Chapter 7
The Heat Flow Calorimeter by Regenass

Just before publication of the described compact TKR calorimeter the so-called heat-flow calorimeter by Regenass was released. Measurement of the thermal reaction power under thermal conditions is carried out by that calorimeter, similarly by remodels [40, 41, 46] and knock-offs as follows.

A hollow jacket encloses both the bottom and about two-thirds of the side wall of the measuring kettle[1] (Fig. 7.1). The liquid of a quickly controllable thermostat flows turbulently through the jacket. The upper part of the measuring kettle, which is not surrounded by the hollow jacket, can either be exposed to the temperature in the laboratory or surrounded by an insulating material. In addition, the cover can be brought to the temperature of the filling within the accuracy range of the temperature sensor. Nevertheless, a relevant zone between the cover and the side is always exposed to the temperature in the laboratory.

The interior of the measuring kettle is equipped with a stirrer coupled and driven by an electric motor usually used in a laboratory (sleeve bearing), some baffles and a temperature sensor. An electric heater is installed for the purpose of calibration. The temperature is measured in the flowing fluid at the outlet of the hollow jacket. The temperature of the measuring kettle is routed to a control unit which regulates the quickly operating thermostat such that the set temperature of the measuring kettle, despite heat release, is maintained constant by an appropriately changed temperature of the fluid passing turbulently through the jacket, i.e. by a change in the heat flow into or out of the measuring kettle.

At the start of an exothermic process, the temperature of the jacket decreases; at the start of an endothermic process, it increases. In the case of a chemical reaction, the change in the heat flow[2] into or out of the jacket is, however, only a gross

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[1] The set up is made of glass.

[2] Determined by multiplication of change in the working average temperature of fluid in jacket and heat transfer coefficient ($k \cdot F$).

W. Litz, *Bench Scale Calorimetry in Chemical Reaction Kinetics*,
DOI 10.1007/978-3-319-12532-9_7

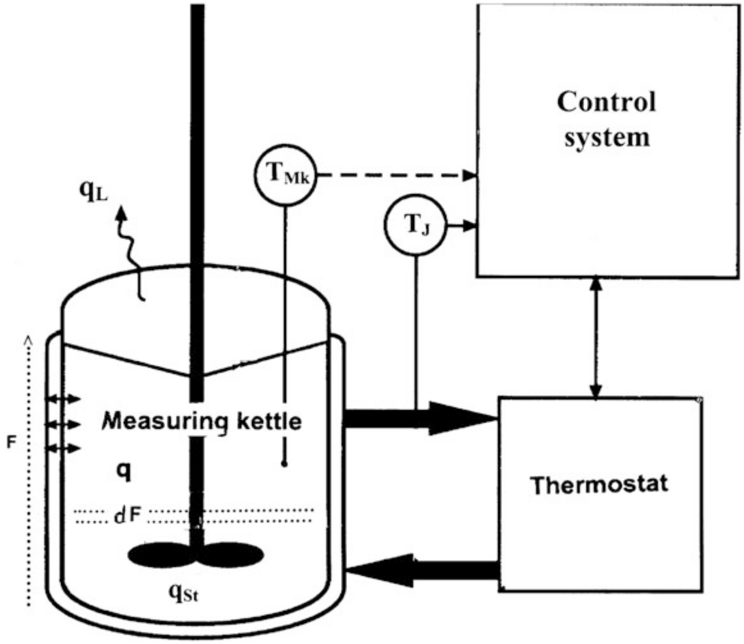

Fig. 7.1 Flowchart of so-called heat-flow calorimeter by Regenass

measure of the thermal reaction power. To determine the exact thermal reaction power q, it should be evaluated as follows. Using

$(k{\cdot}F)$: Heat-transfer coefficient: measuring kettle↔jacket
p_{St}: Stirring power within measuring kettle
p_L: Heat loss to surroundings
q: Thermal reaction power
T_{Mk}: Set temperature within measuring kettle
F: Heat-exchange area
$T_J[F]$: Temperature in the turbulently flowing fluid in jacket at the value of F behind the outlet
T_J: Temperature of the outflow of jacket
$\overline{T}_J$: Balanced average temperature of turbulent flow through the jacket
ΔT: Temperature difference $T_{Mk} - T_J$

the heat balance at controlled equilibrium reads as follows:

	Sum of all thermal powers in measuring kettle	Heat flow between measuring kettle and fluid of jacket
Prior to start of reaction: $t < 0$	$p_{\mathrm{L0}} + p_{\mathrm{St0}}$	$= \int_{F=0 \to F\mathrm{Max}} k \cdot \left(T_{\mathrm{Mk}} - T_{\mathrm{j}}[F]\right) \cdot \mathrm{d}F = (k \cdot F)_0 \cdot \left(T_{\mathrm{Mk}} - \overline{T}_{\mathrm{J0}}\right)$ (7.1)
After start of reaction: $t \geq 0$	$q + p_{\mathrm{L}} + p_{\mathrm{St}}$	$= \int_{F=0 \to F\mathrm{Max}} \left\{k \cdot \left(T_{\mathrm{Mk}} - T_{\mathrm{j}}[F]\right)\right\} \cdot \mathrm{d}F = (k \cdot F) \cdot \left(T_{\mathrm{Mk}} - \overline{T}_{\mathrm{J}}\right)$ (7.2)

The combination of (7.1) and (7.2) leads to the exact determination of the thermal reaction power:

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\begin{aligned}
q &= (k \cdot F) \cdot \left(T_{\mathrm{Mk}} - \overline{T}_{\mathrm{J}}\right) - (k \cdot F)_0 \cdot \left(T_{\mathrm{Mk}} - \overline{T}_{\mathrm{J0}}\right) - (p_{\mathrm{L}} - p_{\mathrm{L0}}) - (p_{\mathrm{St}} - p_{\mathrm{St0}}) \\
&\qquad \text{or using} \\
&\qquad \Delta T_0 = T_{\mathrm{Mk}} - \overline{T}_{\mathrm{J0}} \\
&\qquad \Delta T = T_{\mathrm{Mk}} - \overline{T}_{\mathrm{J}} \\
&\qquad \Delta p_{\mathrm{L}} = p_{\mathrm{L}} - p_{\mathrm{L0}} \\
&\qquad \Delta p_{\mathrm{St}} = p_{\mathrm{St}} - p_{\mathrm{St0}} \\
&= (k \cdot F) \cdot \Delta T - (k \cdot F)_0 \cdot \Delta T_0 - \Delta p_{\mathrm{L}} - \Delta p_{\mathrm{St}}. \\
&= (k \cdot F) \cdot \left[\Delta T - \Delta T_0 \cdot (k \cdot F)_0 / (k \cdot F) - \Delta p_{\mathrm{L}} / (k \cdot F) - \Delta p_{\mathrm{St}} / (k \cdot F)\right] \\
&= [k \cdot F](t) \cdot [\Delta T(t) - \Delta T_{\mathrm{kF}}(t) - \Delta T_{\mathrm{L}}(t) - \Delta T_{\mathrm{St}}(t)] \\
&= [k \cdot F](t) \cdot [\Delta T(t) - \Delta T_{\mathrm{Base}}(t)] \\
&= [k \cdot F](t) \cdot \Delta T_{\mathrm{q}}(t).
\end{aligned}
\tag{7.3}
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- ΔT_{kF} represents the part of the total change in temperature ΔT within the liquid of the jacket which is caused by the change in the initial heat-transfer coefficient $(k{\cdot}F)_0$ due to the inevitable change in the properties of the reaction mixture by the chemical conversion or of the physical conditions (i.e. area of heat exchange due to dosing, incrustation on wall, viscosity, phase inversion).
- ΔT_{L} represents the part of the total change in temperature ΔT within the fluid of the jacket which is brought about by the change in heat loss via the cover by variations in condensation on the cover due to changes in the temperature in the laboratory or by the inevitable change in vapour pressure due to variations in the chemical composition of the reaction mixture during the reaction or dosing and, in addition, due to the change in heat loss through the flange zone between the cover and wall of the measuring kettle when the temperature of the laboratory changes.
- ΔT_{St} represents the part of the total change in temperature ΔT within the fluid of the jacket which is caused by the inevitable change in the physical properties of the reaction mixture due to the chemical conversion or, in addition, to the stirred volume because of dosing.

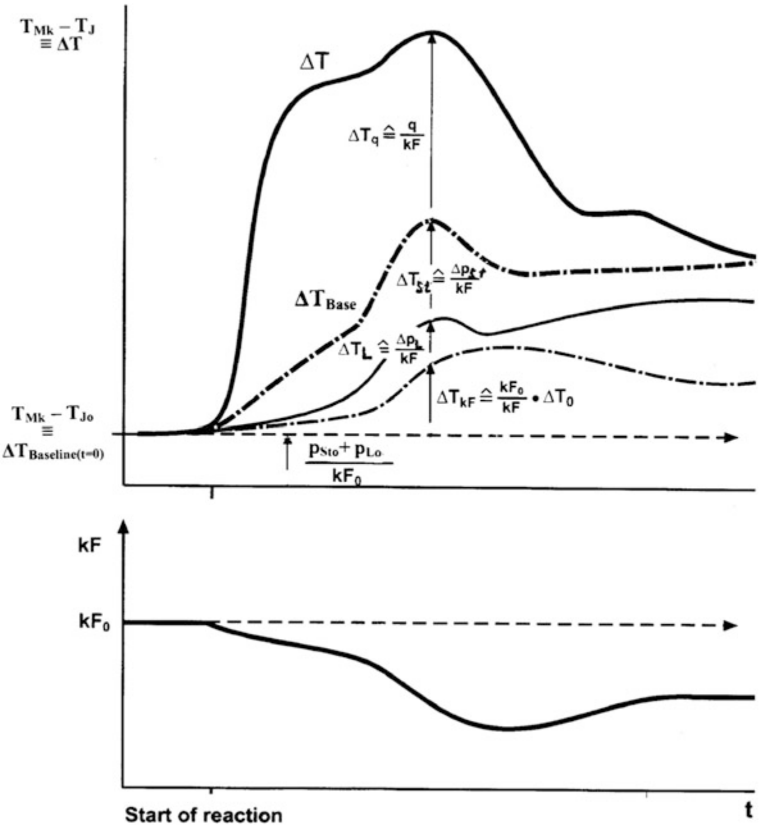

Fig. 7.2 Determining the thermal reaction power q from change in temperature ΔT and baseline ΔT_{Base} as well as course of (K · F) versus reaction time

Only the subtraction of the sum $[\Delta T_{\mathrm{kF}}(t) + \Delta T_{\mathrm{L}}(t) + \Delta T_{\mathrm{St}}(t)]$ from the recorded temperature difference $\Delta T(t)$ gives as a result the temperature difference $\Delta T_{\mathrm{q}}(t)$, the multiplication of which by the heat transfer coefficient $[k{\cdot}F](t)$ brings the desired caloric reaction power $q(t)$. Thus, $[\Delta T_{\mathrm{kF}} + \Delta T_{\mathrm{L}} + \Delta T_{\mathrm{St}}]$ represents the baseline $\Delta T_{\mathrm{Base}}(t)$ for determining the rate of heat release q due to a chemical process from the recorded total change in the temperature $\Delta T(t)$ (Fig. 7.2).

As for determining the thermal reaction power according to Regenass:

- Neither the stirrer power p_{St} nor its temporal change Δp_{St} is measured.
- Certainly, insulation of the cover of the measuring kettle or bringing the temperature of the cover to the temperature of the reaction reduces the heat loss as much as possible, but a finite heat loss is unavoidable, at least as long as the flange zone between the cover and the wall of the measuring kettle is exposed to the temperature of the laboratory. Neither the heat loss p_{L} nor its temporal change Δp_{L} is measured.

- The measured temperature T_J in the outflow of the jacket into the thermostat system is assumed to be representative of the working average temperature within the jacket, i.e. it is assumed to be determinant for the heat flow $(k{\cdot}F)\cdot(T_{Mk}-\overline{T}_J)$ from the measuring kettle to the jacket.
- The heat-transfer coefficient $(k{\cdot}F)$ respectively its temporal change is determined by proceeding point by point. The measurement for each point in time is carried out in the following way. The reaction mixture is supplied by the electric heater with a constant power p for a short time, which is necessary for achieving a thermal steady state. The temperature change $(T_{Mk}-T_{M(p)})-(T_{Mk}-T_M)=\delta T$ is recorded, and the heat-transfer coefficient is calculated according to relation $(k{\cdot}F)=p/\delta T$. On account of the point-by-point elaboration mode, unexpected physicochemical fluctuations in the reaction mixture (e.g. Fig. 2.17) can be recognized only inaccurately or not at all. It is not possible to carry out any number of time-consuming determinations because otherwise an analytically usable ΔT curve could not be recorded. Hence, in the case of a relatively quick reaction, the method is only of questionable merit.

In practical applications, the thermal reaction power was mostly determined in the following way. The limit values ΔT_0 respectively $(k{\cdot}F)_0$ (prior to the start of a reaction) and ΔT_∞ respectively $(k{\cdot}F)_\infty$ (end of reaction) were connected by a plausibly curved line $\Delta T_{\text{Base}}(t)$ respectively $[k{\cdot}F](t)$. On this basis, the thermal reaction power q was calculated according to (7.3).

Progress in digital electronic data processing (EDP) made it possible to reduce some of the inadequacies by using physical and process-technical methods to establish improved quantities nimbly, smartly and elegantly but perhaps unreliably regarding accuracy. The causes for possible unreliability are listed, without assignment to any device, as follows:

- The stirrer power p_{St} respectively the change in the stirrer power Δp_{St} is determined on the basis of the torque respectively torque change of the driving electromotor. Conventional driving motors with armature retroaction are used without exception, i.e. the relation of the mechanical torque and the intensity of the electrical current is not linear. Therefore, the torque is calculated either from the amperage of the motor combined with a calibration curve or from the balanced torsion strain of the clutch motor/stirrer shaft. However, during the reaction the temporal course of a total torque is measured consisting of the useful torque for stirring and the torque losses in the stirrer bearing. Only if the latter remains unchanged during the time of measurement can the change in the stirrer power Δp_{St} be calculated from the change in the total torque. However, a constant value of the loss momentum is doubtful due to the use of a common, classical bearing set-up of the stirrer (e.g. standard sleeve bearing unprotected from soiling) in combination with the manifold conditions of the reaction.
- The temporal change in the heat-transfer coefficient $(k{\cdot}F)$ is estimated on the basis of a continuously agitated, sinusoidal oscillation of the temperature in the reaction mixture. To be precise, this determination occurs quasi point by point of

time because the time sequence of finding the quantity ($k \cdot F$) is on the order of magnitude of several minutes (approximately 6 min or more) because of the attainable shortest wavelength of the oscillation accompanying thermal inertia of the measuring system.

Compared with the total reaction time of a relatively quick reaction, the points of indication are wide apart. Therefore, the degree of accuracy of a quasi-continuous route of the transfer coefficient found in this way, evaluated by extrapolation via the single points of finding, depends on the time constant of the reaction. Only in the case of a slow reaction is a reliably continuous curve obtained.[3]

- Based on a quick flow of the thermostat liquid through the jacket, a linear change in temperature is taken for granted, and therefore, and therefore the working average temperature $\overline{T}_{\mathrm{J}}$ in the fluid of the jacket is determined using the equation $\overline{T}_{\mathrm{J}} = (T_{\mathrm{Jinflow}} + T_{\mathrm{Joutflow}})/2$.[4]
- The heat loss into the surroundings, especially via the flange zone of the cover and wall as well as the inlet and outlet tubes of the measuring kettle, is usually still practically unsupervised, i.e. measured.
- In particular, thermal effects due to evaporation/condensation with respect to the cover as well as the inlets and outlets are usually not considered.
- The measurement error of commercial temperature sensors is approximately 0.3–1 %.

Assessment of Regenass Apparatus, Remodels and Knoff-offs

- Robustness of apparatus at the expense of precision.
- Suitable for good process-technical investigations.
- Less suitable for thermokinetic analyses of quick and, especially, complex chemical conversions.

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[3] Regarding the non-monotone route of baselines which usually depends importantly on the heat transfer, see Figs. 2.17–2.22.

[4] Plausibility lulls one into a false sense of security; measurements give security! See Lord Kelvin's aphorism in at the beginning of the book.