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SYSTEMATIC ERRORS IN THE MEASUREMENT OF HEAT BY FLOW MICROCALORIMETRY

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ABSTRACT

It is shown that a number of systematic errors must be considered when performing heat measurements by flow microcalorimetry because the nature of the flow technique is such that substantial heat loss can be incurred. The conventional procedure of electrical calibration is found to be an inadequate correction parameter. Equations to account for the effects of thermal disequilibrium are derived from the basic principles incorporated in the Tian equation. The predicted relationships are tested by simple experiments and shown to be correct. The various correction parameters are measured for a wide range of flow rate and heat input conditions. A composite equation is presented which allows for the correction of heat loss while deconvoluting electrical heat from a heat of reaction. The total heat output rate from a flow calorimeter can be calculated for most experimental conditions by reference to this equation and to the tabulated correction values.

INTRODUCTION

Heat conduction microcalorimeters have been designed by Calvet [1], Benzinger and Kitzinger [2] and Wadsö [3] and have evolved into commercial instruments marketed by Setaram, Beckmann and LKB Instruments, respectively. The design principle is identical. A cell with a thermopile jacket is located in a heat sink. The hot junctions of the thermopile are in contact with the cell, the cold junction with the heat sink. An identical cell arrangement has its thermopile connected in opposition to the first. This twin arrangement means that any external disturbance will affect both vessels to the same extent and therefore cancel. The time integral of the EMF of the thermopile is proportional to the total heat flux, therefore this differential

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arrangement produces a resultant EMF proportional to the differential heat flux.

Of the heat conduction calorimeters currently available, the flow microcalorimeter has proved a most versatile instrument with an ease and speed of operation which has caused it to be widely adopted for chemical, microbiological and biochemical studies [4–6]. Theoretical and practical techniques have been developed for the acquisition of not only thermodynamic but also kinetic parameters [7,9]. Several types of flow calorimeter have been built [9–11]. The instrument available for our use was an LKB model 10700-1 flow microcalorimeter designed by Monk and Wadsö [12]. In the mixing mode the two reactant streams are equilibrated to the calorimeter temperature by passing through highly efficient heat exchangers into a mixing junction in which the reaction takes place. The instrument also incorporates a flow-through cell suitable for zero order or very slow processes. Reactions are initiated in a vessel external to the calorimeter and passed through the calorimeter cell, which does not have a mixing junction. The effluent from the calorimeter can be allowed to flow to waste or returned to the external incubation vessel.

The flow calorimeter operates on the principle that inflow of reactant solutions at a constant flow rate will give rise to a constant heat effect in the calorimetric cell and eventually reach the steady state condition whereby the heat generated in the cell will, per unit time, be equal to the heat transported from the cell by heat conduction through the surrounding thermopile. Only under these conditions will the measured heat effect be directly proportional to the extent of reaction within the calorimeter cell. However, it has been acknowledged [12] that even at steady state, part of the heat effect generated in the cell will be lost through the air gap between parts of the flow cell surface not in contact with the thermopile and also will leave the cell with the effluent liquid. The electrical calibration constant was found to exhibit a linear variation with flow rate for a constant electrical input. Between zero and maximum flow rate (6.7×10^{-3} cm^3 s^{-1}) the measured calibration constant differed by about 6%, from which it can be concluded that only 94% of the heat generated in the flow cell will pass through the thermopile at such a flow rate.

Despite this evidence no account has been taken of any corrections which may be required if the system is not at thermal equilibrium, nor has such a consideration been included in the theoretical analysis pertaining to the flow technique [7]. The energy output is conventionally achieved simply by multiplication of the observed voltage deflection with the electrical calibration constant. It is apparently assumed that by performing the electrical calibration under the same experimental conditions as the reaction, any effects of thermal disequilibrium will contribute equally to the observed heat change whether the source is electrical or chemical. This fundamentally assumes that the rate of heat dissipation from the cell is constant whether the heat is generated in the whole chamber or in the small heater located in the base of the cell.

If this assumption is correct, then the measured heat of reaction should exhibit a heat loss, related to liquid flow, that is identical to that observed for a constant electrical input. From the results depicted in Fig. 1, it can be seen that this is not the case. In Fig. 1(a) baseline deflection measurements were performed at a constant electrical input but with different total flow rates. Distilled water was pumped at an equal rate in both flow lines. In Fig. 1(b) the baseline deflection was measured as a function of flow rate for a fast chemical process, the dilution of hydrochloric acid. One flow line contained 0.5 mole dm^{-3} HCl, the other water. Both solutions were pumped at an

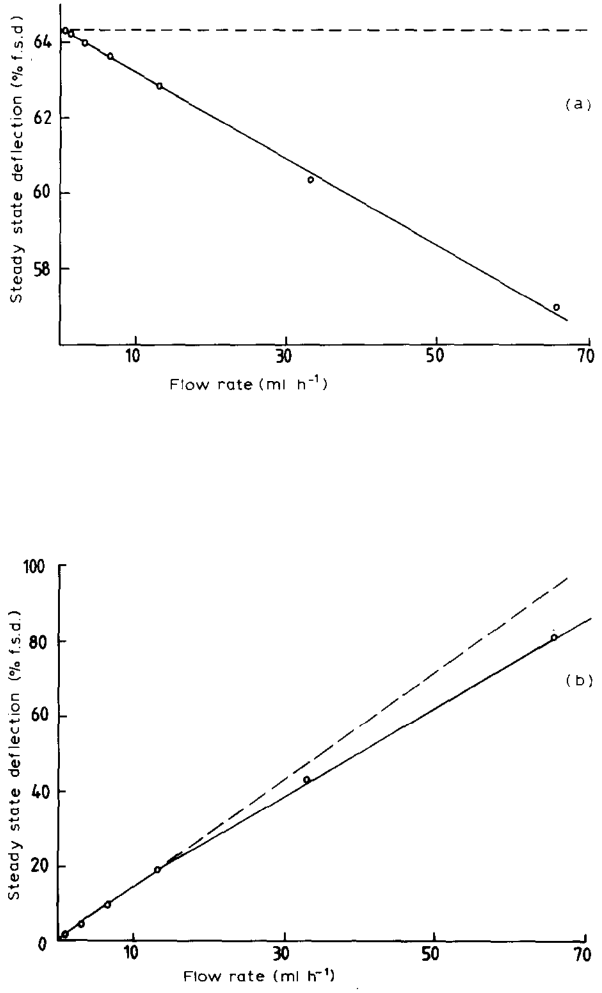

Fig. 1. The effect of flow rate on the steady state deflection for (a) a constant electrical input (288 μW), and (b) a fast reaction (dilution of 0.5 mole dm^{-3} HCl). (— — —) Predicted result for conditions of thermal equilibrium.

equal rate. These simple experiments were performed six times and Fig. 1 represents typical results. The discontinuous lines represent the results that would be expected under conditions of thermal equilibrium, i.e., the heat change observed for a constant electrical input should be independent of flow rate and the heat change observed for a fast chemical process should be directly proportional to flow rate. It is evident from Fig. 1 that significant heat loss occurred even at quite low flow rates and that whereas heat generated electrically was subject to a heat loss directly a flow rate was applied, chemically generated heat was efficiently detected until the flow rate exceeded about 4.2×10^{-3} cm^3 s^{-1}. The geometry of the cell would therefore appear to affect the extent of the heat loss incurred. The heat loss at very slow flow rates is quite small and therefore in this case the error incurred by performing the conventional calibration (at the same flow rate as the reaction) will also be small. However, it is evident from Fig. 1 that there is no condition of flow rate for which the measurement of electrical heat is directly comparable to the measurement of chemical heat. For precise heat measurement, particularly at higher flow rates, this discrepancy should certainly be corrected for. However, to date no detailed analysis of the effect and significance of such systematic error has been presented despite the report by Monk and Wadsö [12] and the discrepancies revealed by simple experiments such as those described here. The nature of the flow calorimeter is such that effluent heat loss is incurred and therefore a knowledge of the size of the heat loss and the dynamic correction factors involved is very important in the accurate evaluation of reaction enthalpy and kinetics. A systematic analysis of heat measurement by flow calorimetry was therefore undertaken in order to fulfil these requirements.

THEORETICAL

The total heat output for a calorimetric measurement is determined under the condition of uniform thermal distribution over the calorimeter cell and heat sink. Such a condition is defined by the Tian equation [1]

$$W = p\Delta/g + \mu(\mathrm{d}\Delta/\mathrm{d}t)g + \beta + P \qquad (1)$$

where W is the rate of heat generation in the calorimeter cell, μ is the heat capacity of the calorimeter cell, p is the rate of heat loss from the cell chamber, Δ is the signal of the galvanometer connected to the thermocouples, β is the rate of heat conduction out of the cell by the flowing solution, P is the rate of heat loss by Peltier cooling and is here assumed to be zero, and g is the calibration constant for the galvanometer such that $\Delta = (T_0 - T_1)g$, where T is the temperature of the heat sink.

The equation can be applied to two special cases.

(i) Heat is supplied at a constant rate until a steady state is reached. Then,

$d\Delta/dt = 0$ and $\Delta = \Delta_\infty$ and hence

$$W = p\Delta_\infty/g + \beta \tag{2}$$

At zero flow rate $\beta = 0$ and $\Delta_\infty = \Delta^0_\infty$ and

$$p/g = W/\Delta^0_\infty. \tag{3}$$

Δ^0_∞ is the steady state deflection at zero flow rate and p/g is the calibration constant for the calorimeter (e.g., for the LKB calorimeter used in the work reported here p/g has the dimensions W/s^{-1} per unit displacement of the recording device) and can therefore be measured directly when W is given by a known amount of electrical energy and the flow rate is zero. When the flow rate is not zero $p\Delta_\infty/g$ is the heat output rate calculated from the steady state signal and differs from the true value by the rate of effluent heat loss β.

Assuming β is a linear function of the heat input rate, W, and the flow rate, R, then

$$W = p\Delta_\infty/g + \alpha WR$$

that is

$$W = p\Delta_\infty/g(1 - \alpha R) \tag{4}$$

where α is a dimensionless constant. However, the experimental correction term $\beta_{\text{expt.}}$ is expressed, in different terms, as $\Delta^0_\infty - \Delta_\infty$. Hence

$$p(\Delta^0_\infty - \Delta_\infty)/g = \beta(R,W) = p\beta_{\text{expt}}/g \tag{5}$$

where $\beta_{\text{expt.}} = \alpha_{\text{expt.}} WR$.

If the above assumptions are correct a plot of the experimentally derived values for $\beta_{\text{expt.}}$ (i.e., $\Delta^0_\infty - \Delta_\infty$) against flow rate should show a linear relationship for a given electrical heat input $W_{\text{el.}}$, and the value of $\alpha_{\text{expt.}}$ obtained from the slope should be independent of $W_{\text{el.}}$.

(ii) The effect of flow rate on the time constant of the calorimeter. If, when the steady state has been achieved, W is made zero then the output signal will decrease to zero. The rate of this exponential decay is characterised by a time constant, θ. Thus

$$p\Delta/g + \mu(d\Delta/dt)/g + p\beta_{\text{expt}}/g = 0 \tag{6}$$

which by rearrangement yields

$$p(\Delta + \beta_{\text{expt.}})/g = -\mu(d\Delta/dt)g$$

$\beta_{\text{expt.}}$ is the rate of heat loss term at zero heat input and is equal to zero when $\Delta = 0$. Since

$$\beta_{\text{expt.}} = \alpha_{\text{expt.}} p\Delta R/g$$

then

$$(d\Delta/dt)/\Delta = -p\big(1 + (\alpha_{\text{expt.}} pR/g)\big)/\mu \tag{7}$$

The cooling rate is characterised by θ which is defined by

$$\theta = \mu/p\left[1 + \left(\alpha_{\text{expt.}} pR/g\right)\right]$$

As

$$\ln\Delta = (-t/\theta) + \text{constant}$$

then

$$\Delta = \Delta_\infty(\exp - t/\theta) \tag{8}$$

The value of θ is thus obtained from the slope of the plot of $\ln(\Delta/\Delta_\infty)$ against t and its relationship to flow rate ascertained. $1/\theta$ should be a linear function of R.

At zero flow rate $\beta = 0$ and therefore $\theta_0 = \mu/p$. That is μ/p is the characteristic time constant, θ_0, for the cooling rate at zero flow rate. Hence $\mu/g = \mathrm{p}\theta_0/g$ and eqn. (1) can be written as

$$W = p\left[\Delta + \left(\theta_0(\mathrm{d}\Delta/\mathrm{d}t)\right)\right]/g + \beta(W,R) \tag{9}$$

These predictions were tested by simple experimentation and the correction parameters established.

EXPERIMENTAL

The flow microcalorimeter (LKB model 10700-1) was operated in the mixing mode at 298 K. An experiment was performed by pumping distilled water into the calorimeter through teflon tubing using peristaltic pumps (Perpex LKB 10200) or a motor-driven syringe pump (Hamilton gas-tight syringes, 20 cm^3 capacity; Braun Perfusor). The flow rate was determined by weighing the amount of water pumped through the calorimeter over a defined time interval and correcting for density. By using a combination of peristaltic pump and perfusor speeds a range of total flow rate from 1.8×10^{-4} to 1.8×10^{-2} $\text{cm}^3\ \text{s}^{-1}$ was achieved. At a given flow rate a steady state deflection was measured by introducing a known quantity of electrical power into the small heater located at the mixing point. To ensure a true evaluation of the steady state, a short burst of excess heat was applied after the apparent steady state voltage had been achieved and the deflection taken as an average of the signal output before and after the heat burst. This 'over' and 'under' estimation has been advocated by Calvet [1]. To eliminate turbulent heat any calorimetric deflection was measured relative to the baseline obtained by pumping water at that particular flow rate in the absence of electrical input. After the steady state deflection had been established the electrical input was cut off and the cooling curve recorded as the heat output decayed to the baseline. Such measurements were performed for a range of electrical input, from 5×10^{-5} to 1.25×10^{-3} W, using the recorder sensitivity levels of 1.47–0.147 mW full scale deflection as ap-

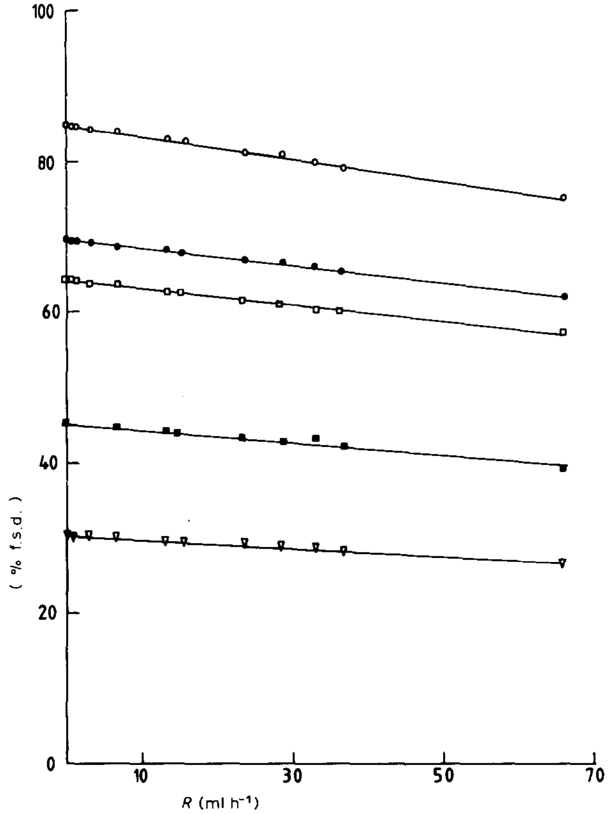

Fig. 2. The effect of flow rate (R) on the steady state deflection (Δ_∞) for a given electrical input ($W_{el.}$). $W_{el.} = 378$ μW (○); 312.5 μW (●); 288 μW (□); 200 μW (■); and 136 μW (▽). Sensitivity range: 441 μW.

TABLE 1

Correction parameters for effluent heat loss, using a recorder sensitivity range of 0.441 mW full scale deflection

Electrical input $W_{el.}(\times 10^4)$(W)	Electrical calibration constant p/g ($\times 10^6$)(W div.$^{-1}$)	Proportionality constant governing heat loss and flow rate $\alpha_{expt.}(\times 10^{-6})$
0.5	4.5254	ND
1.28	4.4759	ND
1.36	4.4736	1.4263
2.0	4.4121	1.5116
2.88	4.4785	1.3820
3.125	4.4804	1.3021
3.78	4.4502	1.3694
Mean value	4.4709×10^{-6} ($\pm 0.3\%$)	1.3983×10^6 ($\pm 2\%$)

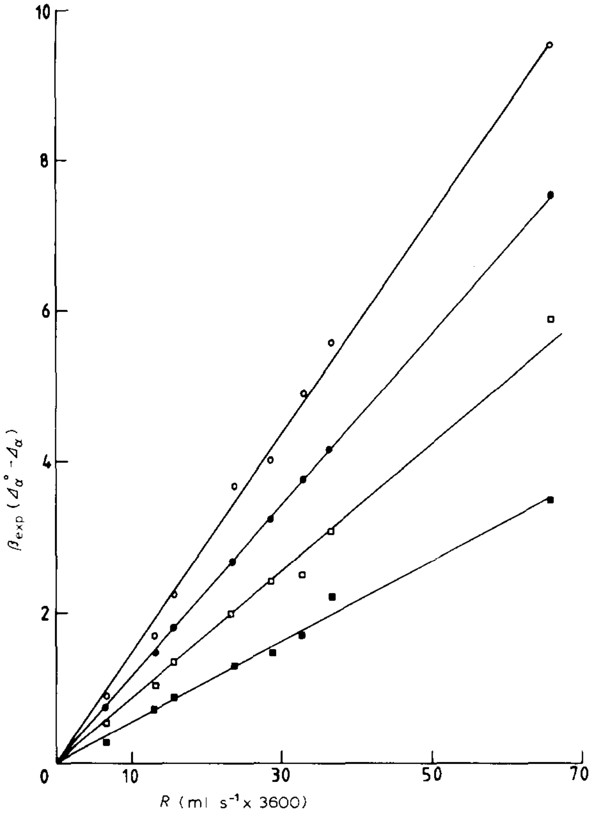

Fig. 3. The heat loss ($\beta_{\text{expt.}}$) as a function of flow rate (R) for a given electrical input ($W_{\text{el.}}$). $W_{\text{el}} = 378$ μW (○); 312.5 μW (●); 200 μW (□); and 136 μW (■). The slope = $\alpha_{\text{expt.}}\ W_{\text{el.}}$. Recorder sensitivity: 441 μW.

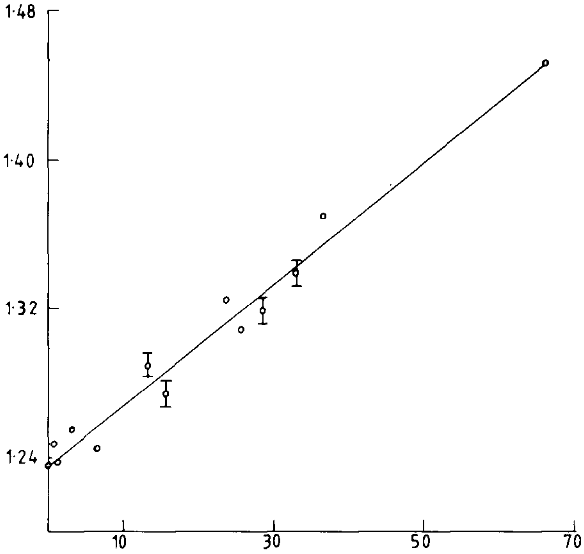

Fig. 4. The relationship between the instrumental time constant for exponential heat decay rate (θ) and the total flow rate (R). $1/\theta$ vs. R.

propriate. Integration of calorimetric data was directly obtained using a printer driver unit (LKB 10758). Results were analysed by simple linear regression using a computer package ISIS (Interactive Statistical Instructional System).

RESULTS

Steady state deflections were obtained for a range of electrical input while water flowed through the calorimeter at various flow rates. Exponential heat decay was monitored when each electrical input was reduced to zero. The data were analysed according to the equations described in the theoretical section and values were derived for each component factor of eqn. (9).

Figure 2 represents typical results for the steady state deflection (Δ_∞) as a function of the flow rate (R) for a given electrical input ($W_{\mathrm{el.}}$). Very good correlation was achieved illustrating the proportionality of the heat loss incurred as the flow rate increased. At the maximum flow rate of 1.8×10^{-2} cm^3 s^{-1} the heat loss term (β) reduced the signal observed at zero flow rate by an average 11%. This heat loss is significant in the assessment of the calibration constant (p/g), i.e., the ratio of electrical input to the steady state deflection. The true value of the calibration constant is thus measured at zero flow rate and employed with the other correction factors to obtain the total heat output rate. Such values of p/g are given in Table 1 and are independent of the size of the heat input, agreeing within 0.3%, at each sensitivity level.

The heat loss term $\beta_{\mathrm{expt.}}$ was found to be proportional to the flow rate and heat input in accordance with the theoretical prediction [eqn. (5)]. Thus a plot of $\beta_{\mathrm{expt.}}$ as a function of flow rate was linear for each electrical input (Fig. 3) and the proportionality constant $\alpha_{\mathrm{expt.}}$, obtained from the slope, was independent of the electrical input (Table 1). $\beta_{\mathrm{expt.}}$ can thus be derived for any experimental condition of flow rate and heat output using the relationship

$$\beta_{\mathrm{expt.}} = \alpha_{\mathrm{expt.}} p \Delta_{\mathrm{obs.}} R/g$$

and referring to the tabulated values of $\beta_{\mathrm{expt.}}$ and p/g. $\Delta_{\mathrm{obs.}}$ is the observed deflection under the experimental conditions.

When the steady state condition was removed, i.e., the heat input was reduced to zero, the instrumental time constant (θ) of the exponential heat decay was found for each condition of flow rate and electrical input. For a given flow rate, θ was measured over a range of electrical input (5×10^{-5}–1.25×10^{-3} W) and was found to be constant within ± 5%. Thus θ was independent of the size of the electrical heat input. However, θ was found to decrease with flow rate and the relationship was approximately linear, as shown by Fig. 4. The value of θ was found to decrease by 15% when the flow rate was increased from 0 to 1.8×10^{-2} cm^3 s^{-1}. For any given flow rate, the observed decay time constant can be corrected for heat loss by the relationship

$$\theta_{\mathrm{corr.}} = \theta_{\mathrm{obs.}}\left[1 + \left(p\alpha_{\mathrm{expt.}}R/g\right)\right]$$

The value of θ measured at zero flow rate thus represents the absolute time constant for exponential heat decay. This value (θ_0) was found to be (80.9 ± 1.2) s and may be compared to the value of 74 s reported by Johansson [13] who used the stopped-flow technique with the mixing cell of a similar type of calorimeter. The value of θ_0 is equal to the value of μ/p, as defined in the theoretical section. The constant μ/g can therefore be calculated and incorporated in the Tian equation.

DISCUSSION

The results illustrate a major systematic error characteristic of the flow microcalorimeter. To date, the only method for correction of this heat loss has been to perform the electrical calibration at the same flow rate as the chemical measurement in the assumption that the effects of thermal disequilibrium would contribute equally in the two types of measurement and therefore be eliminated. We have performed simple experiments which show that there was no condition of flow rate at which the heat loss for a measured heat of reaction was identical to that observed for a constant electrical input. This would appear to illustrate an effect of the geometry of the cell upon the rate of heat dissipation to the thermopile. Thus chemical heat, generated in the main body of the cell, was more efficiently detected than electrical heat, generated in the small resistor at the base of the cell. The conventional procedure for calibration is therefore an inadequate correction process.

This effect of thermal disequilibrium together with a detailed account of the significance of the heat loss and other possible effects on calorimetric parameters have not been previously reported, and would seem to be a fundamental omission in a technique whereby thermal equilibrium is an absolute condition for precise heat measurement. Accordingly the factors underlying the measurement of heat by flow calorimetry have been throughly examined. The analysis reveals that the heat loss incurred during a flow experiment bears a simple relation to the size of the heat input and the flow rate. The proportionality constant governing this heat loss has been measured. The amount of heat undetected by the thermopile during a flow experiment can thus be calculated for any experimental condition and easily corrected for. In addition to assessing the extent of the heat loss, the analysis also establishes the effect on certain important parameters of the calorimeter: the electrical calibration constant and the instrumental time constant.

The true value of the calibration constant is thus measured at zero flow rate and can then be employed in conjunction with the other correction factors to obtain the total heat output. The effect of the heat loss on the time constant characteristic of exponential heat decay has apparently not been appreciated before. However, such a relationship is predicted by the theoretical analysis and indeed it is perhaps to be expected that the rate of heat decay should be faster with increasing flow rate. Thus at slow flow rates, less effluent heat loss is incurred so that more heat will be conducted across the heat sink from the flowing solution within the cell residence time. A greater response is therefore given by the thermopile and the heat decay rate will be observed to be slower.

In all cases the heat loss was found to conform to the predictions given by the equations of the theoretical analysis. A composite equation is therefore presented whereby the total heat output rate can be calculated for any given experimental condition by reference to the observed heat output and the tabulated values of the correction factors. In addition to allowing the correction for heat loss, this equation allows the deconvolution of electrical heat from chemical heat measurement so that any kinetic difference in the respective heat conduction is corrected for.

We feel that this work serves a useful function in removing an important omission in our fundamental knowledge of the flow calorimetric technique. In addition, the inherent heat loss can now be easily assessed and corrected for and this is an absolute requirement in order to measure the total heat output when using this type of instrument. Where applicable, faster flow rates can now be used, with concomitant faster turnover times, without incurring a large error in heat measurement. The correct instrumental time constant can be used for the measurement of reaction kinetics and the correct electrical calibration constant employed for the conversion of the experimental signal into heat units. The precision of thermodynamic and kinetic data obtained by this technique will thus be improved.

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