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Jacques Wiss[1], Francis Stoessel[1]*, and Gérard Killé[2]

Abstract. The accuracy of thermal measurements under reflux conditions strongly depends on the experimental conditions. The temperature difference $T_J–T_R$ imposed on the system and the temperature of the reactor lid and reflux equipment play an important role. The optimization of these parameters and their use in the evaluation of different chemical model reactions is shown.

1. Introduction

In industrial processes, some reactions are advantageously run under reflux conditions, because the boiling point is the highest reaction temperature available at atmospheric pressure. In this way, the highest reaction rate can be achieved in a conventional reactor, increasing the productivity and profitability of an industrial unit. Moreover, using a condenser, the heat removal can be increased considerably compared to the heat exchange accross the reactor wall. This is due to two reasons:

- The heat exchange area of a reactor is limited, while the condenser can be dimensioned independently of the tank geometry.
- The overall heat-transfer coefficient of a condenser is higher than that of a reactor wall, where heat transfer is due to forced convection.

However, such a process is not free of risks. In case of a cooling failure and with inflammable solvents, an explosive cloud may form, or, due to loss of control of the reaction, the boiling rate can dramatically

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most instances, not only the direction of the adjustment is known, but also its approximate order of magnitude, since detailed processing studies allow estimation of this adjustment based upon the differences of the required and actual properties. After adjusting the vector of the operating conditions, *Eqns. 1* and *2* are solved, until the new steady-state value of the activity vector is found; the desired property again determined and checked against its required value. If the new value for the property satisfies *Eqn. 4*, the calculation is terminated. If this is not the case, the vector of the operating condition is again adjusted. Linear interpolation can now be used to determine this adjustment, since two previous values of the desired property together with the values of the appropriate vectors of the operating conditions are known. The computational scheme is now continued. That is, the steady-state value of the activity vector is determined, the value of the property calculated and checked against the required value. If an additional adjustment in the vector of the operating conditions should be necessary, interpolation is carried out between those two values of the property, and associated vectors of operating conditions, that are closest to the required property. The algorithm is eventually terminated when the constraint *Eqn. 4* is satisfied.

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Abstract. The accuracy of thermal measurements under reflux conditions strongly depends on the experimental conditions. The temperature difference $T_J - T_R$ imposed on the system and the temperature of the reactor lid and reflux equipment play an important role. The optimization of these parameters and their use in the evaluation of different chemical model reactions is shown.

1. Introduction

In industrial processes, some reactions are advantageously run under reflux conditions, because the boiling point is the highest reaction temperature available at atmospheric pressure. In this way, the highest reaction rate can be achieved in a conventional reactor, increasing the productivity and profitability of an industrial unit. Moreover, using a condenser, the heat removal can be increased considerably compared to the heat exchange accross the reactor wall. This is due to two reasons:

- The heat exchange area of a reactor is limited, while the condenser can be dimensioned independently of the tank geometry.
- The overall heat-transfer coefficient of a condenser is higher than that of a reactor wall, where heat transfer is due to forced convection.

However, such a process is not free of risks. In case of a cooling failure and with inflammable solvents, an explosive cloud may form, or, due to loss of control of the reaction, the boiling rate can dramatically

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increase, leading to a large pressure build up.

Reflux may also become important for reactions carried out below the boiling point: after a cooling failure a possible runaway may lead to reflux temperature. In this case, the evaporation of the solvent can be used effectively as an additional emergency cooling. Nevertheless, it is essential to know, if the system provides enough cooling power to stop the runaway.

To design reflux processes and to dimension the condenser and distillation system properly, it is necessary to know the heat of reaction and the variation of the heat release rate as a function of time [1] [2].

To obtain such information on the desired reaction, reaction calorimetry [3] is an appropriate chemical engineering tool. The objectives of this work were, on the one hand, to show that a heat flow calorimeter lends itself to the determination of heats of reaction and heat release rates under reflux conditions, and, on the other hand, to define the optimal conditions for the measurement and evaluation of thermal reaction data.

2. Calculation of the Heat Flow under Reflux Conditions

The heat flow calorimeter chosen for our experiments was the commercial model *Mettler RC1* [4].

The reaction calorimeter *RC1* works according to the heat flow principle [4–6]: the temperature difference $\Delta T = T_J - T_R$ between the jacket, J, and the contents of the reactor, R, is continually measured. A fast thermostat regulates the jacket temperature for a quick exchange of the heat accross the reactor wall, so that the entire heat exchanged accross the reactor wall is measured. The integration of the heat flow over time leads to the enthalpy of reaction.

The determination of the heat release rates is based on the heat and mass balances for the reactor. When a reaction is carried out below the boiling point of the reaction mixture, the overall heat flow balance is (see *Fig. 1*):

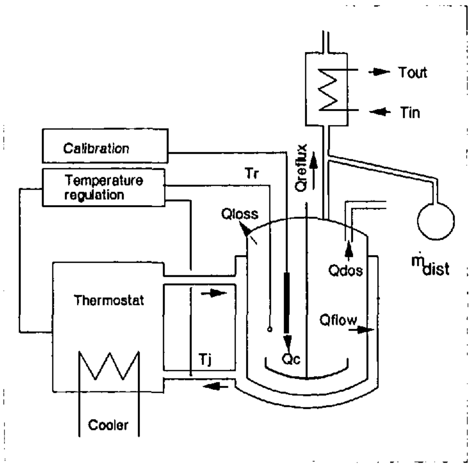


Fig. 1. *The heat flow calorimeter*

$$q_R = q_{ex} + q_{accu} + q_{dos} + q_{loss} - q_c \qquad (1)$$

where

q_R heat release rate of reaction
q_{ex} heat flow accross the wall
q_{accu} heat accumulation in the reaction mass through temperature increase
q_{dos} heat due to the dosage of reactives
q_{loss} heat dissipated through internal accessories
q_c heat supplied by calibration heating

When a reaction is run under reflux conditions, the heat flow calorimeter *Mettler RC1* is equipped with a refluxing-distillation set. In this case, an additional term, q_{reflux}, has to be taken into account in the heat balance and the temperature difference $T_J - T_R$ is normally kept constant. Then, the heat of reaction cannot be measured by the heat flow through the wall. Instead, the temperature difference $\Delta T_{Cond} = T_{out} - T_{in}$ between the cooling water outlet and inlet in the condenser has to be measured, while the mass flow of the cooling water is kept constant by a flow-controller. Thus, the heat flow balance can be written:

$$q_R = q_{ex} + q_{accu} + q_{dos} + q_{loss} + q_{reflux} - q_c \qquad (2)$$

with

$$q_{reflux} = (T_{out} - T_{in}) \cdot C_p \cdot \mathrm{dm/dt} \qquad (3)$$

where C_p is the specific heat capacity, and dm/dt is the mass flow of the cooling water.

In industrial practice, two categories of reflux reactions can be distinguished:

- the reactions started by addition of reagents or catalyst under reflux conditions: isothermal processes;
- the reactions started below the boiling point: non-isothermal processes.

The optimization of the measuring conditions for these two types of reflux reactions will be discussed in the two following sections.

3. Optimization of Measuring Conditions for Reactions Started under Reflux Conditions

3.1. *Influence of Imposed* ΔT

During experiments under reflux conditions, an important experimental parameter is the temperature difference $\Delta T = T_J - T_R$ which must be imposed on the system. This parameter can strongly influence the results:

- If the imposed ΔT is too small, part of the vapor condenses before reaching the condenser and the values of the heat flow which are obtained are too low.
- If ΔT is too large, irregular boiling occurs, leading to false results.

The influence of the imposed ΔT on the accuracy of the measurements of q_{reflux} was studied first. A series of different pure solvents was distilled in the calorimeter each with different values for the experimental parameter ΔT. For each experiment, a thermal balance calculation, using the latent heat of vaporization of the solvent, was carried out. The energy of distillation (Q_{Dist}) determined by weighing the amount of solvent distilled during the measurement period was compared to Q_{reflux} obtained by integration of q_{reflux} (*Eqn. 3*) over the same period of time.

$$Q_{Dist} = m_{Dist} \cdot (\Delta H_v) \qquad (4)$$

with

m_{Dist}: mass of distilled solvent
ΔH_v: enthalpy of vaporization of the solvent

The results are summarized in the *Table*. For each solvent, we find an optimal $\Delta T = T_J - T_R$ which leads to a minimum error. *Fig. 2* shows that this optimal temperature difference is a linear function of the boiling point of the reaction mass. This temperature should be controlled to ± 2–3°.

Table. *Optimization of* ΔT *for Different Solvents*

Solvent	B.p. [°C]	$T_J - T_R$ [°C]	Error[a]) [%]
Acetone	56.2	4	16.1
		6	1.6
		8	1.9
		20	11.7
MeOH	65.0	6	16.7
		8	2.3
		10	1.5
		12	3.4
EtOH	78.5	15	15.6
		18	7.0
		20	8.1
		25	10.3
H_2O	100.0	28	19.3
		30	2.2
		32	8.7
		34	11.6
Toluene	110.6	25	7.0
		30	4.0
		33	2.0
		35	13.5

[a]) $(Q_{dist} - Q_{reflux})/Q_{dist} \cdot 100$

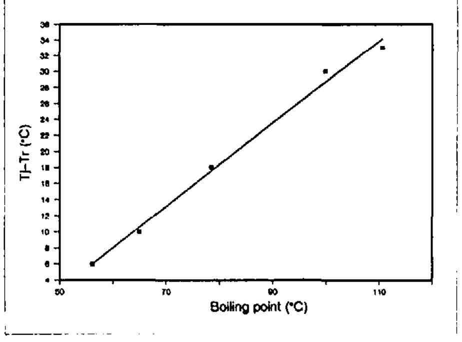


Fig. 2. *Optimal temperature difference* $T_J - T_R$

3.2. Determination of Heat Losses

The optimal experimental parameters described above were determined for a steady state without chemical reaction. The heat input due to a chemical reaction, on the other hand, could lead to the same effect as too large ΔT and result in false values for q_R. Thus, it must be proved that the heat release rate of a reaction (q_R) is entirely retrieved in the condenser (q_{reflux}). The effect of an additional heat input was studied in a series of experiments where the heat production of a reaction was simulated by the electrical calibration heater (q_c instead of q_R). The additional energy input to the system by this means was dissipated through the condenser: the difference between the measured 'heat of reaction' and the supplied energy was always below 1%.

3.3. Some Examples for the Determination of Heats of Reaction under Reflux Conditions (Isothermal Experiments)

The stoichiometric equations are displayed in *Fig. 3*.

3.3.1. Esterification of Ac_2O [7] [8]

The theoretical calculations based on enthalpies of formation give a heat of reaction between 66.2 and 67.1 kJ/mol at 298 K (depending on the parameters chosen from data tables) [9] [10].

The following values were measured in previous studies:

Q_R = 60 kJ/mol: *Cronin* [11], *Riesen* [12]
Q_R = 64 kJ/mol: *Wright* and *Rogers* [13]
Q_R = 63.7–69.5 kJ/mol: *Steele* and *Nolan* [14]

Mode of operation:

- 448 g (14 mol) of MeOH were charged into the reactor and brought to reflux ($T_J - T_R = 10°$ corresponding to a b.p. of 65–68°);
- when q_R remained constant, 459 g (4.5 mol) of Ac_2O were added within 15 to 30 min.

1. Esterification of acetic anhydride

$$(CH_3CO)_2O + CH_3OH \longrightarrow CH_3COOH + CH_3COOCH_3$$

2. Hydrolysis of diethyl propylmalonate

$$CH_3CH_2CH_2CH(CO_2C_2H_5)_2 + 2\ KOH \longrightarrow CH_3CH_2CH_2CH(CO_2H)_2 + 2\ C_2H_5OK$$

3. Hydrolysis of acetic anhydride

$$(CH_3CO)_2O + H_2O \xrightarrow{HCl} 2\ CH_3COOH$$

4. Reduction of 4-t-butyl-2-nitrophenol

$$4\ Ar\text{-}NO_2 + 6\ NaHS + H_2O \longrightarrow 4\ Ar\text{-}NH_2 + 3\ Na_2S_2O_3$$

5. Reduction of 4-nitrotoluene

$$CH_3\text{-}Ar\text{-}NO_2 + Na_2S_x \longrightarrow CHO\text{-}Ar\text{-}NH_2 + CH_3\text{-}Ar\text{-}NH_2$$

Fig. 3. *The stoichiometric equations*

Results (see *Fig. 4*):
Experiment 1: Q_R = 66.8 kJ/mol
2: Q_R = 69.2 kJ/mol
3: Q_R = 66.5 kJ/mol
4: Q_R = 68.2 kJ/mol
Q_R = 67.7 ± 1.5 kJ/mol

The divergence from the theoretical value is below + 2%.

3.3.2. Hydrolysis of Diethyl Propylmalonate

The following values were measured in a previous study:

Q_R = 99.1–107.3 kJ/mol: *Steele* and *Nolan* [14]

Mode of operation:

- 312 g of 50% KOH solution and 400 g of EtOH were charged into the reactor and brought to reflux ($T_J - T_R = 21°$ corresponding to the b.p. of 79–83°);
- 220 g (1.09 mol) of diethyl propylmalonate were dosed in 20 min.

Results (see *Fig. 5*):
Experiment 1: Q_R = 106.9 kJ/mol
2: Q_R = 106.3 kJ/mol
Q_R = 106.6 ± 0.3 kJ/mol

3.3.3. Hydrolysis of Ac_2O

The theoretical calculations predict a heat of reaction of 58.4 kJ/mol at 298 K [7].

The following values were measured in previous studies:

Q_R = 60.4 kJ/mol between 15 and 35°: *Martin* [15]
Q_R = 58.3 kJ/mol at 30°: *Smith* [16]

Mode of operation:

- 1000 g of 0.1N HCl were charged into the reactor and brought to reflux ($T_J - T_R = 30°$ corresponding to the b.p. of 100°);
- A solution of 133.43 g of Ac_2O in 110.76 g of AcOH was added in 10 min.

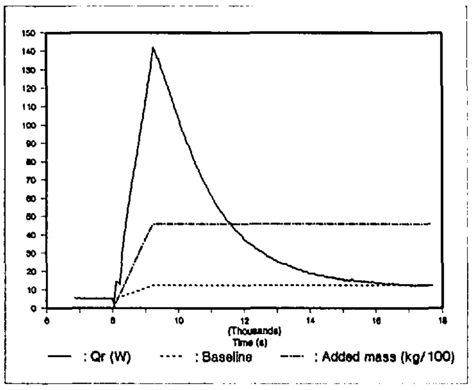
Results (see *Fig. 6*):
Experiment 1: Q_R = 58.8 kJ/mol
2: Q_R = 56.8 kJ/mol
3: Q_R = 60.0 kJ/mol
Q_R = 58.5 ± 1.7 kJ/mol

The divergence from the theoretical value is *ca.* + 0.2%.

3.3.4. Reduction of 4-(tert-Butyl)-2-nitrophenol [17] [18]

Mode of operation:

- The solution of sodium hydrosulfide was charged into the reactor and brought to reflux ($T_J - T_R = 34°$ corresponding to the b.p. of 108–110°);
- The 4-(*tert*-butyl)-2-nitrophenol was added after the *RC1* baseline was horizontal.



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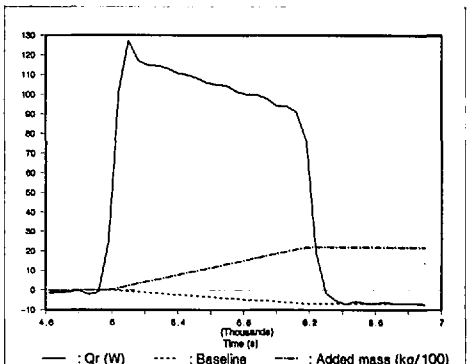

Fig. 5. *Hydrolysis of diethyl propylmalonate*

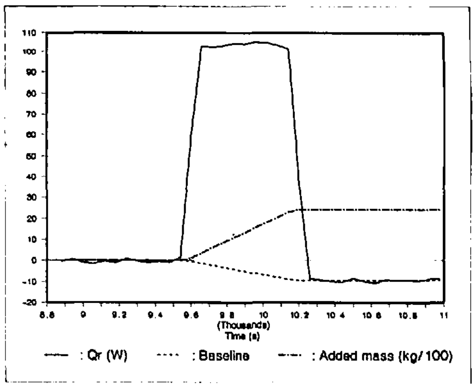

Fig. 6. *Hydrolysis of Ac_2O*

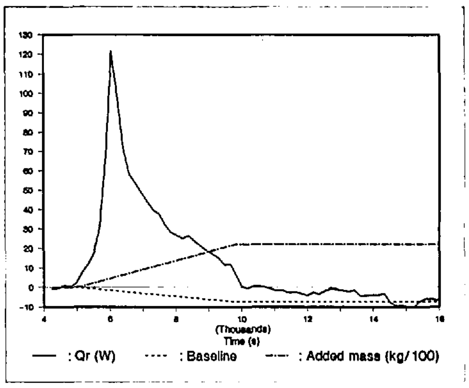

Fig. 7. *Reduction of 4-(* tert-*butyl)-2-nitrophenol*

Results (see *Fig. 7*):
Experiment 1: Q_R = 200.4 kJ/mol
2: Q_R = 197.1 kJ/mol
3: Q_R = 202.1 kJ/mol
Q_R = 199.9 ± 2.8 kJ/mol

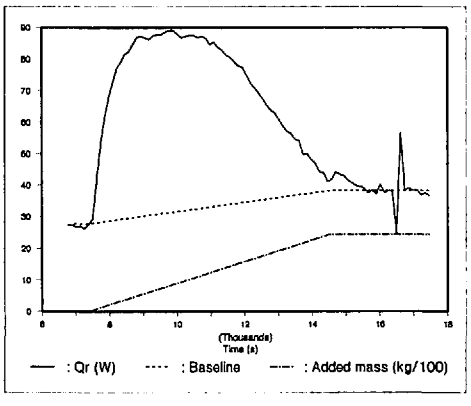

Fig. 8. *Reduction of 4-nitrotoluene*

3.3.5. Reduction of 4-Nitrotoluene

The reduction of the NO_2 group of 4-nitrotoluene with a solution of sodium polysulfide was studied.

Mode of operation:

- A solution of 4-nitrotoluene was charged into the reactor and brought to reflux (T_J–T_R = 21° corresponding to the b.p. of 82°);
- The polysulfide solution was added to the mixture.

Results (see *Fig. 8*):

The determined heat of reaction is: Q_R = 320 kJ/mol

4. Optimization of Measuring Conditions for Reactions Started below the Boiling Point

4.1. Experiments Using a Standard Glass Reactor Lid

Often in industrial processes, the reaction is started below the boiling point. The thermal measurements, corresponding to such processes, cover two distinct periods:

- The heating phase:
  To perform accurate thermal measurements during the heating period the best way is to use a linear temperature program. According to its working principle, the *RC1* calorimeter, while heating up to the boiling point, is set to the Tr mode, where (T_J – T_R) is measured.
- The reflux phase:
  During this period, the calorimeter works in the distillation mode (Ad mode) with (T_J–T_R) kept constant. In this case, the temperature difference ΔT_{Cond} is measured.

Therefore, at the beginning of reflux, the calorimeter has to be switched from the Tr mode to the Ad mode. The consequence of this change in the control mode of the calorimeter is a time gap in the measurement of heat-release rate during which the baseline is not defined. To evaluate the experiment and, particularly, to define the baseline, it is necessary to run a blank test. This experiment can be performed without dosage of the reactant or, rather, with dosage of an inert product to compensate for the increase of the heat-exchange area in the reactor.

The test example of the esterification of Ac_2O with MeOH was measured under these conditions. Two different values for the heat release rate were obtained on each side of the gap:

q_R = 54 W at time = 4900 s in the Tr mode (see *Fig. 9*)

q_R = 22.7 W at time = 5100 s in the Ad mode (see *Fig. 10*)

Obviously, q_R should have approximately the same value just before and after the reflux temperature is reached, and both parts of the heat release curve should form a continuous curve. To decide which of the two values is correct, two isothermal control experiments were performed: the first just below the boiling point, the second with the reaction started at the boiling point. Both gave a heat release rate of *ca.* 23 W at the degree of conversion, corresponding to the gap in the non-isothermal experiment.

This means that the values of the heat flow measured in the Tr mode just before the boiling point are inaccurate because of the energy required to heat the reactor lid and the refluxing-distillation set.

4.2. Experiments with a Heated Metallic Reactor Lid

The problem just mentioned can be resolved by the use of the metallic reactor lid which can be heated with a thermostat. The refluxing-distillation set is also heated with an electrical heat-band. Both parts are thermostated to 1–2° below the boiling temperature of the reaction mass. Another determination of the optimal imposed ΔT was carried out with this new equipment.

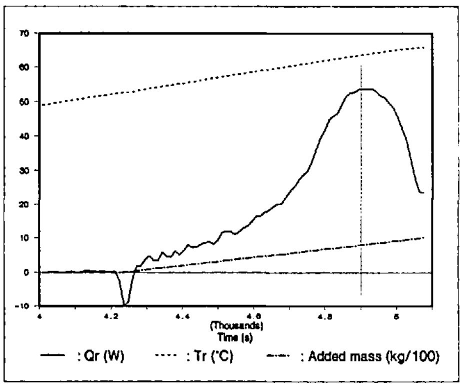

Fig. 9. *Esterification of Ac_2O.* Mode Tr.

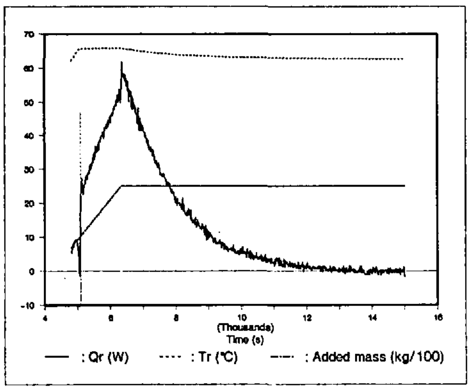

Fig. 10. *Esterification of Ac_2O.* Mode Ad.

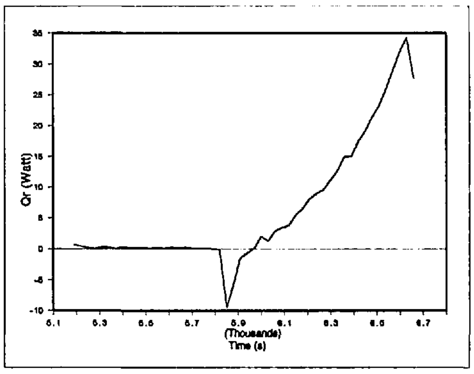

Fig. 11. *Esterification of Ac_2O.* Mode Tr. Heated metallic reactor lid.

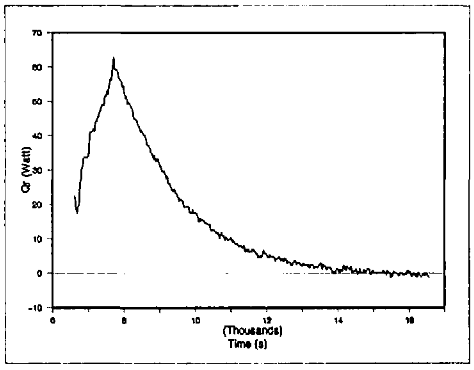

Fig. 12. *Esterification of Ac_2O.* Mode Ad. Heated metallic reactor lid.

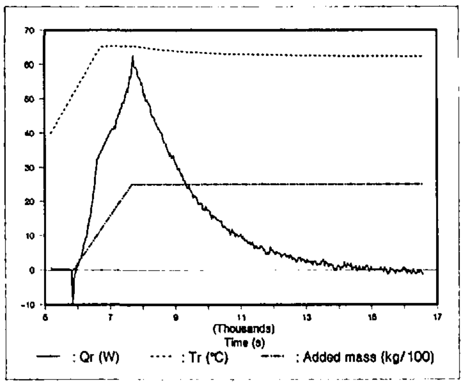

Fig. 13. *Esterification of Ac_2O.* Heated metallic reactor lid.

4.2.1. Esterification of Ac_2O

The experiments were conducted under the same conditions as described in *Sect. 3.3.1.*

The temperature of the reactor head and of the refluxing set was about 64–65°. The temperature difference T_J – T_R was now 6°. The measured heat flows are shown in *Figs. 11* and *12*.

Now, the q_R values measured in the Tr mode are correct. The graphs of the heat flows in both modes coincide well, and it is possible to plot the heat flow as a function of the time for the duration of the whole reaction (see *Fig. 13*).

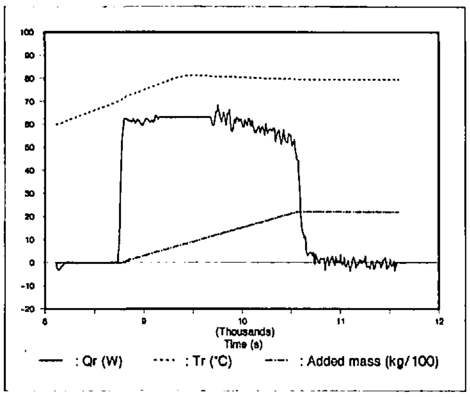

Fig. 14. *Hydrolysis of diethyl propylmalonate.* Heated metallic reactor lid.

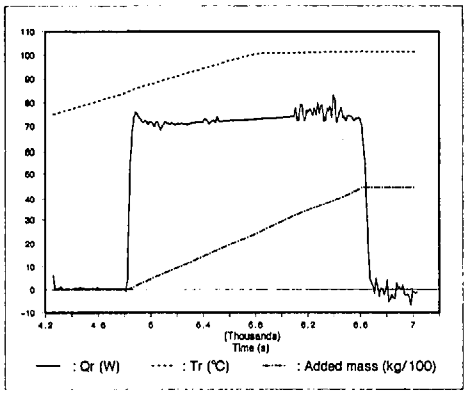

Fig. 15. *Hydrolysis of* Ac_2O.
Heated metallic reactor lid.

The integration of this heat flow curve over time leads to the heat of reaction, Q_R.

Results:
Experiment 1: $Q_R = 66.6$ kJ/mol
2: $Q_R = 69.4$ kJ/mol
3: $Q_R = 68.4$ kJ/mol
$Q_R = 68.1 \pm 1.7$ kJ/mol

The divergence from the theoretical value is *ca.* +1.5–3%.

4.4.2. *Hydrolysis of Diethyl Propylmalonate*

The experiment was conducted unter the same conditions as described in *Sect. 3.3.2.*

The measured heat of reaction (see *Fig. 14*) is:
$Q_R = 102.2$ kJ/mol

4.2.3. *Hydrolysis of* Ac_2O

The experiment was run under the same conditions as described in *Sect. 3.3.3*, except that 448 g of the Ac_2O/AcOH solution was added in 30 min. The temperature of the reactor lid and of the refluxing set was about 99°. The temperature difference $T_J - T_R$ was now 30°. The heat flow as a function of the time for the duration of the whole reaction is shown in *Fig. 15*.

Results:
The calculated heat of reaction is:
Experiment 1: $Q_R = 54.0$ kJ/mol
2: $Q_R = 55.2$ kJ/mol
$Q_R = 54.6 \pm 0.6$ kJ/mol

The divergence from the theoretical value is −6.5%.

4.3. *Reactions under Adiabatic Conditions*

Some industrial reactions are effected under partially adiabatic conditions: the heat of reaction is used to heat the reaction mixture up to the boiling point. This kind of reaction can be investigated by the calorimeter *RC1* in the adiabatic mode. In that mode, the reactor temperature follows the reaction profile. The temperature difference ($T_J - T_R$) is adjusted in such a manner that the heat of reaction is entirely used to heat up the reaction mixture while the reactor behaves like an insulated vessel.

Thus, heat losses which are temperature-dependent have to be compensated by the jacket temperature. In the *RC1* reaction calorimeter, the set value of the temperature difference ($T_J - T_R$) is calculated as a linear function of the reactor temperature.

The adiabatic control mode gives satisfactory heats of reaction, if the end temperature of the experiment lies below the boiling point. However, when this temperature is reached, the reaction mixture begins to boil and the imposed temperature difference $\Delta T = T_J - T_R$ is too small in comparison with the optimal value (see *Sect. 3.1*). As a consequence, the calculated enthalpy of reaction is systematically too low.

In practice, it is necessary to correct the imposed ΔT to the optimized value (see *Fig. 2*) when the boiling point is reached. In this case too, a time gap in the measurement of heat release rate will be observed and the baseline must be corrected as in experiments with a linear temperature ramp.

5. Conclusion

In this work, we have shown that the calorimeter *Mettler RC1* lends itself for the determination of heats of reaction under reflux conditions.

As a novel improvement in the measurement technique, we have demonstrated that under stationary conditions, it is necessary to adjust the temperature difference $T_J - T_R$ to optimized values linearly dependent on the boiling point of the reaction mass. This optimal value can be determined by means of a thermal balance of a distillation. This optimization should be repeated for every important change of the equipment.

For reactions started below the boiling point and ended at reflux, we have developed a new method to determine heat release rates under non-stationary conditions. The experimental equipment must be modified to include a heated reactor lid and a heating device for the distillation set to avoid energy losses, when the temperature approaches the boiling point. For the evaluation of this kind of measurement, it is necessary to perform a blank experiment for the definition of the baseline in the transition phase between heating and reflux.

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