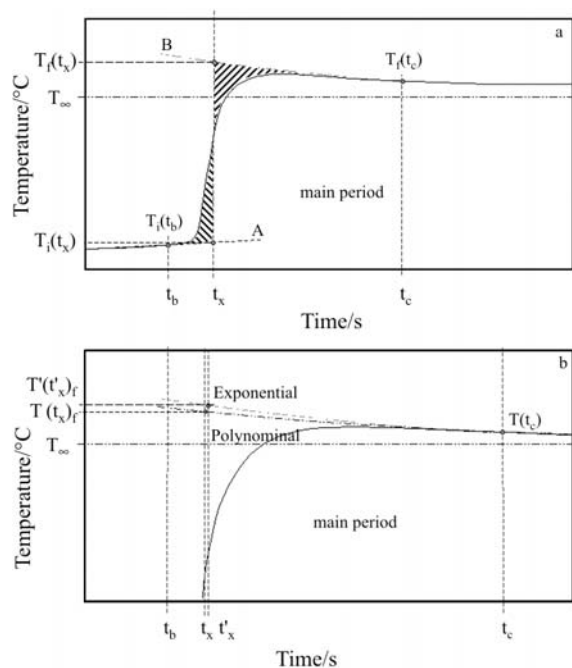
Fig. 2 Schematic temperature-time curve in isoperibol calorimetry: a – the temperature–time lines (A, B) are extrapolated to a common point in time, (t_x). The time (t_x) is selected in a way which will make the two shaded areas in the graph equally sized; b – fitting extrapolations in vicinity of the main period region (exponential and polynomial)

$$[T(t)]_{ci} = A_i + B_i t + C_i t^2 + D_i t^3 \tag{15}$$

and the final period, t_c to t_d

$$[T(t)]_{cf} = A_f + B_f t + C_f t^2 + D_f t^3 \tag{16}$$

Alternatively, an exponential function, in the form of Eq. (5), could be iteratively fitted.

- Utilizing the analytical derivatives of the Eqs (15) and (16) at the mean times of the initial and final periods, t_{mi} and t_{mf}, respectively, to derive the analytical solution for the thermal leakage modulus, k, based on Eq. (8);

$$k = \frac{B_i - B_f + 2C_i t_{mi} - 2C_f t_{mf} + 3D_i t_{mi}^2 - 3D_f t_{mf}^2}{A_f - A_i + B_f t_{mf} - B_i t_{mi} + C_f t_{mf}^2 - C_i t_{mi}^2 + D_f t_{mf}^3 - D_i t_{mi}^3} \tag{17}$$

- Calculation of the convergence temperature, T_∞, from Eq. (9), using the analytical derivative of the temperature in the mean time of the initial period, $T(t_{mi})$, and the interpolated temperature from Eq. (15) and the value of k, from Eq. (17).

$$T_\infty = A_i + B_i t_{mi} + C_i t_{mi}^2 + D_i t_{mi}^3 + \\ + (B_i + 2C_i t_{mi} + 3D_i t_{mi}^2) / k \tag{18}$$

- Derivation of the analytical solutions of the function that describes the initial and final periods, Eq. (5), using the previous values of k and T_∞ and anchoring the exponential functions at the interpolated temperatures at the mean time of the initial period $T(t_{mi})$

$$[T(t)]_i = A_i + B_i t_{mi} + C_i t_{mi}^2 + D_i t_{mi}^3 \\ + (B_i + 2C_i t_{mi} + 3D_i t_{mi}^2) / k \tag{19} \\ - [(B_i + 2C_i t_{mi} + 3D_i t_{mi}^2) / k] \exp[-k(t - t_{mi})]$$

and at the mean time of the final period, $T(t_{mf})$

$$[T(t)]_f = A_f + B_f t_{mf} + C_f t_{mf}^2 + D_f t_{mf}^3 \\ + (B_f + 2C_f t_{mf} + 3D_f t_{mf}^2) / k \tag{20} \\ - [(B_f + 2C_f t_{mf} + 3D_f t_{mf}^2) / k] \exp[-k(t - t_{mf})]$$

Implementation of the numerical procedure

The described methodology procedures were implemented in the windows software application Labtermo [16]. Labtermo performs the calculation of the corrected temperature rise from results obtained in isoperibol calorimeters using the following procedures.

Regnault–Pfaundler method (integration method) (RP)

- step 1 – Polynomial or exponential fitting of the initial and final periods, Eqs (15) and (16);
- step 2 – Calculation of k, from Eq. (17);
- step 3 – Numerical integration of the temperature exchange correction, ΔT_{exc}, Eq. (11);
- step 4 – Calculation of $T(t_b)$ and $T(t_c)$ from Eqs (19) and (20), respectively;
- step 5 – Calculation of ΔT_{ad}, from Eq. (10), using the data obtained in steps 3 and 4.

Optionally, the thermal leakage modulus k can be pre-defined. This feature offers the possibility of using a k-value obtained from other experiments, or an averaged k-value which is typical for the system.

Extrapolation method (EM)

- step 1 – Polynomial or exponential fitting of the initial and final periods, Eqs (15) and (16);
- step 2 – Calculation of k, Eq. (17);
- step 3 – Numerical iterative calculation of t_x, where the temperature–time integration of the derived Eqs (19) and (20), $[T(t)]_i$ and $[T(t)]_f$, from t_a to t_x and from t_x to t_d, respectively, equals the overall temperature–time integration of the experimental curve data.
- step 4 – Calculation of ΔT_{ad} from Eq. (14), using $[T(t_x)]_i$ and $[T(t_x)]_f$ calculated from Eqs (19) and (20).

In order to evaluate and compare the proposed methodology with the standard methods, the described procedures were applied to the calculation of a typical exothermic experimental data set. The calculations were done for the same experimental temperature *vs.* time data set, based on an independent fitting of the initial and main period to a first, second and third order polynom, using a fixed size time interval for the initial

and final periods (2000 s) and changing the time intervals for the main period (t_b to t_c) A (2990–4240 s); B (2990–4490 s) and C (2990–4740 s). The main period, A (t_b=2990 to t_c=4240 s), was intentionally chosen too short in order to exemplify how the difference between the temperature at the initial time of the final period, t_c, obtained from the polynomial fitted Eq. (16) and the exponential Eq. (20), can be used as a criterion to evaluate when the calorimeter reaches a pseudo steady state in the final period.

Table 1 lists a summary of the results for the numerical treatment of a typical exothermic experimental data set (data obtained in a high-precision isoperibol combustion calorimetry experiment). The presented results indicate that in the case of the considered experimental data set, a linear fit is clearly not adequate to be simultaneously used in high-precision isoperibol calorimetry when long time periods have to

be considered. From the results acquired for the difference between the temperature at the time t_c, $T(t_c)$, T_c (exponential)–T_c (poly), one can conclude that the chosen main period A is too short as the significant decrease of the difference, T_c (exponential)–T_c (poly), reveals, while facing an increase of the time t_c (intervals B and C).

While considering both the Regnault–Pfaundler and the extrapolation method, the use of the exponential functions [Eqs (19) and (20)] results in a higher reliability in the calculation of ΔT_{ad}, as compared to the use of the polynomial fitting functions [Eqs (15) and (16)], which holds for both methods.

Besides the observed small differences in ΔT_{ad} attained via second and third order fittings, the results obtained for both methods are in good agreement (considering $\pm 5 \cdot 10^{-5}$ K as the experimental temperature resolution). Third order fittings result in more ac-

Table 1 Summary of the results for the numerical treatment of a typical experimental data set (exothermic high-precision isoperibol combustion calorimetry), obtained using different sizes of the 'main period' A, B and C. 'initial period': (2000 s); 'final period': (2000 s)

			A	B	C
		Experimental 'main period' (t_b:t_c)/s	2990:4240	2990:4490	2990:4740
Linear fit		k/s^{-1}	0.00010756	0.00010772	0.00010828
		T_∞/°C	25.27656	25.27582	25.27452
		T_b(poly)/°C	25.00181	25.00181	25.00181
		T_b(exponential)/°C	25.00009	25.00009	25.00009
		T_c(poly)/°C	25.34671	25.34488	25.34320
		T_c(exponential)/°C	25.34709	25.34525	25.34357
		T_c(exponential)–T_c(poly)/°C	0.00038	0.00037	0.00037
	ΔT_{ad}/K	RP (poly)	0.34766	0.34780	0.34826
		RP (exponential)	0.34976	0.34990	0.35036
		EM (poly)	0.34573	0.34548	0.34554
		EM (exponential)	0.34983	0.35001	0.35059
2nd order fit		k/s^{-1}	0.00010776	0.00010800	0.00010803
		T_∞/°C	25.27659	25.27590	25.27582
		T_b(poly)/°C	25.00061	25.00061	25.00061
		T_b(exponential)/°C	25.00068	25.00068	25.00068
		T_c(poly)/°C	25.34682	25.34507	25.34325
		T_c(exponential)/°C	25.34700	25.34511	25.34328
		T_c(exponential)–T_c(poly)/°C	0.00018	0.00004	0.00003
	ΔT_{ad}/K	RP (poly)	0.34897	0.34921	0.34925
		RP (exponential)	0.34908	0.34918	0.34921
		EM (poly)	0.34842	0.34902	0.34902
		EM (exponential)	0.34913	0.34922	0.34925
3rd order fit		k/s^{-1}	0.00010814	0.00010799	0.00010800
		T_∞/°C	25.27533	25.27576	25.27572
		T_b(poly)/°C	25.00059	25.00059	25.00059
		T_b(exponential)/°C	25.00063	25.00063	25.00063
		T_c(poly)/°C	25.34671	25.34510	25.34329
		T_c(exponential)/°C	25.34716	25.34518	25.34333
		T_c(exponential)–T_c(poly)/°C	0.00045	0.00008	0.00004
	ΔT_{ad}/K	RP (poly)	0.34906	0.34928	0.34933
		RP (exponential)	0.34947	0.34932	0.34933
		EM (poly)	0.34656	0.34873	0.34873
		EM (exponential)	0.34965	0.34937	0.34938

In the table, the symbols have the same meaning as described in the text.

RP (poly) and RP (exponential) – Regnault–Pfaundler procedure applying $T(t_b)$ and $T(t_c)$ as derived from the polynomial fit [Eqs (15) and (16)] or the exponential function [Eqs (19) and (20)], respectively.

EM (poly) and EM (exponential) – extrapolation method procedure applying $T(t_b)$ and $T(t_c)$ as derived from the polynomial fit [Eqs (15) and (16)] or the exponential function [Eqs (19) and (20)], respectively.

curate interpolations of temperature of both mean times, $T(t_{mi})$ and $T(t_{mf})$, and the corresponding temperature–time derivatives, when compared with a second order fitting interpolation.

As in any established methodology for the calculation of ΔT_{ad}, it is mandatory to use the same procedure in the calibration and the experiment itself, in order to partially cancel out the particular inherent numerical deficiencies.

Final remarks

A new methodology for the accurate calculation of the corrected temperature rise in isoperibol calorimetry is proposed, based on the polynomial fitting of the initial and final periods, followed by the use of the exponential function derived from the analytical derivatives of the fitted cubic polynomial equation, in order to decrease the dependency of the results on the definition of the main period. The advantages of the proposed procedure are the following ones:

- The fittings of the Eqs (15) and (16) are independently done, with a highest number of fitting parameters, and, as a consequence, with an increase in flexibility of the fitting even in the incidental case when the time t_c was prematurely chosen;
- At the mean time of the initial and final periods of the fitted cubic Eqs (15) and (16), both the interpolated temperature, $T(t_m)$, and the value of the derivative, $\{dT/dt\}t_m$, are expected to be very accurate;
- As a consequence of the previous considerations, a reasonably accurate calculation of k and T_∞, from Eqs (17) and (18), is achieved;
- The functions in Eqs (19) and (20) and the value of k are less sensitive to the time t_c;
- A minimal difference between the temperature at the initial time of the final period, t_c, obtained from the polynomial fitted Eq. (16) and the exponential Eq. (20), can be used as a criterion to evaluate when the calorimeter reaches a pseudo steady state in the final period; as shown in Fig. 2b.
- The deviations of the experimental temperature–time data from the derived exponential Eqs (19) and (20) can be used to evaluate the quality of the numerical calculation and the existence of some anomalous perturbations in the experimental data.

A criterion to evaluate the moment, after which the power effect due to the process under investigation can be considered as being completed, is proposed. This is based on the analysis of the difference between the temperatures at the initial time of the final period, t_c, obtained from the fitted polynomial equation, and the derived exponential functional description. The proposed methodology is a robust al-

ternative to other methods for the accurate calculation of the corrected temperature-rise in high precision, nearly ideal isoperibol calorimetry.

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