

## **DEVELOPMENT AND USE OF A CONSTANT FLOW STIRRED THERMOKINETIC REACTOR (STEADY-STATE TKR)**

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In addition to studies of reaction kinetics by a transient method in a batch reactor (non-steady-state), such studies should also be carried out by continuous operation in a stirred-flow reactor (steady-state). Only in this way, for instance, can the extent be recognized to which the simplifying assumptions often made in the evaluation of industrial kinetics from transient investigation are reasonable and whether the kinetics obtained are applicable to complex reactor design. The thermokinetic reactor (TKR), with which it has only been possible to measure the rate of heat evolution in experiments under transient conditions (batch TKR), has now been modified so that investigations can also be carried out in the stirred-flow manner (steady-state TKR).

It is well known that an exact knowledge of the reaction mechanism (i.e. of the system of elementary reactions taking place), the corresponding reaction rate equations and the heats of reaction is absolutely necessary for the optimal and safe design of a reactor. As a rule, this knowledge is obtained from laboratory experiments carried out in a batch reactor under transient conditions (non-steady-state).

In such an experiment, a *series* of data points is obtained; in contrast, a steady-state measurement in a stirred-flow reactor only affords *one* data point. The question therefore arises as to why steady-state laboratory experiments should be carried out at all:

A planned large-scale continuous operation can be studied on a laboratory scale; deactivation processes can be better investigated in a stirred-flow reactor; the kinetics of certain reactions, such as copolymerizations, are appropriately investigated under steady-state conditions. An additional reason is that reaction kinetics obtained by experiment in a batch reactor under transient conditions should be checked for accuracy.

The rate of an elementary reaction in the concentrated reaction mixtures mostly found in industrial processes is, as a rule, a function of the activities of the reactants.

These activities are known to depend on the concentrations of the components of the reaction mixture (i.e. reactants, products, by-products—which arise, for example, by dissociation, solvation, etc.—and the solvent) [1–3]. The reaction rate is therefore a function of the concentrations of *all* the components of the reaction mixture. As a result of analytical and mathematical difficulties, however, simplified approaches in the functional description of the reaction rate are made in practice. Practice-oriented kinetics (industrial kinetics) are obtained by representing the rate of an elementary reaction merely as a function of the reactant concentrations, and including the influences of all other components (main products, by-products and solvent) in pseudo rate factors.

To be precise, “average values” are obtained, since with the transient method the composition of the reaction mixture changes during the reaction. The danger exists that a significant influence exerted by the products and the solvent will only be determined to a limited degree, or even remain undetermined in this procedure. The degree of accuracy of the reaction kinetics obtained using the described transient method should therefore be checked by laboratory testing under a significantly different set of conditions (e.g. by carrying out testing at the steady-state of the reaction). Only thus can it be determined whether the applied simplifications are reasonable and whether the kinetics obtained (i.e. the functional representation of the reaction rate) are applicable to the design of complex reactor installations, or whether they must be modified.

In recent times, different types of calorimetric equipment have been used in the chemical industry for kinetic studies of reactions in which the progress of the reaction cannot be followed by classical analytical methods. However, no calorimetric apparatus is available with which kinetic studies could be carried out on *reactions at the steady-state and under practice-oriented conditions*. Using the thermokinetic reactor (TKR) [4, 5], it was only possible to investigate substantially liquid reaction mixtures in a transient mode (batch TKR) by measuring the changing rate of heat evolution over time and to elicit the reaction kinetics from the measured data [6–8]. The TKR has now been modified so that investigations by the stirred-flow method can also be carried out (steady-state TKR).

### **Operating principle of steady-state TKR**

A throughput vessel, the reactor, equipped with input and output lines for the feed components and the reacted mixture, is enclosed in a jacket containing a liquid in turbulent flow. This jacket of liquid is an intermediate thermostat, since it is in turn immersed in a base thermostat, which is also turbulently stirred (Fig. 1).

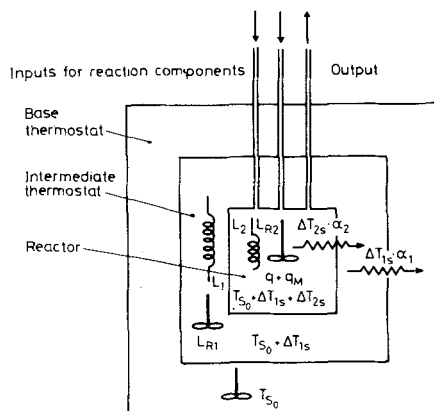


Fig. 1 Operating principle of the steady-state TKR

The throughput vessel is equipped with a stirrer, four baffles, a regulated heating element and a temperature sensor. The intermediate thermostat is similarly equipped. The temperature  $T_s$  of the base thermostat is kept at a constant level. The controlled heating power  $L_1$  of the intermediate thermostat maintains a constant set temperature difference  $\Delta T_{1s}$  between the intermediate thermostat and the base thermostat; the controlled heating power  $L_2$  in the stirred throughput vessel maintains a constant temperature difference  $\Delta T_{2s}$  between the reactor and the intermediate thermostat. The base thermostat is at the lowest temperature,  $T_2$ ; the intermediate thermostat is at the middle temperature,  $T_s + \Delta T_{1s}$ ; and the reactor is at the highest temperature,  $T_s + \Delta T_{1s} + \Delta T_{2s}$ . With the use of a controlled thermostating facility, the reaction components which are separately and continuously metered in are individually preheated to the constant reactor temperature  $T_s + \Delta T_{1s} + \Delta T_{2s}$  before entering the reactor; this avoids possible pre-reaction in the input line and ensures that no change in enthalpy takes place in the reactor due to temperature differences between the input and the reactor contents.

If  $\beta \cdot F \equiv \alpha$  represents the heat transferability, the heat  $\alpha_2 \cdot \Delta T_{2s}$  flows from the reactor to the intermediate thermostat, while at the same time the heat  $\alpha_1 \cdot \Delta T_{1s}$  is transferred from the intermediate thermostat to the base thermostat.

In the controlled thermal equilibrium, the following equations apply:

a) Reactor:

Sum of all heating powers in the reactor = heat flow from reactor:

$$q + q_M + L_2 + L_{R2} = \alpha_2 \cdot \Delta T_{2s} \quad (1)$$

b) Intermediate thermostat:

Sum of all heating powers in the intermediate thermostat = heat flow from the intermediate thermostat:

$$\alpha_2 \cdot \Delta T_{2s} + L_1 + L_{R1} = \alpha_1 \cdot \Delta T_{1s} \quad (2)$$

It therefore follows that

$$q + q_M = (\alpha_1 \cdot \Delta T_{1s} - L_{R1}) - (L_1 + L_2 + L_{R2})$$

The heat transferability  $\alpha_1$  and the stirring power  $L_{R1}$  of the intermediate thermostat are not affected by the reaction in the throughput vessel, but can be considered as apparatus constants. The value of  $\Delta T_{1s}$  remains constant, since  $L_1$ , which is regulated by means of a control loop changes inversely congruently with any change of the heat flow  $\alpha_2 \cdot \Delta T_{2s}$  from the reaction to the intermediate thermostat\*. It therefore follows that

$$\begin{aligned} q + q_M &= \text{const} - (L_1 + L_2 + L_{R2}) = \\ &= (L_1 + L_2 + L_{R2})_{\text{before}} - (L_1 + L_2 + L_{R2})_{\text{during}} = L_0 - L(t)_{\text{stead}} \\ &\quad \text{metering} \quad \text{metering} \\ &\quad \text{cont.} \quad \text{with } L_0 = \text{const.} \end{aligned}$$

The difference in the sums of the heating power of the reactor, the heating power of the intermediate thermostat and the stirring power in the reactor before and during metering is therefore always equal to the sum of the thermal reaction power  $q$  and the thermal mixing power  $q_M$ . The value of  $q_M$  can be determined if the dosage of reactants is stopped at  $t = t_s$ , the steady-state operation immediately reverts to transient operation. Since no further mixing takes place and hence no further mixing heat arises, the compensating heating power of the stirred vessel changes abruptly by the thermal mixing power  $q_M$  (Fig. 2). Thus,  $q_M$  is given by the difference of the sum of the power under transient conditions at time ( $t_s$ ),  $L(t = t_s)_{\text{trans.}}$ , and the (constant) sum under steady-state conditions,  $L(t < t_s)_{\text{stead.}}$ . This can be written as

$$q_M = L(t_s)_{\text{trans.}} - L(t < t_s)_{\text{stead.}}$$

\* The heat transferability  $\alpha_2$  and the stirring power  $L_{R2}$  always change during the reaction as a result of the inevitable change of the physical properties of the reaction mixture (viscosity, etc.), and also due to variations in the fluid level of the reactor. The heat transferability  $\alpha_2$  also changes due to deposition of constituents of the reaction mixture on the wall of the vessel.

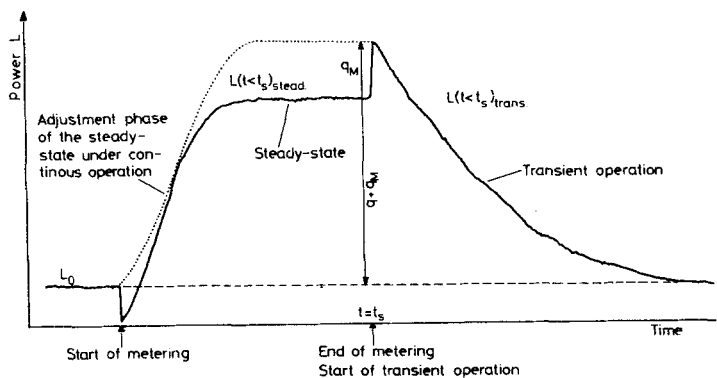
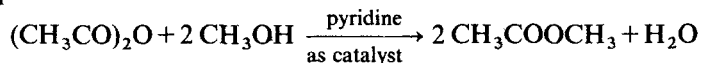


Fig. 2 For evaluation of thermokinetic measurement in the steady-state TKR

### Example

The alcoholysis of acetic anhydride EA with excess methanol using pyridine as a catalyst will be studied as an example. The reaction proceeds according to the overall equation:



For the discontinuous study, 100 ml methanol and 10 ml acetic anhydride were premixed in the batch TKR, heated to 45°, and then 0.4 ml pyridine was injected at once to initiate the reaction. Figure 3 shows the change in the thermal reaction

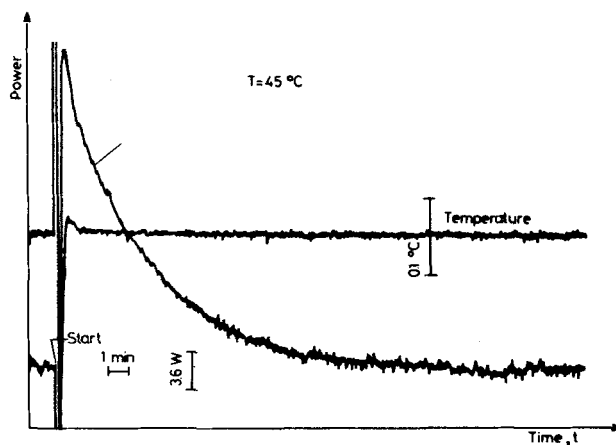
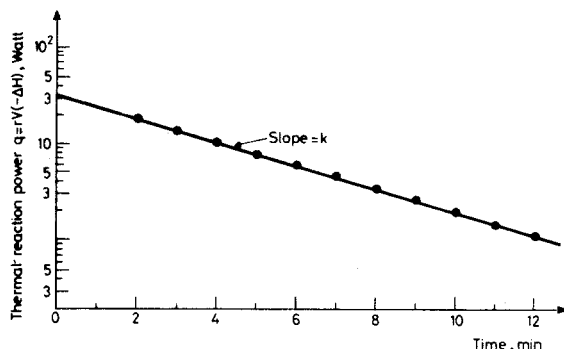


Fig. 3 Measurement trace of the alcoholysis of acetic anhydride (transient operation), 100 ml methanol, 10 ml acetic anhydride, 0.4 ml pyridine

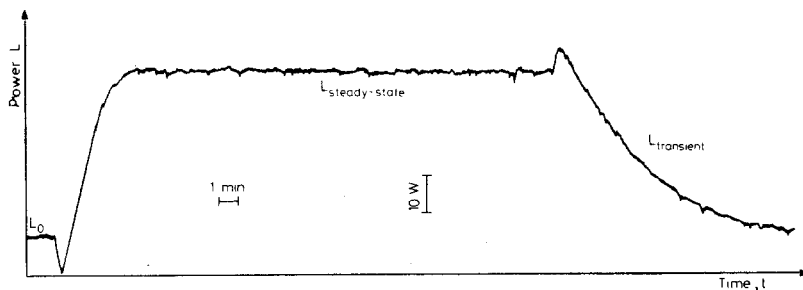
power  $q$  during the reaction. If  $\ln q$  is plotted versus time, a straight line is obtained (Fig. 4). This shows that the reaction rate may be described in empirical kinetics by a first-order law ( $r = k \cdot C^a$  with  $a = 1$ ). The reaction rate constant  $k$  ( $45^\circ$ ) =  $4.6 \cdot 10^{-3} \text{ s}^{-1}$  is obtained from the slope of the straight line, and the heat of reaction  $\Delta H = -62.4 \text{ kJ/mol}$  from the intersection of the straight line with the ordinate.



**Fig. 4** Elicitation of the reaction rate  $r = kC$  from thermokinetic measurements by transient operation, alcoholysis of acetic anhydride

With the same volume ratio of methanol, acetic anhydride and pyridine and the same temperature as in the transient procedure, the reaction was next carried out under stirred-flow conditions in the steady-state TKR. Figure 5 shows a trace of a measurement. The average residence time of the reaction mixture in the reactor was varied.

If a rate equation of the type  $r = k \cdot C^a$  holds true, a straight line should result when  $\ln q/V \cdot (-\Delta H) = \ln r$  is plotted versus  $\ln(1 - q/(n_0 \cdot (-\Delta H))) = \ln(1 - U)$ . The reaction order  $a$  is obtained from the slope of the line, and the rate constant  $k$



**Fig. 5** Measurement of the alcoholysis of acetic anhydride with methanol using pyridine as a catalyst (steady-state operation); volumetric ratio: methanol/acetic anhydride/pyridine = 250/25/1

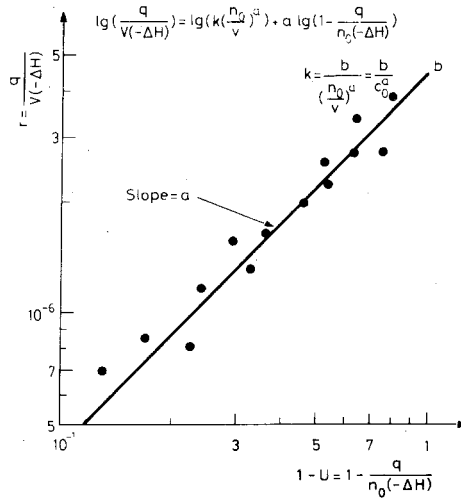


Fig. 6 Elicitation of the reaction rate  $r = k \cdot C^a$  from thermokinetic measurements by steady-state operation: alcoholysis of acetic anhydride  $T = 45^\circ\text{C}$

from the ordinate value  $b$  at the abscissa value 1. Figure 6 reveals that

$$a = 1$$

$$k(45^\circ) = 4.7 \cdot 10^{-3} \text{ s}^{-1}$$

This result agrees with the result from the transient method and, indeed, it stands to reason that it would be very surprising if the kinetics of this dilute reaction system elicited by the transient and the steady-state methods were to differ.

In the steady-state experiments, the conversion changes as a result of the variation in the residence time of the reaction mixture in the reactor. As a result, different mixing heats arise during the individual measurements, since the mixing heat is a function of the composition of the reactor contents, i.e. the partial molar enthalpies. An average mixing heat was determined according to the formula

$$\Delta H_M = \frac{1}{I} \sum_{i=1}^I \frac{q_{mi}}{n_{0i}} = 5.02 \text{ kJ/mol EA}$$

**Explanation of symbols**

$a$	Reaction order
$c$	Concentration
$c_0$	Initial concentration
EA	Acetic anhydride
$F$	Heat exchange surface
$\Delta H$	Reaction enthalpy
$\Delta H_M$	Mixing enthalpy
$k$	Rate constant
$L_1$	Heating power in the intermediate thermostat
$L_2$	Heating power in the stirred throughput vessel
$L_{R1}$	Mixing power in the intermediate thermostat
$L_{R2}$	Mixing power in the stirred throughput vessel
$L$	$L_1 + L_2 + L_{R2}$
$n_0$	Molar input flow
$q$	Thermal reaction power (heat production rate)
$q_M$	Thermal mixing power
$r$	Reaction rate
$\Delta T_{1s}$	Temperature difference between intermediate thermostat and base thermostat
$\Delta T_{2s}$	Temperature difference between stirred throughput vessel and intermediate thermostat
$T_{s0}$	Temperature in the base thermostat
$U$	Conversion
$V$	Volume of the reaction mixture
$v$	Volumetric input flow
$\alpha_1$	Heat transferability of the system intermediate thermostat/base thermostat
$\alpha_2$	Heat transferability of the system reactor/intermediate thermostat
$\beta$	Heat transfer coefficient

**References**

- 1 M. Boudart, Kinetics of Chemical Processes, Prentice-Hall INC., Englewood Cliffs, NY 1968.
- 2 L. P. Hammett, Physical Organic Chemistry, McGraw-Hill Book Company, NY 1970.
- 3 G. Kortüm, Einführung in die Chemische Thermodynamik, Verlag Chemie GmbH, Weinheim 1966.
- 4 W. Litz, J. Thermal Anal., 27 (1983) 215.
- 5 W. Litz, Thermochimica Acta, 85 (1985) 357.
- 6 W. Köhler, O. Riedel and H. Scherer, Chemie-Ing. Techn., 45 (1973) 1289.
- 7 W. Regenass, Chirica, 37 (1983) 430.
- 8 W. Litz, J. Thermal Anal., 30 (1985) 627.



**Zusammenfassung** — Neben reaktionskinetischen Untersuchungen in diskontinuierlicher Arbeitsweise sollten tunlichst solche in kontinuierlicher Arbeitsweise (steady-state) durchgeführt werden. Nur dadurch ist beispielsweise zu erkennen, inwieweit die bei der Ermittlung einer Formalkinetik aus diskontinuierlich durchgeführten Versuchen oft gemachten, vereinfachenden Annahmen vertretbar sind und die erarbeitete Formalkinetik für komplexe Reaktionsplanung verwendbar ist. Der Thermokinetische Reaktor TKR, mit dem es bisher nur möglich war, in diskontinuierlich durchgeführten Versuchen den zeitlichen Verlauf der Wärmeproduktionsrate zu messen (Batch TKR) wurde dahingehend weiterentwickelt, daß nunmehr auch Versuche in kontinuierlicher Arbeitsweise durchgeführt werden können (steady-state TKR).

**Резюме** — Исследования реакционной кинетики методом переходного состояния в загрузочном реакторе (неустановившийся) могут быть также проведены методом непрерывного действия в реакторе со смешанным потоком (установившийся). Однако, это может быть приемлемо только при разумных упрощающих предположениях, часто допускаемых при определении промышленной кинетики в методе переходного состояния, а полученные при этом кинетические данные применимы для конструкции сложного реактора. Термокинетический реактор (ТКР), с помощью которого ранее в методе переходного состояния представлялось возможным измерить только скорость выделения тепла, теперь модифицирован таким образом, что позволяет проводить исследования по методу смешанного потока (установившийся ТКР).