Thermochimica Acta, 49 (1981) 87–100
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

REACTION CALORIMETER FOR APPLICATIONS IN CHEMICAL PROCESS INDUSTRIES: PERFORMANCE AND CALIBRATION

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Summary

Two types of reaction calorimeter for use in evaluation of thermal data for plant design and assessment of thermal safety in the chemical process industries have been developed.

The principle of calorimetric measurement is thermoelectrical compensation of the heat of reaction. One calorimeter is built in stainless steel, the other in glass. Reactor volumes are 200 to 1400 ml. Practicable temperature range is about -50°C to +200°C and admissible pressures range from 0 to 50 bars.

For the chemical calibration of these reaction calorimeters the neutralization reaction of sulfuric acid in excess sodium hydroxide has been chosen. A calibration curve in an appropiate concentration range has been established by precision calorimetry and can be used now as a reference of sufficient accuracy.

Zusammenfassung

Zur wärmetechnischen Auslegung von Produktionsanlagen in der chemischen Industrie müssen die Prozesswärmen, insbesondere die Reaktionswärmen, hinreichend genau bekannt sein. Zu diesem Zweck wurden zwei Varianten eines Reaktionskalorimeters entwickelt, das eine möglichst betriebsgerechte Durchführung chemischer Reaktionen ermöglicht, wobei der Erfassung der zeitabhängigen Wärmeproduktionsrate besondere Bedeutung zukommt. Die so gewinnbaren

kalorimetrischen Daten können zudem für die sicherheitstechnische Beurteilung des Prozesses und unter Umständen zur Ermittlung kinetischer Modelle für die Prozessoptimierung ausgewertet werden.

Die beiden Kalorimeter arbeiten nach dem thermoelektrischen Kompensationsprinzip und werden isotherm betrieben. Das eine ist aus rostfreiem Stahl, das andere aus Glas gebaut. Gute Rührung, Dosierung und Probenahme während der Messung sind möglich. Das Reaktionsvolumen beträgt 200 bis 1400 ml, der Temperaturbereich erstreckt sich von ca. $-50^\circ C$ bis $+200^\circ C$, der Druckbereich von 0 bis 50 bar.

Zur Kalibrierung der Geräte ist eine Reaktion mit angemessen hoher Wärmeleistung erforderlich. Es wurde die Neutralisationswärme von Schwefelsäure in überschüssiger Natronlauge beigezogen und eine Kalibrierkurve etabliert.

INTRODUCTION

In the chemical process industries specific requirements have to be met by reaction calorimetry. Calorimetric measurements are performed to obtain the following information:

1. Determination of heat evolved by processes.
   Heat of processes means, in particular, enthalpy of reactions, but also enthalpy changes of physico-chemical processes such as mixing, diluting, solvation, evaporation, etc. These heats have to be known for thermal plant design. The rate of heat evolution is as important as the total heat evolved. This demands calorimetric data describing heat evolution as a function of time. The calorimetric measurements have to be performed under the same process conditions as the technical process to be designed.

2. Thermokinetics.
   In the chemical process industries, thermokinetics may be of interest in so far as, by means of the calorimetric data, a formal model [1] can be established which allows the heat production rate of the considered process to be described as a function of temperature, concentrations and other reaction parameters that are of practical interest [2].

3. Assessment of thermal safety.
   From calorimetric measurements essential contributions may result to the assessment of the thermal safety of chemical processes. In addition to standard thermal stability tests as well as other routine methods of investigating chemical hazards, reaction calorimetry will quantify these standard test results [3] . One very important point is to recognize any dangerous accumulation of products which can react exothermically.

4. Process optimization.
   In the chemical process development, knowledge of all the aforementioned calorimetric data may be very helpful in optimizing the chemical process.

There exist different instruments suitable for facilitating the solution of the stated problems [4,5,6,7]. The results of our own development work will now be described.

REACTION CALORIMETER UNDER MICROCOMPUTER CONTROL

The reactor of the calorimeter is a usual jacket thermostated and well stirred laboratory reaction vessel with a volume of up to 600 ml. Inside the reactor there is an electrical heater and a temperature sensor. The thermostated reactor lid has different necks allowing the usual operations to be performed such as dosage, gassing, taking samples, measuring pH or pressure, etc.

The reaction calorimeter is a constant-heat flow type where the thermoelectrical heat compensation principle [8] is applied (Fig. 1). The temperature measured in the reaction mass is compared to the preset temperature. The reaction temperature is brought to the preset temperature by means of a PI controller which controls a DC power supply. The electrical DC output is measured. Because the compensation heater is completely immersed in the reaction mass, the electrical heat input is complementarily equal to the heat production rate of the reaction. To assure constant heat flow from the reaction mass to the jacket, a constant temperature difference is maintained. The higher the expected reaction heat rate, the lower the temperature of the jacket that has to be selected.

The difference between the actual electrical heat input and the base electrical heat input before the reaction equals the actual reaction heat output.

The instrument is controlled by a microprocessor system. All measured values are first converted and standardized in the input interfaces. The computer evaluates the adequate control and regulation values. These are directed to the corresponding control and regulation devices through the output interfaces.

The basic configuration (Fig. 2) comprises three temperature controls and the measurement of the electrical input. The main control circuit consists of the compensation heater used to regulate the reaction temperature T_R to the preset temperature. Temperature T_R as well as temperature T_B are measured with an HP-2804 quartz thermometer. A second means of temperature control is necessary to maintain the thermostated circulation at the jacket temperature T_B, which has to be at a specific level below the preset temperature T_R. To avoid any uncontrollable heat flux through the reactor lid, its temperature is kept at T_A equal T_R by a third temperature control.

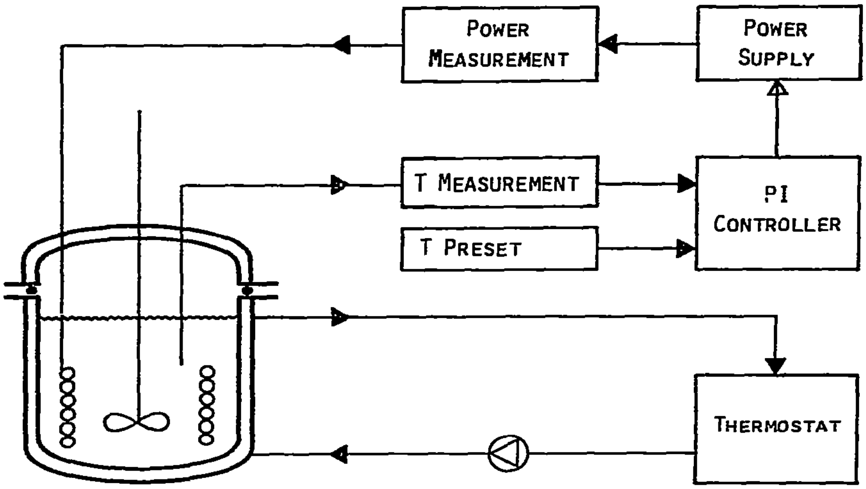

Figure 1: Calorimetric principle. The jacket temperature is lower than the preset reaction temperature.

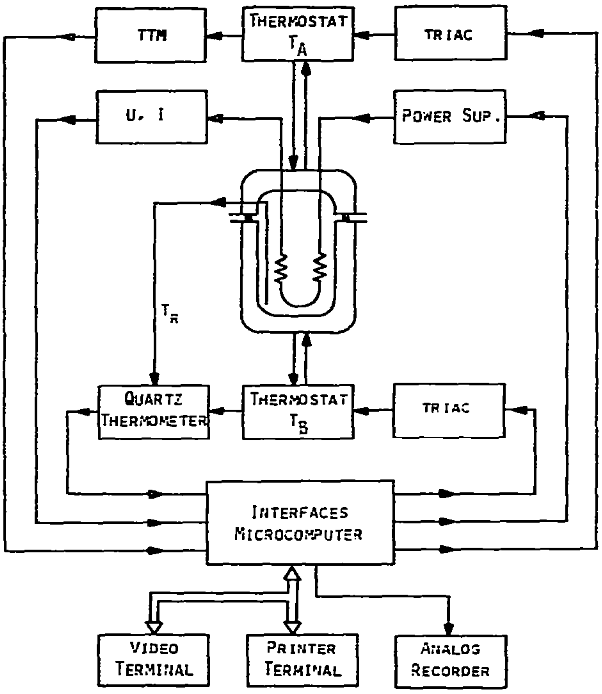

Figure 2: Basic configuration of the reaction calorimeter. TTM: Temperature transmitter; U,I: Voltage and current measurement; other explanations see text.

For the calculation of the electrical heat input, the current I and voltage drop U on the compensation heater have to be measured.

On a typewriter keyboard all instructions for the computer are given in a dialogue conversation or in short mnemonic commands. All actual process data are visualized on a screen. All calorimetrically relevant data are registered continuously on an analog recorder. The specifications of the experiment as well as the final results of the evaluation of the experiment are protocolled on the printer terminal.

The microcomputer used is an INTEL 8080 based modular microprocessor system [9] equipped with 47 k byte PROM and 9 k byte RAM. A small real-time multitasking operating system RTS-80 [10] was further developed [11] . Its major features are multitasking with time-dependent task initiation, task synchronization, task-to task communication and fixed priority task scheduling. The application software is a set of 5 user tasks written in assembler language [12].

The specifications of this calorimeter may be summarized as follows:

Limits of applicability:

Temperature T	$-30^{\circ}C < T < +200^{\circ}C$
Volume V	$200\ ml < V < 600\ ml$
Heat production rate q	$\pm 1\ W < q < \pm 500\ W$

Working mode:

isotherm
scanning mode (optional)

Calorimetric specifications:

Valuable for the heat production rate q of about $10\ W < q < 200\ W$

(Q = integral heat)

	q	Q
reproducibility	±1%	±2%
accuracy	±2%	±2%
sensitivity	±0.2%	10 J
noise - short time	±0.2%	-
· long time drift	±0.5%	

Linearity of the heat transfer factor (base line)

reproducibility	±1%
volume dependence V = 250 – 600 ml	±50%
dependence on quality, especially on viscosity η, of reaction mass η = 25 – 0.25 cP	±50%

Time constant (regulation)

τ (50%)	15 s
τ (99%)	180 s

A PRESSURE RESISTENT CALORIMETER

For the same applications as mentioned above, a reaction calorimeter for pressures up to 50 bar (5 MPa) was developed earlier by use of conventional electronics [13]. The mechanical construction is evidently much more complicated. The compensation heater is housed in the pressure resistent reactor wall. The essential advantage of this special construction is that, to maintain the constant heat flux, the temperature gradient drops through the reactor wall and not through the reaction mass. This implies that, without reaction heat production, a completely homogeneous temperature distribution is reached within the whole reaction volume, including the inner reactor surface. Nevertheless, very high changes in heat production rate of more than 1 kW may be compensated very fast, that is, within 3 minutes.

By this arrangement of the compensation heater, considerable direct heat loss to the thermostated jacket occurs. That is why the efficiency of the compensation heater has to be calibrated by an additional internal electrical calibration heater.

Otherwise the performance of this calorimeter is comparable to the calorimeter described earlier.

CHEMICAL CALIBRATION OF REACTION CALORIMETERS

By electrical calibration of reaction calorimeters of this type, systematic errors may not be excluded a priori. Systematic errors could be caused by an unfavourable construction or location of the calibration heater. From this, asymmetric or unhomogeneous temperature distribution could result and the measured reaction temperature would not be the effective mean temperature. The same error could occur if a fast reacting component that is added continuously is not well mixed and therefore unhomogeneously distributed in the reactor.

To our knowledge, the only chemical reaction suitable for calibrating our calorimeters is the hydrolysis of acetic anhydride. Several thermokinetic measurements have been performed on this reaction [4,14,15,16]. But even the best measurements [15] yield enthalpy values with standard deviations of 3 - 5% and with the given concentrations, heat production rates are rather small, reaching zero within 10 to 30 minutes.

As calibration reaction we have chosen the neutralization of excess sodium hydroxide (2.77 n or 10.0% in weight) with sulfuric acid (4.00 n), for the following reasons.

1. Precisely measured reference values are given in the literature [17]. For our purposes we had to complete these data up to much higher concentrations.

2. By reason of high concentrations chosen, the volume-related heat production is comparable to that of reactions in the chemical process industries.

3. The heat production rate can be adjusted within wide limits by varying the rate of sulfuric acid feed. This can be done because the neutralization reaction is instantaneous.

4. Since the reaction is under feed control, the reaction time can be extended long enough to average out the short-time noise of the heat rate measuring signal. By this means, the heat rate can be measured very precisely.

5. During reaction, the reaction volume increases by about 50%, so that the volume-dependent base line shift (Fig. 3) will be included in the calibration.

The enthalpy of neutralization ΔH_N is found to change very little as a function of the degree of neutralization and can be described by the linear relation

$$\Delta H_N = \Delta H_{NO} + bn_2$$

where ΔH_N = total enthalpy of reaction (enthalpy of neutralization and enthalpies of dilution) per mole sulfuric acid

ΔH_{NO} = total enthalpy of reaction at degree zero of neutralization

n_2 = moles sulfuric acid (2.00 molar) added to 2.50 moles of sodium hydroxide (10.0% in weight or 2.77 molar) $0.1 < n_2 < 1.0$

The measured total heat produced is

$$Q = n_2 \Delta H_N$$

As ΔH_N is a function of n_2, Q and the heat production rate $\dot{Q}$ wil change with the degree of neutralization. $\dot{Q}$ is proportional to the dosage rate of sulfuric acid, dn_2/dt.

$$\dot{Q} = \frac{dQ}{dt} = \frac{dQ}{dn_2} \cdot \frac{dn_2}{dt}$$

This is the expression used for the calibration of the heat rate measurement. dn_2/dt is chosen by the experimenter. dQ/dn_2

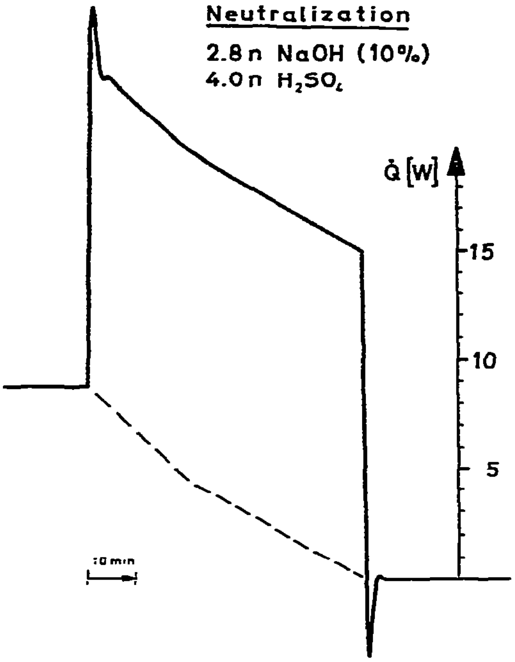

Figure 3: Reaction heat output $\dot{Q}$ of the feed-controlled neutralization reaction.

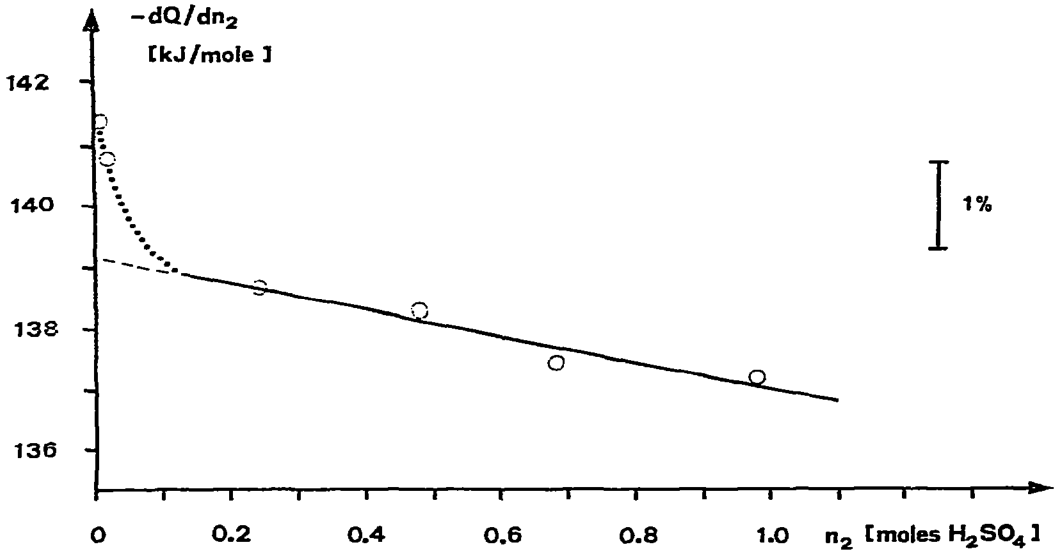

Figure 4: Reference curve established for chemical calibration: enthalpy of neutralization dQ/dn_2 at 25.0°C; titration of 2.50 moles $NaOH \cdot 20H_2O$ (2.77 molar) with n_2 moles $H_2SO_4 \cdot 26H_2O$ (2.00 molar).

is the "differential" reaction enthalpy and may be derived from the "integral" enthalpy of reaction as

$$\frac{dQ}{dn_2} = \Delta H_{No} + 2bn_2$$

Because the change in dQ/dn_2 as a function of n_2 is small and linear, dQ/dn_2 can be well approximated by $\Delta Q/\Delta n_2$. This has been done experimentally on a LKB - 8700 Precision Calorimeter. We have found the following results (see also Fig. 4).

n_2 [mole]	$-\Delta Q/\Delta n_2$ [kJ/mole]	$-dQ/dn_2$ [kJ/mole]	$-\Delta H_N$ [kJ/mole]	$-\Delta H_N$ (corr) [kJ/mole]	$-\Delta H_N$ (iso) [kJ/mole]
0.01	141.40	-	-	-	-
0.02	140.78	-	-	-	-
0.10	-	138.93	139.03	140.1	140.6
0.24	138.65	138.62	138.88	140.0	140.3
0.48	138.26	138.11	138.62	139.7	140.0
0.68	137.39	137.68	138.41	139.5	139.6
0.98	137.17	137.03	138.09	139.2	139.2
1.10	-	136.78	137.96	139.1	139.0

$\Delta Q/\Delta n_2$: means of experimental values

dQ/dn_2, ΔH_N: calculated with the following constants from the linear regression of the experimental data

$\Delta H_{NO} = -(139.14 \pm 0.30)$ kJ/mole sulfuric acid

$b = +(1.07 \pm 0.46)$ kJ/(mole)^2

ΔH_N (corr.) : corrected by -1.1 kJ/mole as described below

ΔH_N (iso.) : from measurements with an isoperibolic reaction calorimeter

All values at $25.0 \pm 0.5^\circ C$

At very low degrees of neutralization ($n_2 < 0.05$) the heat of reaction is a little higher and deviates significantly from the linear function. These values have not been included in the regression analysis. The standard deviation of all other experimental values from the linear function is ±1.1% (12 measurements in the concentration range $0.2 < n_2 < 1.0$).

The error of the calculated integral heat of reaction ΔH_N, due to the deviation from linearity if n_2 approaches zero, is estimated to be -1.1 ± 0.1 kJ/mole. This is confirmed by independent measurements of the integral enthalpy of reaction performed earlier on an isoperibolic reaction calorimeter. Those results differ only by -0.5 to +0.1 kJ/mole in the concentration range $n_2 = 0.1$ to 1.1.

With the reaction calorimeter presented here this calibration curve could be reproduced within ±0.7% for the differential and ±0.1% for the integral heat of reaction.

The accuracy of the measurement of these reference values has been proven to be better than ±0.5% by calibration check of the LKB calorimeter with the reaction of TRIS in 0.1 n HCl [e.g. 18]. The reaction temperature rise has been corrected in the usual way [19] by numeric evaluation.

ACKNOWLEDGEMENT

I wish to thank all those who have contributed to the successful development of these instruments, especially H.H. Ammann (electronics), J. Baur (software), A. Rabenstein (experiments) and K. Schleich for supporting these projects.

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