# Heat flow reaction calorimetry under reflux conditions [1]

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## Abstract

A brief review of the procedures used in heat flow reaction calorimetry experiments under reflux and their evaluation is presented. A method to calibrate global heat transfer coefficients and the mass flow of the cooling condenser fluid under refluxing conditions is validated and discussed through experiments with pure solvents. A study of the influence of the most significant experimental conditions on the accuracy of the measurements is also considered.

## 1. INTRODUCTION

One of the most suitable designs of reaction calorimeters [1] for the study of industrial chemical processes is that proposed by Regenass [2] and commercialised by Mettler under the name of RC1. This is a heat flow reaction calorimeter which requires the evaluation of the global heat transfer coefficient through the reactor wall in order to calculate the heat flow. This determination is called calibration and is accomplished through the injection of a known thermal power into the system.

Most of the papers published on reaction calorimetry examine reaction mixtures of pure solvents at temperatures below their boiling point. However, in organic synthesis a significant number of processes are performed under refluxing conditions.

In 1988, Steele and Nolan [3] introduced the use of a set of accessories which allows the heat from the solvent condensation in reflux experiments to be measured and which reduces the heat losses that are more significant under these conditions than when the reaction temperature is far below boiling point.

In 1989, Mettler introduced reflux and distillation accessories that do

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not include elements for the reduction of heat loss. In 1990, this equipment was supplemented with a heatable metal/Teflon cover, according to the principle established by Steele and Nolan.

Reaction calorimetry under boiling conditions shows significant differences from isothermal heat flow calorimetry, one of the most outstanding being the inability to measure the global heat transfer coefficient according to the established principle for the RC1 when reflux does not occur.

Riesen [4] gives two methods for taking these measurements. The first uses the continuous measure of the temperature increase in the reflux condenser to evaluate the heat associated with the evaporation of volatile components of the reaction mixture. For each experiment a run must be carried out under similar experimental conditions but preventing the chemical reactions from taking place, thus compensating for the increase in heat loss and transient state in order to reach boiling conditions. The second method consists of preventing boiling by using a pressure vessel; this cannot be applied to reactions in which gases that can inhibit the reaction are given off.

All the proposals up until now use heat transfer coefficients determined 5–10 K below the boiling point. Therefore, because the global heat transfer coefficient under reflux operating conditions is unknown, a heat balance corrected for the reality of the heat transfer phenomena cannot be established, especially if $U$ changes significantly during the process. The possibility of carrying out intermediate calibrations is limited because these force a change in the operating mode and fix the reaction temperature below the boiling point. In order to solve these shortcomings and given their incidence in the field of Fine Chemistry (industrial synthesis of high value chemicals), the authors have developed a method of measuring heat transfer coefficients under reflux conditions [5, 6].

This research validates the method proposed for reflux calibrations and compares the results with those obtained by the methods mentioned above. The results obtained should allow the calculation of global heat transfer coefficients under reflux values and measurement of the mass flow of the condenser cooling fluid without additional measuring instruments. The influence of the experimental conditions on the accuracy of the measurements is also considered.

## 2. $UA$ CALIBRATION UNDER REFLUXING CONDITIONS

In the absence of chemical reactions or physical transformations that produce enthalpic changes, the heat balance equation of a system in a stationary state under refluxing conditions is

$$0 = UA_{\text{refl}} \Delta T_{\text{i}} + \dot{m}_{\text{c}}c_{\text{c}} \Delta T_{\text{c}_{\text{i}}} + \dot{Q}_{\text{loss}} + \dot{Q}_{\text{s}} \tag{1}$$

The first term on the right of this equation is the heat flow through the

reactor wall, calculated as the product of the global heat transfer coefficient $U$, the area of heat transference $A$, and the temperature difference $\Delta T$ between the reactor contents $T_r$ and the jacket fluid $T_j$. The second term corresponds to the power due to condensation of vapours in the reflux condenser and equals the product of the mass flow of the cooling fluid $\dot{m}_c$, its specific heat $c_c$, and the measured temperature increase $\Delta T_c$ between the inlet and outlet of the condenser. $\dot{Q}_{loss}$ is the heat lost to the surroundings and $\dot{Q}_s$ is the power introduced by the stirrer in the reaction mixture. The subscript 1 refers to an initial stationary state in the absence of thermal phenomena produced by the system. The subscript 'refl' refers to the value of $UA$ measured in reflux conditions.

If a change in the form of a rectangular pulse in $T_j$ is produced, because the system is at its boiling point $T_r$ remains constant and $\Delta T$ will show a change of the same nature, which produces a response in the variable $\Delta T_c$. Assuming that the pulse lasts long enough to reach a new stationary state and that the variation in $T_j$ is small enough to keep $UA_{refl}$ and $\dot{Q}_{loss}$ constant, as well as $\dot{m}_c c_c$ and $\dot{Q}_s$, the heat balance equation corresponding to this new stationary state indicated by subscript 2 is

$$0 = UA_{refl}\, \Delta T_2 + \dot{m}_c c_c\, \Delta T_{c_2} + \dot{Q}_{loss} + \dot{Q}_s \tag{2}$$

In agreement with the previous hypotheses, it is possible to determine $UA_{refl}$ from

$$UA_{refl} = -\dot{m}_c c_c \frac{(\Delta T_{c_2} - \Delta T_{c_1})}{(\Delta T_2 - \Delta T_1)} \tag{3}$$

This equation implies a linear relation between $\Delta T_c$ and $\Delta T$, both being measured in stationary states of the system but with different values of $T_j$

$$\Delta T_{c_2} = -\frac{UA_{refl}}{\dot{m}_c c_c}(\Delta T_2 - \Delta T_1) + \Delta T_{c_1} \tag{4}$$

To verify experimentally the hypotheses on which the method is based, step-like changes of 1 K in the jacket temperature within a range of ±2 K of a value of $T_j$ were made and the relationship between $\Delta T_c$ and $\Delta T$ within this range was studied. If the relationship is linear, the slope will be $UA_{refl}/\dot{m}_c c_c$, which when multiplied by $\dot{m}_c c_c$ allows the calculation of $UA_{refl}$.

## 3. CALIBRATION OF $\dot{m}_c c_c$ UNDER REFLUXING CONDITIONS

The distillation/reflux accessories developed by Steele and those of the calorimeter RC1 include instruments that measure the mass flow of the condenser cooling fluid. In the study by Steele and Nolan [3] and in a later contribution by Wiss et al. [7], a known heat power is introduced by the calibration heater to verify the accuracy of the reflux heat power using the measured value of the mass flow $\dot{m}_c c_c$. In the first study, it was shown that

the accuracy is greater than 90% for a reflux heat power below 300 W, and in the second the difference between the electrical measurement of the power introduced and the measurement obtained by integration of the reflux heat power was less than 1% with an optimum selection of the value of $\Delta T$.

In this study, the effective value of $\dot{m}_c c_c$ under reflux was determined by activating the calibration heater; this value was used instead of that obtained by an additional measuring instrument of mass flow. Under optimum experimental conditions, these measurements should coincide, within their experimental error. The heat balance corresponding to a stationary state reached during the activation of the calibration heater $\dot{Q}_c$ (subscript 3) is

$$\dot{Q}_c = UA_{\text{refl}}\,\Delta T_3 + \dot{m}_c c_c\,\Delta T_{c_3} + \dot{Q}_{\text{loss}} + \dot{Q}_s \tag{5}$$

If the value of $\Delta T_3$ is the same as the value of the stationary state prior to the activation of the calibration heater $\Delta T_1$, then $\dot{m}_c c_c$ can be determined using the equation

$$\dot{m}_c c_c = \frac{\dot{Q}_c}{(\Delta T_{c_3} - \Delta T_{c_1})} \tag{6}$$

As a consequence, a theoretical base for the calculation of $UA_{\text{refl}}$ and $\dot{m}_c c_c$, two essential parameters in the calculation of the heat balance equation in reflux conditions, can be established.

## 4. CALCULATION METHODS

In order to generalise the explanation of the calculation methods used to calculate global heat transfer coefficients and mass flow of cooling fluid, the magnitude of the response of a signal $y$ to a perturbation in signal $x$ must be calculated.

If a rectangular pulse in a signal $x$ produces a fast enough response to a signal $y$ so that during the perturbation $y$ reaches a new stationary state distinct from the initial stationary state, it is possible to determine the increase of $y(\Delta y)$ by calculating the simple difference between the final and initial states. The presence of noise or fluctuations and drift in the sampled signal makes this determination advisable through averages taken at time intervals where $y$ is stable, i.e. before $(\bar{y}_{A-B})$, during $(\bar{y}_{C-D})$, and after $(\bar{y}_{E-F})$ the perturbation. If these hypotheses are carried out, $\Delta y$ can be calculated using the equation

$$\Delta y = \bar{y}_{C-D} - \tfrac{1}{2}(\bar{y}_{A-B} + \bar{y}_{E-F}) \tag{7}$$

The same procedure can be applied to the increase in the perturbation $x$

$$\Delta x = \bar{x}_{C-D} - \tfrac{1}{2}(\bar{x}_{A-B} + \bar{x}_{E-F}) \tag{8}$$

Calculation by averages can only be applied when a stationary state is
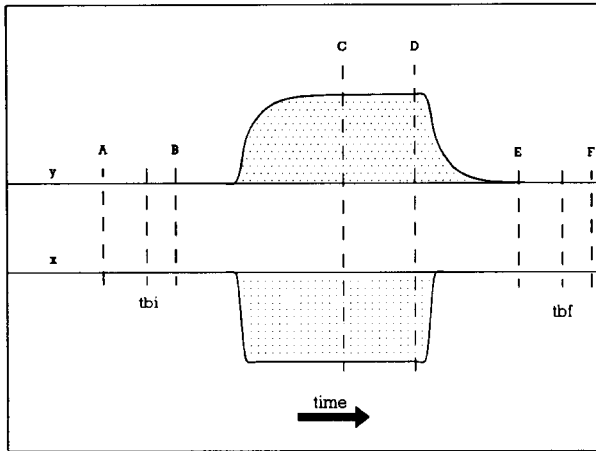
Fig. 1. Response of a signal $y$ to a rectangular impulse in a signal $x$. Stationary states before (A–B), after (E–F), and during the perturbation (C–D) are shown; $t_{bi}$ and $t_{bf}$ are the limits of time for the definition of the base lines.

obtained during perturbation (range C–D, Fig. 1). However, even when this does not occur it is always possible to evaluate the magnitudes of the perturbation and of its response by integration between the initial stationary state and the state reached once the perturbation is over. As the values of the two signals are not necessarily zero when perturbation does not occur, the integration should be defined with respect to a base line which is used to eliminate from the signal all the effects which may be considered independent of the perturbation. The base line is determined from an initial instant $t_{bi}$ to a final instant $t_{bf}$ in accordance with the expression

$$y_b = (1 - k)y(t_{bi}) + ky(t_{bf}) \tag{9}$$

where $y_{bi}$ and $y_{bf}$ are the values of $y$ in the limits of the base line and can be calculated as averages or regression around $t_{bi}$ and $t_{bf}$ (Fig. 1). The parameter $k$ is a function of the type of base line chosen. In this study, linear base lines have been used, so $k$ is calculated by the equation

$$k = \frac{t - t_{bi}}{t_{bf} - t_{bi}} \tag{10}$$

The integral of the response $y$ with respect to the base line is calculated using the equation

$$\int_{t_{bi}}^{t_{bf}} (y - y_b)\, dt = \int_{t_{bi}}^{t_{bf}} \left\{ y - \left[ y(t_{bi}) + \frac{y(t_{bf}) - y(t_{bi})}{t_{bf} - t_{bi}}(t - t_{bi}) \right] \right\} dt \tag{11}$$

By an analogous reasoning, the integral of the signal $x$ can be determined

$$\int_{t_{bi}}^{t_{bf}} (x - x_b)\, dt = \int_{t_{bi}}^{t_{bf}} \left\{ x - \left[ x(t_{bi}) + \frac{x(t_{bf}) - x(t_{bi})}{t_{bf} - t_{bi}}(t - t_{bi}) \right] \right\} dt \tag{12}$$

In Fig. 1, the shaded areas correspond to the integrals of $y$ and $x$ with respect to linear base lines.

The calculation methods described can be applied to the calculation of $UA_{\mathrm{refl}}$, where the perturbation is a rectangular pulse in $\Delta T$ and the response is $\Delta T_c$. If eqn. (1) is integrated in relation to the time between two instants when the system is in a stationary state, before and after the perturbation, then $UA_{\mathrm{refl}}$ can be obtained using the integral method of calculation

$$UA_{\mathrm{refl}} = -\dot{m}_c c_c \frac{\displaystyle\int_{t_{bi}}^{t_{bf}} (\Delta T_c - \Delta T_{c_1})\, \mathrm{d}t}{\displaystyle\int_{t_{bi}}^{t_{bf}} (\Delta T - \Delta T_1)\, \mathrm{d}t} \tag{13}$$

The terms $\dot{Q}_{\mathrm{loss}}$ and $\dot{Q}_s$ are not measured directly and are taken into account in the base line of $\Delta T_c$ and $\Delta T$

$$-\int_{t_{bi}}^{t_{bf}} (\dot{Q}_{\mathrm{loss}} + \dot{Q}_s)\, \mathrm{d}t = \int_{t_{bi}}^{t_{bf}} \dot{m}_c c_c\, \Delta T_{c_1}\, \mathrm{d}t + \int_{t_{bi}}^{t_{bf}} UA_{\mathrm{refl}}\, \Delta T_1\, \mathrm{d}t \tag{14}$$

To calculate $\dot{m}_c c_c$, the perturbation is $\dot{Q}_c$ and the response signal is $\Delta T_c$

$$\dot{m}_c c_c = \frac{\displaystyle\int_{t_{bi}}^{t_{bf}} \dot{Q}_c\, \mathrm{d}t}{\displaystyle\int_{t_{bi}}^{t_{bf}} (\Delta T_c - \Delta T_{c_1})\, \mathrm{d}t} \tag{15}$$

The numerical calculation of the integral can be made using either the evaluation program of the RC1 of the data treatment programs specially built for this purpose.

## 5. EXPERIMENTAL

The equipment used was the RC1 reaction calorimeter equipped with the standard 2 l glass reactor AP01 and the glass cover or the heatable cover MT01. The accessories used were an anchor stirrer, a temperature sensor and calibration heater of 23 W. A glass helix condenser insulated by vacuum insulation and silver coating was also used, with a sensor for measuring temperature variations in the cooling fluid.

The cooling fluid in the condenser was water, with known specific heat $c_c$; its mass flow was regulated by a differential pressure controller and measured with a rotameter. In some experiments the glass cover was insulated with 8 mm thick polyurethane foam.

The experiments were carried out using 1 and 1.7 l of the pure solvents, acetone, ethanol, water, and toluene. In order to determine the viability of

the method, 14 experiments were carried out, making step-like changes of 1 K in the jacket temperature within the range of ±2 K of 6, 20, 30 or 34 K above the solvent's normal boiling point for stirring speeds of 50, 100, 150, 200 and 250 r.p.m. The calibration heater was calibrated for 15 min at the average value of $T_j$ allowing a stabilisation time of 15 min before and after this action. Two further experiments under identical experimental conditions were also carried out with 1.7 l of water to determine the reproducibility of the proposed calibration method, introducing changes in the form of a rectangular pulse of +4 K above a value of 303 K (130°C), at the previous stirring speeds and activating the calibration heater for 15 min. A final experiment was carried out with 5 repetitions of the run with 1.7 l of water at 200 r.p.m., in order to study its accuracy.

## 6. RESULTS AND DISCUSSION

### 6.1. *Linearity of $\Delta T_c$ versus $\Delta T$*

The aim of the experiments with pure solvents in which step-like changes were produced in $T_j$ was to study experimentally the relationship between $\Delta T_c$ and $\Delta T$ to confirm or refute the hypothesis of linearity. With the exception of the experiment with acetone with a value of $\Delta T$ in the range of 6 K at speeds of 50, 100 and 150 r.p.m., where the value of $\Delta T_c$ is within the order of the sensitivity of this measurement, in all cases a good linearity of $\Delta T_c$ versus $\Delta T$ was observed. Linear regressions were established by the least-squares method with mean relative errors of correlation below 1%. Figures 2 and 3 show some of the experimental points obtained.
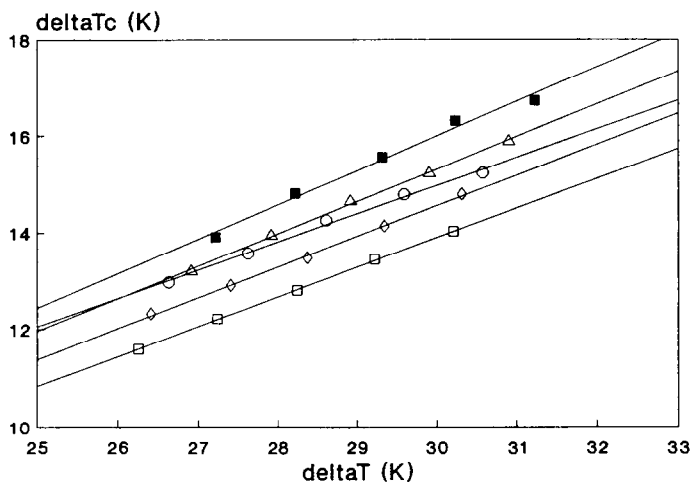


Fig. 2. $\Delta T_c$ vs. $\Delta T$ in an experiment with 1.7 l of ethanol, glass cover without insulation and variations in $T_j$ in a range of 108 ± 2°C at different stirrer speeds: □, 50 r.p.m.; ◇, 100 r.p.m.; ○, 150 r.p.m.; △, 200 r.p.m.; and ■, 250 r.p.m..

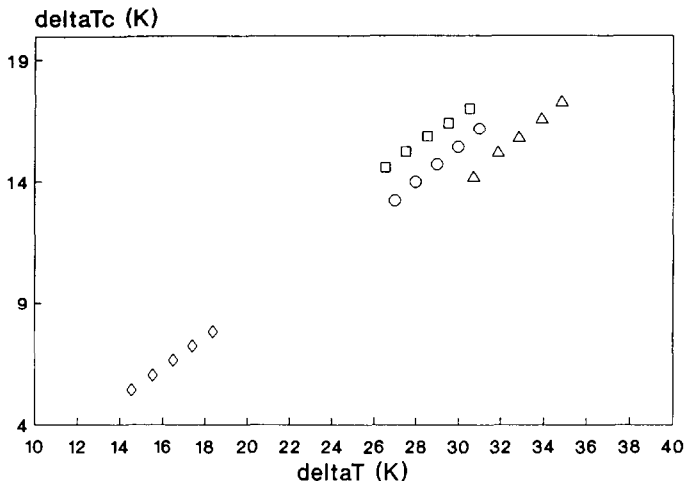Fig. 3. $\Delta T_c$ vs. $\Delta T$ in experiments with 1.7 l of different solvents, glass cover without insulation and 200 r.p.m. stirrer speed: □, acetone; ◇, ethanol; ○, water; and △, toluene.

## 6.2.  Measurement of mass flow by calibration

In all the experiments the mass flow of the condenser cooling fluid was kept constant by a differential pressure controller. The average corresponding value of 35 measurements of $\dot{m}_c$ by calibration in the experiments with 1.0 and 1.7 l of acetone, ethanol, water and toluene, using a glass cover without insulation and $\Delta T$ in the range of 30 K (34 K for toulene), was 0.227 l min$^{-1}$, with a standard deviation of 0.02 l min$^{-1}$. The frequency distribution of these measurements is shown in Fig. 4. The average value
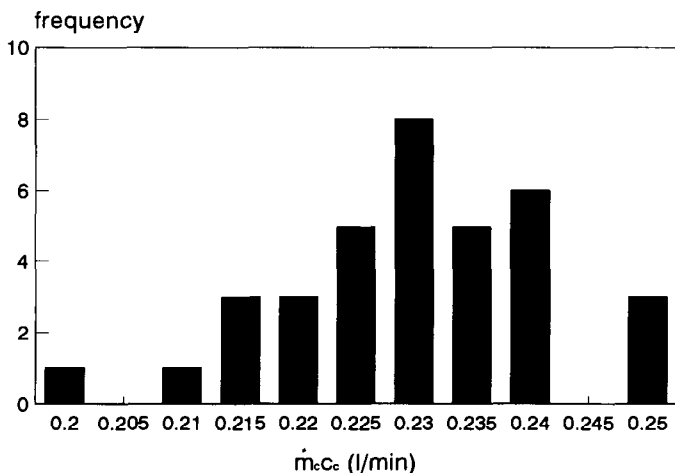


Fig. 4. Frequency distribution of the measurements of $\dot{m}_c$ by reflux calibration on the experiments with acetone, ethanol, water and toluene at different stirrer speeds in experiments with the glass cover, without insualtion.

coincides with that obtained by calibration of the rotameter, $0.228 \pm 0.005 \, 1 \, min^{-1}$. The values furthest from the average were obtained when the fluctuation in the $\Delta T_c$ signal was greater, making it more difficult to define a base line for its integration. In the experiments with 1.0 and 1.7 l of water and the heatable cover MT01, similar results were obtained, within experimental error, the average value being $0.235 \, 1 \, min^{-1}$; with standard deviation $0.007 \, 1 \, min^{-1}$.

### 6.3. Values of $UA_{refl}$

The experiments involving step-like changes in $T_j$ were used to determine the values of $UA_{refl}$ from the slopes of $\Delta T_c$ versus $\Delta T$ multiplied by the value of $\dot{m}_c c_c$ evaluated by the activation of the calibration heater.

If the values of $UA_{refl}$ are compared with those obtained under equivalent experimental conditions, but at 5–10 K below the boiling point, it can be seen that the relative differences decrease as the stirring speed increases (Fig. 5). For stirring speeds of 200–250 r.p.m. these differences are of the order of 10% or less (Fig. 6).

The measurements of $UA_{refl}$ taken from step-like changes in $T_j$ are valid for the confirmation of the basis of the method and for comparison with the values obtained below reflux temperatures, but the procedure is impractical as a standard method for work on reaction calorimetry under reflux.

The standard method is to apply a rectangular pulse in $T_j$ or in $\Delta T$ and, after activating the calibration heater, to measure the factor $\dot{m}_c c_c$ (Fig. 7). An increase of 4 K is applied which corresponds to the total variation of $T_j$
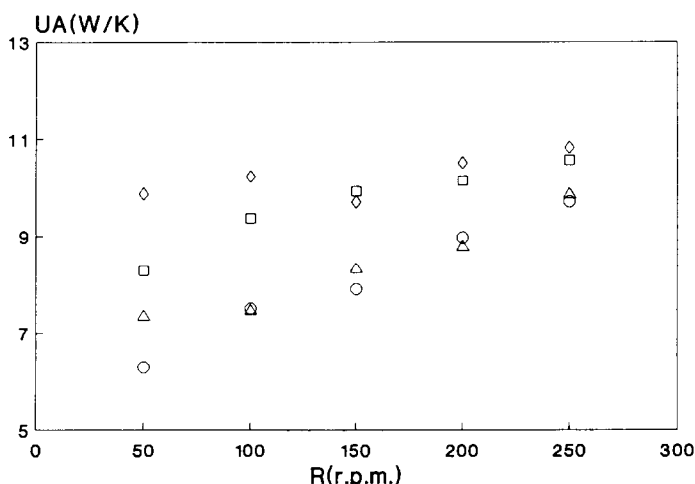


Fig. 5. $UA$ values by calibration at $T_r = 70°C$ and by reflux calibration at $T_j = 108°C$ in experiments with 1 and 1.7 l of ethanol at different stirrer speeds: □, $UA$ 70°C, 1.7 l; ◇, $UA_{refl}$, 1.7 l; ○, $UA$ 70°C, 1 l; and △, $UA_{refl}$, 1 l.
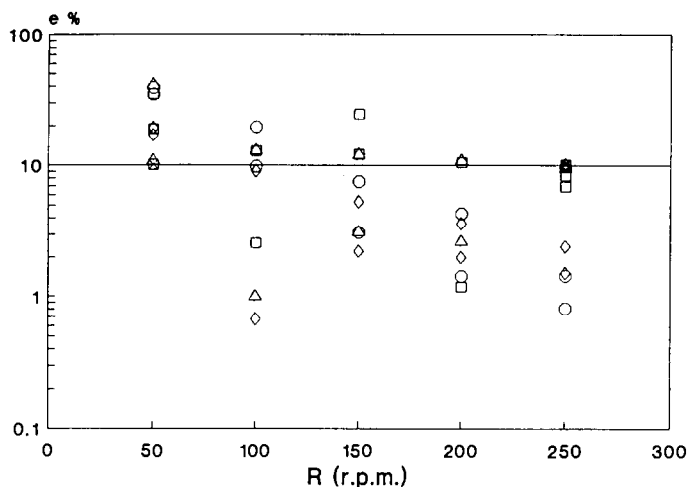
Fig. 6. Relative differences $e\%$ between $UA$ values obtained by reflux calibration and at 5–10 K below the boiling point for different stirrer speeds $R$ in experiments with 1 and 1.7 l of different solvents: □, acetone; ◇, ethanol; ○, water; and △, toluene.

in which the linearity between $\Delta T_c$ and $\Delta T$ has been verified. The calculations can be made using averages or integrals.

In order to study the reproducibility of the proposed method, two experiments using 1.7 l of water at different stirring speeds and using the heatable cover were carried out. The responses in $\Delta T_c$ to the perturbations in $\Delta T$ and $\dot{Q}_c$ were calculated by integration to obtain the values of $UA_{refl}$ and $UA_{refl2}$ corresponding to the two experiments (Table 1). Relative
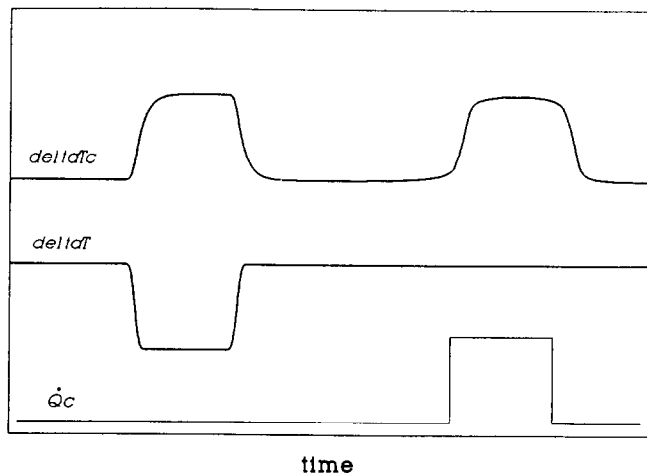


Fig. 7. Method of calibrations of $UA$ and $\dot{m}_c c_c$ under reflux. The response of $\Delta T_c$ to rectangular impulses on $\Delta T$ and $\dot{Q}_c$ in an experiment with 1.7 l of water and the heatable cover MT01 are shown.

TABLE 1

Values of $UA_{refl}$ in W K$^{-1}$ in two experiments under identical conditions, $UA_{refl1}$ and $UA_{refl2}$. The relative difference $e\%$ from the average value $UA_{reflm}$ are calculated

| Stirring speed $R$/r.p.m. | $UA_{refl1}$ | $UA_{refl2}$ | $UA_{reflm}$ | $e\%$ |
|---|---|---|---|---|
| 50 | 11.07 | 10.68 | 10.87 | 1.8 |
| 100 | 11.91 | 11.75 | 11.83 | 0.7 |
| 150 | 10.18 | 11.82 | 11.00 | 7.4 |
| 200 | 12.69 | 11.62 | 12.16 | 4.4 |
| 250 | 12.78 | 12.28 | 12.53 | 2.0 |

differences of up to 7.4% with respect to the average value of the two measurements $UA_{reflm}$, can be observed.

To determine the precision of the method, 5 repetitions of a complete calibration at 200 r.p.m. with 1.7 l of water and the heatable cover were carried out. The changes in the signals were evaluated by calculation of integrals using the evaluation program RC1 ($UA_{RC}$), and on a spreadsheet ($UA_{DT}$). The average value of the $UA_{RC}$ measurements was 12.55 W K$^{-1}$ with a standard deviation of 0.65, and the average value of the $UA_{DT}$ measurements was 12.44 W K$^{-1}$ with a standard deviation of 0.37. The smaller spread in $UA_{DT}$ values is due to the possibility of obtaining a better adjustment in the definition of the base lines for integration.

### 6.4.  Fluctuations in reflux measurements

The curve of reaction heat power $\dot{Q}_r$ measured with the reaction calorimeter presents a noise/signal ratio that is greater when working in reflux conditions than in experiments below the boiling point.

A study of the results of the experiments carried out indicates that the noise is due to fluctuations in the measurements of $\Delta T_c$. To characterise the fluctuations of a measured variable in an experiment under reflux, and taking into account that the fluctuations have a frequency distribution very close to normal, the average value of measurements over a time interval was chosen as a good approximation to the exact value of the variable $y$, and the standard deviation of the series of measurements was taken as a quantifier of the noise $Sy$. The noise/signal ratio $y_{(r/s)}$ can be calculated by the equation

$$y_{(r/s)} = \frac{S_y}{\bar{y}} \tag{16}$$

One consequence of the normal distribution of noise is that the signal can be filtered through transversal filters without causing signal distortion, provided fast changes are not produced, and keeping the value of its integral.
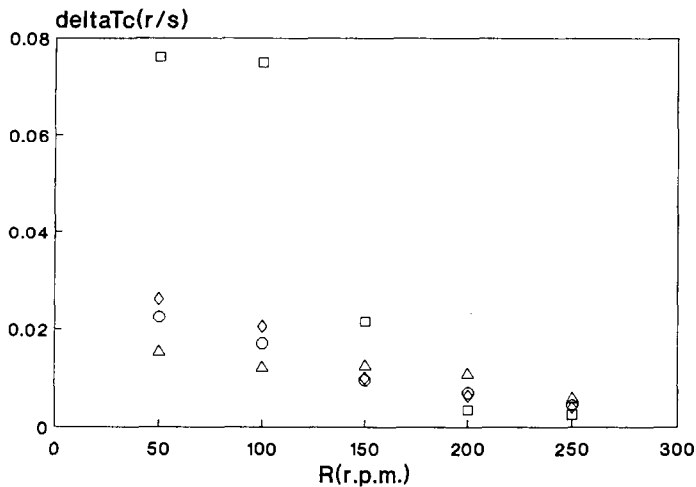
Fig. 8. Noise/signal ratio vs. stirrer speed $R$ in experiments with 1.0 l of pure solvents: □, acetone; ◇, ethanol; ○, water; and △, toluene.

Figure 8 shows the behaviour of the noise/signal ratio in $\Delta T_c$ for the experiments under reflux with 1 l of acetone, ethanol, water and toluene, at different stirring speeds and $\Delta T = 30$ K (34 K for toluene). In all cases it can be seen that this ratio decreases as the stirring speed increases. It is also worth noting the instability of the measurements with 1 l of acetone, which produce a noise/signal ratio much greater than that for the other solvents for speeds of 50, 100 and 150 r.p.m..

In the experiments with 1.7 l of solvent (Fig. 9), there is a decrease in the noise/signal ratio to a value less than 2%, as stirring speed increases. It can
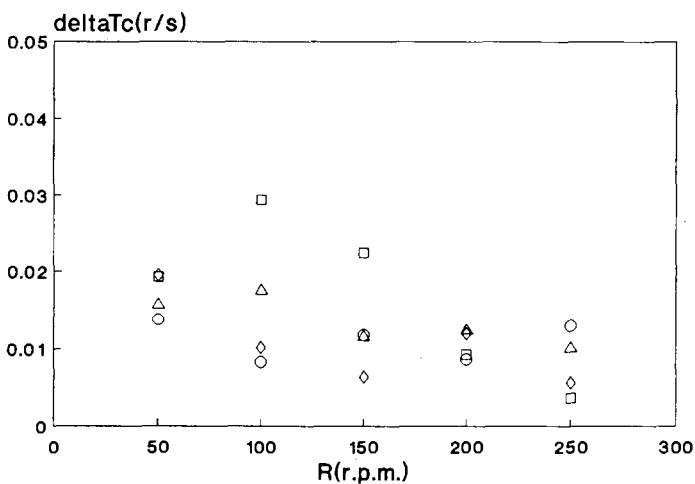


Fig. 9. Noise/signal ratio of $\Delta T_c$ vs. stirrer speed $R$ in experiments with 1.7 l of pure solvents: □, acetone; ◇, ethanol; ○, water; and △, toluene.
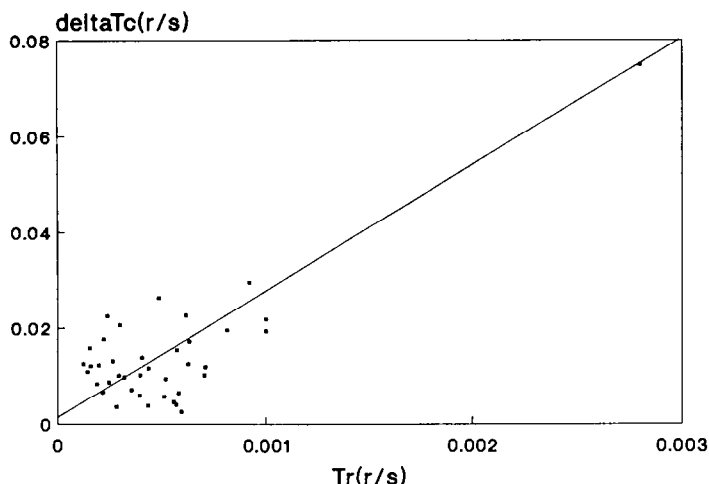
Fig. 10. Noise/signal of $\Delta T_c$ vs. noise/signal ratio in $T_r$ in experiments with 1.0 and 1.7 l of acetone, ethanol, water and toluene.

also be observed that the noise is greater at lower stirring speeds (50, 100, 150 r.p.m.) when the solvent is acetone. Figure 10 shows the noise/signal ratio of $\Delta T_c$ plotted against the noise/signal ratio of $T_r$ for experiments carried out with 1 and 1.7 l of solvent and $\Delta T = 30$ K (34 K for toluene). The noise/signal ratio is approximately 0.1%, an order of magnitude lower than for the variable $\Delta T_c$. When there are more fluctuations in $T_r$, large variations can also be seen in $\Delta T_c$. This indicates that the fluctuations in $\Delta T_c$ are not due to the measuring instrument but to the instability of the boiling phenomenon inside the reactor.

In order to study the influence of $\Delta T$ in the noise/signal ratio, a comparison is made between experiments using 1.7 l of ethanol and acetone with two different values of $\Delta T$: 20 and 30 K for ethanol, and 6 and 30 K for acetone. With the exception of the value for acetone at 50 r.p.m. and $\Delta T = 6$ K, which corresponds to a very low value of $\Delta T_c$, no significant influence of $\Delta T$ on the noise/signal relation could be seen.

Finally, the changes in noise/signal ratio for distinct configurations of the reactor cover was studied. The results for 1.7 l of acetone with and without insulation of the cover and for 1.7 l of water with both the glass and heatable covers were compared. No significant changes in the noise/signal data with respect to the cover configuration were observed.

## 7. CONCLUSIONS

The working hypothesis for the calibration method under reflux conditions is confirmed. As normal procedure, the application of a rectangular pulse in $T_j$ or $\Delta T$ of 4 K above its working value or that increase which produces a response in $\Delta T_c$ equal to the one which produces the

activation of $\dot{Q}_c$, is established. Once the stationary state is regained, an electrical power introduced by the calibration heater is applied. The first action allows the calculation of $UA_{refl}$ while the second allows the effective value of $\dot{m}_c c_c$ to be deduced.

From the data obtained, it can be stated that the values of $UA$ obtained by reflux calibration under the experimental working conditions do not present significant differences to the values of $UA$ obtained through calibration at temperatures below reflux when the stirring speed is high. One advantage of the method proposed is that it enables the carrying out of as many intermediary calibrations as necessary without significantly altering the process.

Fluctuations in reflux measurements depend basically on the stirring speed and are independent of the magnitude of the temperature difference between the jacket and the reactor temperature, and of the insulation or heatability of the reactor cover. These fluctuations are due to the nature of the boiling phenomenon in the reactor.

## ACKNOWLEDGEMENT

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