

Isothermal calorimetry: Impact of measurements error on heat of reaction and kinetic calculations

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Abstract

Heat flow and power compensation calorimetry measures the power generation of a reaction via an energy balance over an appropriately designed isothermal reactor. However, the measurement of the power generated by a reaction is a *relative* measurement, and calibrations are used to eliminate the contribution of a number of *unknown factors*. In this work the effect of the error in the measurement of temperature of electric power used in the calibrations and the heat transfer coefficient and baseline is assessed. It has been shown that the error in all aforementioned quantities reflects on the baseline and it can have a very serious impact on the accuracy of the measurement. The influence of the fluctuation of ambient temperature has been evaluated and a means of a correction that reduces its impact has been implemented. The temperature of dosed material is affected by the heat losses if reaction is performed at high temperature and low dosing rate. An experimental methodology is presented that can provide means of assessment of the actual temperature of the dosed material. Depending on the reacting system, the heat of evaporation could be included in the baseline, especially if non-condensable gases are produced during the course of the reaction.

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1. Introduction

A reaction-calorimeter is a small-scale, programmed, well-stirred, jacketed batch-reactor fitted with a rapid and accurate temperature controller to accomplish heat balancing. The contents in the reactor could be heated or cooled by heat-transfer oil at the same time being stirred well with agitator. It is equipped with a number of additional components such as scales, pumps, electric heaters, etc.

In the current study heat-flow and power compensation measurements performed during the calorimetric study of the *N*-oxidation of alkyipyridines [1–4] are used to perform an error analysis and identify the factors where higher accuracy is imperative. As mentioned in [1–4] the reaction employed in this study is liquid, homogeneous and catalytic with hydrogen peroxide being used as oxidant, which inevitably decomposes producing

gaseous oxygen. The reaction is performed in a semi-batch mode with the slow addition of hydrogen peroxide over the alkyipyridine.

Isothermal calorimetry has been used to measure the heat of reaction and to perform a kinetic study employing the instrument shown in our previous work [1–4].

The instrument can operate at heat-flow, power compensation and reflux modes. In all cases the general equation employed for the calculation of the power generated by the reaction is calculated according to the following energy balance:

$$\frac{dq_{\text{reaction}}}{dt} = \frac{dq_{\text{accum}}}{dt} + \frac{dq_{\text{flow}}}{dt} - \frac{dq_{\text{electric}}}{dt} + \frac{dq_{\text{evaporation}}}{dt} + \frac{dq_{\text{dosing}}}{dt} - \frac{dq_{\text{stirring}}}{dt} + \frac{dq_{\text{losses}}}{dt} \quad (1)$$

All the terms of the above equation indicate power, as the symbols *q* and *t* correspond to heat and time, respectively. The suffices are used to indicate: reaction, the power generated by the reaction, accum, accumulated power, flow, the power exchanged with the cooling medium, electric, the electric power provided by the calibration heater, evaporation, the power loss due to possible evaporation, dosing, power provided to the dosed mass,

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stirring, power added by stirring and losses, any other kind of power losses, respectively.

1.1. Heat-flow operation

In heat-flow mode the temperature of the cooling medium circulating in the reactor jacket changes as required in order to ensure isothermal reactor operation. When the instrument operates at heat-flow mode the terms of the Eq. (1) are obtained as follows:

The power transferred to the circulating cooling medium is calculated from the following relation:

$$\frac{dq_{\text{flow}}}{dt} = UA(T_r - T_j) \quad (2)$$

where U is the heat transfer coefficient between the jacket and reactor, A the heat transfer area, T_r the temperature of the reactor and T_j the temperature of the jacket.

The power loss due to possible evaporation of the reacting mixture is calculated by relation (3):

$$\frac{dq_{\text{evaporation}}}{dt} = \frac{dm}{dt} C_p \Delta T \quad (3)$$

where dm/dt and C_p are the mass flow-rate and the heat capacity of the cooling water circulating in the condenser, respectively. ΔT is its temperature rise.

The power losses due to dosing are calculated by the following equation:

$$\frac{dq_{\text{dosing}}}{dt} = \frac{dm_{\text{dosing}}}{dt} C_{p,\text{dosing}} (T_r - T_{\text{dosing}}) \quad (4)$$

where $d(m_{\text{dosing}})/dt$, $C_{p,\text{dosing}}$, T_{dosing} are respectively the dosing rate, the heat capacity and the temperature of the dosed material, which is normally equal to ambient temperature.

The accumulated power is taken equal to zero at isothermal operation. However, its calculation can be performed according to following relation [5]:

$$\frac{dq_{\text{accum}}}{dt} = \left[(MC_p)_R \left(\frac{dT_r}{dt} \right) \right]_{\text{reactor}} + \left[(MC_p)_J \left(\frac{dT_j}{dt} \right) \right]_{\text{jacket}} \quad (5)$$

where $(MC_p)_R$ is the thermal mass of reactor and contents and $(MC_p)_J$ is the thermal mass of the jacket and the cooling oil.

The directly measured quantities are:

- reactor temperature, T_r ;
- jacket temperature, T_j ;
- ambient or dosing temperature, T_{amb} or T_{dosing} ;
- condenser temperature rise, ΔT ;
- condenser coolant mass flow-rate, (dm/dt) ;
- rate of addition of dosed material, $d(m_{\text{dosing}})/dt$;
- heat transfer area, A ;
- electric power introduced by the calibration heater, dq_{electric}/dt ;

Power due to stirring and power losses are not normally calculated explicitly but they are included in a *baseline*. That

inevitably, renders the measurement relative. The heat transfer coefficient, U , or frequently, as in the case of the current study the product, UA and the quantity $d(q_{\text{stirring}})/dt$ and $d(q_{\text{losses}})/dt$, which constitute the *baseline* are calculated via calibration. The dosed material is maintained at ambient temperature, so T_{dosing} is normally considered equal to T_{amb} .

For the calculation of the *baseline* and UA , a known electric power is applied to the reacting mixture at isothermal steady-state operation. The power removed by the cooling medium at steady state, during calibrations using different electric power, can be used to calculate UA and *baseline* (dq_{bas}/dt). The transient state of the reactor during calibration can be used for the calculation of the thermal mass of reactor and contents and the thermal mass of the jacket and cooling oil and the accumulated power.

1.2. Evaluation of the overall heat transfer coefficient and the baseline

Fig. 1 shows the reactor and jacket temperatures of a typical calibration run. It can be seen that the reactor temperature is disturbed by the introduction of the electric power and for a period of approximately 20 min from the start and the end of the calibration the reactor temperature is in transient state.

The steady-state during and after the calibration can be used for the evaluation of the overall heat transfer coefficient, U , and the *baseline*. The unsteady-state parts of the measurement can be used for the evaluation of the reactor and oil thermal masses as described by Papadaki and Nawada [5].

At steady-state, namely, at constant reactor and jacket temperatures, dq_{accum}/dt is zero. In the absence of reaction, Eq. (1), after rearrangement, simplifies to:

$$\frac{dq_{\text{electric}}}{dt} - \frac{dq_{\text{evaporation}}}{dt} = \frac{dq_{\text{losses}}}{dt} - \frac{dq_{\text{stirring}}}{dt} + UA(T_r - T_j) \quad (6)$$

A plot of $(dq_{\text{electric}}/dt)$ against $(T_r - T_j)$ results in a straight line the slope and the intercept of which are UA and $(dq_{\text{loss}}/dt) - (dq_{\text{stir}}/dt)$, or, *baseline*, respectively. The condenser power is measured directly but it is frequently constant and can be included in the *baseline*. Without loss of generality, it will be considered as such in all the analysis that follows.

The accumulated power and the thermal masses of Eq. (5) can be calculated from the unsteady-state part of the calibration

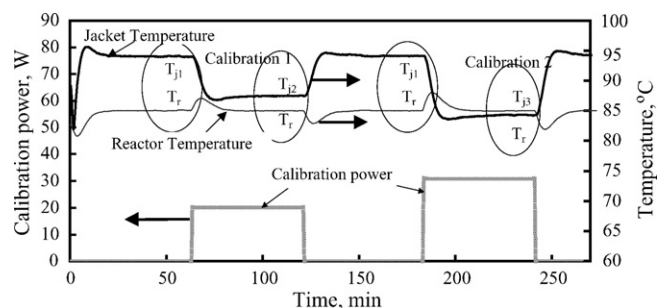


Fig. 1. Reactor and jacket temperature profiles in the presence and absence of calibration power.

run according to the methodology described by Papadaki and Nawada [5].

1.3. Power compensation

The power compensation mode of operation is characterised by constant reactor and jacket temperatures and a constant power generation inside the reactor, which is provided by reaction and/or the electric calibration heater. The calibration heater supplies an adequate amount of power, which is constant prior and after reaction and is removed by the cooling oil. During the course of the reaction the electric power of the calibration heater changes so that power generation inside the reactor maintains its constant value, which is manifested by the isothermal reactor and jacket operation. Due to the rapid response of the heater, both temperatures are essentially constant [6] so that accumulation of power is practically zero. Previous studies with isothermal calorimetry [2] have shown that at constant temperature the heat transfer coefficient of the system is not changing (within the accuracy of the measurement) due to the changes in the chemical composition of the mixture during reaction. However, the heat-transfer area changes due to dosing. The power supplied to the reactor prior and after reaction is given by the following relation:

$$\left[\frac{dq_{\text{electric}}}{dt} \right]_{\text{no_reaction}} = -\frac{dq_{\text{stirring}}}{dt} + \frac{dq_{\text{flow}}}{dt} + \frac{dq_{\text{losses}}}{dt} + \frac{dq_{\text{condenser}}}{dt} = \text{baseline} \quad (7)$$

For the conditions maintained in most measurements (constant stirring torque, constant coolant temperature in the condenser) dq_{stirring}/dt , $dq_{\text{condenser}}/dt$ are considered constant throughout the process. Because of the change in the heat-transfer area between jacket and reactor during reactant addition dq_{flow}/dt is considered to vary linearly with addition of reactant. The linear coefficient is calculated using the initial and final steady-state electrical power values. The heat losses to the environment, dq_{losses}/dt , are either considered to be constant or vary according to ambient temperature. So, from power compensation measurements, the heat of reaction is calculated from the following relation:

$$\frac{dq_{\text{r}}}{dt} = \frac{dq_{\text{accum}}}{dt} + \frac{dq_{\text{dosing}}}{dt} - \frac{dq_{\text{electric}}}{dt} - \text{baseline} \quad (8)$$

The accumulation term is normally negligible. The sensible heat provided to heat up the dosed material from its temperature, T_{dosing} , which, as earlier mentioned is usually taken equal to the ambient temperature, T_{amb} , to the reactor temperature, T_{r} , is calculated from relation (4). Finally, the *baseline* power is calculated from relation (7) applied on the system in the absence of reaction.

1.4. Reflux

Operation under reflux, or boiling reactors, operate at the boiling temperature of reaction mixture and a constant temperature

difference between jacket and reactor results in continuous evaporation of the reacting mixture. The vapours formed condense in the condenser and an energy balance over the condenser provides the power of the reaction. Calibrations as in the heat-flow operation provide the necessary data that allow the development of the relation between heat produced in the reactor and condenser cooling water temperature rise. Although analysis of data with this method is very easy it is highly prone to errors due to changes in the boiling point and enthalpy of evaporation of the reacting system and limitations in the maximum possible rise of temperature in the condenser. This method will not be dealt with in the current work.

1.5. Concentration evaluation

The power of reaction evaluated by any of the above methods can then be used for the calculation of the concentrations of reactants and products [1,2,4].

Relation (9) can be used for the calculation of the power evolution, (dq_2/dt) due to the decomposition reaction only, n_{oxygen} is the number of moles of oxygen produced and $\Delta H_{\text{H}_2\text{O}_2\text{-decomposition}}$ is the enthalpy of the decomposition reaction. The power evolution, $(dq_{1N\text{-oxidation}}/dt)$, owing to the *N*-oxidation reaction can be calculated from the following relation:

$$\frac{dq_{\text{H}_2\text{O}_2\text{-decomposition}}}{dt} = -\Delta H_{\text{H}_2\text{O}_2\text{-decomposition}} \times 2 \times \frac{dn_{\text{oxygen}}}{dt} \quad (9)$$

$$\frac{dq_{N\text{-oxidation}}}{dt} = \frac{dq_{\text{flow}}}{dt} - \frac{dq_{\text{H}_2\text{O}_2\text{-decomposition}}}{dt} \quad (10)$$

The accumulated number of moles of each of the reacting compounds can be evaluated by means of the heat evolution curves, using the following relations:

$$n_{\text{H}_2\text{O}_2,t} = n_{\text{H}_2\text{O}_2\text{-dos},t} - (n_{\text{alkylpyridine},0} - n_{\text{alkylpyridine},t}) - 2n_{\text{oxygen}} \quad (11)$$

$$n_{\text{alkylpyridine},t} = n_{\text{alkylpyridine},0} \left(1 - \frac{q_{N\text{-oxidation},t}}{q_{N\text{-oxidation},t_f}} \right) \quad (12)$$

$(n_{\text{alkylpyridine},0} - n_{\text{alkylpyridine},t})$ are the consumed moles of alkylpyridine until time t , while $n_{\text{alkylpyridine},0}$ and $n_{\text{alkylpyridine},t}$ are respectively the number of moles of alkylpyridine initially loaded into the reactor and the number of its moles present in the reaction mixture at time t ; $n_{\text{H}_2\text{O}_2,t}$ are the number of moles of hydrogen peroxide present in the reactor at time t ; $n_{\text{H}_2\text{O}_2\text{-dos},t}$ is the number of moles of hydrogen peroxide that have been added into the reaction mixture until time t ; n_{oxygen} are the number of moles of oxygen, that have been produced until time t ; $q_{N\text{-oxidation},t}$ and $q_{N\text{-oxidation},t_f}$ is the heat produced by the *N*-oxidation until time t and the total heat produced by the same reaction at completion (or equilibrium), respectively. For the calculation of the concentration of reactants, the accumulated

moles at time t are divided by the corresponding reactor volume V_t .

The accuracy of the whole measurement thus analysed depends on the accuracy of the raw data and this work focuses on this very topic.

2. The accuracy of the measurement

As mentioned earlier the measured quantities are:

- reactor temperature, T_r ;
- jacket temperature, T_j ;
- ambient or dosing temperature T_{amb} or T_{dosing} ;
- condenser temperature rise ΔT ;
- condenser coolant mass flow-rate (dm/dt);
- rate of addition of dosed material $d(m_{dosing})/dt$;
- heat transfer area, A ;
- electric power introduced by the calibration heater, $dq_{electric}/dt$;

while the heat transfer coefficient, the baseline and the required thermal masses are calculated via calibrations or via the measurement of the electric power in the absence of reaction, depending on the mode of operation.

The employed platinum resistance thermometers measure the temperature with accuracy better than 0.5°C , the power is measured with an accuracy better than 0.5 W and the measurement of the mass flow is better than 0.01 g . However, due to the noise in the measurement the scatter of the data is larger, inevitably rendering the measurement less accurate. Causes of these inaccuracies are investigated next.

As previously mentioned the measurement of the power of the reaction can be achieved either via heat-flow or via power compensation.

2.1. Temperature and power measurement error

The measurement of the reactor and jacket temperature, the value of the heat transfer coefficient and the baseline are crucial for the accuracy of the heat-flow measurement as the main amount of power produced by the reaction is transferred to the cooling oil. The accuracy of the evaluation of the heat transfer coefficient and baseline depends on the accuracy of temperature measurement and that of the power of calibration. In power compensation measurements the accuracy of the electric power measurement is the crucial component.

Fig. 2 shows the temperature of the oil entering and leaving the jacket during a measurement. It can be seen that their difference is of the order of $0.1\text{--}0.2^\circ\text{C}$, which suggests that the approximation of a constant jacket temperature is correct. However, the scatter in the measurement is of the order of $\pm 0.5^\circ\text{C}$. The same can be seen in Fig. 3, where the temperature of the reactor, shown in grey on the left-hand axis, at steady state, has a scatter of $\pm 0.5^\circ\text{C}$. In the same figure, in black, on the right-hand axis, the scatter in the measurement of the electric power is shown. As can be seen this has a scatter of 2.2 W , which means that its measurement is no better than $\pm 1.1\text{ W}$.

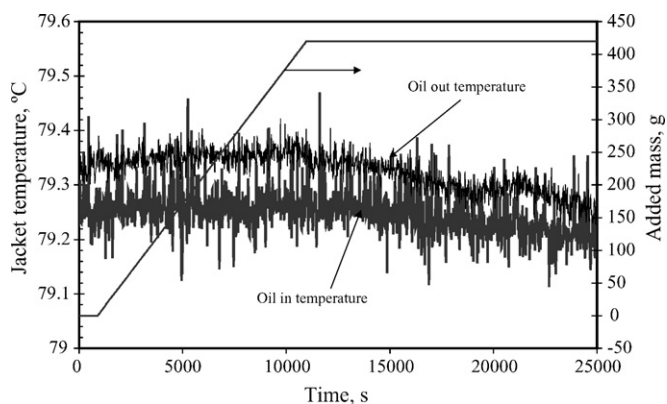


Fig. 2. Temperature of the oil entering and leaving the reactor jacket during reaction.

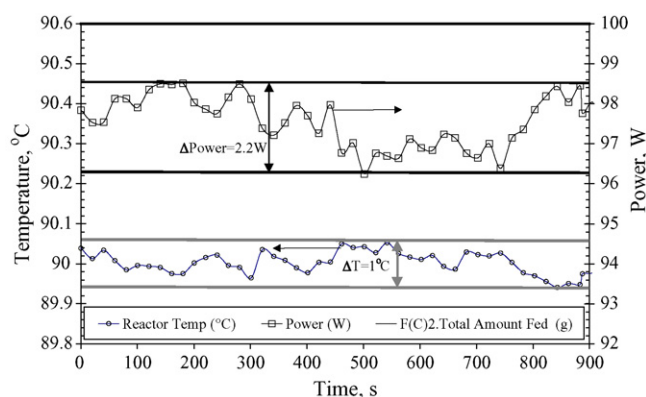


Fig. 3. Temperature and power measurement accuracy in heat-flow and power compensation measurements.

Fig. 4 shows a typical power profile obtained via heat-flow during the N -oxidation of α -picoline at 85°C . As can be seen the duration of the measurement is approximately $50,000\text{ s}$ and the power generated is approximately 650 kJ . In heat flow mode, the evaluation of the overall error requires consideration of the error in the measurement of jacket and reactor temperatures and also the error induced in the calculation of the heat transfer coefficient and the baseline due to inaccuracies in the measured power. Although these errors do not affect the value of the heat transfer

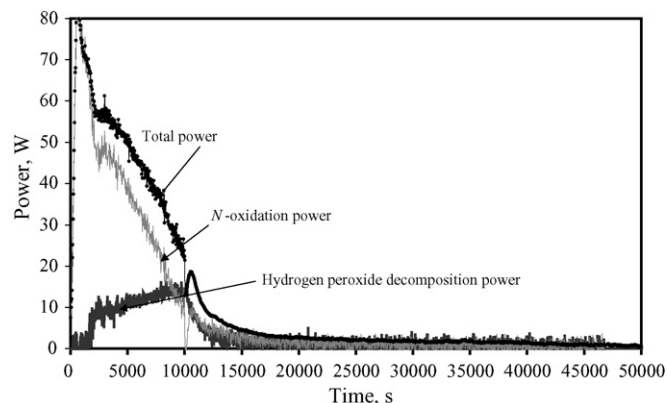


Fig. 4. Typical power profile obtained by heat-flow reaction calorimetry.

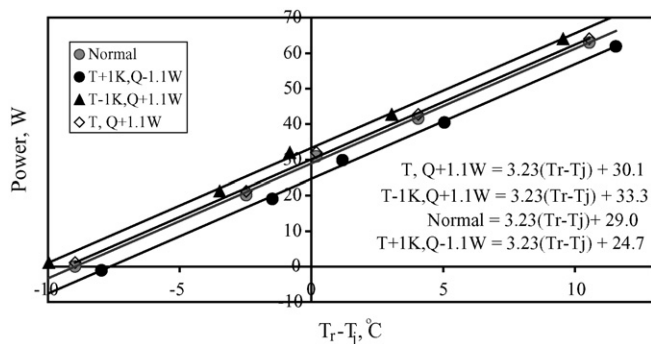


Fig. 5. Error in UA evaluation due to temperature and power error.

coefficient, they substantially affect the value of the baseline, as can be seen in Fig. 5. Fig. 5 shows the influence of temperature and power measurement error on the value of the heat transfer coefficient. The experimental values of the measurement shown in Fig. 4 are shown under the legend “normal”. The heat transfer coefficient and the baseline obtained from these data are 3.23 W K^{-1} and 29.0 , respectively. The error has been calculated in the two extremes where temperature difference ($T_r - T_j$) has $+1 \text{ K}$ error and electric power has -1.1 W error (shown as “ $T + 1 \text{ K}, Q - 1.1 \text{ W}$ ” in Fig. 5 legend) and with $T_r - T_j$ being smaller by 1 K and calibration power being larger by 1.1 W (shown as “ $T - 1 \text{ K}, Q + 1.1 \text{ W}$ ”). A fourth curve is also shown where only the electric power error has been considered. As shown in the figure, the heat transfer coefficient is unaffected by those errors. However, the baseline is strongly affected by $\pm 4.3 \text{ W}$. For a random temperature and electric power error, this would result in a huge $\pm 215 \text{ kJ}$ error in the overall heat of reaction. For a systematic error in the temperature measurement the effect of the 1 K error in the baseline would be cancelled out when multiplied by the temperature difference (relation (2)) and the overall error would be of the order of $\pm 50 \text{ kJ}$.

If power compensation had been employed the error in the heat of reaction caused by the error in the measurement of electric power would be $\pm 55 \text{ kJ}$.

Obviously, in both cases, the overall error depends on the power profile of the reaction. The heat of reaction of rapid, short-lasting reactions can be more accurately evaluated than that of slow, long-lasting ones.

2.2. Influence of ambient temperature

The heat losses, which constitute an important part of the baseline, have been considered constant. However, they vary according to the ambient temperature. Occasionally the entire calorimeter is positioned in a constant temperature oven to ensure constant ambient temperature. However, this is not always practical and calorimeters are usually kept in well-ventilated places where the ambient temperature changes. These changes, which are not very large, can have an important effect on measurements that last long like the measurements employed in the present study. Fig. 6 shows a measurement on the *N*-oxidation of β -picoline employing power-compensation calorimetry. As can be seen the measurement appears to finish at

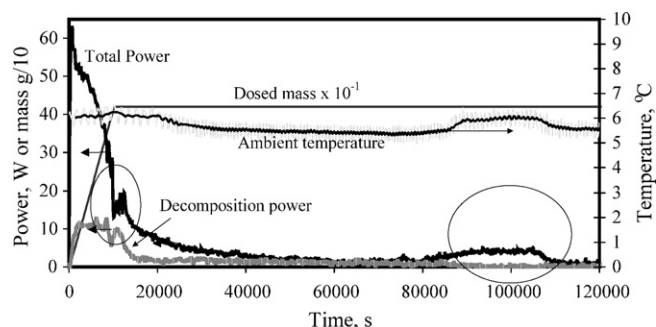


Fig. 6. Effect of ambient temperature in heat of reaction and baseline.

around $60,000 \text{ s}$, but then, a substantial amount of power appears to be produced at around $100,000 \text{ s}$. From the oxygen flow measurement it is known that the measurement has finished before $60,000 \text{ s}$. As can be seen in Fig. 6, the pattern of the ambient temperature variation and the reaction power after the end of the measurement are identical. The ambient temperature variation pattern shown in Fig. 6 is repeated daily in the laboratory where the measurements are taken. Although the ambient temperature variation is not very large ($1 \text{ }^\circ\text{C}$), it has an important influence on the overall power of the reaction due to the long duration of the slow hydrogen peroxide decomposition. To overcome this problem a correction has been applied using equation:

$$\frac{dq_{\text{correction-losses}}}{dt} = U_{\text{amb}}(T_A - T_{AB}) \quad (13)$$

where U_{amb} is a heat transfer coefficient for heat losses the value of which is evaluated from the end of the measurement, T_A is the ambient temperature and T_{AB} is the ambient base-temperature, which is the ambient temperature at the power of the baseline.

The corrected power profile is shown in Fig. 7, where the uncorrected power profile is also shown. This small correction resulted in a reduction of the total measured heat of reaction from 715 to 550 kJ .

2.3. Influence of end of dosing and heat capacity

As can be seen in Fig. 6, the power curve is discontinued at the moment addition of hydrogen peroxide finishes and possible causes have been sought. The power required to bring the dosed solution to the reactor temperature is calculated via relation (4). The mass of the dosed solution is accurately measured and the

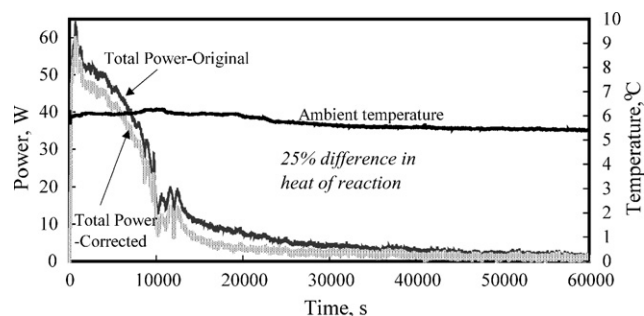


Fig. 7. Comparison of untreated heat of reaction and heat of reaction where the fluctuation of ambient temperature has been accounted for via relation (12).

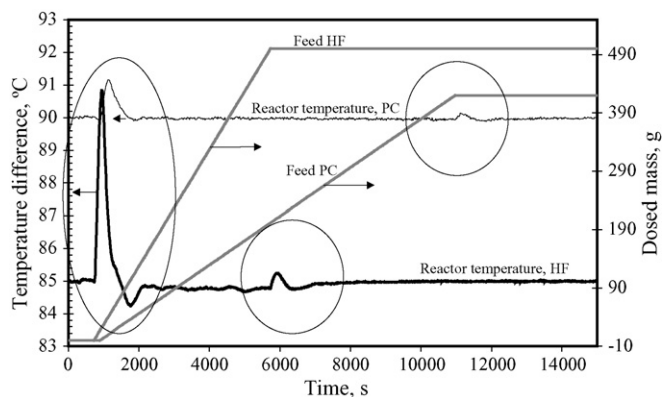


Fig. 8. Reactor temperature changes at start and end of dosing in heat-flow (HF) and power compensation (PC) modes of operation.

temperature of the reactor is known within an accuracy of 1°C . However, although the dosed material is at ambient temperature, its temperature when it enters the system, is not necessarily well known. The heat losses, which have already been taken into account, is heat dissipated around the reactor. Part of that heat may have been used in preheating the dosed material prior to its entrance in the reactor. The extent of such a preheating will obviously depend on the dosing rate and the reactor temperature.

Another possibility is that the irregularity in the measurement at the end of dosing is the effect of the sudden interruption of addition and the subsequent short-lasting rise in the reactor temperature as can be seen in Fig. 8. This irregularity could then possibly be corrected via the appropriate consideration of the accumulation term in the energy balance. In Fig. 8 reactor temperature of two measurements one taken in power compensation (PC) and one in heat flow (HF) mode are shown. However, as can be seen in Fig. 8, the temperature disturbance during the initiation of dosing is far greater than the respective change during its termination. Moreover the major upset occurs in heat-flow rather than in power compensation measurements. However, a quick comparison of Figs. 4(HF) and 6(PC) indicate that this problem is equally important in both modes of operation. Nevertheless, to investigate this phenomenon a number of heat-flow measurements, involving addition of water into water, have been taken at 40, 60, 80 and 90°C and at dosing rates 2, 4, 4.3 and 4.5 g/min . Fig. 9 shows the power versus time profile during the addition

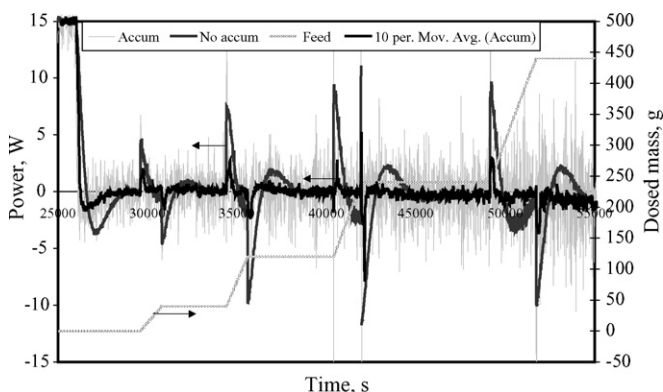


Fig. 9. Heat flow power curves during addition of water in water.

three curves are shown. The first one is the power obtained from Eq. (1) without considering the term of accumulation.

It can be seen that in the beginning and the end of each dosing session the accumulation term (series indicated in the figure legend as “no accum”) has a significant contribution. Applying the methodology presented by Papadaki and Nawada [5], this heat is mostly accounted for and a straight line is obtained (series indicated in the figure legend as “accum”). However, due to the noise introduced by the use of the temperature derivative the respective straight line is very noisy, as is shown by the curve in light grey. The moving average of this curve, in black, shows that there is a residual amount of power that cannot be corrected for.

Fig. 10 shows the power balance during dosing of water in water at a rate of 2 g/min at 90°C . After the heat capacity has been accounted for, the power, in grey, shows “power generation” during dosing, indicating that excessive correction has been applied when the heat spent in heating the dosed mass is calculated by relation (4). However, if the ambient temperature is replaced by a higher value, which, in this case is 25°C higher than the ambient temperature for a dosing rate of 2 g/min at 90°C this problem is resolved as can be seen in the same figure by the black curve. A correction of 7°C is required for a dosing rate of 4.5 g/min , at the same temperature. A smaller correction is needed for measurements performed at 80°C while no change of the ambient temperature is required for measurements performed at 40°C . Thus the error with regard to the dosing power depends on the temperature of the measurement and on the dosing rate, while the error in the heat of reaction also depends on the duration of dosing. Fig. 11 shows the dependence of temperature correction on dosing rate and temperature during the addition of water in water. The relation obtained can be used for the *N*-oxidation as, in most cases, a predominant amount of water is present throughout the reaction. Such a correction improves the end of dosing irregularity but it does not eliminate it. However, its contribution in the overall reaction power is not negligible. As can be seen in Fig. 10 the power correction at a

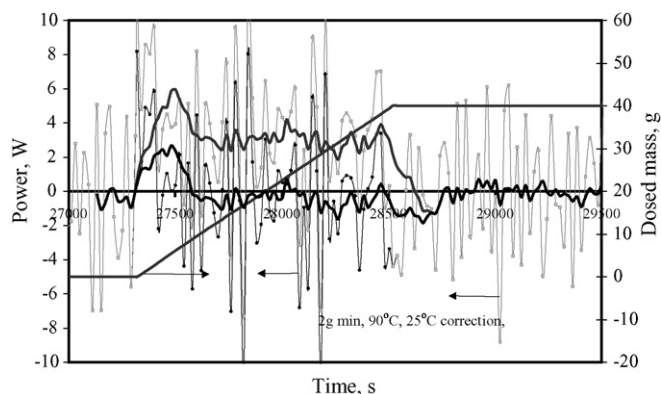


Fig. 10. Heat-flow power balance during the addition of water into water at a rate of 2 g/min . Left-hand axis: grey points: power obtained using reactor temperature and ambient temperature. Grey solid line moving average of the respective scattered points. Black scattered points: curve obtained after implementation of 25°C ambient temperature correction. Solid black line moving average of corrected power curve. Right hand axis: rate of mass addition.

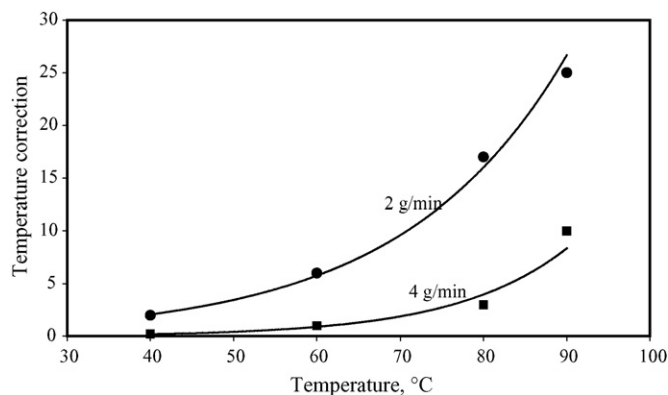


Fig. 11. Correction of dosing temperature as a function of temperature and dosing rate for addition of water in water.

dosing rate of 2 g/min (which is slightly smaller than the one employed in most measurements), at 90 °C, is approximately 4 W, which for a dosing period of 3 h is approximately 40 kJ.

2.4. Power contribution of evaporation

As the solution contains a high amount of water throughout the measurement, the condenser load has been considered constant throughout. Fig. 12 shows the condenser load, during the reaction in a measurement performed at 90 °C. As can be seen the load of the condenser follows a curve similar to the one of the oxygen generation in the respective measurement. It is thus plausible that cooling of the generated oxygen is the cause of the increased condenser load. Therefore it is believed that it should not be considered in the energy balance. Nevertheless, in this particular system its contribution (650 W) is too small to create a significant error.

2.5. Influence of error in hydrogen peroxide heat of reaction

The concentration of unreacted hydrogen peroxide can be calculated from Eq. (12) and the concentration of the alkyipyridine via relation (11). As previously said the concentration of reactants is calculated by means of power curves. Hydrogen peroxide heat of decomposition is used for the calculation of the

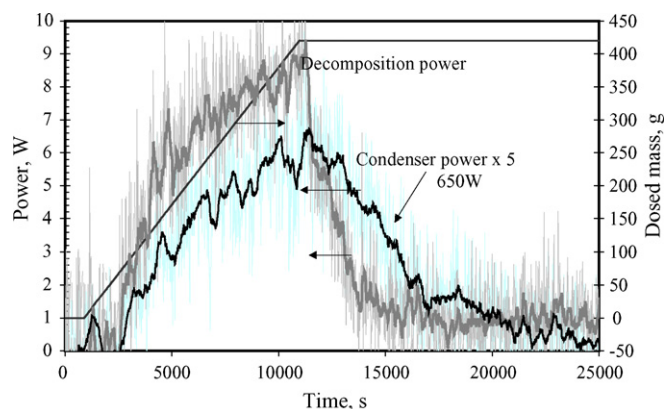


Fig. 12. Heat of evaporation and comparison with the oxygen flow-rate.

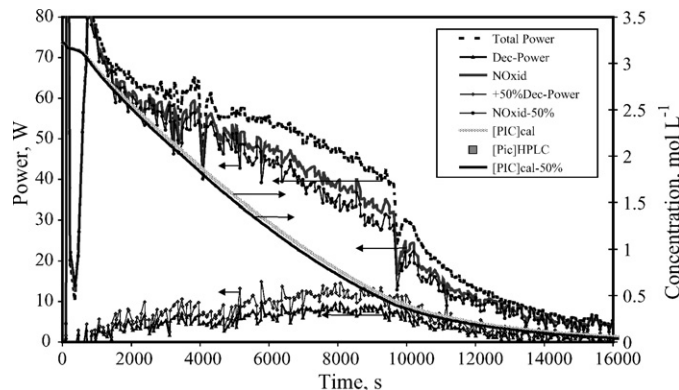


Fig. 13. Influence of +50% error in the heat of decomposition of hydrogen peroxide on the concentration of alkyipyridine.

power of *N*-oxidation and thus for the concentration of all compounds. High performance liquid chromatography (HPLC) has been used for the calculation of the concentration of the organic compounds. In Fig. 13 a typical measurement has been employed to show the effect that +50% error in the heat of decomposition of hydrogen peroxide has on the calorimetrically evaluated concentration of alkyipyridine and its power generation profile. It can be seen that the difference in the concentration is very small.

In the work of Papadaki and JunGao [4] a kinetic model involving seven kinetic coefficients for the *N*-oxidation of alkyipyridines is presented. The evaluation of the effect that the aforementioned errors induce in the accuracy of the kinetic constants of the model is a very complex problem as accuracy is crucial in specific regions of the power profile rather than in the overall profile as explained in Papadaki, Emery et al. [3].

3. Conclusions

Isothermal heat-flow and power compensation calorimetry is a useful tool for safety and kinetic studies of industrially important reactions. They measure the energy of a reaction by calculating the values of the individual components of an energy balance for the equipment. This is done using heat transfer relations involving the temperature differences measured during a reaction. However, the measurement of the power generated by a reaction is a *relative* measurement, and calibrations are used to eliminate the contribution of a number of *unknown factors*. In order to examine the reliability of a kinetic model and/or to improve the accuracy of the measurement, it is important to examine the relative importance of all factors involved in the measurement and to implement improvements. In this work the effect of the error in the measurement of temperature of electric power and the heat transfer coefficient and baseline is assessed. It has been shown that the error in all aforementioned quantities reflects on the baseline and it has a very serious impact on the resulting heat of reaction. The influence of the fluctuation of ambient temperature has been evaluated and a means of a correction that reduces its impact is suggested. The

accumulation term can be important in heat-flow calorimetry. However, when it is considered in the energy balance it renders the measurement very noisy. Accumulation is not important in power compensation measurements. The temperature of dosed material has to be selected so that over-correction is avoided. For aqueous solutions an experimental methodology is presented that can provide means of assessment of the actual temperature of the dosed material. Depending on the reacting system, the heat of evaporation could be included in the baseline, especially if non-condensable gases are produced during the course of the reaction.

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