

Chapter 2

Bench Scale Calorimeter

2.1 Devices for Discontinuous Reactions

2.1.1 Isothermal Reaction

To record the rate q of heat release by a chemical reaction (thermal reaction power) under strictly isothermal condition in the measuring-kettle of a calorimeter, the apparatus must be able

- On one hand to maintain a constant temperature within the kettle despite of both the release of heat by the reaction in itself and other additional causes for change in temperature being concomitant with the reaction performance.
- On the other hand to indicate simultaneously the rate of heat release by reaction in itself.

The following types of equipment make it possible to control the conditions more or less exactly.

1. Controlled cooling by means of an installed Peltier element. The intensity of its electrical current is a measure for the quantity of cooling power, which corresponds to the gross rate of heat release during isothermal reaction. The rate of heat release by the reaction in itself can only be deduced, if in addition a base line can be recorded which corresponds to the sum of all other calorific thermal effects within the kettle: e.g. due to stirring, heat loss and condensation on inlet pipes, etc.
2. Controlled heat flow from the measuring-kettle into its surroundings or from there into the measuring-kettle, compensating all effects of changing the temperature within the kettle. Therefore, they are also only a gross measure for the rate of heat release of the reaction in itself. Its accurate value can only be determined, if in addition a base line can be indicated, the change of which corresponds to the sum of all other calorific thermal effects in the measuring-kettle, such as stirring, heat loss, change of heat transfer condition, effects of rectification on inlet/outlet pipes, etc.

3. Controlled heating power of a heater within the measuring-kettle working already prior to start of the reaction. The change in heating power is a gross measure for the rate of heat release by reaction itself; the thermal reaction power in itself can only be elucidated precisely, when in addition a line of heating power (base line) can be indicated, the change of which corresponds to the sum of all other calorific thermal effects in the kettle, for instance stirring, heat loss, change of heat transfer condition, etc.

Apparatus of Types 1 [49], 2 i.e. [40, 41, 46], and 3 [24, 54] have been developed. The straightforward measuring technique of a Type 1 apparatus is a good argument for using it.

Against its general use in industrial practice are the following factors:

- Only exothermic reactions can be investigated
- Peltier elements in such a setup can reliably be used up to approximately 100 °C. Although higher temperatures are in principle possible, that would will severely limit the lifetime of the element and, hence, of the apparatus.

The robustness of Type 2 apparatus speaks well for its use. However, against its general use for accurately measuring the thermal reaction power itself—a prerequisite for performing a thorough thermokinetic analysis of a complex chemical conversion—are the following factors:

- A precise baseline can only be determined for special conditions (Chap. 7)

The use of Type 3 apparatus is recommended because

- The baseline can always be recorded accurately and simultaneously with the measurement of changes in heating power.

The author chose Type 3 applying the following conception for discontinuous reactions (Fig. 2.1).

A measuring kettle (reactor) is inserted in a thermostat, which, to be precise, is an intermediate thermostat, since it is in turn immersed in a base thermostat. The measuring kettle respectively the intermediate thermostat is filled with a predominantly liquid reaction mixture respectively thermostat fluid. Both the measuring kettle and the intermediate thermostat are provided with a stirrer,¹ some baffles, and an electric heater and temperature sensor, both resistant to corrosion. The stirrers vigorously mix the fillings in the intermediate thermostat and the reactor. The temperature T_S and the rotational velocity of the stirrer in the base thermostat are maintained at chosen set values using a controller. The temperature difference between the measuring kettle and the intermediate thermostat ΔT_2 , as well as the temperature difference between the intermediate thermostat and the base thermostat ΔT_1 , is maintained at a chosen set value by regulation of the corresponding electrical heating powers p_2 and p_1 .

¹Primarily a lattice stirrer is used.

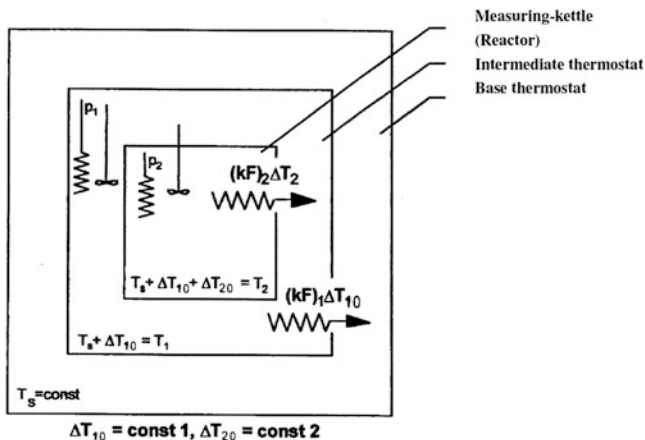


Fig. 2.1 Principle of accurate determination of thermal reaction power during an isothermal, discontinuous reaction [based on the same measuring principle of the calorimeter, this system of intermediate thermostat—fluid, controlled heater, base thermostat (controlled heat sink)—was replaced recently [54] by a new type of intermediate thermostat: metal, bordering controlled Peltier elements, thermostat (controlled heat sink)]

The base thermostat displays the lowest constant temperature T_s , the intermediate thermostat the medium temperature $T_s + \Delta T_1$, and the measuring kettle the highest temperature $T_s + \Delta T_1 + \Delta T_2$.

From the measuring kettle heat flows to the intermediate thermostat and from there to the base thermostat. In controlled equilibrium, the following applies with respect to the balance of heat power:

(a) Measuring kettle (reactor)

$$\begin{array}{ll} \text{Sum of all heat powers} & \text{heat flow out of} \\ \text{in measuring kettle} & \text{measuring kettle} \\ q + p_2 + p_{\text{St}2} & = (k \cdot F)_2 \cdot \Delta T_2 \end{array}$$

(b) Intermediate thermostat (2.1)

$$\begin{array}{ll} \text{Sum of all heat powers} & \text{heat flow out of} \\ \text{in intermediate thermostat} & \text{intermediate thermostat} \\ (k \cdot F)_2 \cdot \Delta T_2 + p_1 + p_{\text{St}1} & = (k \cdot F)_1 \cdot \Delta T_1. \end{array}$$

Because of the chemical process, the physical properties of the reaction mixture (e.g. viscosity, density) inevitably change. Therefore, during the reaction, changes take place in the caloric reaction power q , the stirring power $p_{\text{St}2}$, and the heat-transfer coefficient $(k \cdot F)_2$, i.e. the heat flow from the measuring kettle into the intermediate thermostat. This means that, to maintain the set temperature difference ΔT_2 of the measuring kettle, the electric heating power p_2 compensates not only the change in the thermal reaction power q_2 but also the change in the heat flow $(k \cdot F)_2 \cdot \Delta T_2$ and the change in the stirring power $p_{\text{St}2}$, according to (2.1). On the other hand, the heat-transfer coefficient $(k \cdot F)_1$ and the stirring power $p_{\text{St}1}$ within

the intermediate thermostat are constant because these quantities are not influenced by the chemical conversion in the measuring kettle. Therefore, the change in p_1 compensates only the change in heat flow from the measuring kettle into the intermediate thermostat, according to (2.1).

From (a) and (b) it follows that

$$q = [(k \cdot F)_1 \cdot \Delta T_1 - p_{\text{St1}}] - [p_1 + p_2 + p_{\text{St2}}]. \quad (2.2)$$

Because $(k \cdot F)_1 = \text{const}$ and $p_{\text{St1}} = \text{const}$ we obtain,

$$q(t) = \text{const} - [p_1(t) + p_2(t) + p_{\text{St2}}(t)]$$

or because $q = 0$ prior to the start of the reaction at time $t = 0$,

$$q(t) = \underset{\substack{\text{prior} \\ \text{to start of} \\ \text{reaction at time } t < 0}}{[p_1 + p_2 + p_{\text{St2}}]} - \underset{\substack{\text{during} \\ \text{reaction} \\ \text{at time } t \geq 0}}{[p_1(t) + p_2(t) + p_{\text{St2}}(t)]}.$$

When it is ensured that during the reaction

- The rotational velocity of the motor does not change and the internal motor loss momentum remains constant, (const_{ML})
- The bearing arrangement of the stirrer within the measuring kettle does not become soiled by the reaction mixture or vapour, i.e. the stirrer loss momentum remains constant, ($\text{const}_{\text{StL}}$)
- The motor torque is transferred unchanged to the stirrer shaft, and the relation between the stirring power p_{St2} and the total motor power p_{M2} reads

$$p_{\text{St2}} = p_{\text{M2}} - (\text{const}_{\text{ML}} + \text{const}_{\text{StL}}) = p_{\text{M2}} - \text{const}_{\text{MSL2}}. \quad (2.3)$$

Hence, the thermal reaction power is given as

$$q(t) = \underset{\substack{\text{prior} \\ \text{to start of} \\ \text{reaction at time } t < 0}}{[p_1 + p_2 + p_{\text{M2}}]} - \underset{\substack{\text{during} \\ \text{reaction} \\ \text{at time } t \geq 0}}{[p_1(t) + p_2(t) + p_{\text{M2}}(t)]}$$

or (Fig. 2.2)

$$q(t) = p_0 - p(t) \quad \text{with} \quad p_0 = p_1(t < 0) + p_2(t < 0) + p_{\text{M2}}(t < 0) \\ = \text{const}. \quad (2.4)$$

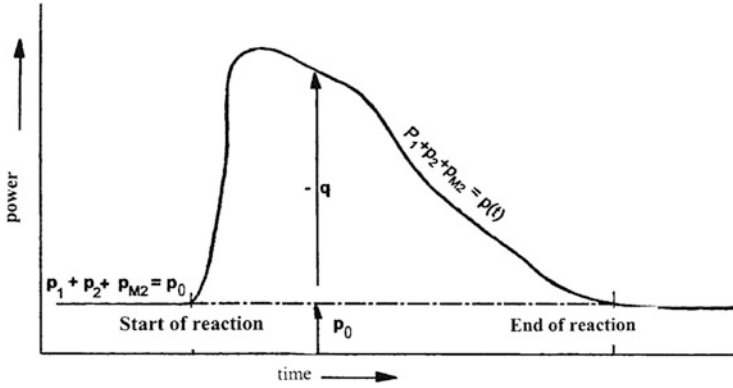


Fig. 2.2 Determination of thermal reaction power q by the difference of $(p_1 + p_2 + p_{M2})_{\text{prior to start of reaction}} = p_0$ and $(p_1 + p_2 + p_{M2})_{\text{during reaction}} = p(t)$

The total amount of heat released from reaction Q results from the integration of (2.4):

$$Q = \int_{0 \rightarrow \infty} q \cdot dt = \int_{0 \rightarrow \infty} [p_0 - p] \cdot dt.$$

The reason and the necessity for using an intermediate thermostat in addition to the measuring kettle to estimate the exact thermal reaction power $q(t)$ appears to the naked eye as follows.

Rearrangement of Eq. (2.4) gives

$$\begin{aligned} q(t) &= \left\{ [p_1 + p_2 + p_{M2}]_{\text{prior to start of reaction}} - [p_1(t) + p_{M2}(t)]_{\text{during reaction}} \right\} - p_2(t)_{\text{during reaction}} \\ &= \{p_1(t < 0) - p_1(t)\} + \{p_{M2}(t < 0) - p_{M2}(t)\} + p_2(t < 0) - p_2(t) \\ &= -\delta p_1(t) - \delta p_{M2}(t) + p_2(t < 0) - p_2(t) \\ &\quad \text{or} \\ &\quad \text{because of (2.1)} \\ &= \{[k \cdot F]_2(t) - [k \cdot F]_2(t < 0)\} \cdot \Delta T_2 + \{p_{M2}(t < 0) - p_{M2}(t)\} + p_2(t < 0) - p_2(t) \\ &= \left\{ \delta(k \cdot F)_2(t) \cdot \Delta T_2 \quad - \quad \delta p_{M2}(t) \equiv \delta p_{s2} \quad + p_2(t < 0) \right\} - p_2(t) \\ &\quad \text{change in heat flow} \quad \text{change in} \\ &\quad \text{out of measuring kettle} \quad \text{motor power} \\ &\quad \text{owing to varied} \quad \text{owing to varied} \\ &\quad \text{heat transfer coefficient} \quad \text{stirring resistance} \end{aligned}$$

or (Fig. 2.3)

$$q(t) = p_B(t) - p_2(t). \quad (2.5)$$

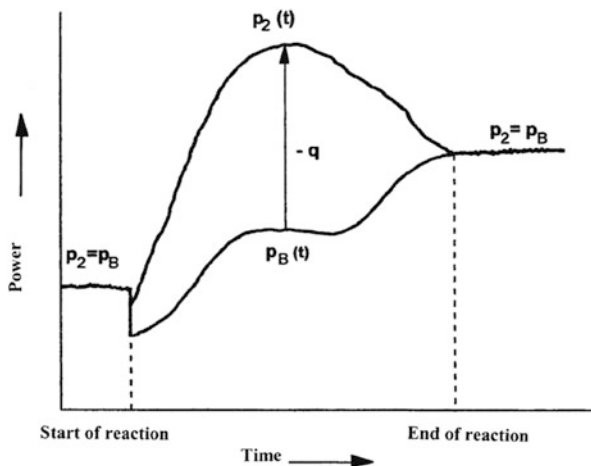


Fig. 2.3 Connection between thermal reaction power q , electric heating power p_2 and baseline p_B

Conclusion

Equation (2.5) shows the only thing that the solely course of the electric heat power $p_2(t)$ in the measuring kettle versus time does not allow for the estimation of the thermal reaction power $q(t)$.² It can be determined only when the course of a reference power, the baseline $p_B(t)$, is known. The intermediate thermostat contributes essentially to its registration.

The course of $p_B(t < 0)$ prior to the start of the reaction corresponds to $p_2(t < 0)$ prior to the start of the reaction, but, as a rule, following the start of the reaction, this is no longer the case. As already mentioned, the deviation of the baseline $p_B(t)$ from the constant value of $p_2(t < 0)$ prior to the start of the reaction is caused

² This relation stands to reason, because it is evident that

1. To maintain $\Delta T_2 = \text{const}$, the partial changes in the total change in the heating power in the measuring kettle following the start of the reaction from their values prior to the start of reaction δp_2 must be
 - Opposite and equal to the thermal power of reaction q
 - Opposite and equal to the change in stirring power $\delta_{\text{St}2}$
 - Equal to the change in heat flow out of the measuring kettle by a change in heat transfer following the start of reaction $\delta(k \cdot F)_2 \cdot \Delta T_2$

$$\delta p_2 = \delta(k \cdot F)_2 \cdot \Delta T_2 - \delta_{\text{St}2} - q = [\delta(k \cdot F)_2 \cdot \Delta T_2 - \delta_{\text{St}2}] - q$$

2. To maintain $\Delta T_1 = \text{const}$, the change in electric heating power of the intermediate thermostat δp_1 must be
 - Opposite and equal to the change in heat flow $\delta(kF)_2 \cdot \Delta T_2$ from the measuring kettle following the start of the reaction from the value prior to the start of

$$\delta(k \cdot F)_2 \cdot \Delta T_{20} = -\delta p_1$$

3. The change in stirring power $\delta_{\text{R}2}$ corresponds to the change in the total motor power $\delta_{\text{M}2}$ when the lost power remains constant.

Hence, $\delta p_2 = -(\delta p_1 + \delta_{\text{M}2}) - q = \delta p_B - q$ (Fig. 2.4).

- By a change in the stirring power p_{St2} ,
- By a change in the heat-transfer coefficient $(k \cdot F)_2$ of the measuring kettle.

To repeat, such changes are caused by changes in the physical properties of the reaction mass due to the reaction (e.g. viscosity, density, surface tension, electric conductivity) or by changes in the measuring conditions (incrustation on the inner kettle wall; phase inversion; change in the volume of the reaction mixture in case of a semi-batch run, in which a large quantity of reactant is dosed into a relatively small batch of mixture, by which, as a rule, the area F_2 , the specific heat-transfer coefficient k_2 and the stirring power p_{S2} enlarge).

For illustration, in the case $q = 0$ and $p_2 = \text{const} = 0$:

- The enlargement of the heat-transfer coefficient $(k \cdot F)_2$ by $\delta(k \cdot F)_2$ would cause a drop in the present difference in temperature ΔT_2
- The enlargement of the stirring power p_{St2} by δp_{St2} and unchanged $(k \cdot F)_2$ would cause an increase in the present difference in temperature ΔT_2 .

However, based on the order of the control system, to keep constant the difference in temperature ΔT_2 , the electric heating power p_2

- In the first case is enlarged by the amount of increased heat flow from the measuring kettle into the intermediate thermostat $\delta(k \cdot F)_2 \cdot \Delta T_2$;
- In the second case is decreased by the amount of the increased stirring power $\delta p_{St2} = \delta p_M$.

The course of the electric heating power $p_2(t)$ corresponds only then to the baseline $p_B(t)$, when the change in the physical properties during a physicochemical process is accompanied only by a marginal calorific occurrence (i.e. $q \cong 0$), for example, in the case of dissolving cellulose in water (Fig. 2.4).

2.1.1.1 Examples of Devices

Two types of construction for the investigation of discontinuous reactions are illustrated.

- In one construction, the compact calorimeter Thermokinetic reactor (TKR) [24] (Figs. 2.5, 2.6, 2.7, 2.8, 2.9, and 2.10), the measuring kettle, and the surrounding intermediate thermostat with a wall made of a welded spiral tube (Fig. 2.5) are completely immersed in a base thermostat. In this way, interfering thermal effects from the surroundings are minimized and a high measuring accuracy is guaranteed. Therefore, this type of construction is very appropriate for kinetic investigations.

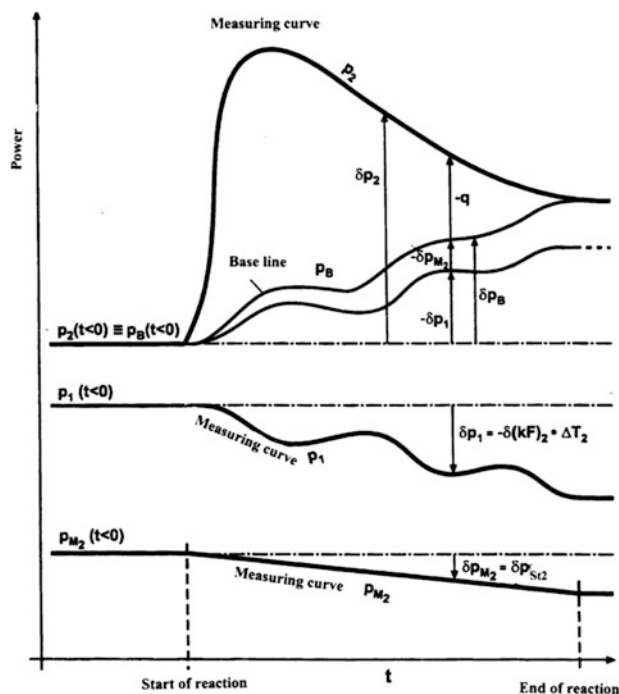


Fig. 2.4 Estimating the thermal reaction power q from the heating power p_2 using the baseline p_B ; composition of p_B

Because of the construction of the TKR, which inhibits a direct view into the reaction chamber, it is impossible to follow visually special events within the measuring kettle (e.g. phase inversion, precipitation) in a simple way, but knowledge of these special events often constitutes important information for chemists. Suitable devices, such as fiberscope endoscope, may allow one to view the reaction chamber.

- Therefore, in the case of a non-compact calorimeter (Fig. 2.11), only a part of the intermediate thermostat encloses the measuring kettle in the form of a hollow jacket. This hollow jacket is connected to the central part of the intermediate thermostat by a thermally insulated pipeline. The central part of the intermediate thermostat is immersed in the base thermostat. The thermostat liquid circulates turbulently via a pipeline through the hollow jacket and lid. For reactions under a pressure of up to 10 bar, the measuring kettle with a hollow jacket consists of glass (Fig. 2.12). A simple visual observation of the reaction mixture is possible.

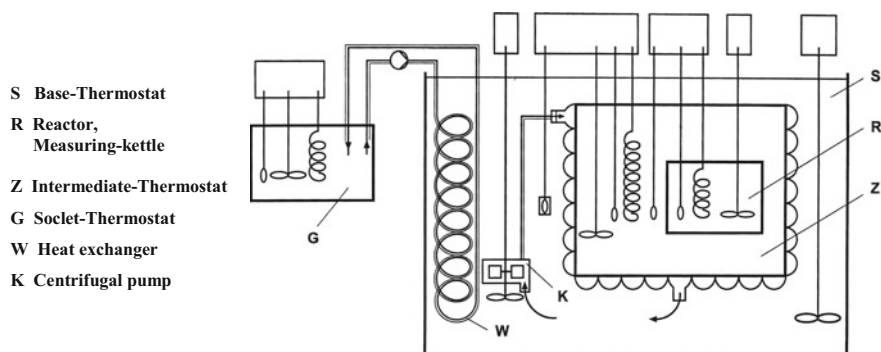


Fig. 2.5 Design principle of compact calorimeter TKR

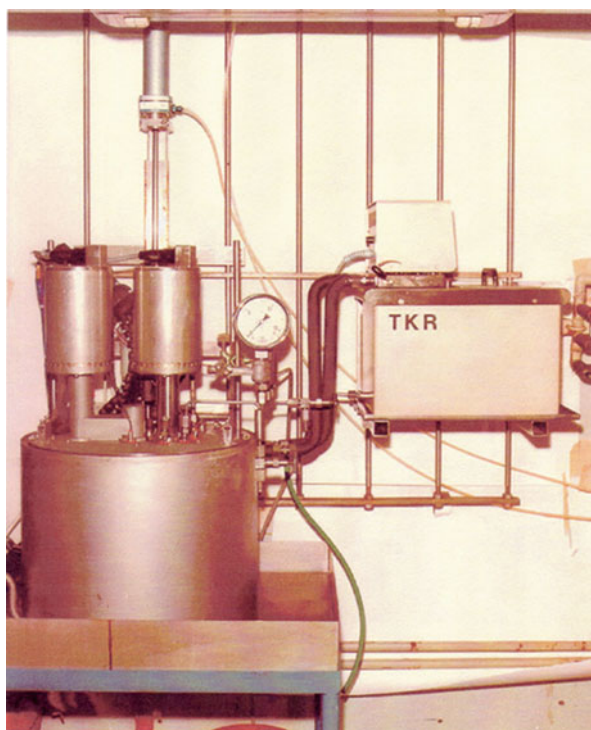


Fig. 2.6 Direct view of apparatus

The pipelines and the outer wall of the hollow jacket are exposed to temperature fluctuations, which occasionally occur within the laboratory. The measurements cannot be shielded completely from external influence despite the thermal

Fig. 2.7 Innards of measuring kettle/ intermediate thermostat

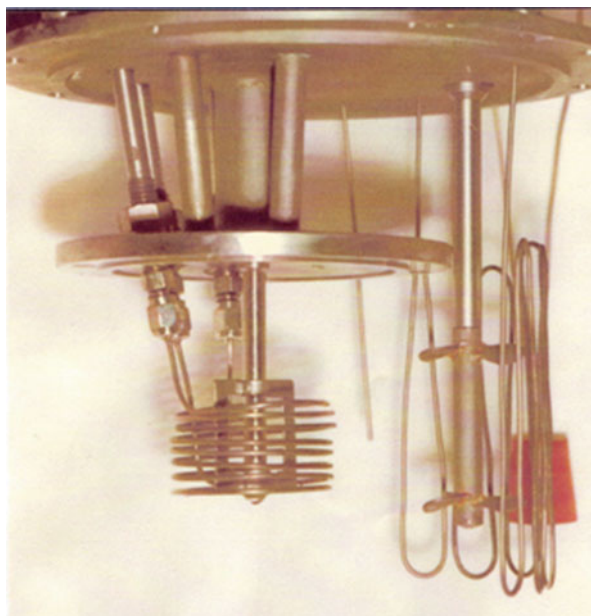


Fig. 2.8 Inside of measuring kettle with baffles



insulation of the pipeline. However, carrying out measurements in a closed hood notably diminishes interference. Nevertheless, this type of construction should be used predominantly for the simulation of a technical process.

Fig. 2.9 Flanged measuring kettle

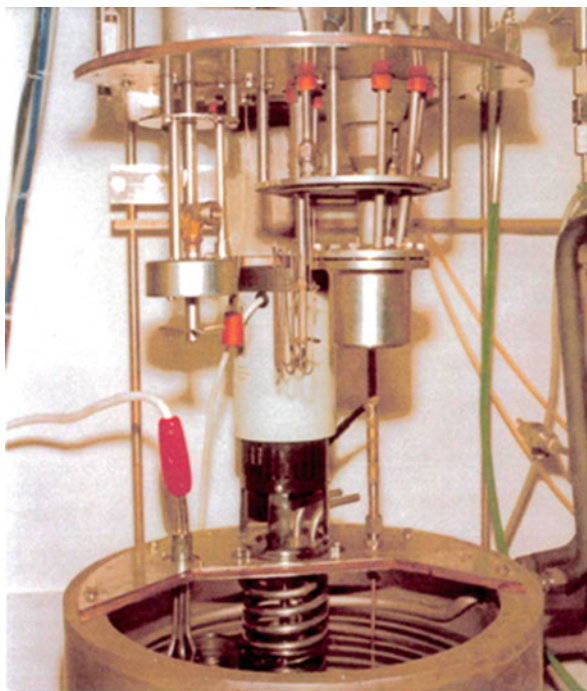
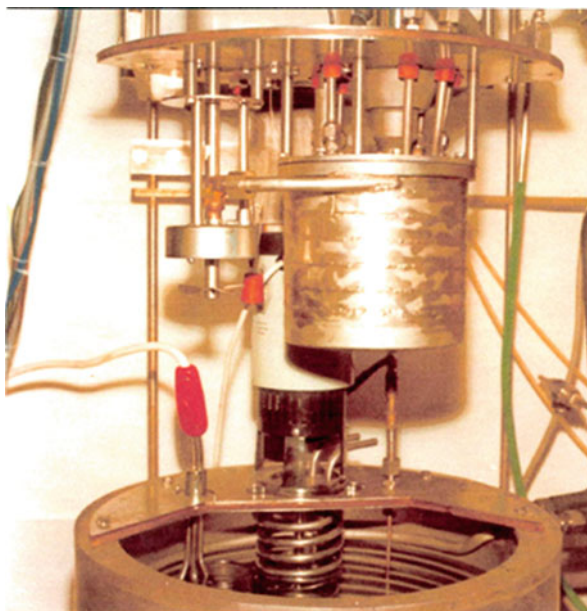


Fig. 2.10 Flanged intermediate thermostat



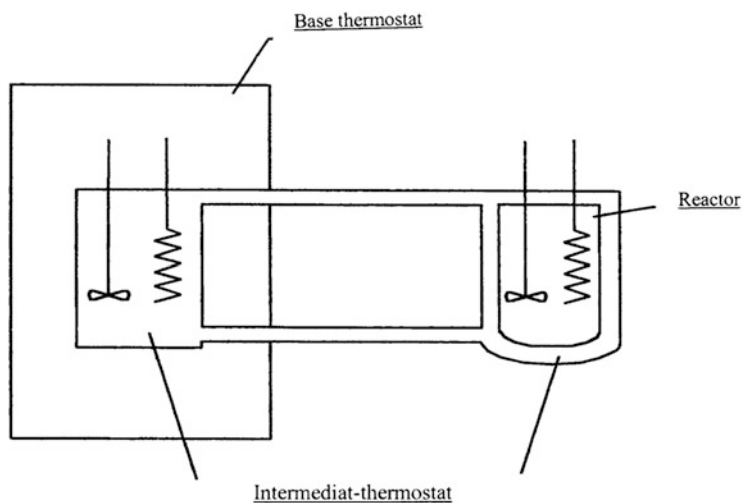


Fig. 2.11 Principle of non-compact calorimeter

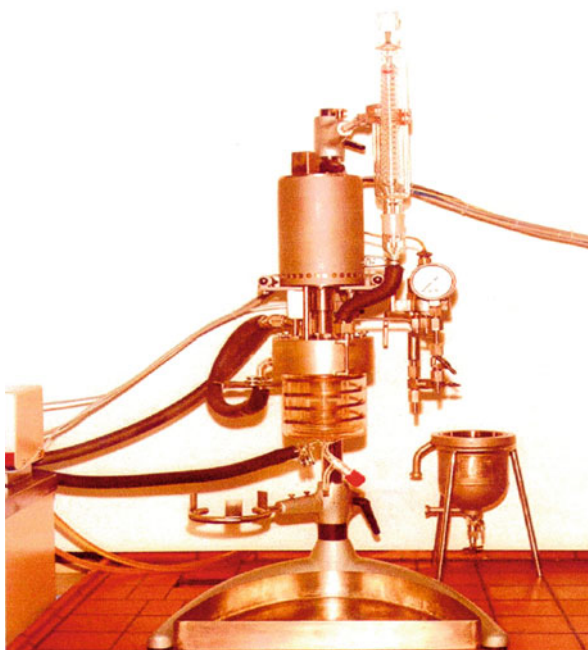


Fig. 2.12 Direct view of non-compact calorimeter. This type should be used predominantly for simulating technical processes

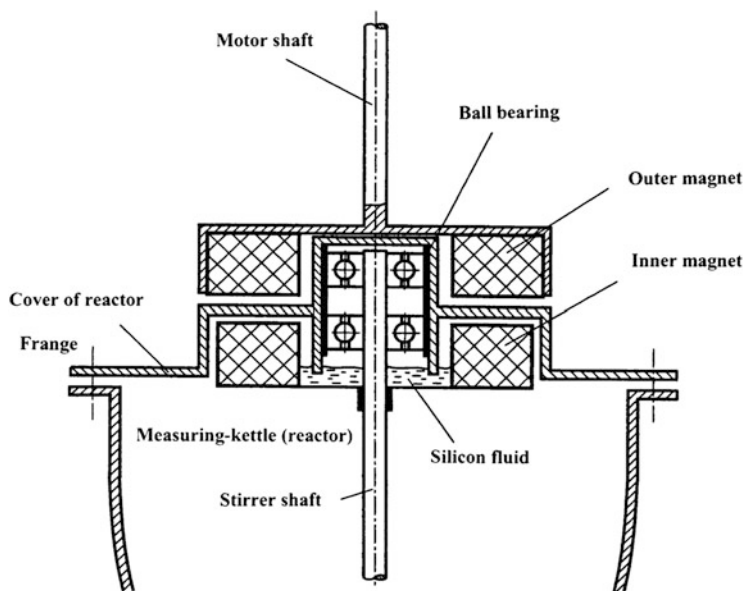


Fig. 2.13 Magnet cluster with ball bearing of stirrer shaft

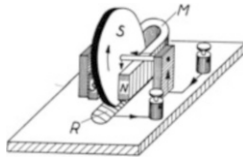
The following types of electric driving motor and clutch motor/stirrer are used. The torque transfer from the motor shaft to the stirrer shaft takes place by a magnetic clutch (Fig. 2.13). This consists of two permanent magnet rings horizontally mounted in bearings above one another, the higher one above the cover of the measuring kettle, the lower one enclosed in a Hastelloy C4 shell within a cylindrical cavity in the cover of the measuring kettle. The shell is open at the top centre, closed at the bottom, and connected to the stirrer shaft at this point. The stirrer shaft is borne and guided by a ball-bearing column, which is located above the lower magnet ring inside an additional cylindrical space, which is partly filled with silicone liquid. Stirrer, stirrer shaft, lower magnet ring and ball-bearing column are a unity, which can be pulled out of the measuring-kettle cavity.

During measurement the centrifugal force of the rotating lower magnet ring within the measuring kettle prevents the reaction mixture penetrating the area surrounding the ball bearings; vapours which reach the region by diffusion are nearly completely absorbed in the silicon confining layer. It stands to reason that the silicon liquid and the ball bearings must sometimes be renewed.

An electromotor without armature retroaction—type DC disk-armature motor connected to a disk-armature tachogenerator (speedometer) (Brown, Boveri & Cie. AG, Mannheim) [7]—equipped with powerful permanent magnets, is used.³

Whose field flows vertically through the unferrous disk-like rotors. The electric conductors are arranged similarly to the spokes of a bicycle rim. The magnetic flow is constant, and the magnetic field structure around the homogeneous and electric self-induction is negligibly small. Because of that, the correlations between the electric and mechanical characteristics are linear, in contrast to conventional electromotors.

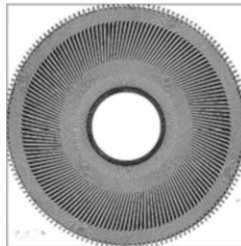
³ Barlow wheel [2]



The Barlow wheel, from 1822, is considered to be the historic forerunner of the DC disk-armature motor. It consists of a pivoted copper disk *S* in a vertically oriented magnetic field of a strong permanent magnet *M*. The conductive connection from the copper disk to the conductive wire takes place via a mercury bath *R*.



The essential constituents of a modern DC disk-armature motor (Brown, Boveri & Cie. AG, Mannheim) connected to a tachometer. Magnetic return path via a feriferous motor jacket.



Arrangement of conductive wires of rotor disk [7]

The mechanical torque D of the motor is a linear function of the intensity I of the electric current⁴

$$D(J) = d_{\text{Torque}} \cdot I,$$

the generated electric voltage U_M of the motor is a linear function of its rotational velocity N ⁵

$$U_M(N) = k_{\text{Motor}} \cdot N,$$

the generated electric voltage U_T of the tachogenerator is a linear function of its rotational velocity N ⁶

$$U_T(N) = k_{\text{Tacho}} \cdot N. \quad (2.6)$$

There is a linear correlation between the mechanical torque factor d_{Torque} and the electromotive factor k_{Motor} of the motor

$$d_{\text{Torque}} = \mathfrak{A} \cdot k_{\text{Motor}}$$

for instance, for d_{Torque} in unit [pcm/A] and k_{Motor} in unit [V/min⁻¹] results in

$$d_{\text{Torque}} [\text{pcm/A}] = 97,465 \cdot k_{\text{Motor}} [\text{V/min}^{-1}]. \quad (2.7)$$

Consequently, the torque constant d_{Torque} can be determined in a simple way.

The generated, total mechanical g torque D of the motor is composed of the usable torque D_U , transmitted via the motor shaft to the stirrer, as well as the loss torque D_L ,

$$D = D_U + D_L.$$

The torque loss D_L consists of the

(a) Torque loss of the inner motor

1. Frictional torque loss D_{FLMotor} (by ball bearing, brush friction), independent of rotational speed N .

⁴ d_{Torque} generated mechanical torque per unit of the electric current strength I .

⁵ k_{Motor} generated electric voltage of the DC disc armature motor (running without load) at one revolution N in unit of time.

⁶ k_{Tacho} generated electric voltage of the DC disk armature tachogenerator (speedometer) at one revolution N in unit of time.

2. Damping torque loss $D_{\text{DLMotor}} = d_{\text{DLMotor}} \cdot N$ (by electric eddy current), depending on the rotational speed N , with

$$d_{\text{DLMotor}} \equiv \text{damping factor} \equiv [D_{\text{DLMotor}}(N = 1)].$$

(b) Outer torque loss in clutch of motor shaft/stirrer shaft

1. Frictional torque of ball bearing of stirrer shaft D_{FLShaft} , independent of rotational speed N .

The correlation of the total motor power p_M and its useful part p_U , i.e. p_{St} , reads

$$\begin{aligned} p_M &= D \cdot \omega = (d_{\text{Torque}} \cdot I) \cdot 2\pi \cdot N = (D_U + D_L) \cdot 2\pi \cdot N = D_U \cdot 2\pi \cdot N \\ &\quad + (D_{\text{FLMotor}} + D_{\text{DLMotor}} + D_{\text{FLShaft}}) \cdot 2\pi \cdot N = p_U + p_L \\ &= p_{\text{St}} + (D_{\text{FLMotor}} + D_{\text{DLMotor}} + D_{\text{FLShaft}}) \cdot 2\pi \cdot N. \end{aligned}$$

Hence, for a constant rotational velocity N it follows that

$$p_M = (d_{\text{Torque}} \cdot I) \cdot 2\pi \cdot N = p_{\text{St}} + \text{const}_{\text{MSIL}}. \quad (2.8 \equiv 2.3)$$

Even classic electronics allows one to record the thermal reaction power q in a simple way:

- Using special heater systems (lead, heating section, lead with resistance ratio 1/400/1; Philips Eindhoven) with virtually no thermal inertia and DC power supplies, both the released heating powers p_2 in the measuring kettle and p_1 in the immediate thermostat are obtained in Watts multiplied by the intensities of the current $I_{2/1}$ [A] and voltage $U_{2/1}$ [V] of the heaters by means of a multiplier unit.
- The motor power p_{M2} [W] is determined (Sect. 6.3) by multiplying the current I [A] of the electromotor, the motor factor k_{Motor} [V/min⁻¹], the voltage U_{Tacho} [V] of the tachogenerator and the reciprocal value of its factor, i.e. $(k_{\text{Tacho}} [\text{V/min}^{-1}])^{-1}$.
- The addition of $p_1(t)$, $p_2(t)$ and $p_M(t)$ by means of a potential recorder gives the course of the total power $p(t)$. The curve $p(t)$ with relation to the constant baseline p_0 imparts $-q$ (Fig. 2.2). If p_0 is compensated by an adjustable voltage source, only the desired q is recorded.

Nowadays, using modern recording and calculation systems on the basis of digital electronics, elegant and simple multiplication and addition can be carried out.

The controlling units can also be implemented on the basis of digital electronics.

2.1.1.2 Specification of Devices

The essential features of the apparatus are as follows:

- Material of measuring kettle/intermediate thermostat stirrer, surfaces of electric heater, temperature sensor Glass, HC4, V4A
- Electric heater with approximately no thermal inertia, temperature sensors with the smallest thermal time constant, thermocouples, quasi-identical, homemade by cutting pieces of thermoelectric wire into two parts and preparing the quasi-identical cut zones as thermocouples HC4, V4A
- Volume of measuring kettle 100 → 1,500 ml
- Range of temperature (thermostat fluid: silicon liquid) essentially the range of temperature is determined by the boiling point resp. freezing point of the thermostat liquid −40 °C → 300 °C
- Maximal number of rotations 4,000 rpm
- PID control unit
- Maximal electric heating power 500 W
- Resolution <1 W
- Maximal operating pressure 32 bar

Reactions in fluid solution mixtures <200 mL within the calorimeter TKR with time constants >1 min run during total time of reaction under virtually isothermal conditions, with the exception of the first moments after starting. Temperature fluctuations around the set point are approximately 0.01 °C.

This strongly isothermal character is the necessary and sufficient condition for the correctness of the measured rate of heat release q .

2.1.1.3 Simplified Apparatus

In addition to the electromotor without armature retroaction, the use of the intermediate thermostat is necessary to determine the baseline by analogous measurement and ultimately to determine the thermal reaction power by physical means in the classic working manner, i.e. by simple potentiometric addition and multiplication of measured quantities. The modern method of recording measured quantities and proceeding on the basis of digital electronics makes it possible—with limitations—to neglect the intermediate thermostat and to determine an adequately precise course of the baseline proceeding from one point in time to another as follows.

When the control unit is in equilibrium t_i the following equation is valid according to (2.1):

$$q(t_i) + p_2(t_i) + p_{St2}(t_i) = (k \cdot F)_2(t_i) \cdot \Delta T_2,$$

and for changes in the set-temperature difference ΔT_2 by $\delta\Delta T_2$ the following equation is valid:

$$q(t_i) + \{p_2(t_i) + \delta p_2(t_i)\} + p_{\text{St2}}(t_i) = (k \cdot F)_2(t_i) \cdot \{\Delta T_2 + \delta\Delta T_2(t_i)\}.$$

From both equations we obtain

$$(k \cdot F)_2(t_i) = \delta p_2(t_i) / \delta\Delta T_2(t_i).$$

Combining this with the first equation yields

$$q(t_i) + p_2(t_i) + p_{\text{St2}}(t_i) = [\delta p_2(t_i) / \delta\Delta T_2(t_i)] \cdot \Delta T_2$$

or, according (2.5),

$$p_{\text{B}}(t_i) + p_{\text{St2}}(t_i) = [\delta p_2(t_i) / \delta\Delta T_2(t_i)] \cdot \Delta T_2.$$

For $t_i < t_0 = 0$ we have $p_{\text{B}}(t_i < 0) = p_2(t < 0)$ because $q(t_i < 0) = 0$; hence

$$p_2(t_i < 0) + p_{\text{St2}}(t_i < 0) = [\delta p_2(t_i < 0) / \delta\Delta T_2(t_i < 0)] \cdot \Delta T_2.$$

The quotient of this and the previous equation leads to

$$\begin{aligned} & [p_{\text{B}}(t_i) + p_{\text{St2}}(t_i)] / [p_2(t_i < 0) + p_{\text{St2}}(t_i < 0)] \\ &= [\delta p_2(t_i) / \delta\Delta T_2(t_i)] / [\delta p_2(t_i < 0) / \delta\Delta T_2(t_i < 0)]. \end{aligned}$$

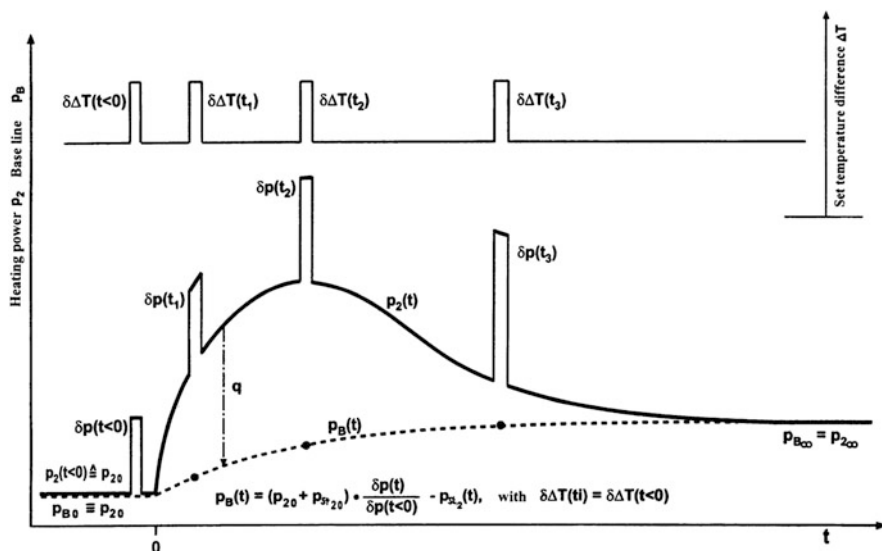
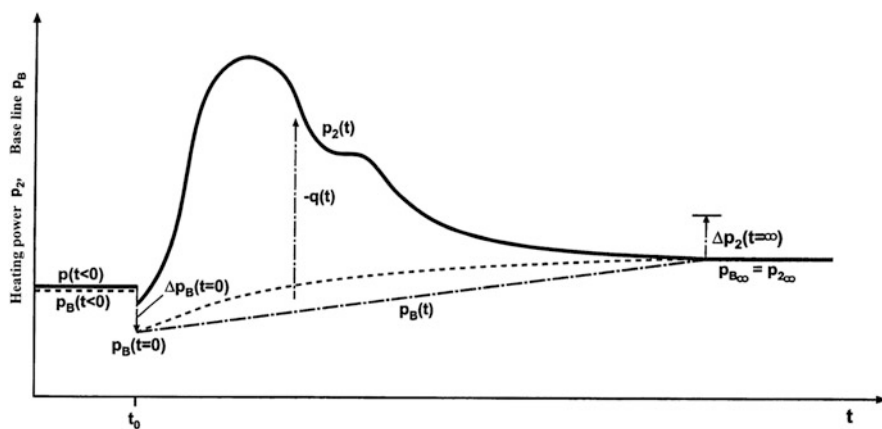
Are all chosen changes in the set temperature difference at different points in time t_i of the same size $\delta\Delta T_2(t_i)$, it follows that

$$[p_{\text{B}}(t_i) + p_{\text{St2}}(t_i)] / [p_2(t < 0) + p_{\text{St2}}(t < 0)] = \delta p_2(t_i) / \delta p_2(t < 0)$$

or

$$p_{\text{B}}(t_i) = [p_2(t < 0) + p_{\text{St2}}(t < 0)] \cdot \delta p_2(t_i) / \delta p_2(t < 0) - p_{\text{St2}}(t_i).$$

Hence, to work out the baseline $p_{\text{B}}(t_i)$ without use of the intermediate thermostat during the reaction run, i.e. proceeding from point in time to point in time, the set temperature difference ΔT_2 is to change at progressive points in time t_i for a short interval by the equal amount $\delta\Delta T_2$ and then at thermal equilibrium the induced change of the electric heating power δp_2 is determined (Fig. 2.14). To obtain an accurate baseline $p_{\text{B}}(t_i)$, it is necessary on the one hand to choose a time interval between the single measurements that is as small as possible, which allows one to obtain as many determinations as possible; on the other hand, for reaction-kinetic reasons, the temporarily changed temperatures may not cause a substantial

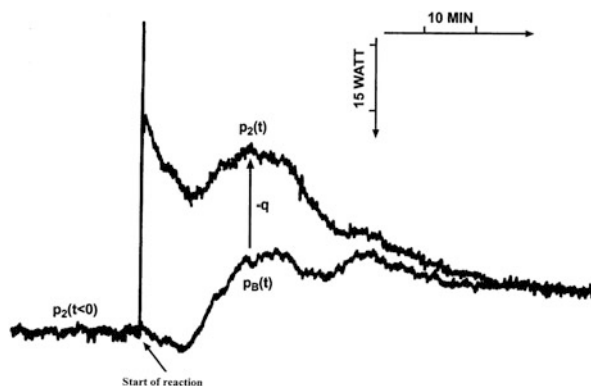
Fig. 2.14 Baseline p_B proceeding from one point in time to anotherFig. 2.15 Establishing approximate course of baseline p_B

deviation of the chemical conversion compared with the strictly isothermal run. Therefore, the following conditions are necessary:

- The reaction must proceed relatively slowly (time constant as large as possible).
- The reaction must be insensitive to temperature (low activity constant).

In the case of a monotonously changing baseline $p_B(t)$, its course can be approximated as follows (Fig. 2.15). When the reaction has completed, the same

Fig. 2.16 Catalytic hydrogenation of a nitrile group



volume of mixture must be taken out of the reaction mixture, which was dosed in order to start the reaction (e.g. co-reactant, catalyst solution). The indicated change in the electric heating power $\Delta p_2(t = \infty)$ is nearly opposite and equal to the change in the baseline $\Delta p_B(t = 0)$ caused by the injection at the start of the reaction, i.e. $\Delta p_B(t = 0) \cong -\Delta p_2(t = \infty)$.

To establish the gross baseline, a straight line is drawn from $p_B(t = 0)$ to $p_B(t = \infty) = p_{2\infty}$. Even better would be to draw an exponentially curved line because the chemical conversion and, hence, the consistency usually change in an exponential way.

This procedure is based on the assumption that the consistency of a reaction mixture changes synchronously and monotonously with the progress of the chemical conversion. Normally this is the case; but it is not necessarily so. For example, the heat-transfer coefficient decreases during the beginning of polymerization because of growing viscosity, but then it can change as a result of gas being stirred into the mixture (producing bubbles), which causes the effective viscosity to start decreasing;

In addition, simultaneously occurring fluctuations in pressure can induce an alternating gas hold-up (change in magnitude of bubbles) causing a fluctuation in the heat-transfer coefficient. A similar change in the hold-up of a gas can also be created during reaction by a change in the density or surface tension of the liquid phase.

Measurements using the compact calorimeter TKR reveal that baselines very often take an unexpected course (Figs. 2.16, 2.17, 2.18, 2.19, 2.20, 2.21, and 2.22).

Conclusion

A precise determination of the thermal reaction power q is only possible when the precise baseline p_B is known. This is valid for any type of calorimeter.

In particular, the prerequisite for a thorough thermokinetic investigation is the precise determination of the thermal reaction power q . This applies for the

Fig. 2.17 Catalytic, intramolecular rearrangement of an amide derivate

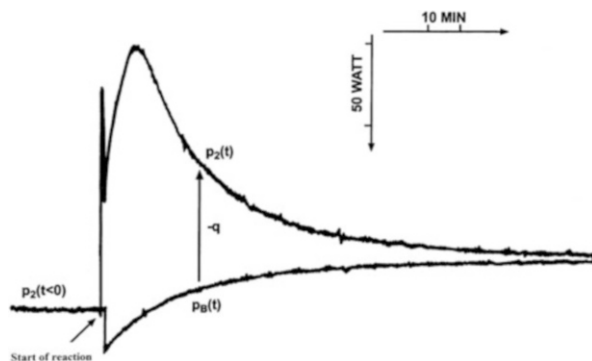


Fig. 2.18 Nucleophilic substitution at a halide of a ketone with an amine derivative in the presence of the auxiliary base KOH in solution

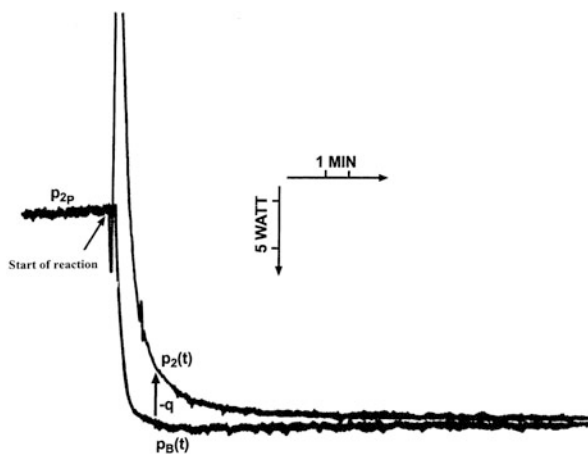


Fig. 2.19 The same reactants as in Fig. 2.18 but with use of auxiliary base K_2CO_3

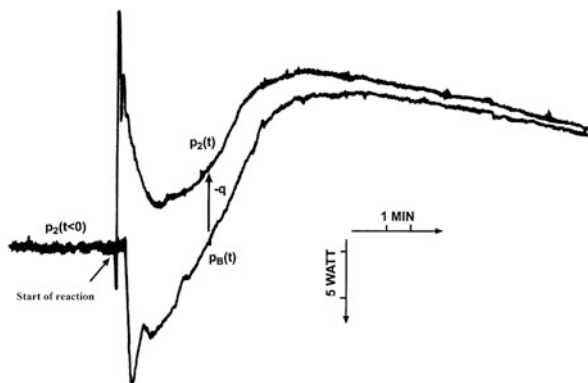


Fig. 2.20 Friedel–Crafts alkylation followed by an autocatalytic decomposition

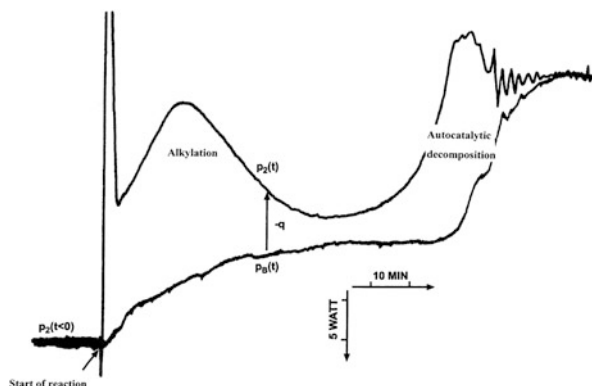


Fig. 2.21 Hydrogenation of an anthraquinone derivative in solution

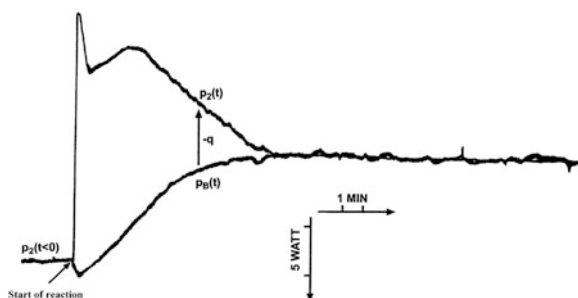
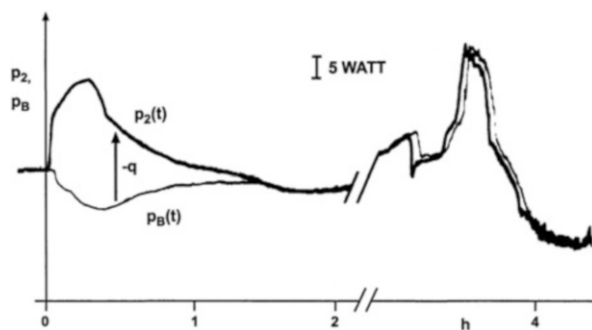
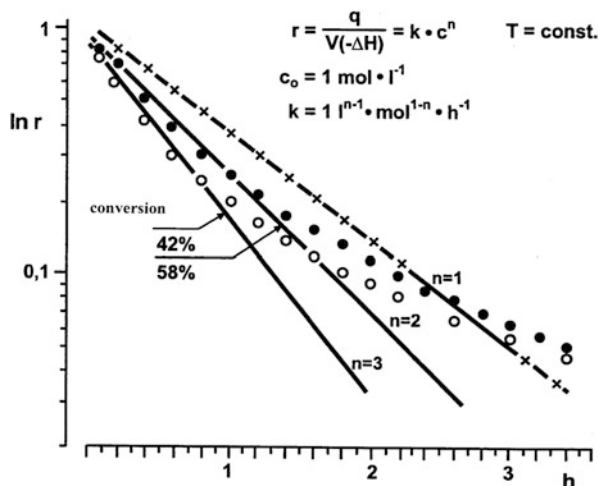


Fig. 2.22 Polymerization in solution



evaluation of a simple rate function, demonstrated as follows (Fig. 2.23). The theoretical courses of the reaction velocity r (respectively the thermal reaction power $q = r \cdot (-\Delta H_\lambda) \cdot V$, see Sect. 4.1) for a rate function of order 1, 2, or 3 are plotted using marks (points, stars, circles) as a logarithmic diagram versus time.

Fig. 2.23 Plot of $\ln\{r\}$ versus time for reaction velocities of order n



It is widely known that a logarithmic plot gives a straight line only for a reaction velocity (thermal reaction power) of order 1. The plots show that there is only a small curvature in the profile of order two and three up to a high degree of conversion.

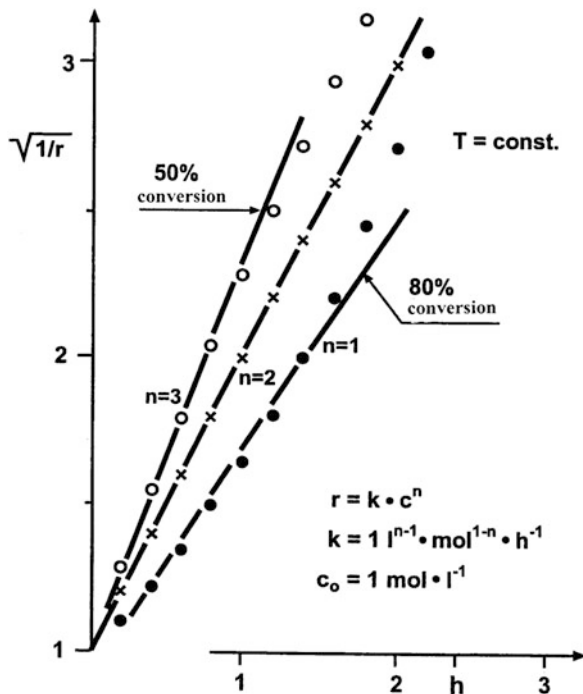
Considering that experimentally found data usually contain many imperfections, a straight line can also be drawn to one's best knowledge and belief through the experimental data of reactions of order greater than one, for instance, up to a conversion of 45 % for reactions of order three and 60 % for reactions of order two.

The situation is similar when $\sqrt{(1/r)}$ respectively $\sqrt{(1/q)}$ is plotted versus time (Fig. 2.24). In this case, a straight line is theoretically valid for a rate function of order two.

This means that, in practice, reaction rates of orders one, two, and three cannot be distinguished up to relatively high conversions. The difference becomes evident only by means of data measured during the final phase of the reaction. However, the calorific effect during this range of reaction is usually rather small. Consequently, the accuracy of the desired net curve is very closely associated with the precision in the course of the baseline.

This principle stands to reason, especially with respect to the thermokinetic analysis of the thermal reaction power of a complex chemical conversion (i.e. analysis of the superposition of thermal reaction powers of individual reactions, see Chap. 4) demands the precise registration of the baseline during the complete reaction run.

Fig. 2.24 Plot of $\sqrt{1/r}$ versus time for reaction velocities of order n



2.1.2 Non-isothermal Reaction

In the case of a non-isothermal reaction, the temperature within the measuring kettle changes during the reaction run. There are three characteristic modes of change in temperature

- Induced change in temperature within the thermally open measuring kettle.
- Change in temperature caused by the reaction itself within the measuring kettle opaque to heat.
- Change in temperature caused by the reaction itself within the thermally open kettle.

2.1.2.1 Induced Change in Temperature Within Thermally Open Measuring Kettle (Temperature Program)

Figure 2.25 shows a flowchart of the apparatus; the control system R2 changes the temperature of the measuring kettle T_2 in such a way that it corresponds correctly to the set temperature $T_p(t)$ of the programming unit, $T_2 = T_p$, despite heat release due to the reaction.

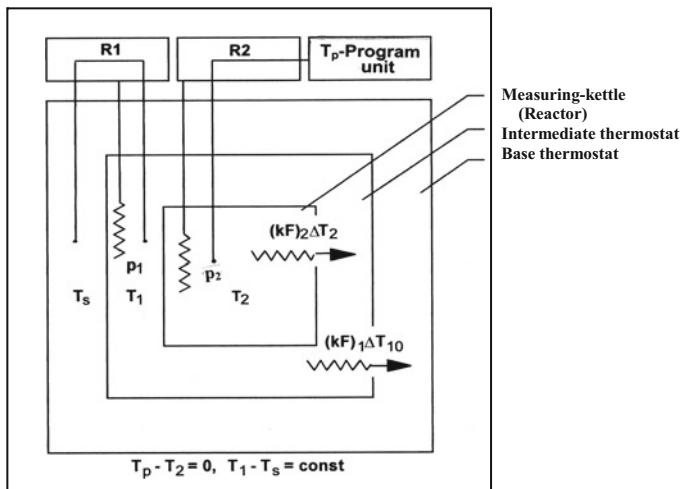


Fig. 2.25 Flowchart of apparatus for non-isothermal reaction (temperature programme)

The temperature of the intermediate thermostat T_1 is maintained as constant as is, for that reason, the temperature difference $T_1 - T_s$ by means of the control system R1, which controls the heating power p_1 . The heat balances of the measuring kettle respectively intermediate thermostat are

$$C_2 \cdot dT_2/dt = q + p_{S12} + p_2 - (k \cdot F)_2 \cdot (T_2 - T_1) \quad (2.9)$$

respectively

$$0 = (k \cdot F)_2 \cdot (T_2 - T_1) + p_{S11} + p_1 - (k \cdot F)_1 \cdot (T_1 - T_s).$$

The combination of both balances gives the thermal reaction power q in the reaction mixture

$$q = [(k \cdot F)_1 \cdot (T_1 - T_s) - p_{S11}] + C_2 \cdot dT_2/dt - [p_1(t) + p_2(t) + p_{S12}(t)].$$

The first parenthetic expression is constant because $(k \cdot F)_1$ and p_{S11} are independent of the chemical conversion in the measuring kettle. The difference $(T_1 - T_s)$ is maintained as constant by the control system R1. Therefore, the equation for the thermal reaction power is obtained as

$$q(t) = \text{const} + C_2 \cdot dT_2/dt - [p_1(t) + p_2(t) + p_{S12}(t)]$$

or with respect to $q=0$ and $dT_2/dt=0$ prior to the start of the temperature programme at time $t=t_0$:

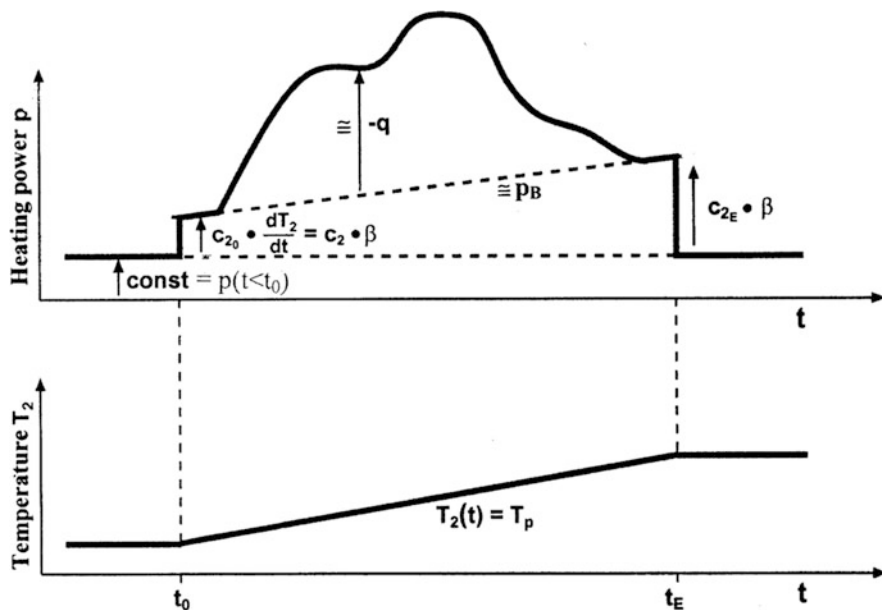


Fig. 2.26 Working out the net curve q of a non-isothermal reaction with an induced, linear change in temperature $T_2(t) = T_{p0} + \beta \cdot (t - t_0)$

$$q(t) = \underbrace{[p_1 + p_2 + p_{St2}]}_{\text{prior to start of temperature programme}} + C_2 \cdot \frac{dT_2}{dt} - \underbrace{[p_1(t) + p_2(t) + p_{St2}(t)]}_{\text{during temperature programme}}$$

or with regard to (2.3) and $p_1(t) + p_2(t) + p_{M2}(t) = p(t)$, $p(t < t_0) = p_0$

$$q(t) = p_0 + C_2 \cdot \frac{dT_2}{dt} - p(t).$$

$p_0 + C_2 \cdot \frac{dT_2}{dt}$ is the baseline p_B for determining the thermal reaction power $q(t)$.

In the case of a constant change in temperature, $\frac{dT_2}{dt} = \beta$, we obtain (Fig. 2.26)⁷

$$q(t) = p_0 + C_2 \cdot \beta - p(t) = p_B - p(t). \quad (2.10)$$

In contrast to the isothermal reaction, $p_B(t)$ cannot be measured synchronously with $p_2(t)$; however, it can be calculated supplementally on the basis of the effective heat

⁷ In fact, the preceding baseline must be completed by a term that takes into account a small heat exchange with the laboratory via the insulated inlet pipes and the cover of the measuring kettle. The heat exchange varies with a temperature programme change T_2 . This term usually varies approximately linearly based on experimentation. Hence, it is sufficiently integrated in the linearly approximated evaluation of $p_B(t)$.

capacity C_2 , which is, in the case of a not too quick change in temperature, a homogeneous composition of the heat capacity C_F of the reaction mass within the measuring kettle and the effective heat capacity C_{Mt} of the measuring kettle itself, i.e. the sprinkled wall of the measuring kettle, stirrer, baffles, temperature sensor and regions of the inlet pipes:

$$C_2 = C_F + C_{Mt}.$$

- C_F changes during the run of the reaction due to the change in the molecular composition of the reaction mixture
- C_F depends on temperature
- C_{Mt} is relatively independent of temperature and can be assumed to be an apparatus constant.

The course of the effective heat capacity C_2 , which as a rule changes monotonously during chemical conversion, is produced approximately as follows. From the abrupt shift in heat power (vertical jump) $\Delta p(t = t_0)$ at the start of the temperature programme $T_p(t)$ at time t_0 as well as $\Delta p(t = t_E)$ at the end of the temperature programme upon completion of the reaction at time t_E ⁸ yields, using (2.9),

$$\begin{aligned} [p(t = t_0) - p(t < t_0)]/\beta &= \Delta p(t = t_0)/\beta = C_{20}, \\ [p(t = t_E) - p(t > t_E)]/\beta &= \Delta p(t = t_E)/\beta = C_{2E}. \end{aligned}$$

With $(C_{2E} - C_{20})/(t_E - t_0) = \gamma$ the temporal profile of the effective heat capacity in the time interval $t_0 \leq t \leq t_E$ can be approximated to the first degree by means of

$$C_2 \cong C_{20} + \gamma \cdot (t - t_0).$$

A very large temperature increase of $T_2 = T_p$ can require a heating power $p_2(t_E)$ which exceeds the capacity of the power supply of the measuring kettle. In addition, the heat flow $(k \cdot F)_2 \cdot [T_2(t) - T_{1(=const)}]$ from the measuring kettle into the intermediate thermostat can increase to such an extent that the heating power prior to the start of the temperature programme $p_1(t < 0)$, which is necessary for maintaining the heat compensation capability during the total width of the running temperature programme, can be beyond the capacity of the power supply of the intermediate thermostat.

Such overstepping of the limits of power supplies can be avoided if one gives up on the idea of measuring accuracy using a simplified design, conveniently a non-compact calorimeter without use of an intermediate thermostat, as follows.

Instead of the temperature T_2 of the measuring kettle, the temperature T_S of the base thermostat is adjusted to the temperature programme: $T_S = T_p(t)$, and now the

⁸ Only when $p(t > t_E)$ agrees with $p(t < 0) = p_0$ the reaction is really finished at the point in time t_E .

temperature difference $T_2(t) - T_S$ is maintained as a constant by the controlled heating power p_2 , i.e. it applies $dT_2/dt = dT_S/dt = dT_p/dt$.

Because of these facts, the heat balance of the measuring kettle reads

$$C_2 \cdot dT_2(t)/dt = q + p_{S12} + p_2 - (k \cdot F)_2 \cdot [T_2(t) - T_S], \quad (2.11)$$

and prior to the start of the temperature programme $T_p(t)$ at $t = t_0$ the following expression holds:

$$0 = p_{S12}(t < t_0) + p_2(t < t_0) - (k \cdot F)_2(t < t_0) \cdot [T_2(t < t_0) - T_S(t < t_0)]. \quad (2.12)$$

Because of the constant temperature difference $[T_2 - T_S]$ prior to, after and during the temperature programme $T_S(t) = T_p(t)$, the expression

$$\begin{aligned} [T_2(t \geq t_0) - T_S(t \geq t_0)] &= [T_2(t < t_0) - T_S(t < t_0)] \\ &= [p_2(t < t_0) + p_{S12}(t < t_0)] / (k \cdot F)_2(t < t_0) \end{aligned}$$

results, along with, due to (2.11),

$$\begin{aligned} q = \{ &C_2(t) \cdot dT_2(t)/dt - p_{S12}(t) + [(k \cdot F)_2(t \geq t_0) / (k \cdot F)_2(t < t_0)] \\ &\cdot [p_2(t < t_0) + p_{S12}(t < t_0)] \} - p_2(t). \end{aligned}$$

$\{C_2(t) \cdot dT_2(t)/dt - p_{S12}(t) + [(k \cdot F)_2(t \geq t_0) / (k \cdot F)_2(t < t_0)] \cdot [p_2(t < t_0) + p_{S12}(t < t_0)]\}$ gives the course of the baseline $p_B(t)$ versus time, knowledge of which is necessary for evaluating the thermal reaction power q from the measured curve $p_2(t)$.

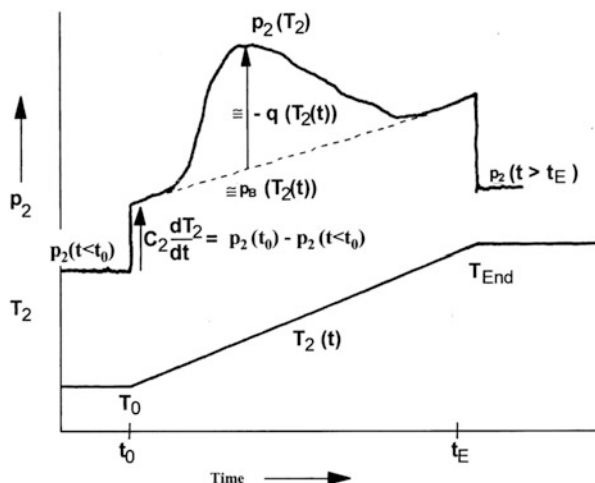
Also in this case p_B cannot be measured synchronously to $p_2(t)$ (Fig. 2.27). To establish the baseline $C_2(t)$, $p_{R2}(t)$ and $(kF)_2(t)$ must be determined (Sect. 2.1.2.3 or 6.3).

Because C_2 , p_{S12} and $(k \cdot F)_2$ change monotonously as a rule during the chemical conversion and in addition approximately linearly with T_2 , to establish $p_B(t)$ in a first approximation, a straight line can be drawn in the time interval $t = t_0$ up to $t = t_E$ from $p_2(t = t_0)$ up to $p_2(t = t_E)$. Because the thermal reaction powers $q(t = t_0)$ respectively $q(t = t_E)$ are still small respectively again small, $p_2(t_0)$ and $p_2(t_E)$ correspond to $p_B(t)$ of the baseline.

In case of a linear temperature programme $dT_2/dt = \beta$, the effective heat capacities C_{20} and C_{2E} result from the jumps in heating power at $t = t_0$ and $t = t_E$. Because of $q(t = t_0) = 0$, $p_{S12}(t = t_0) = p_{S12}(t < t_0)$ and $(k \cdot F)_2(t = t_0) = (k \cdot F)_2(t < t_0)$ respectively $q(t \geq t_E) = 0$, $p_{S12}(t = t_E) = p_{S12}(t > t_E)$ and $(k \cdot F)_2(t = t_E) = (k \cdot F)_2(t > t_0)$ it follows using (2.11) that

$$\begin{aligned} C_2(t = t_0) \cdot dT_2(t = t_0)/dt &= C_{20} \cdot \beta = p_2(t = t_0) - p_2(t < t_0), \\ C_2(t = t_E) \cdot dT_2(t = t_E)/dt &= C_{2E} \cdot \beta = p_2(t = t_E) - p_2(t > t_E). \end{aligned}$$

Fig. 2.27 Non-isothermal reaction (linear temperature programme, simplified apparatus)



2.1.2.2 Change in Temperature Because of Reaction Within Thermally Closed Measuring Kettle (Adiabatic Condition)

Besides the induced and controlled change in temperature, caused by means of an external heat supply (electric heater), a change in temperature without control can take place by the heat release of the reaction itself. In adiabatic conditions, this induced change in temperature occurs without heat loss to the surroundings. To hinder heat transfer into the surroundings of the measuring kettle, the temperature of the surroundings (intermediate thermostat) is adjusted to the changing temperature of the reaction mixture at any moment (Fig. 2.28).

To be precise, this way of proceeding however, cannot attain an exact, thermal insulation of the reaction mixture because of the following facts:

- The reaction mixture is separated from the filling of the intermediate thermostat by a wall of finite heat capacity
- The heat-transfer coefficients from the reaction mixture into the inside surface of the wall and from the thermostat fluid into the outside surface of the wall of the measuring kettle are different
- The heat flows due to the change in temperature simultaneously from the reaction mixture and the filling of the intermediate thermostat into the wall are therefore different
- The mean temperature of the wall changes is temporarily delayed compared with the changing temperature of the measuring kettle and the intermediate thermostat

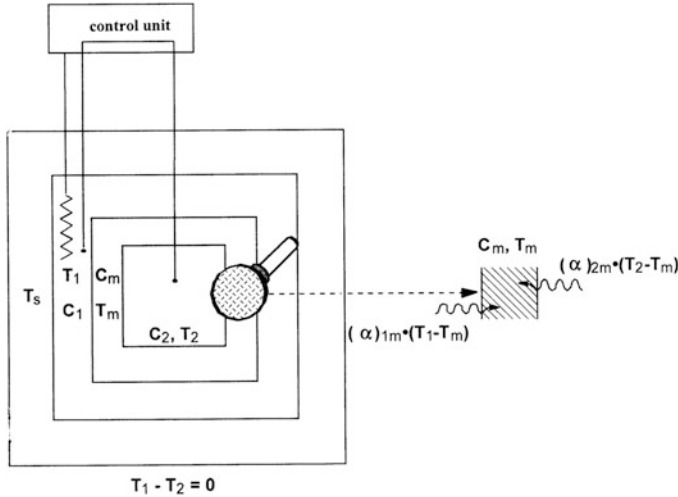


Fig. 2.28 Scheme of apparatus for adiabatic measurement

With

- T_m Mean temperature within wall of measuring kettle⁹
 C_m Corresponding mean heat capacity of measuring-kettle wall (see footnote 12)
 α_{2m} Heat-transfer coefficient: reaction mixture \rightarrow inside wall of measuring kettle
 α_{1m} Heat-transfer coefficient: intermediate thermostat \rightarrow outside wall of measuring kettle
 $(k \cdot F)_1$ Heat-transfer coefficient: intermediate thermostat \rightarrow socle thermostat¹⁰

the heat balances of the reaction mixture, the measuring-kettle wall and the intermediate thermostat are

$$C_2 \cdot dT_2/dt = q + p_{St2} - \alpha_{2m} \cdot (T_2 - T_m) \quad (2.13)$$

$$C_m \cdot dT_m/dt = \alpha_{2m} \cdot (T_2 - T_m) + \alpha_{1m} \cdot (T_1 - T_m) \quad (2.14)$$

$$C_1 \cdot dT_1/dt = -\alpha_{1m} \cdot (T_1 - T_m) + p_{St1} + p_1 - (k \cdot F)_1 \cdot (T_1 - T_s). \quad (2.15)$$

Because the intermediate thermostat is being controlled, we have $T_1 = T_2$ as well as $dT_1/dt = dT_2/dt$ ¹¹, and the sum of (2.13), (2.14) and (2.15) results in

⁹ Existing when the temperature T_2 does not change too quickly.

¹⁰ Intermediate- and socle thermostat consist mainly of welded spiral tubes with turbulent flow, the socle thermostat with an utmost quick throughput of a liquid with the constant entry temperature, e.g. from a public supply (Fig. 2.11).

¹¹ The usual temperature rise produces $dT_2/dt = dT_1/dt \cong dT_m/dt$ as well as $T_1 = T_2 = T_m + \partial T$, with $\partial T \cong \text{const.}$ A very quick temperature rise causes $dT_2/dt = dT_1/dt \neq dT_m/dt$ as well as $T_1 = T_2 = T_m + \partial T$, with $\partial T \neq \text{const.}$

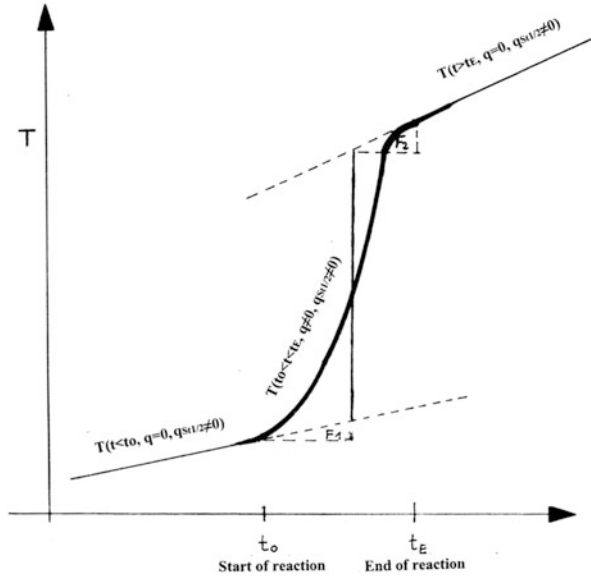


Fig. 2.29 Characteristic course of temperature of an exothermic reaction. Vertical distance between extrapolated straight lines $T(t < t_0, q = 0, p_{S12} \neq 0, p_{M1} \neq 0)$ and $T(t > t_{\text{End of reaction}}, q = 0, p_{S12} \neq 0, p_{M1} \neq 0)$, positioned in such a way that the areas F_1 and F_2 are equal, corresponds in praxis to the jump in temperature by the abruptly released total heat of reaction Q

$$\begin{aligned} (C_2 + C_1) \cdot dT_2/dt + C_m \cdot dT_m/dt &= q + p_{S12} - \alpha_{2m} \cdot (T_2 - T_m) - \alpha_{1m} \\ &\cdot (T_1 - T_m) + p_{S11} + p_1 - (k \cdot F)_1 \cdot (T_1 - T_S) + \alpha_{2m} \cdot (T_2 - T_m) + \alpha_{1m} \\ &\cdot (T_1 - T_m) = q + p_{S12} + p_{S11} + p_1 - (k \cdot F)_1 \cdot (T_2 - T_S). \end{aligned}$$

Fig. 2.29 shows the characteristic change in temperature T_2 during an exothermic reaction. From previous equation follows the equation determining the thermal reaction power: $q[T_1(t)]$.

$$q = (k \cdot F)_1 \cdot (T_1 - T_S) + (C_2 + C_1) \cdot dT_1/dt + C_m \cdot dT_m/dt - p_{S12} - p_{S11} - p_1$$

or, when index 0 marks the start of the reaction,

$$\begin{aligned} q &= (k \cdot F)_1 \cdot (T_1 - T_S) - (k \cdot F)_{10} \cdot (T_{10} - T_S) + (C_2 + C_1) \cdot dT_1/dt \\ &- (C_2 + C_1)_0 \cdot (dT_1/dt)_0 + C_m \cdot dT_1/dt - C_{m0} \cdot (dT_1/dt)_0 - (p_{M2} - p_{M20}) \\ &- (p_{M1} - p_{M10}) - (p_1 - p_{10}). \end{aligned}$$

As a rule, only an approximate determination of the thermal reaction power q is possible because there is insufficient knowledge of the dependence of $(k \cdot F)_1$, C_2 , C_1 , C_m on temperature and the composition of the reaction mixture. As a rule, these quantities must be calculated in a first approximation.

In the case of a relatively small dependence on temperature, $dT_m/dt \cong dT_2/dt = dT_1/dt$ as well as $(p_{M1} - p_{M10}) \cong 0$ the following expression results:

$$q \cong (k \cdot F)_{10} \cdot (T_1 - (T_1)_0) + (C_2 + C_1 + C_m)_0 \cdot (dT_1/dt - (dT_1/dt)_0) - (p_{M2} - p_{M20}) - (p_1 - p_{10}).$$

As a rule, the amount of heat capacity of the measuring-kettle wall C_m cannot be neglected, especially with a pressure kettle. Therefore, the heat contents of the intermediate thermostat and the reaction mixture contribute substantially to the change in temperature within the wall of the measuring kettle, which occurs in the ratio of the transfer coefficients $(\alpha)_{1m}$ and $(\alpha)_{2m}$, in which generally $(\alpha)_{1m}$ is smaller than $(\alpha)_{2m}$.

Due to the heat loss from the reaction mixture into the measuring-kettle wall deviate

- The temporal course of the temperature $T_2 = T_1$
- The temporal course of the thermal reaction power q (due to the temperature dependence of the reaction rate)

—with mutual dependence—from the courses under strictly adiabatic conditions. Only if the heat flow out of the reaction mixture into the measuring-kettle wall is marginal compared with the flow out of the liquid of the intermediate thermostat q is almost completely used up to change the temperature of the reaction mass, i.e. the adiabatic condition is virtually fulfilled. Both the recorded course of the temperature $T_2 = T_1$ and the course of the thermal reaction power q correspond in praxis to those in exact adiabatic conditions.

2.1.2.3 Change in Temperature Because of Reaction Within Thermally Open Measuring Kettle (Isoperibolic Condition)

The thermal inertia of the control loop in an isothermal calorimeter prevents the instantaneous compensation of an abruptly changing release of heat, for instance caused at the start of a reaction by injection of the starting reactant into the reaction batch. The equilibrium of regulation cannot be maintained immediately, i.e. in the first moments we have $\Delta T_2(t) \neq \Delta T_{2(\text{set value})} = \Delta T_2(t < 0)$.

In this situation, e.g. heat is briefly more quickly released than heat—which up to now has been relevant for the maintenance of thermal equilibrium—flows simultaneously from the measuring kettle into the intermediate thermostat. But the momentarily changed temperature difference $T_2(t) - T_{2(\text{set value})}$ between the measuring kettle and the intermediate thermostat now causes for some time a varied heat flow in such a way that the temperature returns after some time to the set value (Fig. 2.30), in accordance with the working principle of the control system.

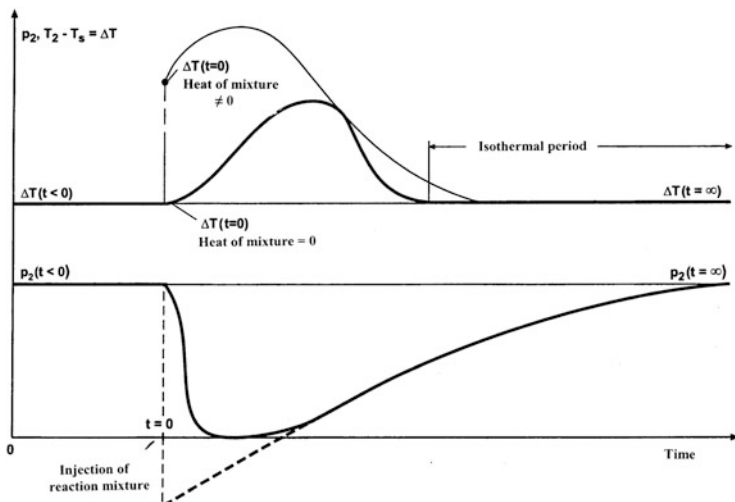


Fig. 2.30 Courses of temperature and heating power p_2 during start of reaction whose power q cannot be immediately compensated due to thermal inertia

When the time interval of the isothermal situation is small compared with the previous non-isothermal phase, for the sake of simplification the measurements are to be performed from the very beginning in non-isothermal conditions, i.e. without heat compensation, hence with the electric heating power turned off, $p_2 = 0$. When the reaction induces only a small change in the heat transfer coefficient, it can be measured without use of the intermediate thermostat (Fig. 2.31).

Simultaneously with the heat release by reaction, a heat outflow or inflow through the measuring-kettle wall takes place; the isoperibolic mode is present. The equation of the thermal reaction power results from the heat balance according to (2.9) with consideration of $p_2 = 0$ and $T_S = \text{const}$ ¹²,

$$(q + q_{Mi}) = (k \cdot F)_2 \cdot [T_2 - T_S] - p_{Si2} + C_2 \cdot d[T_2 - T_S]/dt. \quad (2.16)$$

The temporal course of the function $d(T_2 - T_S)/dt$ is found either by proceeding from one point in time to another using the slopes of tangents at the measured course ($T_2 - T_S$) or by its numeric differentiation. During the reaction changes

¹² q_{Mi} represents the sum of the caloric power of the physical and physicochemical processes during and occasionally after dosing or injection (Chap. 6). The heat of mixture Q_{Mi} is liberated usually instantly during the injection of mixture to start the reaction, with the result that the pre-starting temperature $T_2(t < 0)$ jumps abruptly at $t_0 = 0$ to $T_2(t < 0) + \delta T_0 = T_2(t = 0)$ (Fig. 2.30). $C_2 \cdot \delta T_0$ corresponds to the liberated heat $Q_{Mi} = \int q_{Mi} \cdot dt$. When the mixing process does not occur instantly, a kinetic analysis can only be approximated because $(q + q_{Mi})$ is not easily analysable, i.e. to split into q and q_{Mi} . The course of the rate of heat release q_{Mi} should be determined before the calorikinetical measurements are made, or Q_{Mi} should be compensated as far as possible by the use of an appropriately warmed-up injection mixture to start the reaction kinetic measurements.

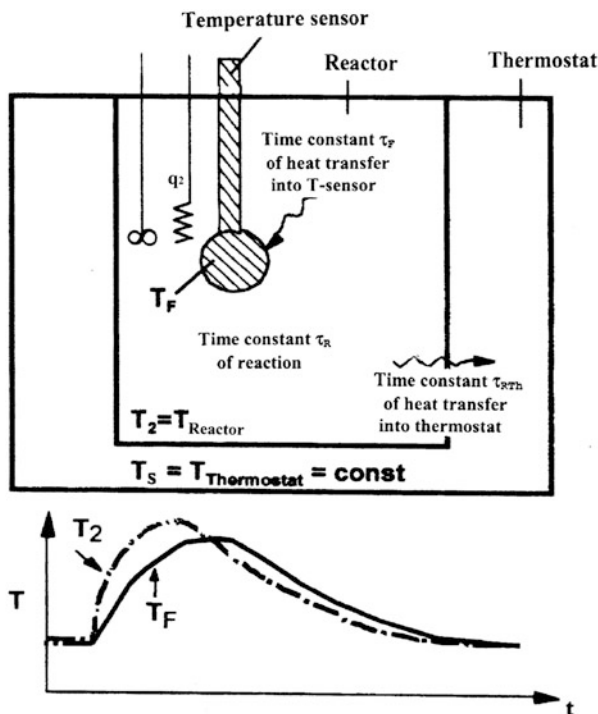


Fig. 2.31 Scheme of isoperibolic measurement equipment. Characteristic course of temperature of an exothermic reaction

occur in the heat capacity C_2 , the heat-transfer coefficient $(k \cdot F)_2$ and the stirring power p_{St2} . The course of their changes for a small degree up to nearly 20 % can be found by approximation as follows:

$(k \cdot F)_2$:

The stirring power prior to start of reaction ($t_0 = 0$) has a constant value of p_{St2} ($t < 0$) and after the reaction has completed ($t > t_E$) a constant value of $p_{St2}(t_E)$. The heat-transfer coefficient $(k \cdot F)_2$ at the start of the reaction and following completion of the reaction¹³ can be determined in such a way that before the start and after the end of the reaction for two switched on heating powers $p_2(1)$ and $p_2(2)$ the corresponding equilibrium temperatures $T_2(1)$ and $T_2(2)$ are recorded and $(k \cdot F)_2$ calculated in accordance with (2.11), i.e. by means of $(k \cdot F)_2 = [p_2(1) - p_2(2)]/[T_2(1) - T_2(2)]$. This results in $(k \cdot F_2)_{t < 0}$ and

¹³ The plot of $\ln T_2$ versus time gives a curve which turns into a straight line. From the transition t_E can be deduced, see e.g. Eqs. (2.25) and (2.26).

For measurements prior to the start of the reaction the measuring kettle must be filled with a solution of all components without the reactant for the start of the reaction, and for measurements after the reaction with the completely reacted mixture, with it filled up each time to the volume equal to that after the start of the reaction.

$(k \cdot F_2)_{t \geq t_E}$. Because of the relatively small amount of injected mixture at the start of the reaction, we have $(k \cdot F_2)_{t=0} \cong (k \cdot F_2)_{t=0}$. Hence, with the first approximation, the course of the heat-transfer coefficient in the time interval of the measurement $0 \leq t \leq t_E$ can be provided by means of $\left[(k \cdot F_2)_{t=t_E} - (k \cdot F_2)_{t=0} \right] / t_E = \beta$ by

$$(kF)_2 \cong (k \cdot F_2)_{t=0} + \beta \cdot t. \quad (2.17)$$

p_{St2} :

According to (2.16) the temperatures prior to the start and after the end of the reaction are $T_{2(t<0)} = T_S + p_{St2(t<0)} / (k \cdot F)_{2(t<0)} = \text{const}_1$ and $T_{2(t \geq t_E)} = T_S + p_{St2(t \geq t_E)} / (k \cdot F)_{2(t \geq t_E)} = \text{const}_2$, in which $p_{St2(t<0)}$ and $p_{St2(t \geq t_E)}$ are determined thanks to the knowledge of $(k \cdot F)_{2(t<0)}$ and $(k \cdot F_2)_{t \geq t_E}$. Because of the small amount of injected mixture at the start of the reaction, we have $p_{St2(t=0)} \cong p_{St2(t<0)}$. Using $\left[p_{St2(t \geq t_E)} - p_{St2(t<0)} \right] / t_E = \alpha$ produces approximately the course of the stirring power in the time period $0 \leq t \leq t_E$

$$p_{St2} \cong p_{St2(t<0)} + \alpha \cdot t. \quad (2.18)$$

C_2 :

The effective heat capacity C_2 of the filling in the measuring kettle is composed of the heat capacity $C_F = c_P \cdot G$ of the reaction mixture and the effective heat capacity C_{Mt} of the measuring kettle itself, i.e. part of measuring-kettle wall sprinkled by the reaction mixture, stirrer, baffle, and temperature sensor,

$$C_2 = C_F + C_{Mt} = c_P \cdot G + C_{Mt}. \quad (2.19)$$

C_2 follows on the basis of

- The time constant $\kappa = C_2 / (k \cdot F)_2$ of the temperature decay following an induced increase in the temperature $\Delta T_2(t)$ of the measuring-kettle filling
- The currently known heat-transfer coefficient $(k \cdot F)_2$.

To produce the curve of temperature decay, the temperature $T_2(t < 0)$ (see second part of footnote 13) prior to the start of the reaction must be increased by switch-on of the heating power p_2 from 0 up to p_2 for a short time, i.e. from its starting value $T_2(t < 0) = T_{20} = T_S + p_{St2} / (k \cdot F)_2$ by ΔT_2 up to $T_2(p_2)$. After the electric heating power p_2 is switched off, the temperature decreases due to (2.16) according to the equation

$$\begin{aligned} T_2(t) - T_{20} &= (T_2(p_2) - T_{20}) \cdot \text{EXP}(-(k \cdot F)_2 / C_2 \cdot t) \\ &= (T_2(p_2) - T_{20}) \cdot \text{EXP}(-t / \kappa). \end{aligned}$$

Plotting the natural logarithm of the temperature decay $[T_2(t) - T_{20}]$ versus time gives a straight line with a slope of $1/\kappa$. From κ we obtain $C_{2(t \leq 0)} = \kappa \cdot (k \cdot F)_2$. The

same procedure with the completely reacted mixture yields $C_{2(t \geq t_E)}$. Using $[C_{2(t \geq t_E)} - C_{2(t \leq 0)}]/t_E = \gamma$, the temporal course of the effective heat capacity C_2 in the time interval $0 < t < t_E$ can be found in a first approximation by

$$C_2 \cong C_{2(t \leq 0)} + \gamma \cdot t. \quad (2.20)$$

In case that C_2 , $(k \cdot F)_2$ and P_{St2} change during the reaction approximately $> 20\%$ the use of the intermediate thermostat is unconditionally necessary to determine the accurate thermal reaction power q . The heat balances of the measuring kettle and the intermediate thermostat are

$$\begin{aligned} C_2 \cdot dT_2/dt &= (q + q_{Mi}) - (k \cdot F)_2 \cdot [T_2 - T_1] + p_{St2}, \\ C_1 \cdot dT_1/dt &= (k \cdot F)_2 \cdot [T_2 - T_1] - (k \cdot F)_1 \cdot [T_1 - T_S] + p_{St1}. \end{aligned}$$

Combining both equations gives

$$(q + q_{Mi}) = C_2 \cdot dT_2/dt + C_1 \cdot dT_1/dt + (k \cdot F)_1 \cdot (T_1 - T_S) - p_{St2} - p_{St1}. \quad (2.21)$$

The heat-transfer coefficient $(k \cdot F)_1$ and the effective heat capacity C_1 of the filling in the intermediate thermostat are constant during the reaction. $(k \cdot F)_1$, C_1 and C_2 can be found using an analogous procedure to that just illustrated. The stirring powers p_{St2} and p_{St1} must be measured (Sect. 6.3).

During very quick reactions the temperature sensor signalizes that the real change in temperature of the filling in the measuring kettle has been temporarily distorted (Fig. 2.31) because of the following circumstances.

The heat-transfer coefficient between the measuring kettle and the thermostat has a defined, finite value in accordance with which the heat transfer between their fillings occurs in a definite way: The process is marked by a characteristic thermal time constant τ_{RTh} . Just so, a definite transfer coefficient exists for the heat flow from the reaction mixture into the temperature sensor, i.e. the heat flow is also marked by a characteristic time constant τ_F .

The change in temperature of the reaction mixture in the measuring kettle is influenced by the heat release to the reaction and the heat flow from the reaction mixture into the thermostat and into the temperature sensor.

Quasi-equality of the temperature T_2 in the measuring kettle and the temperature T_F in the sensor, i.e. its temperature signal, is possible only when the time constant τ_R of heat release by reaction is large compared with the time constant τ_F of the heat flow into the sensor. This is not the case during a very quick reaction, because in that case the actual temperature T_2 in the reaction mixture reaches the sensor with a delayed motion, i.e. the sensor signalizes the temporally distorted T_2 as T_F .

Without restriction of the universal validity, this is illustrated by means of a reaction which runs with a constant rate of heat release ($q = \text{const}$) and without

changes in consistency ($q_{\text{Sl2}}, (k \cdot F)_2 = \text{const}$). With β' as the heat-transfer coefficient from the reaction mixture into the sensor, the rates of change in the actual temperature of the mixture T_2 and in the sensor signal T_F are given by

$$C_F \cdot dT_F/dt = \beta' \cdot (T_2 - T_F) \quad (2.22)$$

and

$$\begin{aligned} C_2 \cdot dT_2/dt &= q + q_{\text{Sl2}} - (k \cdot F)_2 \cdot (T_2 - T_S) - \beta' \cdot (T_2 - T_F) \\ &= q + q_{\text{Sl2}} - (k \cdot F)_2 \cdot (T_2 - T_S) - C_F \cdot dT_F/dt. \end{aligned} \quad (2.23)$$

Because of

- $C_F \ll C_2$, i.e. the sensor represents a negligibly small heat sink, the heat flow from the reaction mixture into the sensor can be neglected
- $q_{\text{Sl2}} = \text{const}$, i.e. $q_{\text{Sl2}} = (k \cdot F)_2 \cdot (T_{20} - T_S)$ respectively $T_{20} = T_S + q_{\text{Sl2}}/(k \cdot F)_2$

follows from (2.23) for the rate of change in the real temperature T_2 of the mixture:

$$C_2 \cdot d(T_2 - T_{20})/dt = q - (k \cdot F)_2 \cdot (T_2 - T_{20}). \quad (2.24)$$

The reaction starts at $t = 0$ and is completed at $t = t_E^{14}$; the solution of Eq. (2.24), i.e. the temporal run of the actual temperature T_2 in the reaction mixture, is

$$\text{for } 0 < t \leq t_E \quad T_2 = a/b \cdot (1 - \text{EXP}[-b \cdot t]) + T_{20} \quad (2.25)$$

and

$$\text{for } t > t_E \quad T_2 = a/b \cdot (1 - \text{EXP}[-b \cdot t_E] \cdot \text{EXP}[-b \cdot (t - t_E)]) + T_{20}, \quad (2.26)$$

with

$$\begin{aligned} a &= q/C_2 = \text{const}, \quad b = (k \cdot F)_2/C_2 = 1/t_{\text{Th}} \\ &\equiv \text{reciprocal time constant of heat-transfer kettle} \rightarrow \text{thermostat.} \end{aligned}$$

Combining (2.25) respectively (2.26) with (2.22) and solving the equations gives T_F , i.e. the course of temperature T_2 in the reaction mixture over time signaled by the temperature sensor,

$$T_F = \kappa \cdot \{\text{EXP}[-\beta \cdot t] - \text{EXP}[-b \cdot t]\} + \gamma \cdot \{1 - \text{EXP}[-\beta \cdot t]\} + T_{20} \quad \text{for } 0 < t \leq t_E$$

¹⁴ See Sect. 4.2.1.1.1.1.

and

$$T_F = \kappa \cdot \{1 - \text{EXP}[-b \cdot t_E] \cdot \text{EXP}[-b \cdot (t - t_E)]\} + (\kappa - \gamma) \cdot \text{EXP}[-\beta \cdot t] \\ + (\kappa - \gamma) \cdot \text{EXP}[-\beta \cdot (t - t_E)] + T_{20} \quad \text{for } t > t_E,$$

with

$$\beta = \beta' / C_F = 1 / \tau_F$$

≡ reciprocal time constant of heat transfer from reaction mixture into sensor,

$$\kappa = a \cdot \beta / b / (\beta - b) \text{ and } \gamma = a / b.$$

Figure 2.32 illustrates the typical temporal course of the signal difference $T_{F(\text{during reaction})} - T_{F(\text{prior to start of reaction})} = T_F - T_{F0} (\equiv T_{20})$ depending on the time constant τ_F of the temperature sensor.

Summary

For kinetic analysis of recorded temperature curves of very quick reactions, the thermal inertia of the sensor must be taken into consideration, i.e. to work out the temporal course of the actual temperature T_2 at the location of measurement the distortion of the recorded temporal course T_F must be antidistorted.

To be precise, the relation $(k \cdot F)_2 \cdot [T_2 - T_S]$ for the description of the heat flow from the measuring kettle is useable only under steady conditions, i.e. for a steady temperature distribution in the wall of the measuring kettle, hence for $T_2 = \text{constant}$. The relation is valid with good approximation just about when T_2 changes in a quasi-static way. For an extremely quick release of heat by the reaction, which causes an extremely quick change in the temperature of the reaction mixture, the adjustment of the temperature distribution in the wall follows in a delayed manner resulting from the wall's ability to store heat. In that case, for the

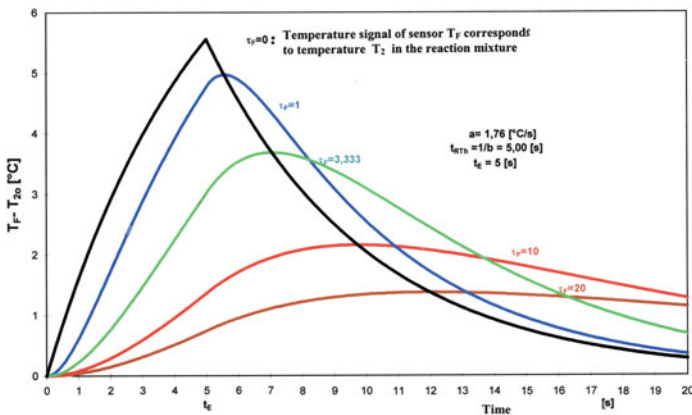


Fig. 2.32 Signal difference $T_F - T_{F,0} (\equiv T_{20})$ of sensor temperature for different time constant τ_F of sensor during a constant thermal reaction power, end of heat release at time point t_E

change in the heat flow one must take into consideration the dynamics of the temperature distribution, i.e. the Fourier equation of heat conduction

$$\delta T / \delta t = a \cdot \nabla T$$

with

$a \equiv$ temperature coefficient of the wall, $\nabla \equiv$ Nabla operator.

2.2 Device for Continuous Reaction

2.2.1 Isothermal Flow Calorimeter TKR

The design of the calorimeter for a continuous, isothermal reaction (Fig. 2.33) corresponds essentially to the calorimeter for discontinuous reactions. A flow measuring kettle,¹⁵ provided with thermally insulated inflow and outflow pipes for the reaction mixture, is inserted in an intermediate thermostat, which in turn is immersed in a base thermostat. The thermostats are filled with thermostat liquid. Both the flow measuring kettle and the intermediate thermostat are provided with a stirrer, baffles, an electric heater and a temperature sensor. The temperature T_S of the base thermostat is maintained at a chosen set value. The temperature differences between the measuring kettle and the intermediate thermostat ΔT_2 and between the intermediate thermostat and the base thermostat ΔT_1 are maintained at the chosen set values by control of the corresponding electric heating powers p_2 and p_1 . When the control is in equilibrium the base thermostat displays the lowest temperature T_S , the intermediate thermostat a medium temperature $T_S + \Delta T_1$ and the flow measuring kettle the highest temperature $T_S + \Delta T_1 + \Delta T_2$. Heat flows from the measuring kettle to the intermediate thermostat and from there to the base thermostat. The single mixtures of reactant are continuously transported at a constant rate in separate pipes. By regulation of a heater enclosing the pipes, the fluid mixtures are brought to the correct temperature, $T_S + \Delta T_1 + \Delta T_2$, just before entering the flow measuring kettle (control system analogous to that in Fig. 2.37). In that way

¹⁵ Using a conventional stirrer, the flow takes place continuously but weakly pulsating as a result of the following causes:

- (a) A low-pressure supply of inert gas on the filling of kettle
- (b) A lengthened outflow pipe sticking through the cover of the measuring kettle by approximately 1 cm.

For a flooded flow measuring kettle a circular pendulum mixer is recommended for use instead of a conventional stirrer (Sect. 2.5, Fig. 2.39).

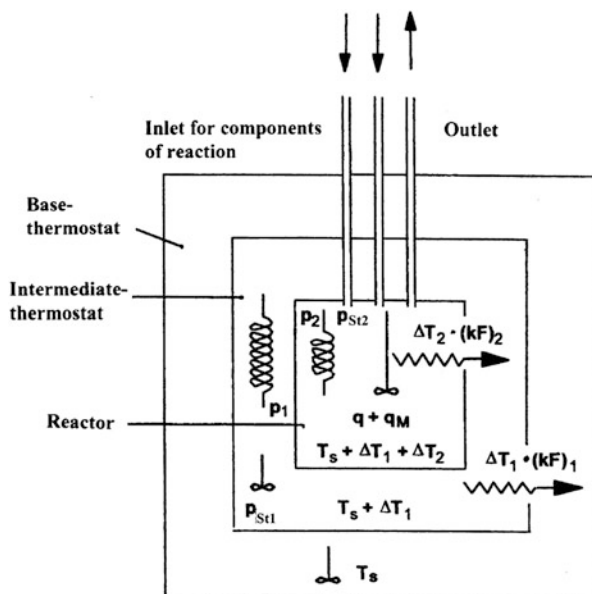


Fig. 2.33 Principle of flow calorimeter TKR

any pre-reaction within the inlet flow is avoided and in addition any heat effect within the measuring kettle based on a temperature difference between inflow and filling is excluded.

The heat $(kF)_2 \cdot \Delta T_2$ flows from the measuring kettle into the intermediate thermostat owing to the temperature difference ΔT_2 , and the heat $(k \cdot F)_1 \cdot \Delta T_1$ flows from the intermediate thermostat to the base thermostat owing to the temperature difference ΔT_1 . q_{Mi} is the rate of physicochemical heat release by mixing, and following the balance of heat powers in equilibrium of control the following conditions apply:¹⁶

(a) Measuring kettle

$$\begin{array}{rcl} \text{Sum of all heat powers} & = & \text{heat flow out of} \\ \text{in measuring kettle} & & \text{measuring kettle} \\ q + q_{Mi} + p_2 + p_{St2} & = & (k \cdot F)_2 \cdot \Delta T_2 \end{array}$$

(b) Intermediate thermostat

¹⁶ If the reactant solutions being dosed are not brought to the temperature of the measuring kettle, then q_{Mi} consists of the rates of heat release due to both physical dosing (physical heat $g \cdot c_p \cdot (T_{\text{Laboratory}} - T_2)$) and physicochemical mixing (physicochemical heat).

$$\begin{array}{lcl}
 \text{Sum of all heat powers} & = & \text{heat flow out of} \\
 \text{in intermediate thermostat} & = & \text{intermediate thermostat} \\
 (k \cdot F)_2 \cdot \Delta T_2 + p_1 + p_{St1} & = & (k \cdot F)_1 \cdot \Delta T_1.
 \end{array}$$

This results in

$$q + q_{Mi} = [(k \cdot F)_1 \cdot \Delta T_1 - p_{St1}] - [p_1 + p_2 + p_{St2}]$$

The heat-transfer coefficient $(k \cdot F)_1$ and the stirring power p_{St1} of the intermediate thermostat are not influenced by the reaction within the measuring kettle; they are to a certain extent apparatus constants. ΔT_1 remains constant because p_1 changes, regulated by a control procedure, opposite and equal to the change in the heat flow $(k \cdot F)_2 \cdot \Delta T_2$ from the measuring kettle into the intermediate thermostat.

Hence

$$\begin{aligned}
 q + q_{Mi} &= \text{const} - (p_1 + p_2 + p_{St2}) \\
 &\quad \text{with (2.3)} \\
 &= \underset{\text{prior to start}}{(p_1 + p_2 + p_{M2})} - \underset{\text{during continuous dosing}}{(p_1 + p_2 + p_{M2})} \\
 &\quad \text{of dosing at } t_{D0s} \qquad \qquad \text{dosing}
 \end{aligned}$$

or

$$q + q_{Mi} = p_0 - p \quad (2.27)$$

with

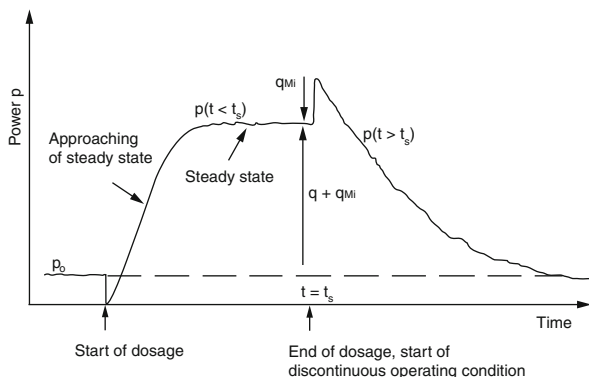
$$p_0 = (p_1 + p_2 + p_{M2})_{t < t_{D0s}} \quad \text{and} \quad p = (p_1 + p_2 + p_{M2}).$$

The sum of the rates of heat release by reaction q and by mixing q_{Mi} in the measuring kettle is determined by the subtraction of the sum of the electric heating powers in the measuring kettle and in the intermediate thermostat as well as the motor power of the measuring kettle during continuous dosing from the sum of these powers prior to the start of continuous dosing (Fig. 2.34).

q_{Mi} is found in the following way. When the dosing is stopped at time t_s , the continuous mode of operation changes abruptly to the discontinuous mode. Since no mixing occurs now, no heat from the mixture is released, i.e. at time t_s the heating electric power in the measuring kettle changes abruptly so that it is opposite and equal to the rate of heat release by mixing q_{Mi} . Its quantity is a result of the subtraction of the sum of the thermal powers of the continuous reaction $p(t < t_s)_{\text{CONT}}$ from the sum of the thermal powers of the discontinuous reaction at time t_s $p(t = t_s)_{\text{DISC}}$. Hence,

$$q_{Mi} = p(t_s)_{\text{DISC}} - p(t < t_s)_{\text{CONT}}.$$

Fig. 2.34 Determination of thermal reaction power q and thermal mixing power q_{Mi} of an isothermal, continuous chemical conversion



2.3 Device with Reflux Condenser for Isothermal, Discontinuous Reaction (Isothermal Condition)

A reflux condenser (condenser-kettle embedded in an intermediate thermostat) within a base thermostat is combined via a thermally insulated pipe with the measuring kettle of a calorimeter for a discontinuous reaction (Fig. 2.35). Provided that in the measuring kettle evaporable components are generated by a not-too-fast chemical conversion, between the measuring kettle and the condenser there exists with regard to the evaporable components a quasi-continual equilibrium.¹⁷

The following heat balances hold

$$\text{Measuring kettle} \quad q + q_E + p_2 + p_{St2} = (k \cdot F)_2 \cdot \Delta T_2 \quad (2.28)$$

$$\text{Intermediate thermostat} \quad (k \cdot F)_2 \cdot \Delta T_2 + p_1 + p_{St1} = (k \cdot F)_1 \cdot \Delta T_1 \quad (2.29)$$

$$\text{Condenser/intermediate thermostat} \quad q_C + p_3 + p_{St3} = (k \cdot F)_3 \cdot \Delta T_3 \quad (2.30)$$

$$q_C = -q_E \quad (2.31)$$

The addition of (2.28), (2.29), (2.30), and incorporating (2.31), results in

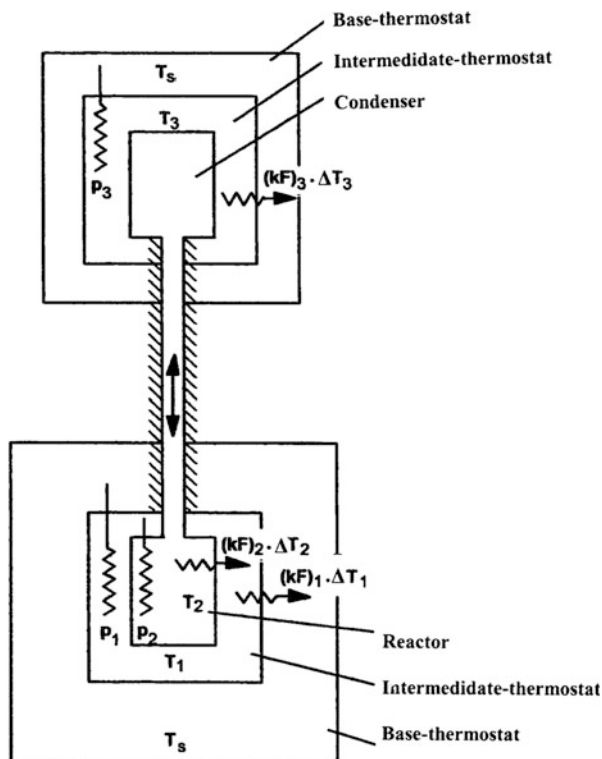
$$q = \{(k \cdot F)_1 \cdot \Delta T_1 + (k \cdot F)_3 \cdot \Delta T_3 - p_{St1} - p_{St3}\} - [p_1 + p_2 + p_3 + p_{St2}]$$

The terms in the first brackets are not influenced by the chemical conversion in the measuring kettle, that is to say, they are apparatus constants. Hence, taking into account (2.3) leads to

$$q = \text{const} - [p_1 + p_2 + p_3 + p_{M2}]$$

¹⁷ During quasi-continual equilibrium, the absolute amounts of the caloric evaporation power q_E in the measuring kettle (temperature T_2) corresponds to the thermal condensation power q_C in the condenser kettle (temperature T_3), that is, the sum of the powers cooling the vapour from temperature T_2 down to T_3 and subsequent condensation with temperature T_3 .

Fig. 2.35 Compact calorimeter and reflux condenser for discontinuous, isothermal reaction



or

$$q = p_0 - [p_1 + p_2 + p_3 + p_{M2}] \quad (2.32)$$

with

$$p_0 = [p_1 + p_2 + p_3 + p_{M2}]_{t < 0} = \text{const.}$$

2.4 Device with Reflux Condenser for Isothermal, Discontinuous Reaction (Boiling Condition)

While boiling a component of the reaction mixture (as a rule, the solvent) the temperature does not change despite heat release from the reaction. As is well known, the temperature remains unchanged as a result of more or less boiling. Consequently, it is not possible to measure the nascent heat directly, i.e. by changes in the compensating power of the electric heater¹⁸ in the measuring kettle.

¹⁸The prerequisite of such a measuring mode is the initiation of a change in temperature.

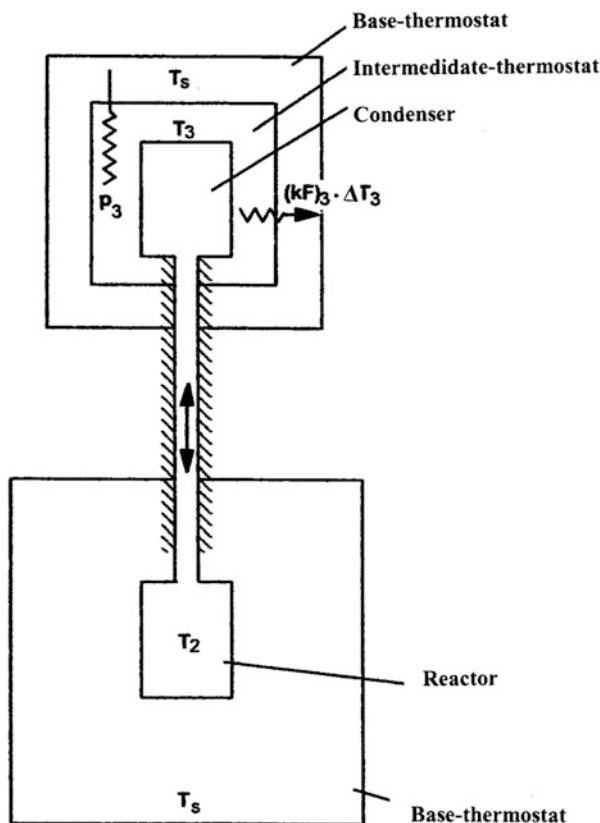


Fig. 2.36 Schematic representation of measuring apparatus for reaction with reflux of a boiling component of reaction mixture

However, under certain conditions, this measurement can be carried out indirectly by measuring the rate of heat release from the condensation of vapour in the condenser, which is recorded by the condenser/ intermediate thermostat (Fig. 2.36). The conditions for equality of the thermal reaction power and the rate of heat release by condensation are as follows:

- The time constant of the reaction must be large compared to the time constant of the heat transfer from the condenser to the condenser/intermediate thermostat;
- The time constant of the reaction must be large compared to the time constant for the adjustment of the thermal equilibrium in the coupled measuring kettle/ condenser system. In this way, the power compensation in the condenser/ intermediate thermostat occurs on the basis of quasi-continual thermal equilibrium. In that case, the amount of substance leaving the measuring kettle as vapour in accordance with the released heat of the reaction per unit of time corresponds to the amount of condensate in the condenser per unit of time.

- The boiling point must be practically unaffected by the change in composition of the reaction mixture caused by the chemical conversion. Otherwise, the reaction heat would not be used solely for boiling but also to change the temperature within the reaction mixture, i.e. the recorded rate of heat release by condensation would differ from the exact rate of heat release by the reaction. Therefore, a reaction mixture which is not too concentrated should be used.

If the boiling point changes very slowly or only slightly, in practice, the absolute rates of heat release by the reaction and by condensation are equal.

2.5 Online Calorimeter (Sensor)

A prerequisite for the optimum, model-supported control of a chemical process is a comprehensive knowledge of the state of the reaction mixture at all times during the process. As a rule, only a few of the variables representing the state can be directly measured.

Modern system theory [43] offers mathematical methods, which—on the basis of these variables together with thermodynamics, chemical kinetics and a reactor model—enable the estimation of additional state variables (e.g. Kalman–Bucy filter, Luenberger observer). The more accurate the process model which is assumed as a base, and the more numerous and meaningful the starting measured variables are, the greater is the number and accuracy of the additional, estimated state variables. Consequently, variables which are usually available (e.g. temperature, pressure) should, if possible, be supplemented by further variables which are more meaningful.

Usually, chemical conversion takes place by parallel or consecutive, elementary reactions¹⁹ accompanied by a release of heat. The amount of heat released during an elementary reaction is directly proportional to the degree of conversion, and the rate of its release is directly proportional to the rate of reaction. The proportionality factor is a characteristic quantity for each elementary reaction, the enthalpy of reaction. The recorded thermal reaction power is the superposition of the specific thermal powers of those elementary reactions. The same holds for melting, condensing and mixing processes, which are often coupled with the chemical process itself. Therefore, thermal reaction power is both a meaningful and always accessible quantity to be measured for the model-supported determination of the state of a sought chemical process.

The rate of heat production in a tank reactor is generally determined by the thermal balance of the system. Experience has shown that, when drawing up a thermal balance for the reactor itself and its cooling jacket, both the stirrer power

¹⁹ See Sect. 4.1.

and the heat loss rates due to convection and radiation cannot be accounted for accurately.

To find the thermal reaction power in an ideally mixed tank reactor, it is recommended to use an appropriately designed flow calorimeter placed as a sensor in a short, thermally insulated by-pass. To equalize the specific rates of heat production in the tank reactor and sensor, the latter must be designed in such a way that both the composition and the temperature of the reaction mixture in the sensor correspond to those in the tank reactor.

2.5.1 Working Mode and Design

The following measurement setup is proposed for the online determination of the thermal reaction power (Figs. 2.37 and 2.38).

The setup is largely comprised of a continuous-flow, compensating calorimeter which consists of a flooded measuring kettle housed in an intermediate thermostat, which is enveloped by a base thermostat. The base thermostat and the intermediate thermostat are filled with a thermostat liquid. The base thermostat, the intermediate thermostat and the flow measuring kettle are each provided with a mixer, baffles and temperature sensors. The mixer of the base and intermediate thermostats are classic stirrers, and the mixer in the flooded measuring kettle is a circular pendulum mixer. Its bearing is protected from contamination with the reaction mixture by corrugated metal bellows, which is joined to the cover of the shaft to form a seal.

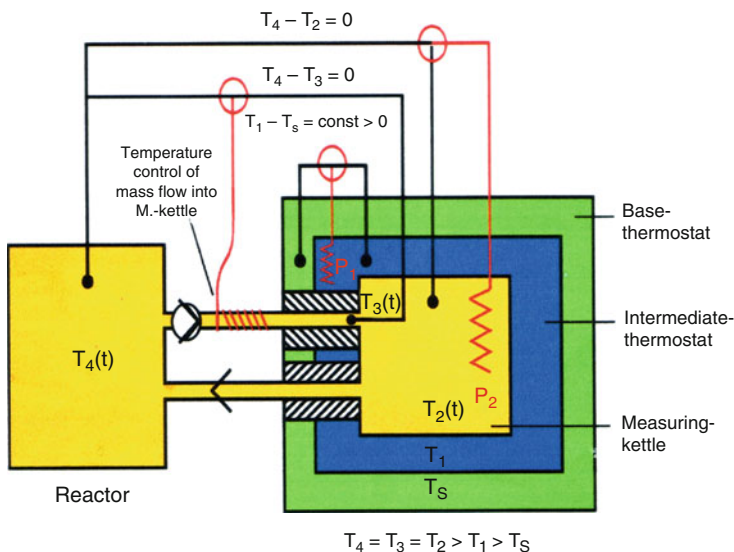


Fig. 2.37 Scheme of online calorimeter (calorimeter sensor)

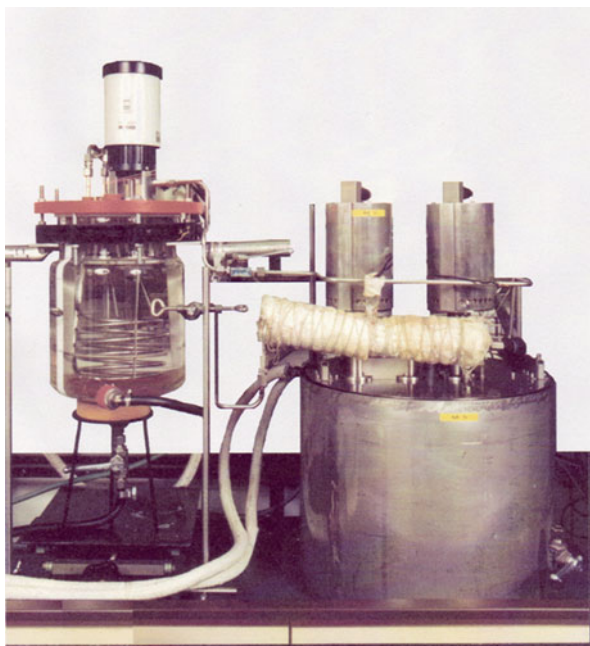


Fig. 2.38 Direct view of online calorimeter (*right*), coupled with tank reactor (*left*)

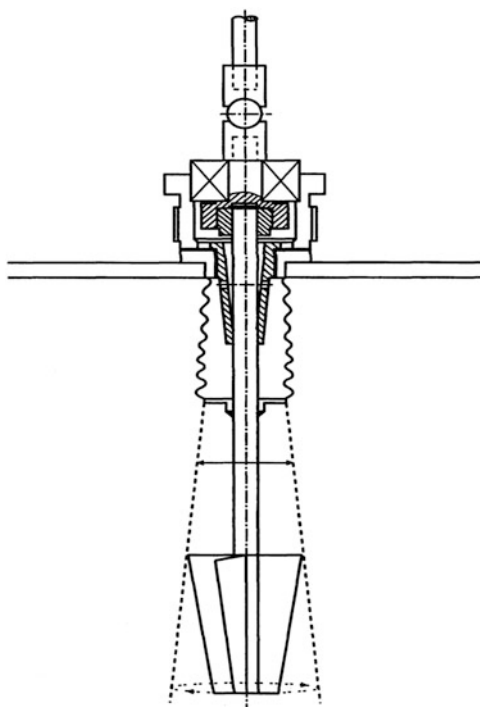


Fig. 2.39 Circular pendulum mixer; *top*: bearing of mixer, *bottom*: design of mixer

The mixer has the form of a three-dimensional, conically formed star with three jags (Fig. 2.39). The rotational velocity of the stirrer in the base and intermediate thermostats and the frequency of the circular pendulum in the measuring kettle are kept constant by controlled electric motors without armature retroaction. The measuring kettle and the intermediate thermostat are additionally provided with a corrosion-resistant special electrical heater (lead, heating section, lead with a resistance ratio of 1/400/1; Philips). DC power supplies are used, and the heating power is given by the product of the voltage and intensity of the current. The reaction mixture flows continuously from the tank reactor via a temperature-controlled pipeline into the ideally mixed measuring kettle and from there back into the reactor. The temperature of the base thermostat T_S , which is chosen to be substantially lower than the temperature T_4 of the tank reactor, has a constant value. The temperature difference between the intermediate thermostat and the base thermostat ($T_1 - T_S$) is measured by temperature sensors and fed to a control unit, which maintains a constant set value by control of the heating power p_1 in the intermediate thermostat. The value of the difference in set temperatures is chosen such that the temperature T_1 in the intermediate thermostat is lower than the temperature T_2 in the measuring kettle.

The temperature difference between the measuring kettle and the tank reactor ($T_2 - T_4$) is also measured and fed to a control unit, which by control of the heating power p_2 in the measuring kettle ensures that the temperature of the measuring kettle T_2 corresponds to the temperature T_4 of the tank reactor. The difference in temperature between the reactor and at the inlet to the measuring kettle ($T_4 - T_3$) is also fed to a control unit, which by regulation of an electric heating envelope of the pipe ensures that the temperature T_3 of the flowing reaction mass at the inlet into the measuring kettle corresponds to the temperature in the reactor T_4 and, thus, to the temperature in the measuring kettle T_2 . The temperature drops in a stepwise manner from the measuring kettle via the intermediate thermostat to the base thermostat: $T_4 = T_3 = T_2 > T_1 > T_S$.

The heat flow from the measuring kettle into the intermediate thermostat changes generally with time due to

- Temperature fluctuation $T_4 (= T_3 = T_2)$ of the tank reactor
- Change in the heat-transfer coefficient (measuring kettle \rightarrow intermediate thermostat) caused by the inevitable change in the physical properties of the content in the measuring kettle according to chemical reaction or, often, because of an accumulation of material on the wall of the measuring kettle (fouling).

Within the intermediate thermostat a change in the heat inflow is compensated for by an opposite and equal change in the electric heating power p_1 , so that the set temperature T_1 remains constant, i.e. a constant heat flow from the intermediate thermostat into the base thermostat is maintained. Provided the residence time in the feed pipe can be neglected, the composition of the reaction mixture in the measuring kettle corresponds to that in the tank reactor. This holds for a discontinuous reaction and with a sufficient degree for semi-continuous and continuous reactions as long as the mean residence time of the reaction mixture in the

measuring kettle is small in comparison to the time constant of the reaction. Consequently, both the difference in the flow of enthalpy into and out of the measuring kettle and the heat from mixing by the entry of the reaction mixture into the measuring kettle are negligible.²⁰

Therefore, the heat balance of the measuring kettle reads

$$C_2 \cdot dT_2/dt = q + p_{S12} + p_2 - (k \cdot F)_2 \cdot [T_2 - T_1]. \quad (2.33)$$

The heat balance of the intermediate thermostat in control equilibrium is given by

$$0 = (k \cdot F)_2(T_1) \cdot [T_2 - T_1] + p_{S11} + p_1 - (k \cdot F)_1 \cdot [T_1 - T_S].$$

Combining both equations yields the following relationship for the caloric reaction power q :

$$q = \{ (k \cdot F)_1 \cdot [T_1 - T_S] - p_{S11} \} - \{ p_1 + p_2 + p_{S12} \} + C_2 \cdot dT_2/dt.$$

The temperature T_1 of the intermediate thermostat, the temperature T_S of the base thermostat, the rotational velocity of the stirrer and the viscosity of the liquid in the intermediate thermostat, i.e. the stirring power p_{S11} and the heat-transfer coefficient $(k \cdot F)_1$ do not change. Therefore, the expression in parentheses on the left is constant, allowing for a simplification of the equation:

²⁰ This is illustrated, without restriction of the universal validity, by a monomolecular reaction of order 1, see 4.2.1.1.1.3

- Discontinuous reaction in tank reactor:

$$c_{\text{Reactor}} = c_{R0} \cdot \text{EXP}(-kt), \quad c_{\text{Mkettle}} = c_{R0} \cdot \text{EXP}(-kt) \\ c_R = c_{\text{Mk}}.$$

- Semi-continuous reaction in tank reactor:

when $c_{R0} = 0$ it follows that $c_R = g/M/V/k \cdot [1 - \text{EXP}(-kt)]$,

$$c_{\text{Mk}} = g/M/V/k \cdot [1/(1 + k\tau) - \text{EXP}(-kt) + \{k\tau/(1 + k\tau)\} \text{EXP}(-(1/\tau + k))];$$

i.e. when $k\tau < 0.01$, it follows with an error of $<1\%$ that

$$c_R = c_{\text{Mk}}.$$

- Continuous reaction in tank reactor:

$$c_R = c_{R\text{stat}}, \quad c_{\text{Mk}} = c_{R\text{stat}}/(1 + k\tau);$$

i.e. when $k\tau < 0.01$, it follows with an error of $<1\%$ that

$$c_R = c_{\text{Mk}}.$$

$$q = \text{const}'(T_1, T_S) - \{p_1 + p_2 + p_{\text{St2}}\} + C_2 \cdot dT_2/dt.$$

Since the power loss in the bearing of the circular pendulum mixer in the measuring kettle is guaranteed to remain unchanged during measurement and electric motors without armature retroaction, i.e. DC disk-armature motors are used, relationship (2.7) holds between the total motor power p_{M2} and the mixing power p_{St2} . Therefore, the following expression results:

$$q = \text{const}(T_1, T_S, N_2) - p + C_2 \cdot dT_2/dt \quad (2.34)$$

with

$$p = p_1 + p_2 + p_{\text{M2}}.$$

$\text{const}(T_1, T_S, N_2)$ is in a certain way an apparatus constant, which can be determined for chosen values of T_1 , T_S and N_2 as follows. Before connection of the measuring kettle [which is filled with a reactionless ($q = 0$) fluid] with the tank reactor, the controlling unit of p_2 is switched off, and instead, the heating power p_2 is set at a constant value. After temperature equilibrium ($dT_2/dt = 0$) is achieved, the sum of the powers p_1 , p_2 and p_{M2} corresponds to the desired constant, i.e.

$$p_1 + p_2 + p_{\text{M2}} = p = \text{const}(T_1, T_S, N_2).$$

The value of $\text{const}(T_1, T_S, N_2)$ remains unchanged as long as

- The thermostat liquid
- The contents of the liquid in the base and intermediate thermostats
- The speed of the mixers in the base and intermediate thermostats as well as the measuring kettle, and
- The temperatures T_S and T_1 of the base and intermediate thermostats remain unchanged.

The effective heat capacity C_2 of the content in the flow measuring kettle comprises the heat capacity C_F of the reaction mixture and the effective heat capacity C_{Mt} of the mixer, baffles, temperature sensor, wall of the measuring kettle, and so forth:

$$C_2 = C_F + C_{\text{Mt}}.$$

C_{Mt} is, in contrast to C_F , an apparatus constant²¹ which can be elaborated by means of the heat capacity C_F of any liquid used to fill up the measuring kettle and the associated effective heat capacity C_2 as follows:

²¹ C_{Mt} is relatively independent of temperature, more or less. C_F , however, varies with changes in temperature. However, because of the generally moderate temperature fluctuations in the tank reactor, its influence can by first approximation also be neglected.

- C_F is given from the volume V of the measuring kettle, the known specific heat c_p of a chosen filling and its density ρ according to $C_F = V \cdot \rho \cdot c_p = G \cdot c_p$.
- The associated effective heat capacity C_2 results from the time constant $\kappa = C_2 / (k \cdot F)_2$ of a temperature decay $T_2 \rightarrow T_1$ over time of the flooded measuring kettle and its heat-transfer coefficient $(k \cdot F)_2$. The determination of $(k \cdot F)_2$ and κ takes place according to (2.33) as follows:

The heating power p_2 in the measuring kettle is switched off; the slope of the logarithmic plot of the temporal decay of the temperature difference $T_2(t) - (T_1 + p_{St2} / (k \cdot F)_2)$ corresponds to the time constant κ and C_2 can be calculated by $C_2 = \kappa \cdot (k \cdot F)_2$.

At the beginning of the decrease it progresses as $T_2(t) - (T_1 + p_{St2} / (k \cdot F)_2) \cong T_2(t) - T_1$ due to $p_{St2} / (k \cdot F)_2 \ll T_1$.

For two constant heating powers $p_2(1)$ and $p_2(2)$ the temperatures $T_2(1)$ and $T_2(2)$ during control equilibrium should be registered.

This yields the heat-transfer coefficient according to (2.33)

$$(k \cdot F)_2 = [p_2(1) - p_2(2)] / [T_2(1) - T_2(2)].$$

In the case of a discontinuous, semi-continuous or continuous reaction in the tank reactor, the satisfactory values of the heat capacity C_F and mass G in the filling of the connected flooded measuring kettle are to be found by means of the weighted-average method.²²

²² The batch of the tank reactor is as follows:

Substance 1 with mass m_1 , density ρ_1 , specific heat c_{p1}
 Substance 2 with mass m_2 , density ρ_2 , specific heat c_{p2}
 Substance n with mass m_n , density ρ_n , specific heat c_{pn} .

The dosage with constant mass rates g_i is as follows:

Substance 3 with rate g_3 , density ρ_3 , specific heat c_{p3}
 Substance m with rate g_m , density ρ_m , specific heat c_{pm} .

The weighted average method yields the following results (neglecting the effect of changes in individual substances due to the reaction):

Average specific heat $c_p(t)$ of reaction mass:

$$c_p(t) = \frac{m_1 \cdot c_{p1} + m_2 \cdot c_{p2} + m_n \cdot c_{pn} + \dots + g_3 \cdot t \cdot c_{p3} + \dots + g_m \cdot t \cdot c_{pm} + \dots}{m_1 + m_2 + m_n + \dots + g_3 \cdot t + \dots + g_m \cdot t + \dots}$$

Average density $\rho(t)$ of reaction mass:

$$\rho(t)^{-1} = \frac{m_1 / \rho_1 + m_2 / \rho_2 + m_n / \rho_n + \dots + g_3 \cdot t / \rho_3 + \dots + g_m \cdot t / \rho_m + \dots}{m_1 / m_2 + m_n + \dots + g_3 \cdot t + \dots + g_m \cdot t + \dots}$$

$$C_F = \rho(t) \cdot V \cdot c_p(t) = C_p(t) \cdot G(t).$$

Consequently, in Eq. (2.34) determining the rate of heat release q in the measuring kettle, $\text{const}(T_1, T_s, N_2)$ and the effective heat capacity C_2 are known. $p(t)$ and $T_2(t)$ are measured online. $dT_2(t)/dt$ can be determined using a numeric online differentiation of $T_2(t)$. Experience has shown that the result of such a numeric operation is usually unsatisfactory because of unavoidable fluctuations in the measured course of $T_2(t)$. A determination of the thermal reaction power q by means of numeric differentiation of T_2 can be avoided using the stochastic estimate algorithm of the Kalman–Bucy filter [6].

The quotient of the determined thermal reaction power q and the reaction mass G in the measuring kettle yields the desired specific rate q_s .

The most important prerequisite for using the online calorimeter to yield meaningful results is that the content of the tank reactor should be uniformly mixed at a uniform temperature. This applies to all types of sensors, which are designed to display a measured value which is representative of the entire tank reactor. With reaction mixtures which are homogenous or almost homogenous the measuring system can be used without problems. The only condition is that the reaction mixture must not be too viscous ($\nu < 500$ cSt); otherwise, temperature streaks would result, which would interfere with the controlling mechanism. With heterogeneous reaction mixtures, in which mass transfer between phases usually affects the rate of chemical conversion, the stirring characteristics of the tank reactor should be adjusted in the measuring kettle based on the rules of scale transfer in stirring systems.

2.5.2 Specification

The essential features of the online calorimeter are as follows:

- | | |
|--|---|
| • Material of measuring kettle, mixer, surface of heater, etc. | Hastelloy C4 |
| • Volume of flow measuring kettle | 1,500 ml |
| • Temperature range (thermostat liquid: silicon fluid) essentially the temperature range is determined by the boiling point respectively freezing point of the thermostat liquid | $-20\text{ }^{\circ}\text{C} \rightarrow 250\text{ }^{\circ}\text{C}$ |
| • Maximum frequency of circular pendulum mixer | 40 Hz |
| • PID control system | |
| • Maximum electric heating power | 500 W |
| • Resolution | $< 2\text{ W}$ |
| • Maximum operating pressure | 32 bar |
| • Time constant of reaction | $> 1\text{ h}$ |
| • Kinematic viscosity | $\nu < 500\text{ cSt}$ |

The endo- and exothermic chemical and physicochemical processes of the following phase systems can be investigated:

- Liquid; liquid/liquid, liquid/solid.
- Sufficiently accurate: liquid/gas; liquid/solid/gas, in all cases: liquid as main constituent.

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