Wilfried Litz

Bench Scale Calorimetry in Chemical Reaction Kinetics

An Alternative Approach to Liquid Phase Reaction Kinetics

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ISBN 978-3-319-12531-2 ISBN 978-3-319-12532-9 (eBook)
DOI 10.1007/978-3-319-12532-9

Library of Congress Control Number: 2015943588

Springer Cham Heidelberg New York Dordrecht London

Printed on acid-free paper

Springer International Publishing AG Switzerland is part of Springer Science+Business Media (www.springer.com)

Dedicated to
Dr. phil. Dr. Ing. h.c. Juri Pawlowski †
a role model scientist indeed

> *"I often say that when you can measure what you are speaking about, and express it in numbers, you know something about it; but when you cannot express it in numbers, your knowledge is of a meagre and unsatisfactory kind."*
>
> *Lord Kelvin*
> *1824–1907*

Preface

It is well known that all physicochemical processes are accompanied by a heat tone. The amount of positive or negative heat released respectively the velocity of its release is principally a measure of the progress respectively the velocity of the process. Both in combination represent—depending on the complexity of the process—a more or less abundant source for a description of changes in physicochemical states. As a rule, the thermal quantities can always be measured.

This book is concerned with carrying out the precise measurement of quantities as well as their utility for chemical engineering, especially their application in the kinetic analysis of reactions within the liquid phase.[1]

The introduction[2] of the book (Chap. 1) explains why caloric investigations aimed at determining the chemical kinetics of liquid-phase reactions can be carried out most efficiently using bench scale calorimeters.

Chapter 2 presents calorimeters for measuring accurately the rate of heat release during discontinuous and continuous reactions versus time under isothermal and nonisothermal conditions. In addition, the chapter contains a description of an apparatus that can be used to record online the rate of heat release within a stirred tank reactor during a reaction.

Chapter 3 offers hints for the practical use of the proposed calorimeters.

Chapter 4 describes the fundamental principles for conducting a kinetic analysis of calorimetric results. The aim of a thermokinetic analysis is the elaboration of the fundamental rules that set the tone for running a chemical conversion in liquid, homogeneous reaction mixtures, i.e.,

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[1] Liquid phase system: liquid, liquid/gas, liquid/solid, liquid/solid/gas; in all cases, a liquid is the main constituent.

[2] List of symbols.

- Independent stoichiometric equations,
- Related rate functions,
- Related reaction enthalpies.

A thermokinetic analysis takes place

- Based on mathematical-analytical relations (examples of several different reaction systems are given)
- Based on numerical calculations (examples of software that has been tested are introduced).

The more complex a chemical process is, the more plentiful must be the variations in calorimetric measurements for kinetic analysis.[3] This holds especially for chemical conversions in concentrated reaction mixtures because increasing concentration complicates the thermokinetic analysis.

Chapter 5 discusses examples of applications to thermokinetic analysis.

Chapter 6 treats the possibilities of bench scale calorimetry in the determination of additional, relevant quantities in chemical engineering.

Chapter 7 discusses the so-called heat flow calorimeter by Regenass respectively subsequently improved models.

The book ends with a list of literature cited in the book that is recommended for further reading, a list of symbols used, and a subject index.

To what end and for whom was the book written?

The book was written first and foremost to stimulate students' interest of chemical engineering and chemistry in the kinetic analysis of liquid-phase reactions on the basis of a calorimetric investigation. Therefore, the illustrations accompanying the chapters are essential, detailed, and coherent. The precise depictions of apparatus and the advantages of their use, as demonstrated by a variety of examples, might encourage scientists and engineers to incorporate one of the apparatus in their professional practice.

The author would consider the book a great success if readers experienced a eureka moment and realized that thermokinetic analysis could be used to solve their existing kinetic problems.

The treatise represents the fusion of literature and experience gained in the domain of bench scale calorimetry, which the author started while working in the applied physics laboratory at Bayer AG Leverkusen in the 1970s.

The author would like to express his special thanks to Dr. Juri Pawlowski for his vivid interest in the progress of the project, Mr. Eberhard Gottschall, Mr. Reinhold Rose, and Mr. Ernst Dykstra for their many ideas and their excellent craftsmanship in mechanics, Dipl.Ing. Dietrich Biehler, Dipl.Ing. Wilfried Braun, and Dipl.Ing. Horst Zwick for their excellent ideas with respect to electronics.

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[3] The same holds for the elaboration of kinetics on the basis of classical chemical analysis.

Last but not least, the author would like to acknowledge a very special debt to his parents, especially to his mother, now age 96, who for several weekends suffered the author's bad temper as a result of sudden revelation of unforeseeable, complex obstacles during the development of the apparatus. In accordance with Murphy's Law, this occurred mostly during or around the weekend.

Cologne, Germany Wilfried Litz

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Part I Fundamentals, Basic Information and Description of Bench Scale Calorimeters

Part II Practical Information and Applications

List of Symbols Used

The relations in the text are not number equations based on fixed values of units but physicochemical quantity equations. Therefore, neither the equations in the text nor the following symbols are characterized by units. For their practical use, units should be chosen uniformly.

a	Activity respectively temperature coefficient
C_2	Effective heat capacity of filling in measuring kettle
C_1	Effective heat capacity of liquid in intermediate thermostat
C_F	Heat capacity of filling in measuring kettle
C_{Mt}	Effective heat capacity of measuring-kettle wall + stirrer + etc.
$\boldsymbol{C}_{\mathbf{p}\zeta}$	Molar heat of reaction constituent ζ
C_ζ	Partial molar heat of reaction constituent ζ
c_p	Mean specific heat of filling in measuring kettle consisting of many components
c	Concentration
c_0	Initial concentration
c_R	Concentration of filling in batch tank reactor
$c_{R,0}$	$c_R(t=0)$
c_{Rstat}	Steady-state concentration in tank reactor for continuous reaction
c_{Mk}	Steady-state concentration in measuring kettle
d_{torque}	Torque constant
d_{Rw}	Thickness of reactor wall
d_{St}	Characteristic diameter of stirrer
D	Total torque of electric motor
D_R	Characteristic inner diameter of reactor
E	Activation energy
F	Area of heat exchange
f	Activity coefficient
G	Mass of filling in measuring kettle

g	Rate of mass flow
$I_{\text{on load}}$	Current of electromotor driving stirrer of filled measuring kettle
$I_{\text{without load}}$	Current of electromotor driving stirrer of empty measuring kettle
i	Product index
j	Reactant index
H	Enthalpy of reaction mixture
$\boldsymbol{H}_{\zeta}$	Molar enthalpy of reaction constituent ζ
H_{ζ}	Partial molar enthalpy of reaction constituent ζ
$(k \cdot F)_1$	Heat-transfer coefficient: intermediate thermostat → base thermostat
$(k \cdot F)_2$	Heat-transfer coefficient: measuring kettle → intermediate thermostat
$(k \cdot F)_{\mathrm{H}}$	Heat-transfer coefficient: pipe coil → measuring kettle
k	Rate coefficient of reaction respectively specific heat-transfer coefficient
$k(c_{\varepsilon})$	Rate coefficient of reaction in highly concentrated solution, generally not constant
k_{Motor}	Generated voltage of rotating electromotor without load per one revolution in unit of time
k_{Tacho}	Generated voltage of rotating tachogenerator per one revolution in unit of time
K_{K}	Kinetic equilibrium quantity, generally not constant
K_{Th}	Thermodynamic equilibrium constant
M	Molecular weight
m_{ζ}	Mass of constituent ζ in reaction mixture
$N_{j,i}$	Number of moles of reactant j respectively products i
N_{ζ}	Number of moles of species ζ in reaction mixture
N	Number of revolutions of stirrer per minute, rpm
n, m	Order or partial order of rate function of a reaction
p_1	Power of electric heater within intermediate thermostat
p_2	Power of electric heater within measuring kettle
p_3	Power of electric heater within condenser/intermediate thermostat
p_{St1}	Stirrer power in filling of intermediate thermostat
p_{St2}	Power of stirrer in filling of measuring kettle
p_{M2}	Total power of electromotor driving stirrer in filling of measuring kettle
p_{MStL2}	Power loss in arrangement of motor stirrer (internal loss of motor and stirrer gearing)
p	Sum of powers p_1, p_2, p_3, q_{M2}
q	Thermal reaction power in measuring kettle or tank reactor
q_{E}	Thermal evaporation power
Q_{∞}	Total heat released during course of a reaction
$q_{(\mathrm{B+C}\rightarrow)0}$	Thermal reaction power at start of reversible reaction $\mathrm{A} \leftrightarrow \mathrm{B} + \mathrm{C}$ starting from $\mathrm{B} + \mathrm{C}$

$Q_{(\mathrm{B+C}\rightarrow)\infty}$	Total amount of heat of reversible reaction A ↔ B + C starting from B + C
R	General gas constant
r	Rate of reaction $(\mathrm{d}\lambda/\mathrm{d}t)/V$
t	Time
t_{E}	Finite time of reaction for a rate function of order 0
t_{RZ}	Total time of reaction (99 % conversion)
T_0	Temperature in socle thermostat
T_{S}	Temperature in base thermostat
T_1	Temperature in intermediate thermostat
T_2	Temperature in measuring kettle
T_{20}	Temperature in measuring kettle prior to start of reaction at time $t = t_0 = 0$
T_3	Temperature of flowing reaction mix from tank reactor to on-line calorimeter at end of inlet pipe, just entering measuring kettle
T_4	Temporally fluctuating temperature of tank reactor
T_{H}	Temperature of superheated fluid within pipe coil installed in measuring kettle
T_{Mk}	Set temperature within measuring kettle of Regenass calorimeter
U_{j}	Fractional conversion $(N_{j\mathrm{o}} - N_j)/N_{j\mathrm{o}}$, simply called conversion of reaction
U_{Motor}	Generated voltage of rotating electromotor without load
U_{Tacho}	Generated voltage of rotating tachogenerator (speedometer)
V	Volume of reaction mixture respectively of measuring kettle
v	Rate of volume flow
α_{Rm}	Coefficient of heat transfer from reaction mixture into inside wall of reactor
α_{C}	Coefficient of heat transfer from outside wall of reactor into cooling fluid
α_{TC}	Combined coefficient of heat conductance within reactor wall and heat transfer from outside wall of reactor into cooling agent
α_{j}	Exponents of reactant concentration c_j in rate function r
β	Rate of temperature increase
β'	Heat-transfer coefficient from reaction mixture into temperature sensor
ΔH_{λ}	Enthalpy of reaction per stoichiometric conversion (formula conversion)
$\Delta H_{j,i} = \Delta H_{\lambda}/v_{j,i}$	Enthalpy of reaction per mol of component j or i; sign of quantity depends on whether component is consumed or produced
ε	Summary term for all constituents of reaction mixture: Reactants, intermediate products, products, by-products, catalysts, solvent
ϕ	Point of interception of a straight line with ordinate
Φ	Heat potential
Ω	Quotient of two rate coefficients

Θ_ζ	Distance of concentration of component ζ from its value $c_{\zeta\infty}$ at equilibrium ($c_\zeta - c_{\zeta\infty} = \Theta_\zeta$)
γ	Quotient $\nu_{j+\sigma}/\nu_j$ of stoichiometric coefficients $\nu_{j+\sigma}$ and ν_j
τ_F	Time constant of heat exchange between reaction mixture and temperature sensor
τ_RTh	Time constant of heat exchange between measuring kettle and thermostat
τ_R	Time constant of reaction
$\iota_{1/2}$	Reaction half-life
ρ	Mean density of filling in measuring kettle consisting of components of different densities
λ	Normalized degree of progress of reaction with stoichiometric equation $\ldots + \nu_j + \ldots \rightarrow \ldots + \cdots + \nu_i \ldots + \ldots$; defined by $(N_{j/i}(t) - N_{j/i}\mathrm{o})/\nu_{j/i}$; number of formula conversion
λ_Rw	Heat conductivity of material of reactor wall
λ_Rm	Heat conductivity of reaction mixture
η	Dynamic viscosity of reaction mix with temperature of main filling of reactor
η_wall	Dynamic viscosity of reaction mixture for temperature on inside wall of reactor
ν	Kinematic viscosity
$\nu_{j,i}$	Stoichiometric integer coefficient: <0 for reactants j, >0 for products i
τ	Mean residence time of reaction mass in flow measuring kettle
ω	Angular velocity
υ	Relative volume change of reaction mixture due to complete conversion of rate determining reactant
ξ	Common index for reactions
ζ	Common index for reaction constituents (reactant, intermediate products, products)

Part I

Fundamentals, Basic Information and Description of Bench Scale Calorimeters

Chapter 1
Introduction

The interaction between chemical and coupled physical processes (mass and heat transfer) gives the tone to the progress of a chemical conversion in a reactor. Therefore, a prerequisite for designing a plant reactor is the knowledge of

- Substance characteristics
- Apparatus characteristics
- Laws which control physical processes (thermodynamics, hydrodynamics)
- Laws which regulate the dynamics of the chemical process itself, i.e. a thorough knowledge of reaction kinetics

Only the combination of all laws puts the chemical engineer in a position to make a well-founded statement on the yield of a reaction and the security in any plant, i.e. it causes an acceleration of the transfer from the first laboratory experiment via a pilot reactor to the plant reactor.

The standard procedure in kinetic analysis is as follows:

- Take samples during the chemical reaction.
- Analyse the samples immediately or soon after preparation by conventional methods of analysis such as liquid chromatography, gas chromatography, spectral photometry and titration, for example.
- Determine the reaction mechanism and the related rate functions from the measured course of reactant and product concentrations versus time on the basis of graphic or numeric operations.

Obviously, this generally accepted working method is both time-consuming and prone to error, in particular when it represents an investigation of a rapid reaction. In addition, it proves that the conventional analysis of samples with chemical environments of technical mixtures provides no or only insufficient results—more often than is generally known. This also holds for the increasingly used online ATR-IR spectroscopy [17].

Hence, clearly, a method of kinetic analysis must be used which

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DOI 10.1007/978-3-319-12532-9_1

- Is always useable, as a rule;
- Works online and without interacting with the reaction;
- In simple cases, immediately reveals the reaction rate or a quantity directly proportional to it;
- In very complex cases, provides at least a gross kinetics ("pulse of chemical conversion");
- Allows for the measurement of additional information and quantities in chemical engineering, for reasons of security at least the enthalpy of a reaction.

The possibility for developing such a method is based on a theorem from chemical thermodynamics that with a chemical conversion occurring in one step, for instance $R \rightarrow P$, the heat Q released during any time interval is directly proportional to the number N_R of consumed mols of reactant R. The proportionality factor corresponds to the released heat $(-\Delta H)_R$ per consumed mol of reactant, i.e. $Q = (-\Delta H)_R \cdot N_R$. It stands to reason that the heat release per unit of time dQ/dt, i.e. the rate of nascent heat[1], is directly proportional to the absolute amount of change in mols of reactant per unit of time $|dN_R|/dt$, i.e. to the rate of reaction.[2]

Commercially available micro calorimeters, for example differential scanning calorimeter (DSC), isothermal-stage thermal analysis (ISTA), differential thermal analysis (DTA) [21, 50], are designed to solve particular questions (especially with respect to security). As a rule, and for a variety of reasons, there is only limited use for a precise kinetic analysis of complex reactions in liquid reaction mixtures. The main reasons for this are listed, without assignment to any device, as follows.

- The measurements take place within small samples (<1 g) in pots. With respect to the possible catalytic influence of the pot wall, the surface/volume ratio is clearly different from that of the plant reactor.
- There is no mixing in the sample; therefore, an inhomogeneity exists in the temperature and concentration despite the smallness of the pot.
- The original test value within a sample over time is in most cases recorded with distortions, which complicates the kinetic evaluation because the recorded signal must be antidistorted.
- The starting point of a reaction cannot be precisely prescribed.
- It is impossible to work according to some technical routine, for example, by dosing an additional reactant or catalyst or sampling while a reaction is taking place.
- At the start of or during a reaction, the reaction mixture is not allowed to undergo any major changes in its physical properties (e.g. volume of sample mass, degree of dispersion, viscosity, density, specific heat, heat conductivity).
- The reaction mixture is not allowed to deposit material on the pot wall.
- To estimate the analysis curve (netto curve) from the recorded curve (gross curve), one must have a baseline. However, it cannot be measured.

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[1] Called thermal reaction power.

[2] See detailed treatment in Chap. 4.

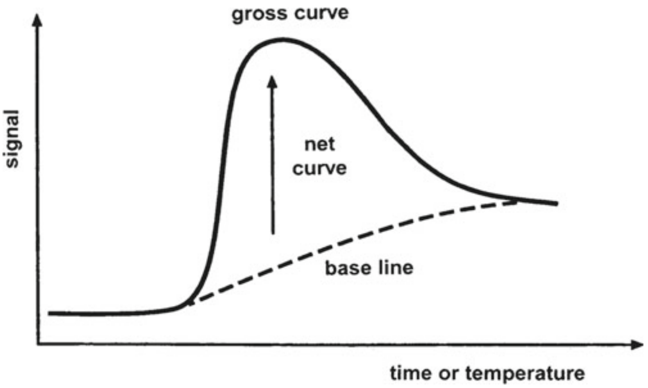

Fig. 1.1 Correlation between gross curve, net curve (curve for analysis), and baseline (reference curve)

Nevertheless, in practice, devices are used for the kinetic analysis of very different liquid reaction mixtures, in which some of the stated engraved weaknesses are tacitly ignored, or an attempt is made to eliminate them by dubious measures. For instance (Fig. 1.1), the determination of the baseline takes place in such a way that the course of the recorded curve (gross curve) prior to the start and following the completion of the reaction is connected by a “plausibly curved” line[3,4] in which sometimes the end of the reaction is plausibly assumed to relate to the course of the recorded curve. Such measures and ones like it, however, can only moderate the existing inadequacies and the combined systematic errors in kinetic analysis. Moreover, the evaluated net curves cannot be used in the kinetic analysis of complex reaction systems.

The imperfections of micro calorimeters can be attributed to the simplifications made for the purpose of miniaturization.

Therefore, it is obvious that calorimeters must be developed for liquid reaction mixtures that do not have the aforementioned weaknesses for calorikinetic investigations. To that end, it must be taken into consideration that the diversity of chemical processes makes it necessary to allow for measurements under various conditions of chemical operation. Therefore, different apparatus for liquid reaction mixtures must be developed for optimal performance.

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[3] Plausibility can lull one into a false sense of security; measurement gives security! See Lord Kelvin’s aphorism in the preface.

[4] For the variety of baselines see Sect. 2.1.1.3.

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.

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DOI 10.1007/978-3-319-12532-9_2

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.

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[1] Primarily a lattice stirrer is used.

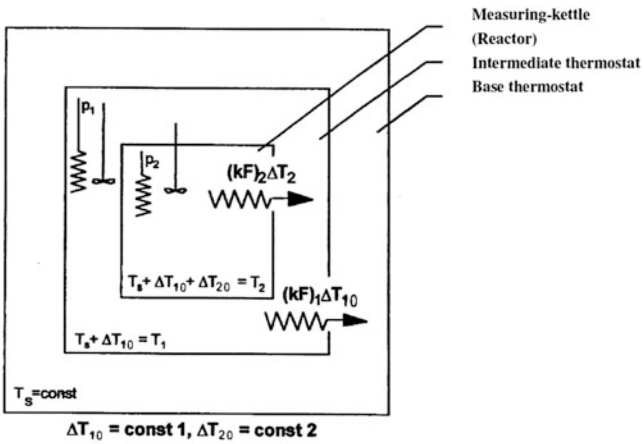

Fig. 2.1 Principle of accurate determination of thermal reaction power during an isothermal, discontinuous reaction [based on *the same measuring principle* of the calorimeter, this system of intermediate thermostat—*fluid, controlled heater, base thermostat* (controlled heat sink)—was replaced recently [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:

$$\begin{array}{l} \text{(a) Measuring kettle (reactor)} \\ \begin{array}{ccc} \text{Sum of all heat powers} & & \text{heat flow out of} \\ \text{in measuring kettle} & & \text{measuring kettle} \\ q + p_2 + p_{St2} & = & (k \cdot F)_2 \cdot \Delta T_2 \end{array} \\ \text{(b) Intermediate thermostat} \\ \begin{array}{ccc} \text{Sum of all heat powers} & & \text{heat flow out of} \\ \text{in intermediate thermostat} & & \text{intermediate thermostat} \\ (k \cdot F)_2 \cdot \Delta T_2 + p_1 + p_{St1} & = & (k \cdot F)_1 \cdot \Delta T_1. \end{array} \end{array} \qquad (2.1)$$

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_{St2}, 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_{St2}, according to (2.1). On the other hand, the heat-transfer coefficient $(k \cdot F)_1$ and the stirring power p_{St1} 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

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

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

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

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

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

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, ($\text{const}_{\mathrm{ML}}$)
- 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, ($\text{const}_{\mathrm{StL}}$)
- 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

$$p_{\mathrm{St2}} = p_{\mathrm{M2}} - (\text{const}_{\mathrm{ML}} + \text{const}_{\mathrm{StL}}) = p_{\mathrm{M2}} - \text{const}_{\mathrm{MStL2}}. \tag{2.3}$$

Hence, the thermal reaction power is given as

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

or (Fig. 2.2)

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

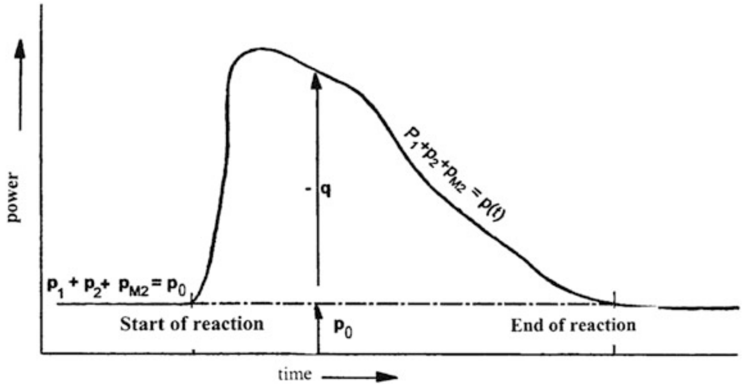

Fig. 2.2 Determination of thermal reaction power q by the difference of $(p_1+p_2+p_{M2})_{\text{prior to start of reaction}} = p_0$ and $(p_1+p_2+p_{M2})_{\text{during reaction}} = p(t)$

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

$$Q = \int_{0\to\infty} q \cdot \mathrm{d}t = \int_{0\to\infty} [p_0 - p] \cdot \mathrm{d}t.$$

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

$$\begin{aligned} q(t) &= \Big\{\underset{\substack{\text{prior to}\\ \text{start of reaction}}}{[p_1+p_2+p_{M2}]} - \underset{\substack{\text{during}\\ \text{reaction}}}{[p_1(t)+p_{M2}(t)]}\Big\} - \underset{\substack{\text{during}\\ \text{reaction}}}{p_2(t)} \\ &= \{p_1(t<0) - p_1(t)\} + \{p_{M2}(t<0) - p_{M2}(t)\} + p_2(t<0) - p_2(t) \\ &= -\delta p_1(t) + -\delta p_{M2}(t) + p_2(t<0) - p_2(t) \end{aligned}$$

or

because of (2.1)

$$= \Big\{[k\cdot F]_2(t) - [k\cdot F]_2(t<0)\Big\}\cdot \Delta T_2 + \{p_{M2}(t<0) - p_{M2}(t)\} + p_2(t<0) - p_2(t)$$

$$= \Big\{\underset{\substack{\text{change in heat flow}\\ \text{out of measuring kettle}\\ \text{owing to varied}\\ \text{heat transfer coefficient}}}{\delta(k\cdot F)_2(t)\cdot \Delta T_2} - \underset{\substack{\text{change } in\\ \text{motor power}\\ \text{owing to varied}\\ \text{stirring resistance}}}{\delta p_{M2}(t)_{\equiv \delta p_{s2}}} + p_2(t<0)\Big\} - p_2(t)$$

or (Fig. 2.3)

$$q(t) = p_B(t) - p_2(t). \tag{2.5}$$

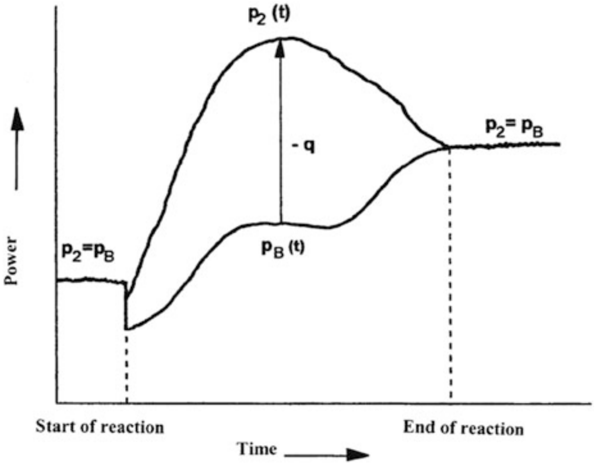

Fig. 2.3 Connection between thermal reaction power q, electric heating power p_2 and baseline p_B

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

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[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 δ_{St2}
   - Equal to the change in heat flow out of the measuring kettle by a change in heat transfer following the start of reaction $\delta(k \cdot F)_2 \cdot \Delta T_2$

$$\delta p_2 = \delta(k \cdot F)_2 \cdot \Delta T_2 - \delta_{S2} - q = \left[\delta(k \cdot F)_2 \cdot \Delta T_2 - \delta_{St2}\right] - q$$

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 δ_{R2} corresponds to the change in the total motor power δ_{M2} when the lost power remains constant.

   Hence, $\delta p_2 = -(\delta p_1 + \delta_{M2}) - q = \delta p_B - q$ (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.

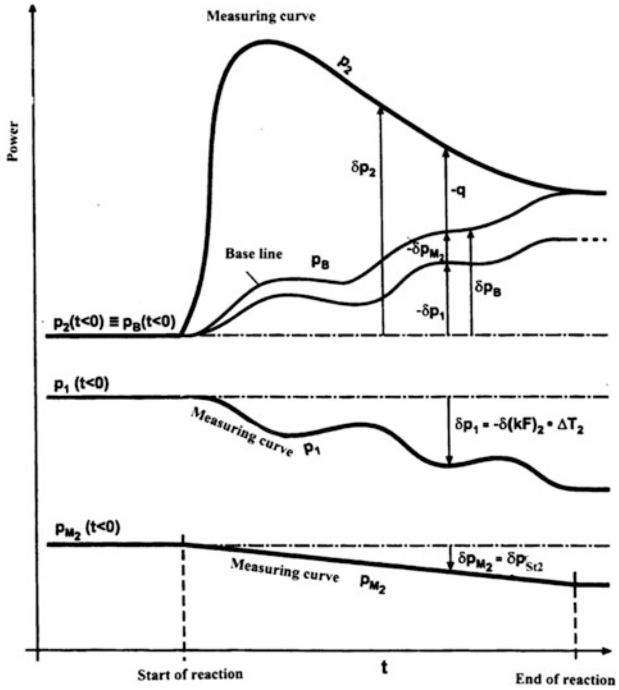


Fig. 2.4 Estimating the thermal reaction power q from the heating power p_2 using the baseline p_B; composition of p_B

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.

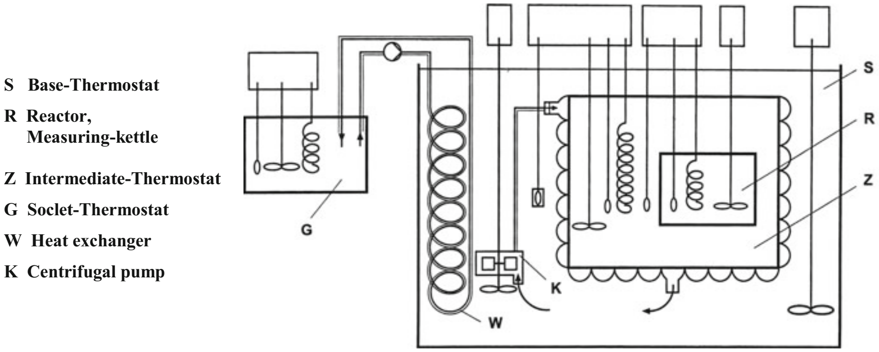


Fig. 2.5 Design principle of compact calorimeter TKR

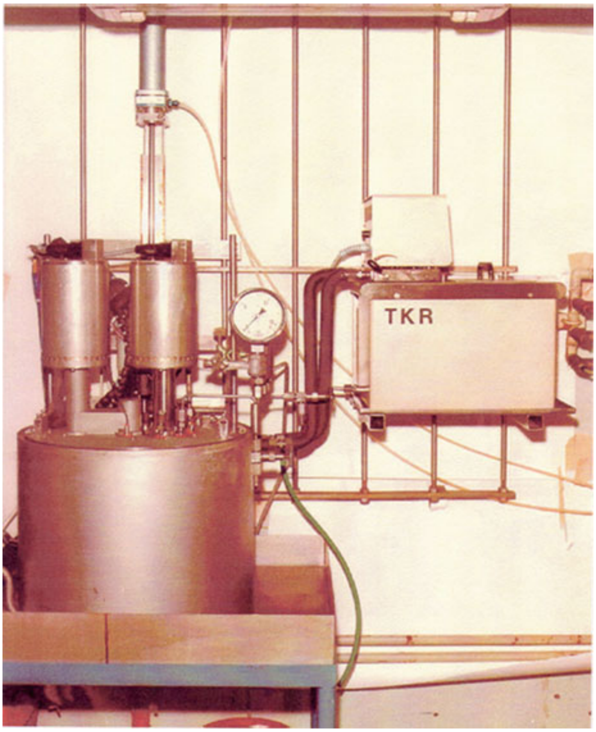


Fig. 2.6 Direct view of apparatus

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

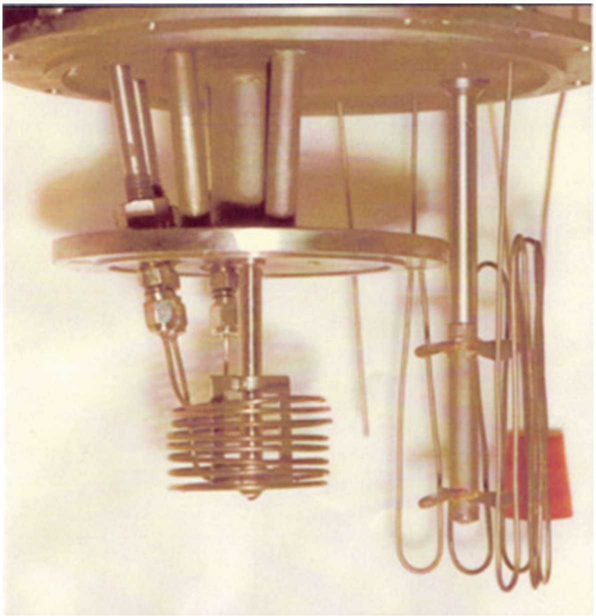


Fig. 2.7 Innards of measuring kettle/intermediate thermostat

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

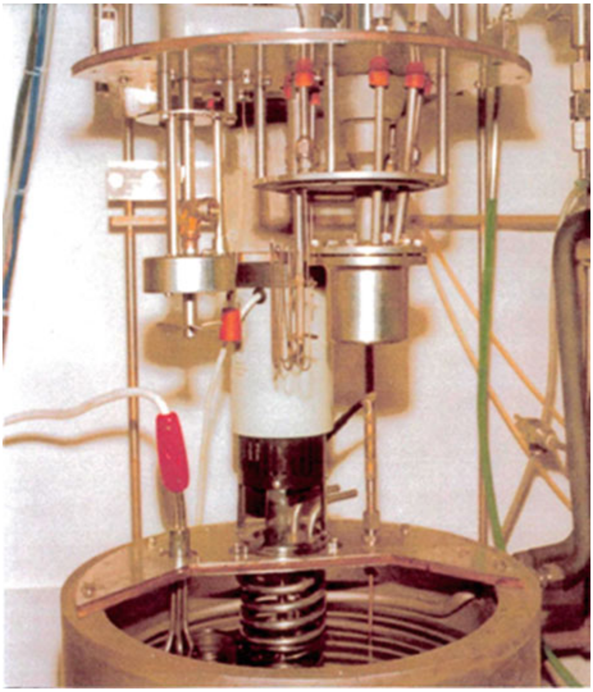
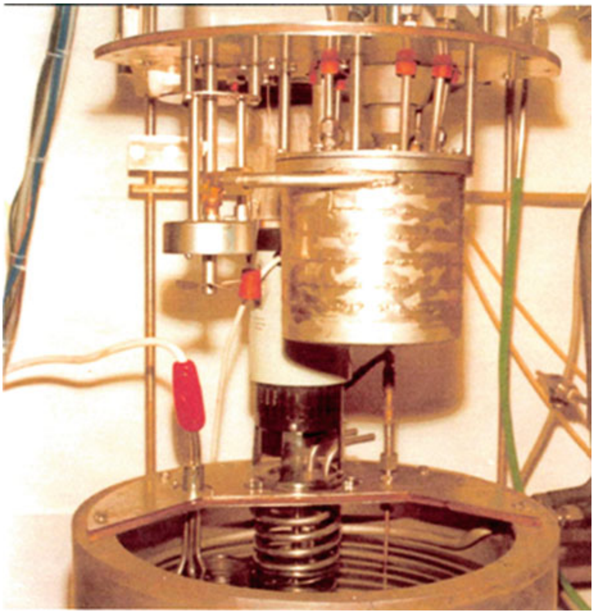


Fig. 2.10 Flanged intermediate thermostat



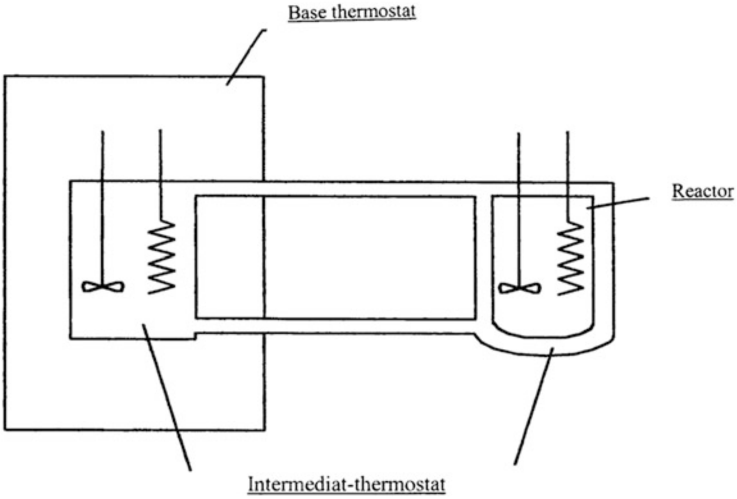


Fig. 2.11 Principle of non-compact calorimeter

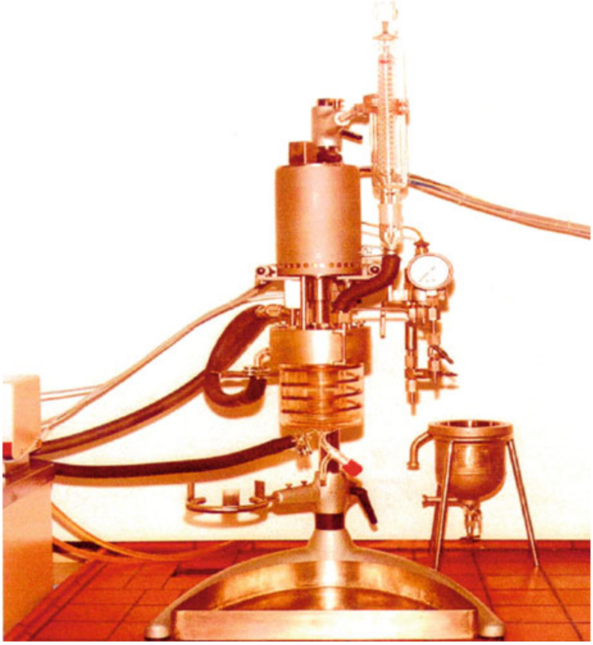


Fig. 2.12 Direct view of non-compact calorimeter. This type should be used predominantly for simulating technical processes

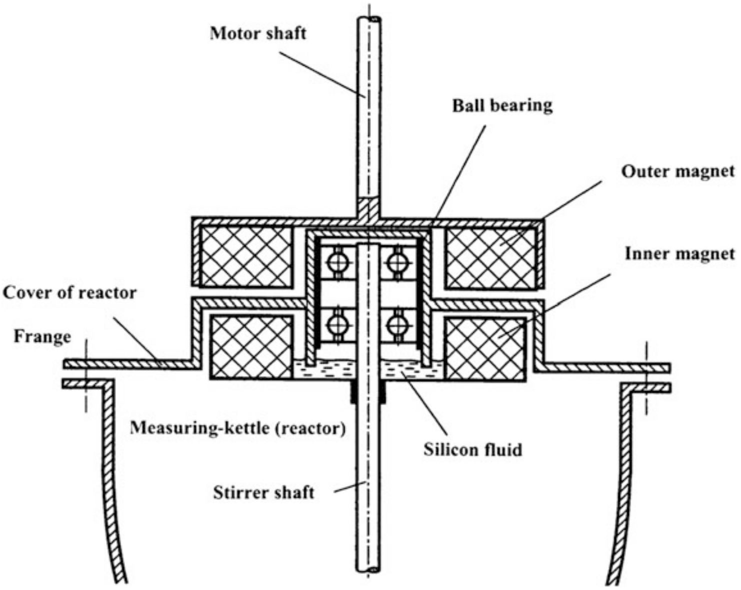


Fig. 2.13 Magnet cluster with ball bearing of stirrer shaft

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.

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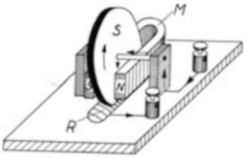
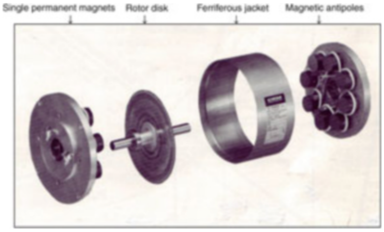
[3] Barlow wheel [2]



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 batch 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 ferriferous 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 current[4]

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

the generated electric voltage U_{M} of the motor is a linear function of its rotational velocity N[5]

$$U_{\mathrm{M}}(N) = k_{\mathrm{Motor}} \cdot N,$$

the generated electric voltage U_{T} of the tachogenerator is a linear function of its rotational velocity N[6]

$$U_{\mathrm{T}}(N) = k_{\mathrm{Tacho}} \cdot N. \tag{2.6}$$

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

$$d_{\mathrm{Torque}} = \text{æ} \cdot k_{\mathrm{Motor}}$$

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

$$d_{\mathrm{Torque}}[\mathrm{pcm/A}] = 97{,}465 \cdot k_{\mathrm{Motor}}\left[\mathrm{V/min}^{-1}\right]. \tag{2.7}$$

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 $D_{\mathbf{U}}$, transmitted via the motor shaft to the stirrer, as well as the loss torque $D_{\mathbf{L}}$,

$$D = D_{\mathbf{U}} + D_{\mathbf{L}}.$$

The torque loss $D_{\mathbf{L}}$ 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.

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[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 $D_{\mathrm{DLMotor}} = d_{\mathrm{DLMotor}} \cdot N$ (by electric eddy current), depending on the rotational speed N, with

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

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

1. Frictional torque of ball bearing of stirrer shaft $D_{\mathbf{FLShaft}}$, 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

$$\begin{aligned} p_{\mathrm{M}} &= D \cdot \omega = \left(d_{\mathrm{Torque}} \cdot I\right) \cdot 2\pi \cdot N = (D_{\mathbf{U}} + D_{\mathbf{L}}) \cdot 2\pi \cdot N = D_{\mathbf{U}} \cdot 2\pi \cdot N \\ &\quad + \left(D_{\mathrm{FLMotor}} + D_{\mathrm{DLMotor}} + D_{\mathrm{FLShaft}}\right) \cdot 2\pi \cdot N = p_{\mathrm{U}} + p_{\mathrm{L}} \\ &= p_{\mathrm{St}} + \left(D_{\mathrm{FLMotor}} + D_{\mathrm{DLMotor}} + D_{\mathrm{FLShaft}}\right) \cdot 2\pi \cdot N. \end{aligned}$$

Hence, for a constant rotational velocity N it follows that

$$p_M = \left(d_{\mathrm{Torque}} \cdot I\right) \cdot 2\pi \cdot N = p_{\mathrm{St}} + \mathrm{const}_{\mathrm{MStL}}. \qquad (2.8 \equiv 2.3)$$

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_{Tacho} [V/min^{-1}])$^{-1}$.
- The addition of $p_1(t)$, $p_2(t)$ and $p_{\mathrm{M}}(t)$ 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	Glass, HC4, V4A
stirrer, surfaces of electric heater, temperature sensor	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):

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

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

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

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

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

or, according (2.5),

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

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

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

The quotient of this and the previous equation leads to

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

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

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

or

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

Hence, to work out the baseline $p_{\mathrm{B}}(t_i)$ 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 $p_{\mathrm{B}}(t_i)$, 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

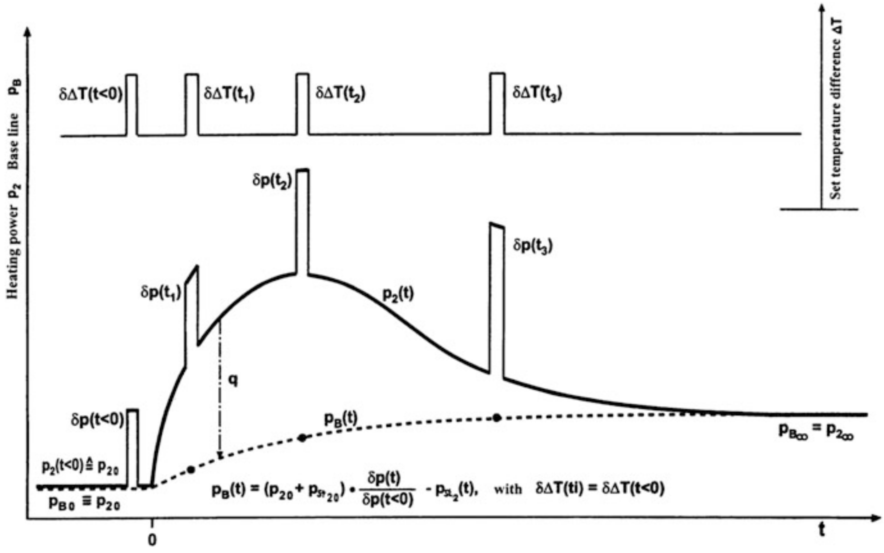


Fig. 2.14 Baseline p_B proceeding from one point in time to another

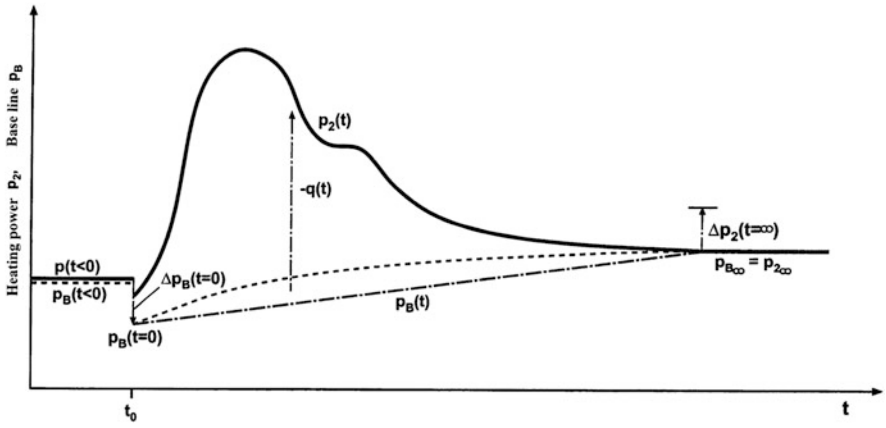


Fig. 2.15 Establishing approximate course of baseline p_B

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

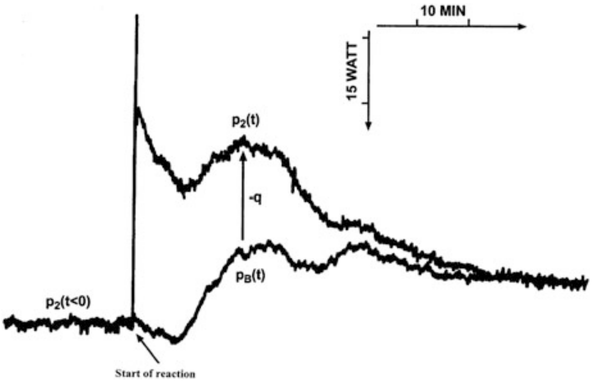


Fig. 2.16 Catalytic hydrogenation of a nitrile group

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 $\Delta p_\mathrm{B}(t = 0)$ caused by the injection at the start of the reaction, i.e. $\Delta p_\mathrm{B}(t = 0) \cong -\Delta p_2(t = \infty)$.

To establish the gross baseline, a straight line is drawn from $p_\mathrm{B}(t = 0)$ to $p_\mathrm{B}(t = \infty) = p_{2\infty}$. 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

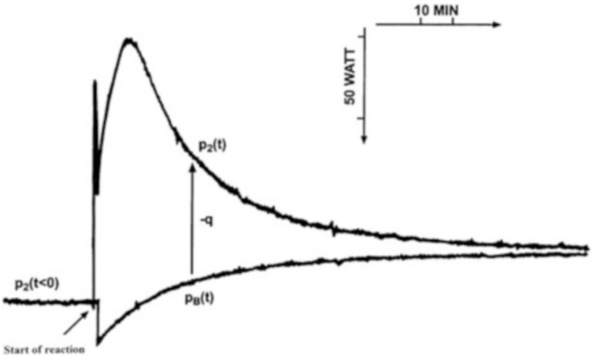


Fig. 2.17 Catalytic, intramolecular rearrangement of an amide derivate

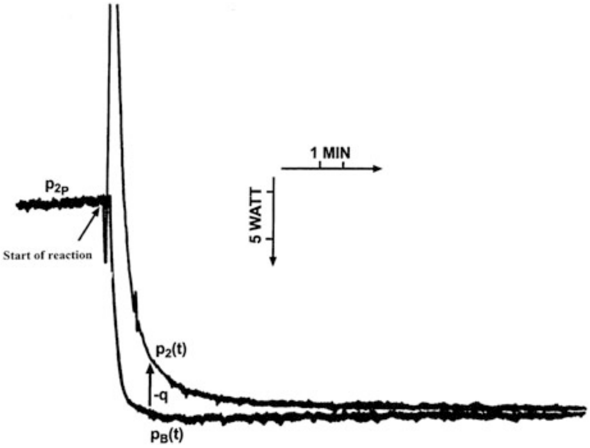


Fig. 2.18 Nucleophilic substitution at a halide of a ketone with an amine derivative in the presence of the auxiliary base KOH in solution

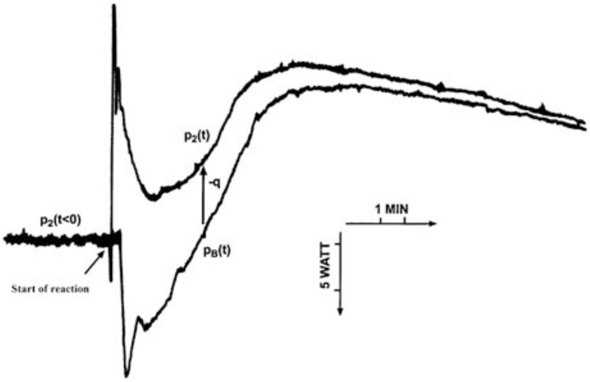


Fig. 2.19 The same reactants as in Fig. 2.18 but with use of auxiliary base K_2CO_3

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

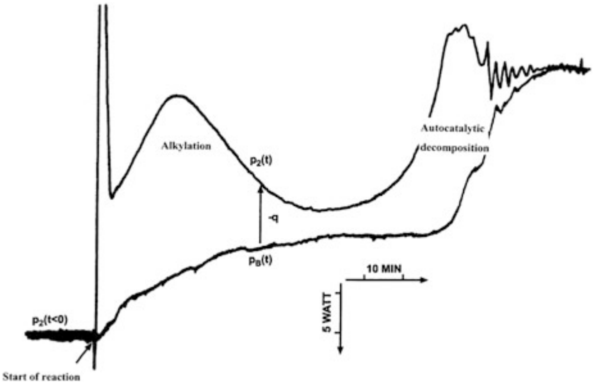


Fig. 2.21 Hydrogenation of an anthrachinon derivative in solution

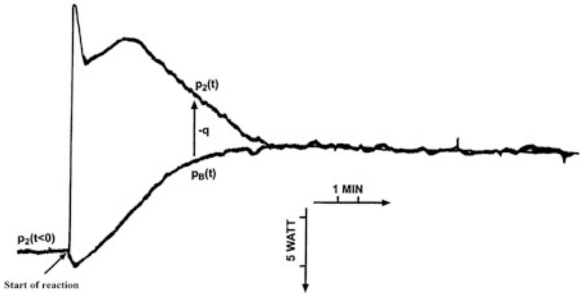
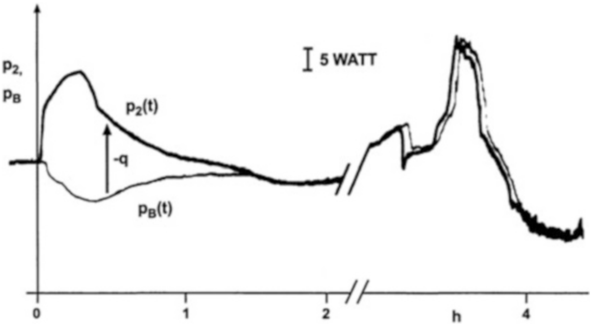
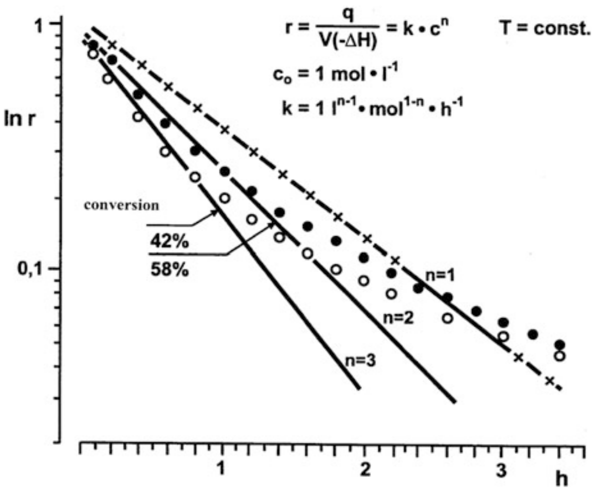


Fig. 2.22 Polymerization in solution



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.

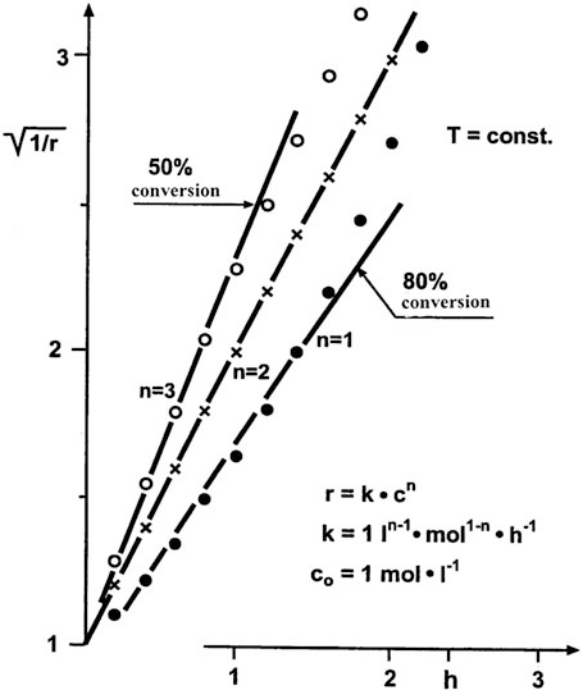
Considering that experimentally found data usually contain many imperfections, a straight line can also be drawn to one's best knowledge and belief through the experimental data of reactions of order greater than one, for instance, up to a conversion of 45 % for reactions of order three and 60 % for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

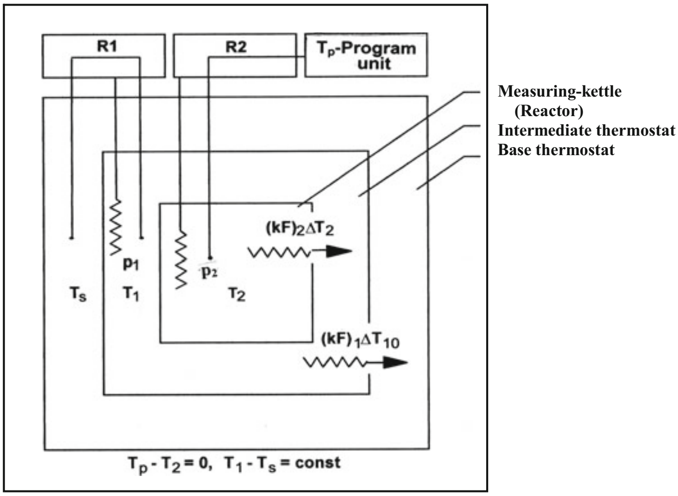


Fig. 2.25 Flowchart of apparatus for non-isothermal reaction (temperature programme)

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

$$C_2 \cdot \mathrm{d}T_2/\mathrm{d}t = q + p_{\mathrm{St2}} + p_2 - (k \cdot F)_2 \cdot (T_2 - T_1) \tag{2.9}$$

respectively

$$0 = (k \cdot F)_2 \cdot (T_2 - T_1) + p_{\mathrm{St1}} + p_1 - (k \cdot F)_1 \cdot (T_1 - T_S).$$

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

$$q = \left[(k \cdot F)_1 \cdot (T_1 - T_S) - p_{\mathrm{St1}}\right] + C_2 \cdot \mathrm{d}T_2/\mathrm{d}t - [p_1(t) + p_2(t) + p_{\mathrm{St2}}(t)].$$

The first parenthetic expression is constant because $(k \cdot F)_1$ and p_{St1} 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

$$q(t) = \mathrm{const} + C_2 \cdot \mathrm{d}T_2/\mathrm{d}t - [p_1(t) + p_2(t) + p_{\mathrm{St2}}(t)]$$

or with respect to $q = 0$ and $\mathrm{d}T_2/\mathrm{d}t = 0$ prior to the start of the temperature programme at time $t = t_0$:

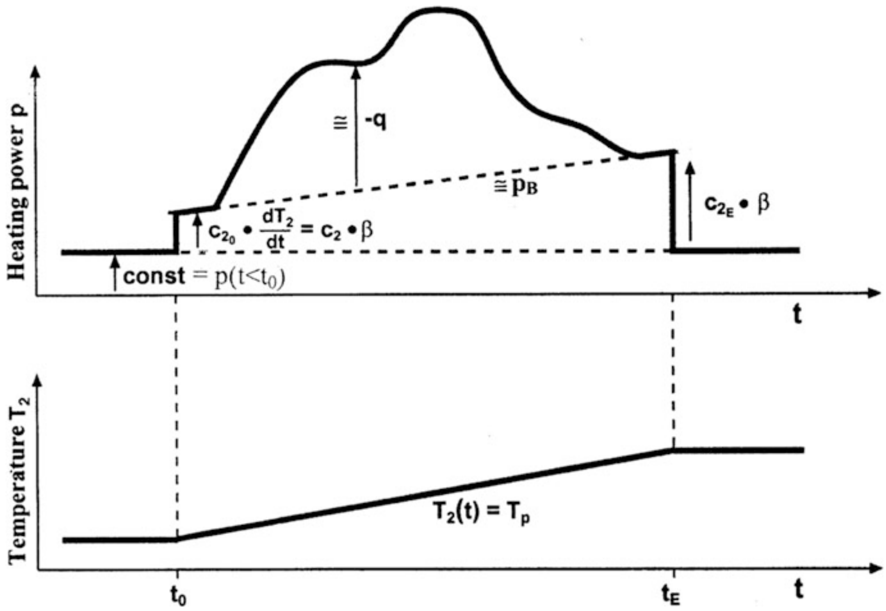


Fig. 2.26 Working out the net curve q of a non-isothermal reaction with an induced, linear change in temperature $T_2(t) = T_{p0} + \beta \cdot (t - t_0)$

$$q(t) = \underset{\substack{\text{prior}\\ \text{to start of}\\ \text{temperature programme}}}{[p_1 + p_2 + p_{St2}]} + C_2 \cdot \mathrm{d}T_2/\mathrm{d}t - \underset{\substack{\text{during}\\ \text{temperature programme}}}{[p_1(t) + p_2(t) + p_{St2}(t)]}$$

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

$$q(t) = p_0 + C_2 \cdot \mathrm{d}T_2/\mathrm{d}t - p(t).$$

$p_0 + C_2 \cdot \mathrm{d}T_2/\mathrm{d}t$ is the baseline p_B for determining the thermal reaction power $q(t)$.

In the case of a constant change in temperature, $\mathrm{d}T_2/\mathrm{d}t = \beta$, we obtain (Fig. 2.26)[7]

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

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 $(k \cdot F)_2 \cdot \left[T_2(t) - T_{1(=\text{const})}\right]$ 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

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[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 $\mathrm{d}T_2/\mathrm{d}t = \mathrm{d}T_S/\mathrm{d}t = \mathrm{d}T_p/\mathrm{d}t$.

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

$$C_2 \cdot \mathrm{d}T_2(t)/\mathrm{d}t = q + p_{St2} + p_2 - (k \cdot F)_2 \cdot [T_2(t) - T_S], \tag{2.11}$$

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

$$0 = p_{St2}(t < t_0) + p_2(t < t_0) - (k \cdot F)_2(t < t_0) \cdot [T_2(t < t_0) - T_S(t < t_0)]. \tag{2.12}$$

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

$$\begin{aligned}[T_2(t \geq t_0) - T_S(t \geq t_0)] &= [T_2(t < t_0) - T_S(t < t_0)] \\ &= [p_2(t < t_0) + p_{St2}(t < t_0)]/(k \cdot F)_2(t < t_0)\end{aligned}$$

results, along with, due to (2.11),

$$\begin{aligned}q = \{&C_2(t) \cdot dT_2(t)/dt - p_{St2}(t) + [(k \cdot F)_2(t \geq t_0)/(k \cdot F)_2(t < t_0)] \\ &\cdot [p_2(t < t_0) + p_{St2}(t < t_0)]\} - p_2(t).\end{aligned}$$

$\{C_2(t) \cdot \mathrm{d}T_2(t)/\mathrm{d}t - p_{St2}(t) + [(k \cdot F)_2(t \geq t_0)/(k \cdot F)_2(t < t_0)] \cdot [p_2(t < t_0) + p_{St2}(t < t_0)]\}$ 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_{St2} 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 $\mathrm{d}T_2/\mathrm{d}t = \beta$, 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 $q(t = t_0) = 0$, $p_{St2}(t = t_0) = p_{St2}(t < t_0)$ and $(k \cdot F)_2(t = t_0) = (k \cdot F)_2(t < t_0)$ respectively $q(t \geq t_E) = 0$, $p_{St2}(t = t_E) = p_{St2}(t > t_E)$ and $(k \cdot F)_2(t = t_E) = (k \cdot F)_2(t > t_0)$ it follows using (2.11) that

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

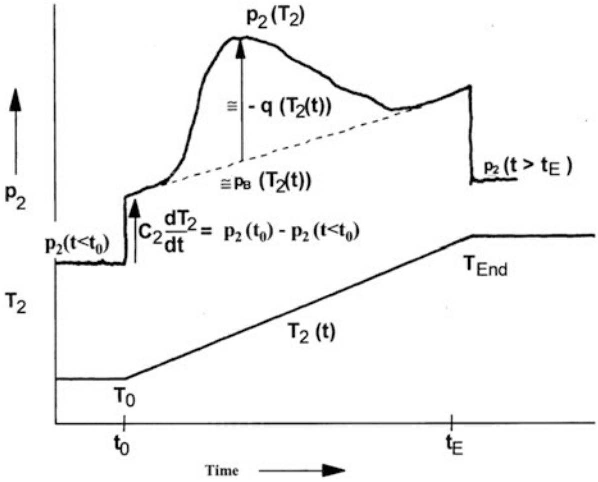

Fig. 2.27 Non-isothermal reaction (linear temperature programme, simplified apparatus)

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 temporarilly delayed compared with the changing temperature of the measuring kettle and the intermediate thermostat

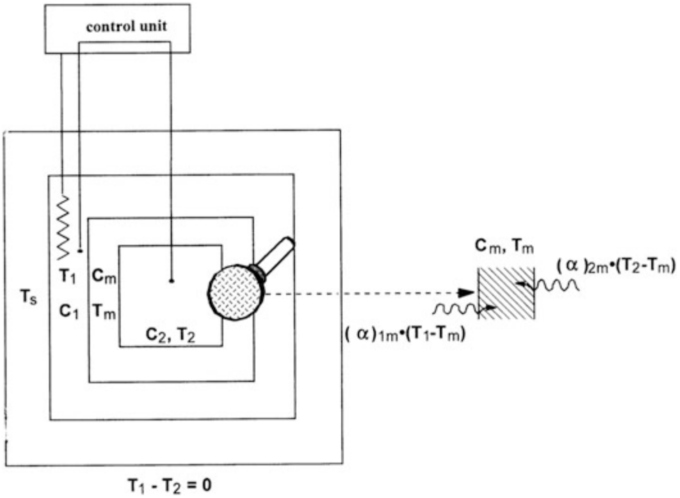

Fig. 2.28 Scheme of apparatus for adiabatic measurement

With

T_m	Mean temperature within wall of measuring kettle[9]
C_m	Corresponding mean heat capacity of measuring-kettle wall (see footnote 12)
α_{2m}	Heat-transfer coefficient: reaction mixture → inside wall of measuring kettle
α_{1m}	Heat-transfer coefficient: intermediate thermostat → outside wall of measuring kettle
$(k{\cdot}F)_1$	Heat-transfer coefficient: intermediate thermostat → socle thermostat[10]

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

$$C_2 \cdot \mathrm{d}T_2/\mathrm{d}t = q + p_{\mathrm{St2}} - \alpha_{2\mathrm{m}} \cdot (T_2 - T_\mathrm{m}) \tag{2.13}$$

$$C_\mathrm{m} \cdot \mathrm{d}T_\mathrm{m}/\mathrm{d}t = \alpha_{2\mathrm{m}} \cdot (T_2 - T_\mathrm{m}) + \alpha_{1\mathrm{m}} \cdot (T_1 - T_\mathrm{m}) \tag{2.14}$$

$$C_1 \cdot \mathrm{d}T_1/\mathrm{d}t = -\alpha_{1\mathrm{m}} \cdot (T_1 - T_\mathrm{m}) + p_{\mathrm{St1}} + p_1 - (k \cdot F)_1 \cdot (T_1 - T_\mathrm{S}). \tag{2.15}$$

Because the intermediate thermostat is being controlled, we have $T_1 = T_2$ as well as $\mathrm{d}T_1/\mathrm{d}t = \mathrm{d}T_2/\mathrm{d}t$[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 $\mathrm{d}T_2/\mathrm{d}t = \mathrm{d}T_1/\mathrm{d}t \cong \mathrm{d}T_\mathrm{m}/\mathrm{d}t$ as well as $T_1 = T_2 = T_\mathrm{m} + \partial T$, with $\partial T \cong \mathrm{const.}$ A very quick temperature rise causes $\mathrm{d}T_2/\mathrm{d}t = \mathrm{d}T_1/\mathrm{d}t \neq \mathrm{d}T_\mathrm{m}/\mathrm{d}t$ as well as $T_1 = T_2 = T_\mathrm{m} + \partial T$, with $\partial T \neq \mathrm{const.}$

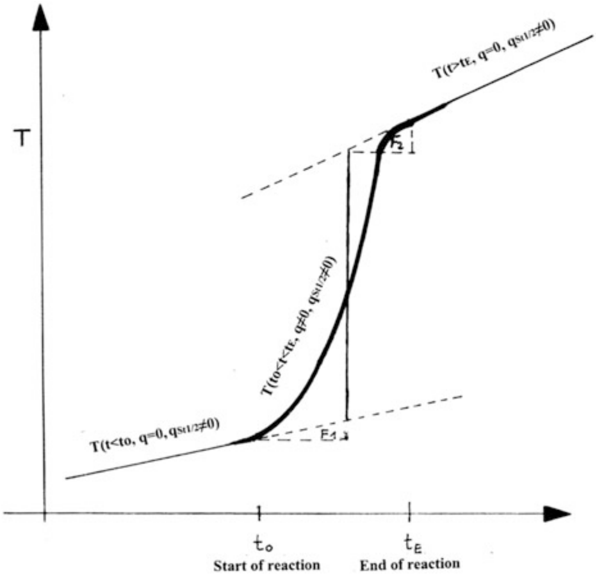

Fig. 2.29 Characteristic course of temperature of an exothermic reaction. Vertical distance between extrapolated straight lines $T(t < t_0, q = 0, p_{\mathrm{St2}} \neq 0,\ p_{\mathrm{M1}} \neq 0)$ and $T(t > t_{\mathrm{End\ of\ reaction}}, q = 0,\ p_{\mathrm{St2}} \neq 0,\ p_{\mathrm{M1}} \neq 0)$, 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

$$\begin{aligned}(C_2 + C_1) \cdot \mathrm{d}T_2/\mathrm{d}t + C_\mathrm{m} \cdot \mathrm{d}T_\mathrm{m}/\mathrm{d}t = q + p_{\mathrm{St2}} - \alpha_{2\mathrm{m}} \cdot (T_2 - T_\mathrm{m}) - \alpha_{1\mathrm{m}} \\ \cdot (T_1 - T_\mathrm{m}) + p_{\mathrm{St1}} + p_1 - (k \cdot F)_1 \cdot (T_1 - T_\mathrm{S}) + \alpha_{2\mathrm{m}} \cdot (T_2 - T_\mathrm{m}) + \alpha_{1\mathrm{m}} \\ \cdot (T_1 - T_\mathrm{m}) = q + p_{\mathrm{St2}} + p_{\mathrm{St1}} + p_1 - (k \cdot F)_1 \cdot (T_2 - T_\mathrm{S}).\end{aligned}$$

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: $q[T_1(t)]$.

$$q = (k \cdot F)_1 \cdot (T_1 - T_\mathrm{S}) + (C_2 + C_1) \cdot \mathrm{d}T_1/\mathrm{d}t + C_\mathrm{m} \cdot \mathrm{d}T_\mathrm{m}/\mathrm{d}t - p_{\mathrm{St2}} - p_{\mathrm{St1}} - p_1$$

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

$$\begin{aligned}q = (k \cdot F)_1 \cdot (T_1 - T_\mathrm{S}) - (k \cdot F)_{10} \cdot (T_{10} - T_\mathrm{S}) + (C_2 + C_1) \cdot \mathrm{d}T_1/\mathrm{d}t \\ - (C_2 + C_1)_0 \cdot (\mathrm{d}T_1/\mathrm{d}t)_0 + C_\mathrm{m} \cdot \mathrm{d}T_1/\mathrm{d}t - C_{\mathrm{m}0} \cdot (\mathrm{d}T_1/\mathrm{d}t)_0 - (p_{\mathrm{M2}} - p_{\mathrm{M20}}) \\ - (p_{\mathrm{M1}} - p_{\mathrm{M10}}) - (p_1 - p_{10}).\end{aligned}$$

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, $\mathrm{d}T_\mathrm{m}/\mathrm{d}t \cong \mathrm{d}T_2/\mathrm{d}t = \mathrm{d}T_1/\mathrm{d}t$ as well as $(p_\mathrm{M1} - p_\mathrm{M10}) \cong 0$ the following expression results:

$$
\begin{aligned}
q \cong{} & (k \cdot F)_{10} \cdot \big(T_1 - (T_1)_0\big) + (C_2 + C_1 + C_\mathrm{m})_0 \cdot \big(\mathrm{d}T_1/\mathrm{d}t - (\mathrm{d}T_1/\mathrm{d}t)_0\big) \\
& - (p_\mathrm{M2} - p_\mathrm{M20}) - (p_1 - p_{10}).
\end{aligned}
$$

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 $(\alpha)_\mathrm{1m}$ and $(\alpha)_\mathrm{2m}$, in which generally $(\alpha)_\mathrm{1m}$ is smaller than $(\alpha)_\mathrm{2m}$.

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.

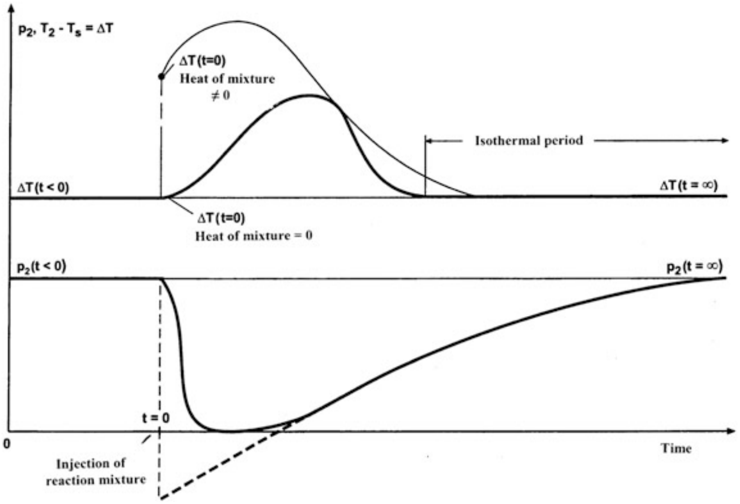

Fig. 2.30 Courses of temperature and heating power p_2 during start of reaction whose power q cannot be immediately compensated due to thermal inertia

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],

$$(q + q_{Mi}) = (k \cdot F)_2 \cdot [T_2 - T_S] - p_{St2} + C_2 \cdot d[T_2 - T_S]/dt. \tag{2.16}$$

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 calorikinetic 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.

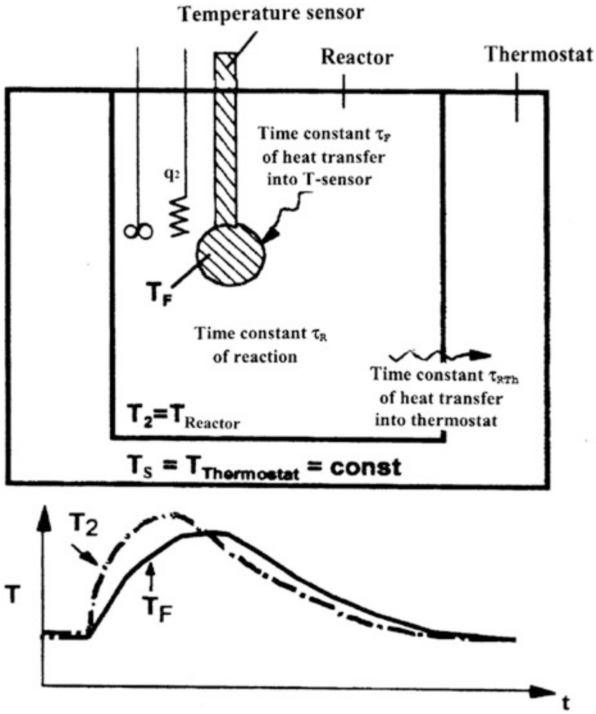

Fig. 2.31 Scheme of isoperibolic measurement equipment. Characteristic course of temperature of an exothermic reaction

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 reaction[13] 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

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[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 $\left[(k \cdot F_2)_{t=t_E} - (k \cdot F_2)_{t<0}\right] \Big/ t_E = \beta$ by

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

$\boldsymbol{p_{St2}}$**:**

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 $T_{2(t \geq E)} = T_S + p_{St2(t \geq t_E)}/(k \cdot F)_{2(t \geq t_E)} = \text{const}_2$, 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 $0 \leq t \leq t_E$

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

$\boldsymbol{C_2}$**:**

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,

$$C_2 = C_F + C_{Mt} = c_P \cdot G + C_{Mt}. \tag{2.19}$$

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 $T_2(\mathrm{p}_2)$. After the electric heating power p_2 is switched off, the temperature decreases due to (2.16) according to the equation

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

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 $C_{2(t \geq t_\mathrm{E})}$. Using $\left[C_{2(t \geq t_\mathrm{E})} - C_{2(t \leq 0)}\right]/t_\mathrm{E} = \gamma$, the temporal course of the effective heat capacity C_2 in the time interval $0 < t < t_\mathrm{E}$ can be found in a first approximation by

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

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

$$\begin{aligned} C_2 \cdot \mathrm{d}T_2/\mathrm{d}t &= (q + q_\mathrm{Mi}) - (k \cdot F)_2 \cdot [T_2 - T_1] + p_\mathrm{St2}, \\ C_1 \cdot \mathrm{d}T_1/\mathrm{d}t &= (k \cdot F)_2 \cdot [T_2 - T_1] - (k \cdot F)_1 \cdot [T_1 - T_\mathrm{S}] + p_\mathrm{St1}. \end{aligned}$$

Combining both equations gives

$$(q + q_\mathrm{Mi}) = C_2 \cdot \mathrm{d}T_2/\mathrm{d}t + C_1 \cdot \mathrm{d}T_1/\mathrm{d}t + (k \cdot F)_1 \cdot (T_1 - T_\mathrm{S}) - p_\mathrm{St2} - p_\mathrm{St1}. \tag{2.21}$$

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 $(q = \mathrm{const})$ and without changes in consistency $\left(q_{\mathrm{St2}}, (k \cdot F)_2 = \mathrm{const}\right)$. 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

$$C_\mathrm{F} \cdot \mathrm{d}T_\mathrm{F}/\mathrm{d}t = \beta' \cdot (T_2 - T_\mathrm{F}) \tag{2.22}$$

and

$$\begin{aligned} C_2 \cdot \mathrm{d}T_2/\mathrm{d}t &= q + q_{\mathrm{St2}} - (k \cdot F)_2 \cdot (T_2 - T_\mathrm{S}) - \beta' \cdot (T_2 - T_\mathrm{F}) \\ &= q + q_{\mathrm{St2}} - (k \cdot F)_2 \cdot (T_2 - T_\mathrm{S}) - C_\mathrm{F} \cdot \mathrm{d}T_\mathrm{F}/\mathrm{d}t. \end{aligned} \tag{2.23}$$

Because of

- $C_\mathrm{F} \ll C_2$, i.e. the sensor represents a negligibly small heat sink, the heat flow from the reaction mixture into the sensor can be neglected
- $q_{\mathrm{St2}} = \mathrm{const}$, i.e. $q_{\mathrm{St2}} = (k \cdot F)_2 \cdot (T_{20} - T_\mathrm{S})$ respectively $T_{20} = T_\mathrm{S} + q_{\mathrm{St2}}/(k \cdot F)_2$

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

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

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

$$\text{for } 0 < t \le t_\mathrm{E} \quad T_2 = a/b \cdot (1 - \mathrm{EXP}[-b \cdot t]) + T_{20} \tag{2.25}$$

and

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

with

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

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 signalized by the temperature sensor,

$$T_\mathrm{F} = \kappa \cdot \{\mathrm{EXP}[-\beta \cdot t] - \mathrm{EXP}[-b \cdot t]\} + \gamma \cdot \{1 - \mathrm{EXP}[-\beta \cdot t]\} + T_{20} \quad \text{for } 0 < t \le t_\mathrm{E}$$

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[14] See Sect. 4.2.1.1.1.1.

and

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

with

$\beta = \beta' / C_F = 1/\tau_F$
$\equiv$ reciprocal time constant of heat transfer from reaction mixture into sensor,
$\kappa = a \cdot \beta / b / (\beta - b)$ 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

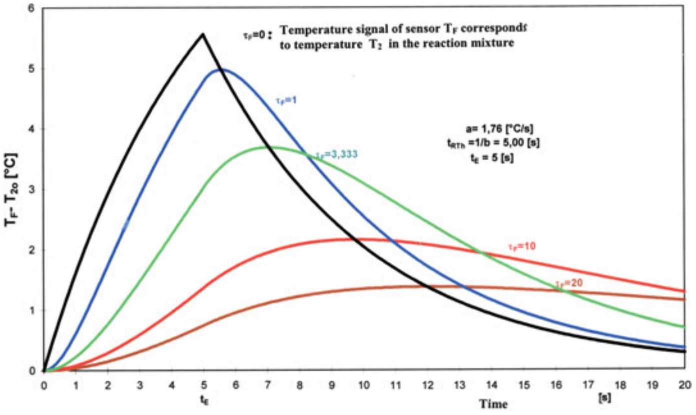

Fig. 2.32 Signal difference $T_F - T_{F,0}(\equiv T_{20})$ of sensor temperature for different time constant τ_F of sensor during a constant thermal reaction power, end of heat release at time point t_E

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

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

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

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[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).

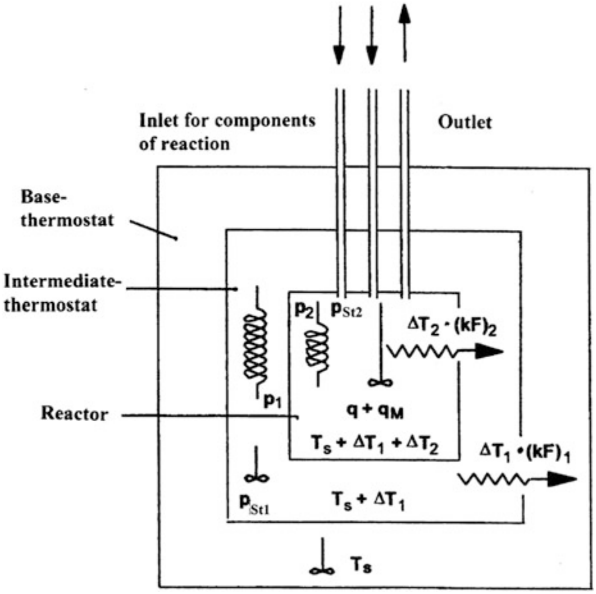

Fig. 2.33 Principle of flow calorimeter TKR

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

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

(b) Intermediate thermostat

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[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 $g \cdot c_p \cdot \left(T_{\mathrm{Laboratory}} - T_2\right)$ and physicochemical mixing (physicochemical heat).

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

This results in

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

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

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

or

$$q + q_{\mathrm{Mi}} = p_0 - p \tag{2.27}$$

with

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

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 $p(t < t_{\mathrm{s}})_{\mathrm{CONT}}$ from the sum of the thermal powers of the discontinuous reaction at time t_{s} $p(t = t_{\mathrm{s}})_{\mathrm{DISC}}$. Hence,

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

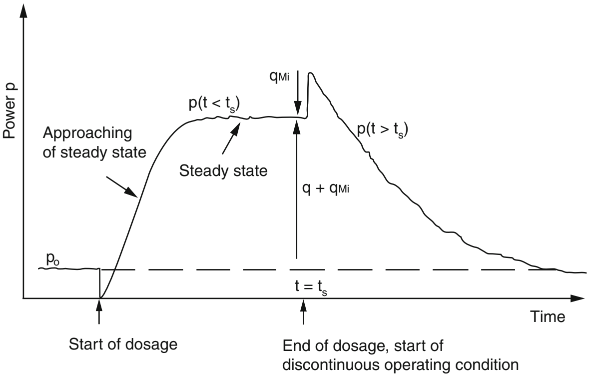

Fig. 2.34 Determination of thermal reaction power q and thermal mixing power q_{Mi} of an isothermal, continuous chemical conversion

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

$$\text{Measuring kettle} \qquad q + q_{\mathrm{E}} + p_2 + p_{\mathrm{St2}} = (k \cdot F)_2 \cdot \Delta T_2 \tag{2.28}$$

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

$$\text{Condenser/intermediate thermostat} \qquad q_{\mathrm{C}} + p_3 + p_{\mathrm{St3}} = (k \cdot F)_3 \cdot \Delta T_3 \tag{2.30}$$

$$q_{\mathrm{C}} = -q_{\mathrm{E}} \tag{2.31}$$

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

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

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

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

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[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.

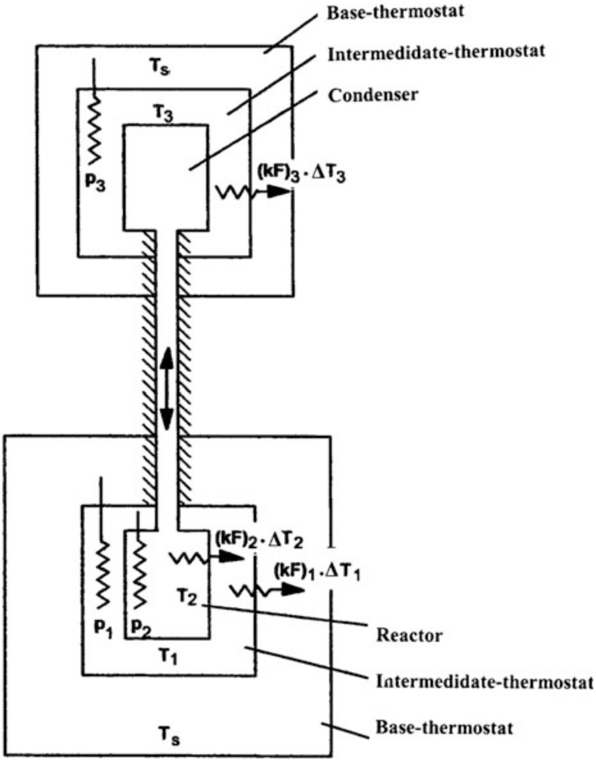

Fig. 2.35 Compact calorimeter and reflux condenser for discontinuous, isothermal reaction

or

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

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 heater[18] in the measuring kettle.

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

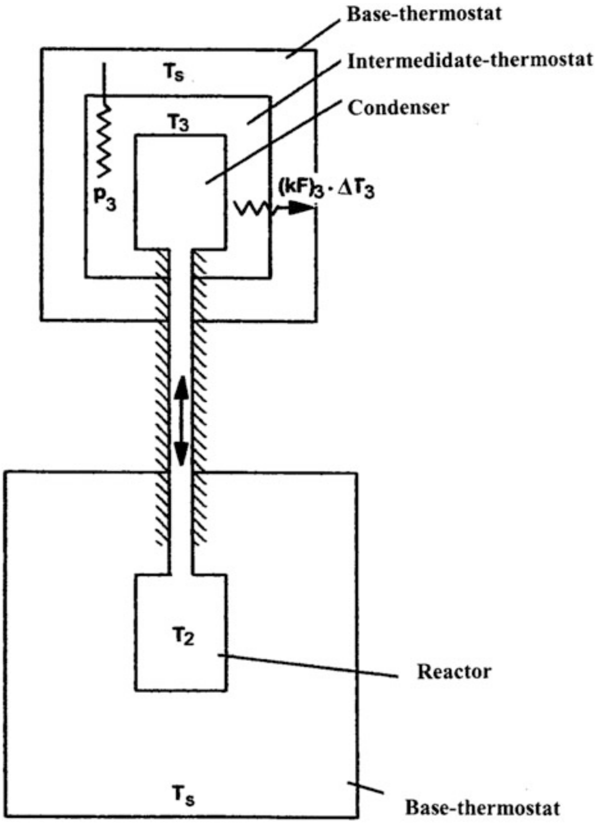

Fig. 2.36 Schematic representation of measuring apparatus for reaction with reflux of a boiling component of reaction mixture

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 reactions[19] 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

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[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.

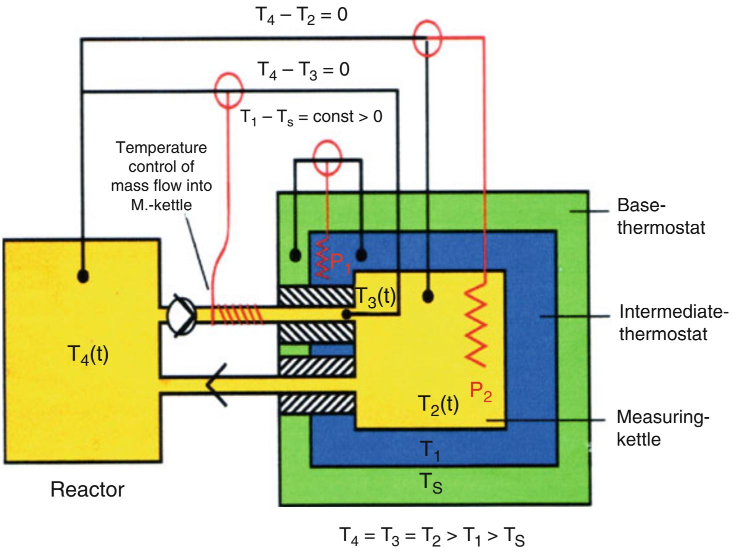

Fig. 2.37 Scheme of online calorimeter (calorimeter sensor)

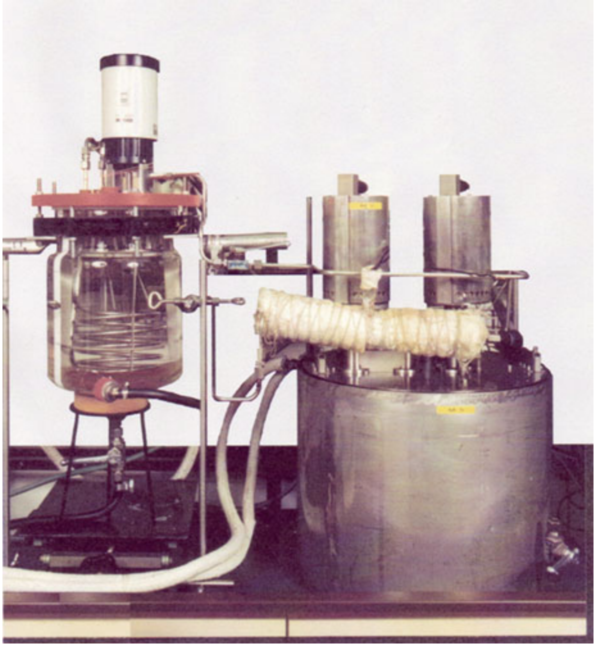

Fig. 2.38 Direct view of online calorimeter (*right*), coupled with tank reactor (*left*)

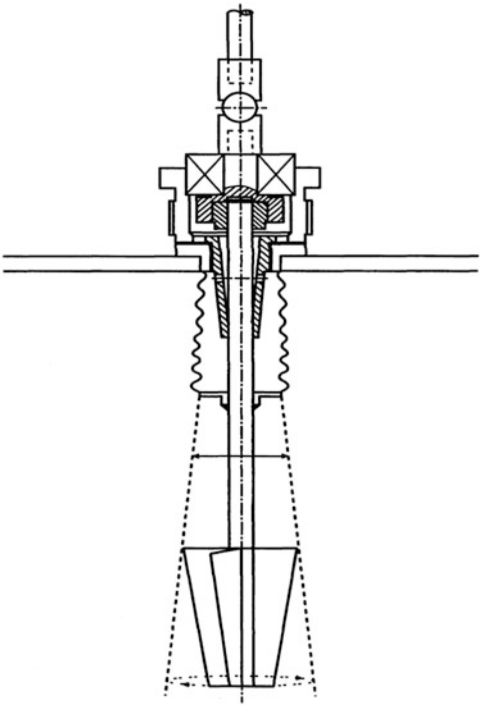

Fig. 2.39 Circular pendulum mixer; *top*: bearing of mixer, *bottom*: design of mixer

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 → 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

$$C_2 \cdot \mathrm{d}T_2/\mathrm{d}t = q + p_{\mathrm{St2}} + p_2 - (k \cdot F)_2 \cdot [T_2 - T_1]. \tag{2.33}$$

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

$$0 = (k \cdot F)_2(T_1) \cdot [T_2 - T_1] + p_{\mathrm{St1}} + p_1 - (k \cdot F)_1 \cdot [T_1 - T_{\mathrm{S}}].$$

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

$$q = \left\{(k \cdot F)_1 \cdot [T_1 - T_{\mathrm{S}}] - p_{\mathrm{St1}}\right\} - \{p_1 + p_2 + p_{\mathrm{St2}}\} + C_2 \cdot \mathrm{d}T_2/\mathrm{d}t.$$

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_{St1} 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:

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[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:

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

- Semi-continuous reaction in tank reactor:
  when $c_{\mathrm{R0}} = 0$ it follows that $c_{\mathrm{R}} = g/M/V/k \cdot [1 - \mathrm{EXP}(-kt)]$,

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

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

$$c_{\mathrm{R}} = c_{\mathrm{Mk}}.$$

- Continuous reaction in tank reactor:

$$c_{\mathrm{R}} = c_{\mathrm{Rstat}}, \quad c_{\mathrm{Mk}} = c_{\mathrm{Rstat}}/(1 + k\tau);$$

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

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

$$q = \mathrm{const}'(T_1, T_S) - \{p_1 + p_2 + p_{St2}\} + C_2 \cdot \mathrm{d}T_2/\mathrm{d}t.$$

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:

$$q = \mathrm{const}(T_1, T_S, N_2) - p + C_2 \cdot \mathrm{d}T_2/\mathrm{d}t \tag{2.34}$$

with

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

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 $(\mathrm{d}T_2/\mathrm{d}t = 0)$ is achieved, the sum of the powers p_1, p_2 and p_{M2} corresponds to the desired constant, i.e.

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

The value of 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:

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

C_{Mt} is, in contrast to C_F, an apparatus constant[21] 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:

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[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 $T_2(t) - \left(T_1 + p_{St2}/(k \cdot F)_2\right)$ 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 $T_2(t) - \left(T_1 + p_{St2}/(k \cdot F)_2\right) \cong T_2(t) - T_1$ due to $\mathrm{p_{St2}/(k \cdot F)_2 \ll T_1}$.

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]

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[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:

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

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

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

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

Consequently, in Eq. (2.34) determining the rate of heat release q in the measuring kettle, 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. $\mathrm{d}T_2(t)/\mathrm{d}t$ 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 ($v < 500$ 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 °C → 250 °C
• Maximum frequency of circular pendulum mixer	40 Hz
• PID control system	
• Maximum electric heating power	500 W
• Resolution	<2 W
• Maximum operating pressure	32 bar
• Time constant of reaction	>1 h
• Kinematic viscosity	$v < 500$ 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.

Chapter 3
Practical Hints

3.1 Standardization of Signal Accuracy of Electric Heating Powers in a Measuring Kettle, Intermediate Thermostat, and Reflux Condenser as well as the Stirring Power in a Measuring Kettle

Despite the thoroughness of amperemeter, voltmeter, amplifier, analog-digital converter etc. today, the possibility cannot be excluded that several homemade recording units, though possessing such electric elements, give for the same actual test value signals with differences that are beyond the range of tolerance. This is important when the signals are intermediate values when establishing target quantities. For the measurements of calorimeters this fact must also be taken into account. With calorimeters for isothermal reactions, the accuracy of signals of the different actual powers p_1, p_2 and p_{St2} must be checked and, if necessary, be standardized as follows.

As described earlier, for set points

- Temperatures T_{S}, ΔT_1, ΔT_2
- Rotational velocity of stirrer
- Degree of fillings of base thermostat, intermediate thermostat and measuring kettle

the actual quantities $p_1, p_2, p_{\mathrm{St2}}$ achieve fixed values at the control equilibrium. The sum $p_1 + p_2 + p_{\mathrm{St2}} + \mathrm{const}_{\mathrm{MStL2}} = p_1 + p_2 + p_{\mathrm{M}}$ corresponds to $(kF)_1 \cdot \Delta T_1 - p_{\mathrm{St1}} + \mathrm{const}_{\mathrm{MStL2}} = \mathrm{const} = p_0$. According to (2.1)–(2.4) the sum remains unchanged after an induced change in p_2 or p_{St2}.[1] For example, variation in the heating power p_2 in the measuring kettle by δp_2 causes a change in the heat flow out of the measuring kettle into the intermediate thermostat by δp_2. To maintain the

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[1] For instance, variation in p_2 due to changes in the set value ΔT_2 to $(\Delta T_2 + \delta\Delta T_2)$, its change due to varied manual setting, a variation in p_{St2} due to a change in the consistency in the filling of the measuring kettle.

W. Litz, *Bench Scale Calorimetry in Chemical Reaction Kinetics*,
DOI 10.1007/978-3-319-12532-9_3

temperature difference ΔT_1, the control system of the intermediate thermostat changes the electric heating power p_1 by making δp_2 equal but opposite to it, i.e., $\delta p_1 = -\delta p_2$.

The same goes for changes in the stirring power p_{St2}. Because of the variation in the stirring power by δp_{St2}, the control system of the measuring kettle changes the heating power p_2 by an opposite and equal amount, maintaining the temperature difference ΔT_2, i.e. we have $\delta p_2 = -\delta p_{\mathrm{St2}} = -\delta p_{\mathrm{M2}}$.

As a rule, the first use of installed recording units indicates signals[2] with differences between $\boldsymbol{\delta p_2}$ and $-\boldsymbol{\delta p_1}$ or $\boldsymbol{\delta p_2}$ and $-\boldsymbol{\delta p_{\mathrm{St2}}}$ respectively $-\boldsymbol{\delta p_{\mathrm{M2}}}$, which are small but outside the range of tolerance. To eliminate the discrepancies in the signal accuracies of the recording units, the accuracies for the signals of the heating power $\boldsymbol{p_1}$ in the intermediate thermostat and of the stirring power $\boldsymbol{p_{\mathrm{St2}}}$ in the measuring kettle must be adjusted to the signal accuracy of the recording unit of power $\boldsymbol{p_2}$ in the measuring kettle. For that, factors f are installed in these measuring systems using hardware or software by which the imperfect, inner outcomes are multiplied for the purpose of improving the accuracy of the signals.

3.1.1 Heating Power in Intermediate Thermostat

The adjustment of the signal accuracy of the heating power $\boldsymbol{p_1}$ in the intermediate thermostat must be performed first of all as follows: ΔT_1 and ΔT_2 (stirring power $p_{\mathrm{St1}} = \mathrm{const}$) are set to such values that the value $\boldsymbol{p_{10}}$ is as small as possible (e.g. 3 W) and the value $\boldsymbol{p_{20}}$ as large as possible (e.g. $\cong 200$ W) (Fig. 3.1).

ΔT_2 must then be reduced by such an amount $\delta\Delta T_2$ that $\boldsymbol{q_2}$ decreases by a magnitude δp_2 as large as possible (e.g. $\cong 180$ W). The signal of the compensating increase $\boldsymbol{\delta p_1}$ of the heating power $\boldsymbol{p_1}$ in the intermediate thermostat is, for instance, $\boldsymbol{\delta p_1} < -\boldsymbol{\delta p_2}$. This means that, although the sum of the actual quantities $p_1 + p_2 + p_{\mathrm{St2}}$ remains unchanged $\boldsymbol{p_0}$, the signal indicates wrongly, instead of $\boldsymbol{p_0}$, a decreased sum $\boldsymbol{p_0'}$. To adjust the signal $\boldsymbol{p_1}$ the factor f_1 for the inner outcome in the recording unit must be enlarged until the following result is obtained:

$$\boldsymbol{p_0'} = \boldsymbol{p_0},$$

i.e.

$$\boldsymbol{\delta p_1} = -\boldsymbol{\delta p_2}.$$

3.1.2 Stirrer Power in Measuring Kettle

Now we can start to adjust the signal accuracy of the recording unit for the stirring power p_{St2}. Because the stirring power cannot be measured directly but only

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[2] In what follows, **signals** of the actual quantities are denoted by **boldface** type.

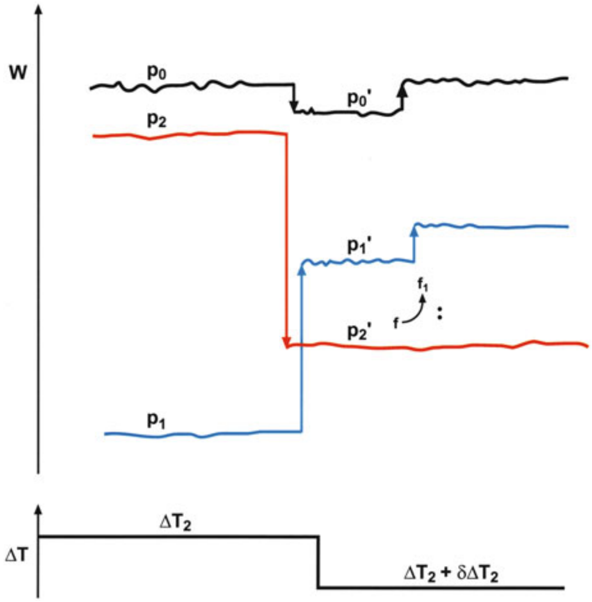

Fig. 3.1 Adjustment of signal accuracy for heating power $\boldsymbol{p_1}$ in intermediate thermostat to signal accuracy for heating power $\boldsymbol{p_2}$ in measuring kettle

indirectly by means of the power $p_{\mathrm{M2}} = p_{\mathrm{St2}} + p_{\mathrm{Loss}} = p_{\mathrm{St2}} + \mathrm{const}_{\mathrm{MStL2}}$ (see Sect. 2.1.1) of the driving motor, the adjustment must be taken place via iterative mode as follows.

The measuring kettle is filled with a substance of high viscosity η under normal pressure, for instance silicone fluid M1000. The rotational velocity of the stirrer should be set at a high level, for example 1,500 rpm. A small volume of nitrogen gas should be injected into the filling of the measuring kettle. Because of the high turbulence in the liquid filling, this volume splits into countless small bubbles, so that the initial high viscosity η decreases to a very small effective viscosity η_{eff}. The controlled equilibrium for chosen set points T_{S}, ΔT_1, ΔT_2 is represented by the actual values p_1, p_2, p_{St2} respectively $p_{\mathrm{M2}} = p_{\mathrm{St2}} + \mathrm{const}_{\mathrm{MStL2}}$ as well as their constant sum p_0 (Fig. 3.2). The signal of the motor power is $\boldsymbol{p_{\mathrm{M2}} = p_{\mathrm{St2}} + \mathrm{const}_{\mathrm{MStL2}}}$, the signals of the heating power in measuring kettle and intermediate thermostat is $\boldsymbol{p_2}$ respectively $\boldsymbol{p_{1(\mathrm{adjusted})}}$. Hence the sum of the signalized powers is

$$\begin{aligned}\boldsymbol{p_1}_{(\text{adjusted})} + \boldsymbol{p_2} + \boldsymbol{p_{\mathrm{M2}}}_{(\text{not adjusted}, f=1)} &= \boldsymbol{p_1}_{(\text{adjusted})} + \boldsymbol{p_2} \\ &\quad + (\boldsymbol{p_{\mathrm{St2}}} + \boldsymbol{\mathrm{const}_{\mathrm{MStL2}}})_{(\text{not adjusted}, f=1)} \\ &= \boldsymbol{p_0} = \text{const}.\end{aligned}$$

A pressure stroke in the measuring kettle compresses the small nitrogen bubbles into tiny vesicles, so that the previous high viscosity η results. Because of that, the stirring power increases by δp_{St2}. The control system of the measuring kettle

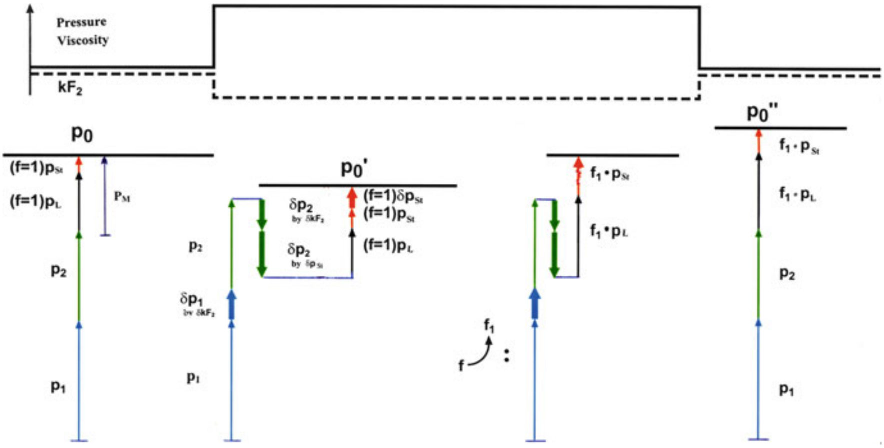

Fig. 3.2 Iterative adjustment of signal accuracy of stirring power $\boldsymbol{p_{St2}}$ to signal accuracy of heating power $\boldsymbol{p_2}$ of measuring kettle

changes p_2 to an opposite and equal value, i.e. we have $\delta p_{St2} = -\delta p_2$, and the sum of the actual quantities $p_1 + p_2 + p_{M2}$ remains unchanged p_0. If the recording unit indicates a motor power signal that is smaller than the value $p_{M2} = p_{St2} + \mathrm{const}_{MStL2}$, i.e. $\boldsymbol{\delta p_{St2}} < \delta p_{St2}$, then the signal $\boldsymbol{p}$ decreases from $\boldsymbol{p_0}$ to $\boldsymbol{p_0'}$ (Fig. 3.2).[3] To obtain $\boldsymbol{p_0'} = \boldsymbol{p_0}$, the adjustment factor f must be increased up to a value f_1. However, this first instance of equality does not mean that we now have $\boldsymbol{\delta p_{St2}} = -\boldsymbol{\delta p_2}$, but only $\boldsymbol{\delta p_{M2}} = -\boldsymbol{\delta p_2}$, because the $\boldsymbol{p_{St2}}$ part of $\boldsymbol{p_{M2}'}$ is less enlarged than the $\mathbf{const}'_{\mathbf{MStL2}}$ part because $\boldsymbol{p_{St2}'} < \mathbf{const}'_{\mathbf{MStL2}(\boldsymbol{p_2})} = \boldsymbol{P_{L2}}$. Hence, the adjustment must be continued in succession in an iterative mode.

To this end, the measuring kettle is decompressed. This leads to an expansion of the tiny vesicles, by which a small viscosity η_{eff} is renewed. Because of $f_1 > f$, the indicated $\boldsymbol{p_0''}$ is now larger than $\boldsymbol{p_0}$. This value $\boldsymbol{p_0''}$ is to be used as the new starting value p_0 for the adjusting procedure. The adjusting work is successful, i.e. $\boldsymbol{\delta p_{St2}} = -\boldsymbol{\delta p_2}$, when further (i) pressure rises/drops, vice versa, produce no change in the sum of the signalized powers $\boldsymbol{p_1}$, $\boldsymbol{p_2}$ and $\boldsymbol{p_{M2}} = \boldsymbol{p_{St2}} + \boldsymbol{p_{L2}}$; hence

$$\boldsymbol{p_0}(\boldsymbol{i}) = \boldsymbol{p_0}\left(\boldsymbol{i'}\right) = \boldsymbol{p_0}\left(\boldsymbol{i''}\right) = \cdots = \cdots$$

---

[3] The compensation of the heat flow change $\delta\Delta T_2 \cdot (k \cdot F)_2$ by δp_1 is correctly indicated because $\boldsymbol{p_1}$ has already been adjusted.

3.1.3 Intermediate Thermostat of the Reflux Condenser

Following adjustment of the accuracy of the measuring signals of the stirring power $\boldsymbol{p}_{\mathbf{St2}}$ and the electric heating power $\boldsymbol{p}_{\mathbf{1}}$ in the intermediate thermostat, the accuracy of the signal of the heating power $\boldsymbol{p}_{\mathbf{3}}$ in the intermediate thermostat of the reflux condenser can be adjusted. The procedure is the same as with the signal of the heating power $\boldsymbol{p}_{\mathbf{1}}$ in the intermediate thermostat, as follows.

The batch in the measuring kettle must be a solution of a low-boiling-point component in a high-boiling-point liquid (for instance ethyl alcohol in ethylene glycol). The set points of the temperatures T_S, ΔT_1, ΔT_2 in the calorimeter respectively T_{SC}, ΔT_3 in the reflux condenser unit are chosen to be of such magnitudes that, for example, during evaporation in the measuring kettle and condensation in the reflux condenser the heating power p_2 in the measuring kettle is large respectively the heating power p_3 in the intermediate thermostat of the condenser is as small as possible. A change of the set temperature in the measuring kettle by $\delta\Delta T_2$ to $T_2 + \delta\Delta T_2$ changes

- The thermal evaporation power in the measuring kettle by δp_E,
- The heat flow out of the measuring kettle into the intermediate thermostat by $\delta\Delta T_2 \cdot (k \cdot F)_2$,
- The thermal condensation power by δp_3.

The first two variations are compensated by the change δp_2 in the electric heating power p_2 in the measuring kettle. According to (2.28), for the two parts of δp_2 the following expressions are valid:

$$\delta_1 p_2 = -\delta p_E$$
$$\delta_2 p_2 = \delta\Delta T_2 \cdot (k \cdot F)_2.$$

Because of (2.28)–(2.31) we obtain the results

$$\delta_1 p_2 = -\delta p_3 \quad \text{and} \quad \delta_2 p_2 = -\delta p_1,$$

i.e. the part $\delta_1 p_2$ of δp_2 concerning evaporation is opposite and equal to the change in the heating power p_3 of the intermediate thermostat of the condenser, the part $\delta_2 p_2$ concerning heat flow is opposite and equal to the change in the heating power p_1 in the intermediate thermostat of the calorimeter. Hence, according to (2.32), the sum $[p_1 + p_2 + p_3 + p_{M2}]$ of the actual powers remains unchanged at value p_0.

When the signal $[\boldsymbol{p}_{\mathbf{1}(\text{adjusted})} + \boldsymbol{p}_{\mathbf{2}} + \boldsymbol{p}_{\mathbf{3}(\text{not adjusted})} + \boldsymbol{p}_{\mathbf{M2}(\text{adjusted})}]$ offers a value $\boldsymbol{p}'_{\mathbf{0}}$ which is smaller, for instance, than $\boldsymbol{p}_{\mathbf{0}}$, i.e. $\boldsymbol{\delta p_3} < -\boldsymbol{\delta_1 p_2}$, the adjusting factor f_3 improving the signal p_3 of the intermediate thermostat of the condenser must be[4] increased until $\boldsymbol{p}'_{\mathbf{0}}$ is equal to $\boldsymbol{p}_{\mathbf{0}}$, i.e. $\boldsymbol{\delta p_3} = -\boldsymbol{\delta_1 p_2}$.

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[4] The compensation of the heat flow change $\delta\Delta T_2 \cdot (k \cdot F)_2$ by $\boldsymbol{\delta p_1}$ is correctly indicated because $\boldsymbol{p}_{\mathbf{1}}$ has already been adjusted.

3.2 Attenuation of Interference Due to the Occasional Phenomenon of Vaporization and Condensation Within the Calorimeter During Isothermal Reactions

The inner surface of the measuring kettle wall always has a lower temperature than the filling within the measuring kettle. When the laboratory temperature is considerably lower than the temperature in the measuring kettle, the temperature in certain regions of the pipes[5] which extend from the cover of the measuring kettle via the intermediate and base thermostats up to the laboratory (see Figs. 2.5 and 2.10) can differ from the temperature in the measuring kettle. Therefore, depending on the vapour pressure of the different species in the reaction mixture, more or less distinct evaporation and condensation on the fluctuatingly exposed areas of the inner wall of the measuring kettle and in zones of the pipes take place. Evaporated components condense there fluctuatingly, and the heat from the condensation passes into the metal. When the condensation occurs only

- On the inner surface of the measuring-kettle wall
- On the zones of the pipes within the intermediate thermostat

the deranging heat effect is involved in the total heat balance, hence the correct estimation of the thermal reaction power is assured according to (2.4). Of course, this is the case all the more when the intensity of evaporation decreases because of a diminution of vapour pressure caused by an injection of reactants at the start of the reaction or because of the change in the composition of the reaction mixture by the chemical conversion.

However, when the vapour extends owing to a high diffusion rate to the zones of the pipes located in the base thermostat or even in the laboratory, it is necessary to quiet the evaporation dynamics. This takes place by increasing the pressure with an inert gas because the diffusion coefficient becomes inversely proportional to the increasing pressure according to the kinetic theory of ideal gases. Much more effective is this brake effect with the vapour phase. Because of the diminution of the rate of diffusion by means of a sufficiently high increase in pressure, the region of condensation can be restricted to zones within the intermediate thermostat. As a rule, tests show that a pressure load of two to three times the boiling pressure of the involved species is sufficient to prevent from falsification of the measuring results.

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[5] Used for dosage of the reaction mixture, measurement of pressure and as a holder system of the stirrer bearing/shaft.

3.3 Instantaneous Dosing of Granule Material

Both for conventional and calorimetric investigations, to elaborate the reaction kinetics, it is usually advantageous to use the mode of discontinuous working. For this, the reactor should be prefilled with a mixture of defined, reactionless composition, the mixture brought to the temperature of the chemical conversion and the reaction started by an instantaneous dosing of the starting reactants, which should also be brought to the temperature of the mixture. Then certain defined physicochemical processes (mixing, solving, dispersing, evaporating, precipitating) occur in the reaction mixture, coupled with the chemical conversion.

It is widely known that this process can be carried out without a problem using a liquid injection mass by means of, for instance, a piston syringe with temperature control, pushed by gas pressure or by means of a powerful quick-action pressure-feed pump with temperature control. However, the quasi-instantaneous dosing of granule material, brought to the exact temperature of the batch, against pressure is not possible by means of conventional dosing equipment (conveyor worm). For this kind of dosage, the rotary dosing unit is suitable (Fig. 3.3). A cylindrical chamber is installed in the measuring kettle. Its cover is removable for the purpose of filling. The bottom, however, is fixed to the stirrer shaft. Symmetrically one-half of a lattice stirrer is in a higher position on the bottom within the chamber; the other half is in a lower position of the bottom and juts out into the measuring kettle. The cylindrical jacket—secured by means of sealing rings (which do not tend to swell up) on the cover and bottom pressure—can be pulled up parallel to the stirrer shaft using a hydraulic lifting unit. For this action the motor is stopped for a moment but is started again after a very short period of time at the previous rotational velocity. The batch of the chamber is centrifuged outward and, by rapid stirring, dispersed instantaneously. This way of dosing combines

- The exact conformity of the temperatures in the batch and the added substance
- Quasi-instantaneous dosing and quasi-instantaneous distribution.

3.4 Instantaneous Dosing of Slurry

During the time necessary to achieve exact thermal equilibrium in the calorimeter (approximately 1 h), which is the prerequisite for the start of a strictly isothermal measurement, a thermally instable substance in the chamber of the rotary dosing unit is changed to an unknown degree. A thermally instable substance must therefore be brought to the temperature of the reaction in as short a time as possible and then dosed as quickly as possible. It is advisable to dose thermally instable solids in the form of slurry using a dosing unit described as follows.

A longish chamber is installed in the vertical direction above the dosage inlet of the measuring kettle in the calorimeter. It is surrounded by an electric heating jacket. The end of the chamber above the inlet is conically formed and closed by a

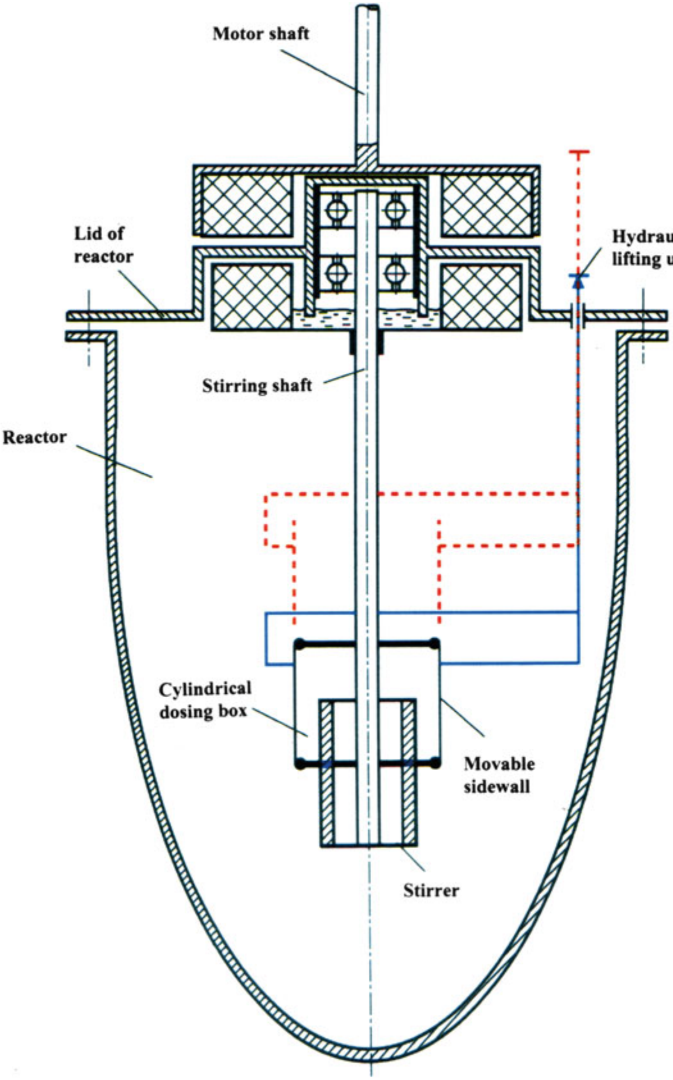

Fig. 3.3 Rotary dosing unit within measuring kettle for instantaneous mixing of a mass (liquid, granule material) at the exact temperature of the batch

pressure-tight, relatively great ball valve. The upper part of the chamber is removable for filling with slurry. The cover has an inlet pipe for pressure strokes. A small stirrer driven by an electric motor via a magnet cluster ensures that

- A batch of solid/liquid disperses to produce slurry
- The dispersed solids do not clump but a homogenously distributed slurry is maintained

- The slurry is brought very quickly to the reaction temperature by the controlled heating jacket
- The slurry is dosed quasi-instantly without complications after the ball valve is opened

3.5 Diminution of Interferences on Evaluation of Non-isothermal Net Measuring Results

The prerequisite for the usability of the determining equations for the thermal reaction power q or the temperature,[6] derived earlier, is that the temperature T_S of the base thermostat remains at a constant level during measurement or changes at least quasi-statically, i.e. in a quasi-continual equilibrium state of the total system.

The following possibilities are appropriate for this purpose:

(a) Use of a base thermostat with a high-heat-capacity filling
(infinitely large heat reservoir)
(b) Control of temperature T_S by means of a regulation system.

Tests with a calorimeter (measuring kettle, intermediate thermostat and base thermostat) reveal

for (a)	Only a base thermostat of an unusable size has a sufficiently high heat capacity
for (b)	Sporadic temperature fluctuations of irregular intensity, which mutually and strongly interfere with the electric heating powers and temperatures, cannot be eliminated even if one has installed additional baffles, several stirrers and a centrifugal pump.[7]

Because of this fact, indirect control of the temperature T_S is used. For that, a relatively small, precisely regulated socle thermostat with a temperature T_0 having maximum fluctuations of $\delta T_0 \cong 0.02$ °C brings the temperature of the base thermostat (30 L volume for a small measuring kettle, 50 L for a large one) to the temperature T_S by means of a heat exchanger. The heat exchanger is uniformly distributed within the base thermostat. The temperature fluctuations δT_0 in the socle thermostat are transmitted in an extremely attenuated form to the base thermostat, so that for a base thermostat without a load, $\delta T_S \cong 0$ holds.

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[6] With the exception of non-isothermal experiments by an induced change in the temperature of a simplified apparatus (Sect. 2.1.2.1).

[7] The small change in the temperature T_S of the base thermostat in the beginning due to the initial stirrer power or heat exchange with the occasionally slow and steadily changing surroundings (temperature in laboratory) occurs in a quasi-static way owing to the high heat capacity.

This temperature constancy of the base thermostat, coupled with the controlled temperatures of the intermediate thermostat and measuring kettle,[8] holds true

- Strictly for isothermal processes within the boundary conditions of the control dynamics,
- With restrictions for non-isothermal process.

The temperature $T_{2\text{Set}}$ in the measuring kettle in the case of both the isothermal and non-isothermal runs of the reaction must be obtained in an iterative manner.

In the first step

- The temperature T_0 of the socle thermostat is adjusted lower than the temperature $T_{2\text{set}}$ of the measuring kettle, i.e. the temperature of the isothermal reaction respectively the start of the temperature programme
- The electric heating power p_1 in the intermediate thermostat and p_2 in the measuring kettle are fixed,

p_1 at a low respectively high value (depending on whether a decrease or an increase in the heat-transfer coefficient $(k{\cdot}F)_2$ during the chemical conversion is expected)

p_2 at a value higher than the assumed peak in the thermal reaction power during the run of reaction.

After thermal equilibrium is established[9] the values $\Delta T_{1\text{stationary}}$ as well as $\Delta T_{2\text{stationary}}$ are registered. As a rule, the temperature $T_{2\text{stationary}}$ deviates from the desired temperature $T_{2\text{set}}$. Therefore, the temperature T_0 of the socle thermostat must be increased or diminished two or three times until the temperature T_2 of the measuring kettle equals the value $T_{2\text{set}}$.

- For the isothermal process (Fig. 2.1), the control is started with the last registered ΔT values, $\Delta T_{1\text{set}} = \Delta T_{1\text{stationary}}$ and $\Delta T_{2\text{set}} = \Delta T_{2\text{stationary}}$. During the course of a

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[8] With constant rotational velocity of all stirrers.

[9] Thermal equilibrium means that there are constant heat flows over time, i.e. stationary heat flows in the calorimeter system:

• From the measuring kettle **into the intermediate thermostat**	– supplied by the electric heating power p_2 and stirring power $p_{\text{St}2}$ –
• From the intermediate thermostat **into the base thermostat**	– increased by the electric heating power p_1 and the stirring power $p_{\text{St}1}$ minus a tiny heat loss to the laboratory due to the dosing pipes and the stirrer bearing application –
• From the base thermostat **into the socle thermostat**	– changed by the stirring power of the base thermostat as well as heat loss by radiation and convection into the laboratory –

physicochemical process[10] the heat transfer coefficient $(k{\cdot}F)_2$ changes, and therefore the heat flow from the measuring kettle into the intermediate thermostat changes as well. In the case of a not-too-dynamic process, the change in heat flow is compensated by an opposite and equal change in the electric heating power p_1 in the intermediate thermostat.

Hence, the heat flow from the intermediate thermostat into the base thermostat does not change, and the temperature T_S is maintained.

- During a non-isothermal process in the regular apparatus (Fig. 2.26), the temperature T_2 of the measuring kettle changes in such a way that, despite heat release due to the reaction, T_2 corresponds to the set temperature $T_p(t)$ of a programming unit, i.e. $T_2(t) = T_p(t)$. When a change in temperature takes place with a moderate gradient, the varying heat flow into the intermediate thermostat can be compensated by the electric heating power p_1 despite thermal inertia.

  Hence, the heat flow from the intermediate thermostat into the base thermostat remains unchanged, i.e. its temperature $\mathrm{T_S}$ remains constant.

In a simplified apparatus, the temperature T_S of the base thermostat is changed in a well-controlled manner according to set-temperature programme $T_p(t)$.

In the isoperibolic working mode in the regular apparatus, p_2 is set to be constant,[11] with the consequence that the start of heat release cannot be compensated. More precisely, ΔT_2 changes and initiates a variation in the initially constant heat flow[12] from the measuring kettle to the intermediate thermostat. If only a moderate change in the heat flow takes place, the heating power of the intermediate thermostat p_1 is able to compensate the variation by an opposite and equal alteration. In such cases, the temperature T_1 of the intermediate thermostat as well as the temperature of the base thermostat T_S remain unchanged. However, the case of an intensive, abruptly starting or frequently fluctuating calorific process within the measuring kettle leads only to an incomplete compensation of the thermal effects in the intermediate thermostat. The control equilibrium cannot be maintained because of the relatively high thermal inertia of the system. As a result, a change occurs in the temperature T_1 of the intermediate thermostat with a reversion to the temperature T_2 in the measuring kettle as well as to the heat flow into the base thermostat. This also varies principally more or less the temperature T_S of the base thermostat, again with a feedback effect on T_1 and T_2.

Therefore, to obtain net measuring results that are useful for kinetic interpretations of isoperibolic operations, it is advisable to work without an intermediate thermostat (Fig. 2.31), because then we have

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[10] The rate of heat release (e.g., heat of mixing, heat of reaction) in the measuring kettle is compensated by opposite and equal changes in the electric heating power p_2.

[11] It is advisable to set $p_2 = 0$.

[12] In addition, the heat flow can vary also due to the changing heat-transfer coefficient $(k{\cdot}F)_2$ owing to the reaction.

- The measuring kettle is in close contact with the (base-)thermostat with a high heat capacity
- There is a relatively simple relation between the temperature T_2 of the measuring kettle and the temperature T_S of the base thermostat
- The interpretation values can be elaborated by only two mutually interfering temperature profiles

To determine the transfer value $(k{\cdot}F)_2$ (Sect. 2.1), the electric heating power p_2 is, for example, switched on with the constant power p_{20}. Therefore, T_2 and T_S change according to

$$\begin{aligned} \mathrm{d}T_2/\mathrm{d}t &= \left[p_{20} + p_{St2} - (T_2 - T_S)\cdot(k\cdot F)_2\right]/C_2 \\ \mathrm{d}T_S/\mathrm{d}t &= \left[(T_2 - T_S)\cdot(k\cdot F)_2\right] - \left[(T_S - T_0)\cdot(k\cdot F)_S\right]/C_S. \end{aligned}$$

With $A = [p_{20} + p_{St2}]/C_2$, $B = (k\cdot F)_2/C_2$, $C = (k\cdot F)_2/C_S$, $D = T_0$, $E = (k\cdot F)_S/C_S$ we obtain

$$\begin{aligned} \mathrm{d}T_2/\mathrm{d}t &= A + B\cdot T_S - B\cdot T_2 \\ \mathrm{d}T_S/\mathrm{d}t &= D\cdot E - (C+E)\cdot T_S + C\cdot T_2. \end{aligned}$$

The solution of the equation system gives the functional equations of $T_S(t)$ and $T_2(t)$

$$\begin{aligned} T_S = {} & (A\cdot C + B\cdot D\cdot E)/B/E \\ & + k_1\cdot C\cdot \mathrm{EXP}\left[-(B+C+E)/2 + \sqrt{\left\{(B-C-E)^2/4 + B\cdot C\right\}}\cdot t\right] \\ & + k_2\cdot C\cdot \mathrm{EXP}\left[-(B+C+E)/2 + \sqrt{\left\{(B-C-E)^2/4 + B\cdot C\right\}}\cdot t\right]. \end{aligned}$$

$$\begin{aligned} T_2 = {} & (B\cdot D\cdot E + A\cdot C + A\cdot E)/B/E \\ & + k_1\cdot\left[(C+E-B)/2 + \sqrt{\left\{(B-C-E)^2/4 + B\cdot C\right\}}\right] \\ & \cdot \mathrm{EXP}\left[-(B+C+E)/2 + \sqrt{\left\{(B-C-E)^2/4 + B\cdot C\right\}}\cdot t\right] \\ & + k_2\cdot\left[(C+E-B)/2 - \sqrt{\left\{(B-C-E)^2/4 + B\cdot C\right\}}\right] \\ & \cdot \mathrm{EXP}\left[-(B+C+E)/2 - \sqrt{\left\{(B-C-E)^2/4 + B\cdot C\right\}}\cdot t\right]. \end{aligned}$$

The discussion of the result shows that $T_2(t)$ changes at the beginning owing to $(k{\cdot}F)_S < (k{\cdot}F)_2$ respectively $C_2 \ll C_S$,[13] i.e. $E \ll C < B$, much quicker than $T_S(t)$ (Fig. 3.3). $T_S(t)$ is nearly constant during some range of the starting phase; the

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[13] Around 400 W/°C or 1600 W/°C respectively around 120000 J/°C or 2000000 J/°C.

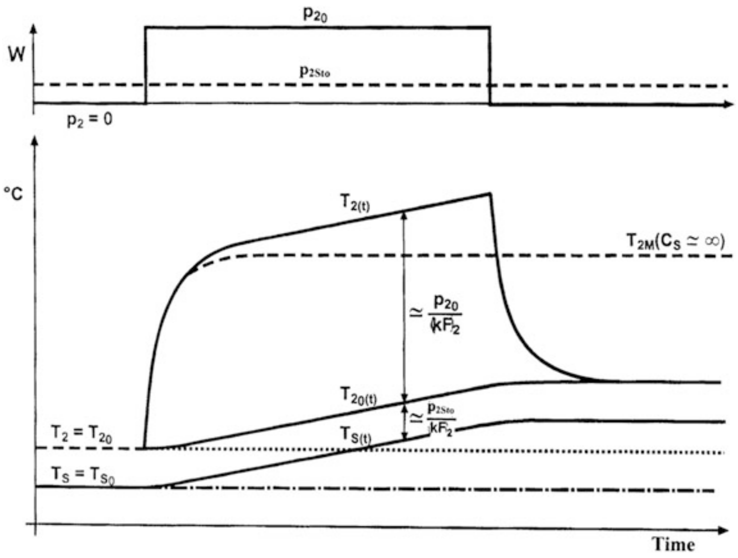

Fig. 3.4 Temporal course of temperatures T_2 in measuring kettle and T_S in (directly contiguous) base thermostat with high heat capacity after switching on respectively off the constant heating power p_{20} within measuring kettle. The heat capacity of the base thermostat is considerably higher than that of the measuring kettle

change in temperature $T_S(t)$ of the base thermostat is at least very small, in comparison to the change in temperature $T_2(t)$ of the measuring kettle.

In the following phase, $T_S(t)$ also changes perceptibly, and soon a quasi-constant difference is achieved:

$$\left[T_2(t) - T_S(t) \cong (p_{St2} + p_{20})/(k \cdot F)_2\right].$$

This difference is, so to speak, mowing on the level of the continuously changing temperature $T_S(t)$ of the base thermostat.[14]

$T_S(t)$ and $T_2(t)$ asymptotically approach in the following time the peak values: $T_{SM}(t = \infty)$ respectively $T_{2M}(t = \infty) = T_{SM}(t = \infty) + (p_{St2} + p_{20})/(k \cdot F)_2$.[15]

In the starting phase, the temperature T_2 of the measuring kettle and the temperature T_S of the base thermostat are still undistorted, especially $T_S \cong T_{S0}$. In this range, useful interpretive data can be measured to determine the rate of heat

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[14] These changes entail maintaining a quasi-equilibrium state, phenomenologically in comparison with the raising of a ship due to a rising water level, with the distance of the deck to the water level remaining quasi-constant.

[15] If the heating power p_{20} is switched off, then the process reverses, i.e. the temperature T_2 of the measuring kettle and the temperature T_S of the base thermostat return to their initial values. For example, switch off of p_2 takes place in order to determine the effective heat capacity C_2. See Sect. 2.1.2.3.

release according to the determining equation (2.16). However, if the interpretive data are measured in a situation of already perceptibly changed T_S, only a gross elaboration of q is possible, even if T_{S0} is replaced by $T_S(t)$, because both T_2 and T_S are already differently distorted (Fig. 3.4).

The determination of interpretive data from the measured curves becomes more accurate again for times with $T_{20}(t) - T_{20} \cong T_S(t) - T_{S0}$; nevertheless, errors in the order of magnitude of some percent are to be expected.

Conclusion

The following circumstances are favourable for investigating chemical conversions under isoperibolic conditions:

- Low concentration of reaction mixture,
- Low time constant of reaction.

The total amount of heat released is relatively small, and therefore a change in the temperature of a base thermostat with a high heat capacity is almost unnoticeable while taking measurements.

Chapter 4
Thermokinetic Analysis

4.1 Introduction

The terminus chemical reaction kinetics encompasses the fundamental laws according to the course of a chemical conversion.

An elementary reaction is a chemical conversion in which only one reaction takes place by a single molecular process, i.e. without forming intermediate products, and it is irreversible.

Its reaction kinetics, provided a conversion in a liquid and homogeneous mix, is elaborated when the stoichiometry and the relevant function of the reaction velocity is determined. Stoichiometry is the description of the minimum, integral, molar conversion of reacting moles (reactants) j to the produced moles (products or resultants) i in accordance with the scheme $v_1 + v_2 + \ldots + v_{j-1} + v_j + \ldots \rightarrow \ldots + v_{i-1} + v_i \ldots$. The integral quantities $v_{j/i}$ are called stoichiometric coefficients. They have different signs, i.e. the numerical values v_j of the reactants j are negatively defined, and the numerical values v_i of the products i are positively defined. The reaction is finished after a large number of conversions according to the stoichiometry (formula conversions).

Its entire or extensive reaction rate is defined as the number λ[1] of stoichiometric conversions (formula conversions) in the total amount of reaction mixture per unit of time [36],

$$r_{\text{entire}} = \mathrm{d}\lambda/\mathrm{d}t.$$

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[1] $\lambda \equiv$ normalized degree of progress $\equiv \left[N_{i/j} - \left(N_{i/j}\right)_0\right]/v_{i/j}$ of an elementary reaction with the stoichiometry $v_1 + v_2 + \ldots + v_{j-1} + v_j + \ldots \rightarrow \ldots + v_{i-1} + v_i + \ldots \equiv$ number of formula conversions.

W. Litz, *Bench Scale Calorimetry in Chemical Reaction Kinetics*,
DOI 10.1007/978-3-319-12532-9_4

This definition is unhelpful in practical applications, because the operating method always requires knowledge of the total amount of the reaction mixture. Moreover, a local reaction rate cannot be stated; but this is necessary for the description of an open reactor. Therefore, it is advisable to link the formula conversions per unit of time with a quantity which gives the dimensions of the reaction system. For liquid, homogeneous systems, the volume V of the reaction mixture is used. In practical applications, this specific or intensive reaction velocity is simply denoted by the reaction rate

$$r_{\text{specific}} = r_{\text{entire}}/V = \mathrm{d}\lambda/\mathrm{d}t/V = r. \tag{4.1}$$

The thermoanalytical procedure for determining the reaction kinetics is based on the law of thermodynamics that the released amount of heat Q during an elementary reaction is proportional to the number λ of the performed conversions according to the stoichiometry (formula conversions). The proportionality factor is the amount of heat by reaction which is released due to one formula conversion. $Q_{\lambda=1}$ corresponds to the negative change in enthalpy per formula conversion. It reads as

$$Q = \lambda \cdot (-\Delta H_{\lambda}). \tag{4.2}$$

According to (4.1) the rate of heat release or thermal reaction power q, i.e. the heat released in volume V per unit of time, is given by

$$q = r \cdot (-\Delta H_{\lambda}) \cdot V. \tag{4.3}$$

Between the change in the number of formula conversions $\mathrm{d}\lambda$ and the change in the number of moles $\mathrm{d}N$ of reactants j respectively of products i exists the relation

$$\mathrm{d}N_{\mathrm{j/i}} = v_{\mathrm{j/i}} \cdot \mathrm{d}\lambda. \tag{4.4}$$

Corresponding to this, the heat of reaction with relation to the reacted moles (reactants) j respectively to the resultant moles (products) i is[2]

$$\left(-\Delta H_{\mathrm{j/i}}\right) = (-\Delta H_{\lambda})/v_{\mathrm{j/i}}. \tag{4.5}$$

Therefore, the numerical values of ΔH_{j} and ΔH_{i} are often different with respect to the absolute value and always have opposite signs (see footnote[2]).

The numerical values of the totally released amount of heat

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[2] In practise the value $(-\Delta H_{\lambda})/\left|v_{\mathrm{j}}\right|$ is used as the heat of reaction $\left(-\Delta H_{\mathrm{j}}\right)$.

$$Q_{(\mathrm{j/i})\infty} = N_{\mathrm{j}(t=0)/\mathrm{i}(t=\infty)} \cdot \left(-\Delta H_{\mathrm{j/i}}\right) = c_{\mathrm{j}(t=0)/\mathrm{i}(t=\infty)} \cdot V \cdot (-\Delta H_{\lambda})/\nu_{\mathrm{j/i}}, \tag{4.6}$$

with $c_{\mathrm{j}(t\,=\,0)}$, $c_{\mathrm{i}(t\,=\,\infty)}$ i.e. concentration of the reactants j at $t = 0$ or of the products i at $t = \infty$, which are in stoichiometric relation, are equal with respect to their absolute values and always have different signs.

As a rule, a chemical conversion occurs via a system of elementary reactions ξ running in parallel or consecutive stages. The superposition of the individual thermal powers $q_\xi(t)$ of the elementary reactions gives the measurable rate of heat release

$$q(t) = \Sigma q_\xi(t).$$

Applying the principle of superposition yields

$$q = \Sigma\left[r_\xi \cdot \left(-\Delta H_{\lambda\xi}\right)\right] \cdot V, \tag{4.7}$$

$$Q_{\infty \mathrm{j/i}} = \sum Q_{\xi\infty \mathrm{j/i}} = \sum c_{\mathrm{j}(t=0)/\mathrm{i}(t=\infty)} \cdot V \cdot \left(-\Delta H_{\lambda\xi}\right)/\nu_{\xi \mathrm{j/i}}, \tag{4.8}$$

with

- r_ξ the rate function of the elementary reaction ξ.
- $\left(-\Delta H_{\lambda\xi}\right)$ is the heat of the reaction per formula conversion of the elementary reaction ξ.

In the case of a not-too-complex system of reaction, the mechanism of reaction, together with the relevant rates of reaction r_ξ and the heats of reaction $\left(-\Delta H_{\lambda\xi}\right)$, can be worked out from the courses of the recorded thermal reaction powers over time, measured under varied conditions. The elaboration can be made easier with the aid of additional life signs of the conversion during a run, for example

- Measuring the pressure change within the measuring kettle during a reaction;
- Determining additional test values, for instance the composition of the reaction mixture following completion of the reaction.[3]
- Kinetic analysis of partial reactions;
- Injecting certain other reactants of the reaction mixture during the reaction run.

or with other aids.

The exact aid which should be used changes from reaction system to reaction system and cannot, as a rule, be predicted. Indications of suitable aids usually become evident during the interpretation and discussion of the first kinetic measurements.

As already mentioned, the reactants of a mixture usually take part simultaneously in two, three or more elementary conversions, forming temporary intermediate products. The practise of the chemical industry often follows from work based

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[3] In any case performable by conventional methods of analysis.

on simplified assumptions about the technically oriented, formal kinetics, i.e. an overall stoichiometry and a relevant simplified overall rate of reaction[4] which accomplish somewhat sufficiently the special requirements of technical production.

However, the classical kineticist usually makes every effort to break down a chemical process to its elementary reactions, so that the process under different boundary conditions (e.g. temperature, type of reactor, procedure of production) can be predicted in detail.

Conclusion

Just like the elaboration of chemical reaction kinetics by conventional modes, a thermokinetic analysis is not as a rule brought to a conclusion by the performance of only certain measurements. Thermokinetic analysis requires intensive interpretation effort, directly coupled with experimentation. A complex mechanism cannot be broken down by an inflexible a priori plan for experiments or an a priori concept for elucidation,[5] but only by the use of knowledge, empathy, feeling for detection, and, last but not least, intuition (see Sect. 4.3).

According to the theory and its verification by means of experimental examination, an elementary reaction is characterized by the following features [5, 11, 14, 16, 36, 44]:

- The chemical reaction takes place by a single molecular process, i.e. without forming perceptible intermediate products, in accordance with the stoichiometry
  $\ldots + \nu_{\mathrm{j}-1} + \nu_{\mathrm{j}} + \ldots + \ldots \rightarrow \ldots + \nu_{\mathrm{i}-1} + \nu_{\mathrm{i}} + \ldots + \ldots$
- In an ideal diluted solution the concentrations (real mol number of educts in the volume unit of the reaction mixture) sets the tone for the drive for a reaction (see Sect. 4.4).

  The general rate functional in the reaction velocity equation is a power function of the concentrations of reactants c_{j} whose powers α_{j} correspond to the absolute values of the integer coefficients ν_{j} of the relevant stoichiometric equation[6]

$$\left[\cdot \cdot \cdot c_{\mathrm{j}-1}{}^{\alpha\mathrm{j}-1} \cdot c_{\mathrm{j}}^{\alpha\mathrm{j}} \cdot \cdot \cdot\right] = \left[\cdot \cdot \cdot c_{\mathrm{j}-1}{}^{|\nu\mathrm{j}-1|} \cdot c_{\mathrm{j}}{}^{|\nu\mathrm{j}|} \cdot \cdot \cdot\right].$$

  The proportional factor, the rate coefficient k, is constant in an ideal diluted solution and characteristic of the reaction system.

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[4] The formation and disappearance of temporary intermediate species are not expressed in the stoichiometry. It is an overall statement.

[5] Especially by stereotype, misunderstood use of software.

[6] In the technically oriented, formal kinetics, characterized by overall stoichiometry and overall reaction velocity, the powers α_{j} in the function of the rate equation usually do not correspond to the stoichiometric coefficients ν_{j}.

- Hence, the rate function r for the ideal diluted reaction mixture reads[7,8]

$$r = \mathrm{d}\lambda/\mathrm{d}t/V = \mathrm{d}N_\mathrm{j}/\nu_\mathrm{j}/\mathrm{d}t/V = k \cdot \left[\cdot\cdot \cdot c_{\mathrm{j}-1}{}^{|\nu\mathrm{j}-1|} \cdot c_\mathrm{j}{}^{|\nu\mathrm{j}|} \cdot \cdot\cdot\right]. \tag{4.9}$$

- The enthalpy of reaction ΔH_λ is given by the stoichiometric sum of the molar enthalpies $\mathrm{H}_\zeta = \left(\delta H/\delta N_\zeta\right)_{\mathrm{p,T}}$ of the moles ζ participating in the reaction[9]

$$\Delta H_\lambda = \Sigma\nu_\zeta \cdot \mathrm{H}_\zeta. \tag{4.10}$$

- The rate coefficient k respectively the enthalpy of reaction ΔH_λ depends on the temperature, in practise, according to

$$\text{Arrhenius equation}: \; k = k_0 \cdot \mathrm{EXP}(-E/RT)$$

with

frequency factor k_0, activation energy E, ideal gas constant R
respectively

$$\text{Kirchhoff's law}: \; \Delta H_\lambda(T_2) = \Delta H_\lambda(T_1) + \int_{T1\to T2} \Delta C_\mathrm{p} \cdot \mathrm{d}T,$$

with

$\Delta \mathrm{C}_\mathrm{p} = \Sigma\nu_\zeta \cdot \mathrm{C}_{\mathrm{p}\zeta}$, in which $\mathrm{C}_{\mathrm{p}\zeta} = \left(\delta H_\zeta/\delta \mathrm{T}\right)_{\mathrm{p,N}}$ is the molar heat of the reaction component ζ at constant pressure p

According to (4.9) it is perfectly obvious to carry out thermal measurements under isothermal conditions. By such separate investigations the following items can be worked out:

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[7] The criteria are certainly necessary but not sufficient to explain the fact that a chemical conversion is an elementary reaction: When a chemical conversion is an elementary reaction, it is fact that a single molecular process of the stoichiometry $\nu_\mathrm{j} \to \nu_\mathrm{i}$ by the reaction rate $r = k\Pi c_\mathrm{j}{}^{|\nu_\mathrm{j}|}$ takes place; but from the experimental result that a chemical conversion takes place by the stoichiometry $\nu_\mathrm{j} \to \nu_\mathrm{i}$ and the reaction rate $r = k\Pi c_\mathrm{j}{}^{|\nu_\mathrm{j}|}$, it does not follow inescapably that it is an elementary reaction, because the conversion by a system of elementary reactions can also lead to this experimental result (pp. 80 and 82). The possibility of detection of an elementary reaction depends in the end, whether the process can be dissected. Hence, the idea of the elementary reaction has a somewhat philosophical character, to be compared with the initial idea of an atom as the smallest elementary building block.

[8] When all α are zero, with exception of α_j, and we have, for example, $\alpha_\mathrm{j} = 0$ respectively 0.5 respectively 1 respectively 2, then we have a reaction rate (or function) of order 0 respectively 0.5 respectively 1 respectively 2.

[9] H is the total enthalpy of the reaction mixture.

- The dependency of the reaction rate on the concentrations of the reactants, i.e. the part of rate function $\left(\ldots \cdot c_{j-1}^{vj-1} \cdot c_{j}^{vj} \cdot c_{j+1}^{vj+1} \cdot \ldots\right)$;
- The dependency of the reaction rate on the temperature, i.e. $k(T)$;
- The dependency of the enthalpy of reaction on the temperature, i.e. $\Delta H_{\lambda}(T)$.

In comparison, we must perform a thermokinetic analysis of the interpretive data, extracted with unreliable accuracy [21, 44] from measured q and T curves of non-isothermal reactions by the simultaneous evaluation of the part of the reaction rate function $(\cdot\cdot\cdot c_{j}^{vj}\cdot\cdot\cdot)$, of the rate coefficient $k(T)$ and of the reaction enthalpy $\Delta H_{\lambda}(T)$. This analytical method is therefore considerably far more prone to error [44]. As a rule, the elaboration of the precise kinetics of complex chemical conversions based on non-isothermal investigation cannot be performed.

By increasing the level of concentration, a mutual interference of all constituents in the reaction mixture arises. The interference affects both the rate of reaction and the enthalpy of reaction.

In highly concentrated reaction mixtures the change in the interference resulting from a change in the composition by reaction is ascertainable even during the course of the chemical conversion (see Sect. 4.4).

4.2 Elucidation of Rate and Enthalpy of Reaction on the Basis of Mathematical–Analytical Relations

4.2.1 Isothermal, Discontinuous Reaction

To measure the thermal reaction power q during a discontinuous reaction, the measuring kettle is pre-filled with part of the reactants, and to start the reaction, the last part is instantaneously injected. The mixing usually occurs instantly compared with the following reaction time. The reaction mixture is homogenized with respect to both concentration and temperature by intensive stirring. The homogenous reacting mixture remains for a certain amount of time in the measuring kettle, after which the run of the conversion is completed. The change in the composition of the reaction mixture takes place uniformly, i.e. the measuring kettle has the characteristics of an ideal mixed batch reactor.

The thermokinetic analysis of the measuring results starts with a hypothesis. A mechanism, the stoichiometry and the relevant function equations of the reaction rates are assumed [4, 10, 14, 16, 36, 44]. From that, the run of both concentrations and thermal reaction power versus time are calculated on the basis of (4.2)–(4.9) [1, 9, 18]. Then we examine whether the measuring results are in accordance with the calculated ones. If there is insufficient congruence between the two, the hypothesis must be revised. Hence, the thermokinetic elaboration of the kinetics of a chemical conversion is based on the principle of validation, that all measured temporal courses of the thermal reaction power and the concentrations of reactants and products measured during many different kinds of experiments are in harmony with the assumed rate functions r_ξ and heats of reaction $\left(-\Delta H_{\lambda\xi}\right)$.

To be able to validate the results quickly, it is advisable that a large variety of mathematical-analytical results be available. Such a variety is established at first by a thermokinetic discussion of different reaction systems in an ideal diluted solution.

To that end, the fact that all physical properties fundamentally change during the chemical conversion, as does the volume V of reaction, must be taken into account. This means that the concentration $c_{\mathrm{j/i}}$, i.e. the mol number of the components j respectively i per unit of volume reaction mixture, changes not only as a result of a decrease respectively increase in the mol number of component j respectively i, but also as a result of the synchronous change in the volume of the mixture due to the reaction. Hence, the total change in the concentration per unit of time is composed of the partial change $\left(\mathrm{d}c_{\mathrm{j/i}}/\mathrm{d}t\right)_{V=\mathrm{const}}$ due to the reaction and the partial change $\left(\mathrm{d}c_{\mathrm{j/i}}/\mathrm{d}t\right)_{r=0}$ due to expansion $(\mathrm{d}V/\mathrm{d}t > 0)$ or contraction $(\mathrm{d}V/\mathrm{d}t < 0)$. Hence, it reads

$$\mathrm{d}c_{\mathrm{j/i}}/\mathrm{d}t = \nu_{\mathrm{j/i}} \cdot r - c_{\mathrm{j/i}}\mathrm{d}V/\mathrm{d}t/V. \tag{4.11}$$

This equation represents the correlation between the rate of change in concentration, the rate of change in formula conversion and the rate of change in volume.

The change in the constituents in solutions during a chemical reaction generally has only a small effect on the density of the reaction mixture. As a rule, the change in volume can be neglected: $\mathrm{d}V/\mathrm{d}t \cong 0$.

4.2.1.1 Constant-Volume Reaction

In what follows, a constant-volume reaction is supposed; owing to (4.11) it holds that

$$\mathrm{d}c_{\mathrm{j}}/\mathrm{d}t/\nu_{\mathrm{j}} = r. \tag{4.12}$$

4.2.1.1.1 System of Reactions Kinetically Characterized by a Single Rate Function

4.2.1.1.1.1 Rate Function of Order 0

When the rate of an irreversible chemical conversion of the stoichiometry $\nu_1 + \ldots + \nu_{\mathrm{j}-1} + \nu_{\mathrm{j}} + \ldots \rightarrow \ldots + \nu_{\mathrm{i}-1} + \nu_{\mathrm{i}} \ldots + .$ does not depend explicitly on any reactant concentrations c_{j}, the rate of reaction is constant. The simplest rate equation is a rate function of order 0.

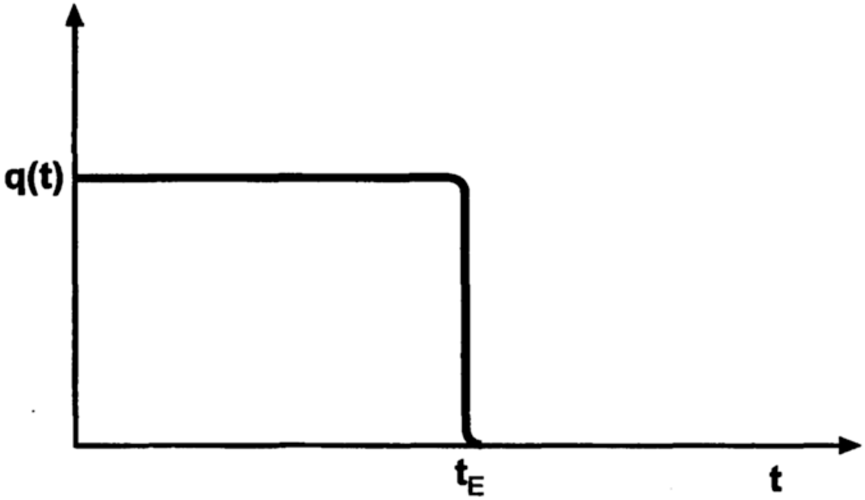

Fig. 4.1 Rate function of order 0; Isothermal, discontinuous, constant-volume reaction $q = k \cdot (-\Delta H_\lambda) \cdot V$

According to (4.2), (4.4) and (4.12) the function of r is[10]

$$r = \mathrm{d}\lambda/\mathrm{d}t/V = \mathrm{d}N_\mathrm{j}/\nu_\mathrm{j}/\mathrm{d}t/V = \mathrm{d}c_\mathrm{j}/\mathrm{d}t/\nu_\mathrm{j} = k \tag{4.13}$$

and according to (4.3) the thermal reaction power is

$$q(t) = r \cdot (-\Delta H_\lambda) \cdot V = k \cdot V \cdot (-\Delta H_\lambda) = \mathrm{const.} \tag{4.14}$$

The conversion runs at a constant velocity until at point in time t_E all reactant mols N_j are consumed respectively all stoichiometric product mols N_i are formed (Fig. 4.1).

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[10] This chemical conversion is not an elementary reaction. r is, rather, the overall rate function of a conversion by a system of elementary reactions, in which the effects of the concentrations due to special physicochemical circumstances do not apply explicitly during the course of the process. The origin of a reaction rate of order 0 is illustrated by the example of a reaction system with the simple overall stoichiometry $-1\mathrm{A} \rightarrow 1\mathrm{B}$ (Michaelis–Menten Mechanisms) [36]:

Reactant A (a large amount) reacts by an elementary reaction with an educt C (a small amount) reversibly (Sect. 4.2.1.1.2.7) to the intermediate product D, which reacts by an elementary reaction to product B, by which C is replenished: $\mathrm{A} + \mathrm{C} \leftrightarrow \mathrm{D}, \mathrm{D} \rightarrow \mathrm{B} + \mathrm{C}$. The rate of production of B and the rate of change in the intermediate product D are $\mathrm{d}c_\mathrm{B}/\mathrm{d}t = k_3 \cdot c_\mathrm{D}$ (1) and $\mathrm{d}c_\mathrm{D}/\mathrm{d}t = k_1 \cdot c_\mathrm{A} \cdot c_\mathrm{C} - k_2 \cdot c_\mathrm{D} - k_3 \cdot c_\mathrm{D}$ respectively. Because the amount of reactant C and, therefore, the amount of the intermediate product D are very small, naturally there is little free variation for their temporal changes, and soon we have, when $k_3 \ll k_2 \ll k_1$ (2), $\mathrm{d}c_\mathrm{D}/\mathrm{d}t = 0$, i.e. $c_\mathrm{D} = k_1 \cdot c_\mathrm{A} \cdot c_\mathrm{C}/(k_2 + k_3)$. Because of $c_\mathrm{C} = c_\mathrm{C0} - c_\mathrm{D}$ it follows that $c_\mathrm{D} = k_1 \cdot c_\mathrm{A} \cdot (c_\mathrm{C0} - c_\mathrm{D})/(k_2 + k_3)$ or $\mathrm{c_D} = \mathrm{k_1} \cdot \mathrm{c_A} \cdot c_\mathrm{C0}/(\mathrm{k_2} + \mathrm{k_3} + \mathrm{k_1} \cdot \mathrm{c_A})$. Equations (1) and (2) result in $\mathrm{d}c_\mathrm{B}/\mathrm{d}t = k_1 \cdot k_3 \cdot c_\mathrm{A} \cdot c_\mathrm{C0}/(k_2 + k_3 + k_1 \cdot c_\mathrm{A}) = k_3 \cdot k_1/k_2 \cdot c_\mathrm{A} \cdot c_\mathrm{C0}/(1 + k_1/k_2 \cdot c_\mathrm{A})$. When $c_\mathrm{A} \gg k_1/k_2$, we obtain $\mathrm{d}c_\mathrm{B}/\mathrm{d}t = k_3 \cdot c_\mathrm{C0}$, i.e. the production of B occurs by a constant rate. Only when c_A is decreased down to $c_\mathrm{A} \ll k_1/k_2$ does the production occur at a rate of order 1. The greater k_1/k_2 is, the smaller the transition zone is.

The integration of (4.13) gives

$$c_{\mathrm{j}} = c_{\mathrm{j}}(t = 0) + v_{\mathrm{j}} \cdot k \cdot t = c_{\mathrm{j0}} + v_{\mathrm{j}} \cdot k \cdot t. \tag{4.15}$$

From this follows the value of the rate coefficient

$$k = -c_{\mathrm{j0}}/v_{\mathrm{j}}/t_{\mathrm{E}}. \tag{4.16}$$

The heat of the reaction from (4.14) results in

$$(-\Delta H_{\lambda}) = q/k/V.$$

4.2.1.1.1.2 Rate Function of Order 0.5

The rate of a chemical conversion with the stoichiometry $v_1 + \ldots + v_{\mathrm{j}-1} + v_{\mathrm{j}} + \ldots \rightarrow \ldots + v_{\mathrm{i}-1} + v_{\mathrm{i}} + \ldots +$. must be proportional to the root of reactant *j*. The rate function is of order 0.5[11]:

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[11] Because of $\alpha_{\mathrm{j}} = 0.5 \neq |v_{\mathrm{j}}|$ and all $\alpha \neq \alpha_{\mathrm{j}} \equiv 0$, the conversion is not an elementary reaction. The conversion occurs via a system of elementary reactions. *r* is the overall reaction rate. The origin of a rate function with order 0.5 is illustrated by the conversion of the stoichiometry $-1\mathrm{A} \rightarrow 1\mathrm{P}_1 + 1\mathrm{P}_2 + 1\mathrm{BP}_1 + 1\mathrm{BP}_2$ [in which $\mathrm{BP}_1 + \mathrm{BP}_2$ (by-products) $\ll \mathrm{P}_1 + \mathrm{P}_2$ (desired products)], with an elementary starting reaction, a loop of two much quicker elementary reactions and a certain relatively slow terminating elementary reaction (Rice–Hertzfeld mechanisms) [36].

The conversion starts by splitting A into two components:

$\mathrm{A}-_{k1}\rightarrow \mathrm{D} + \mathrm{BP}_1$ starting reaction (1)

BP_1 does not take part in the subsequent reaction. In contrast, D starts a relatively quick loop:

$\mathrm{D} + \mathrm{A}-_{k2}\rightarrow \mathrm{E} + \mathrm{P}_1$ producing reaction (2)

$\mathrm{E}-_{k3}\rightarrow \mathrm{D} + \mathrm{P}_2$ producing reaction (3)

The conversion is terminated by the formation of the by-product BP_2

$2\mathrm{E}-_{k4}\rightarrow \mathrm{BP}_2$ terminating reaction (4)

By step 2, D reacts with A to form product P_1 and the intermediate product E, which forms product P_2 and replenishes D by step 3. D initiates a new loop (2, 3) to form the desired products. Simultaneously, E decreases by the combination step 4, in which the by-product BP_2 is formed. According to (4.9) and (4.34) (Sect. 4.2.1.1.2), the decrease rate of A and the change rates of D and E are

$$\begin{aligned} -\mathrm{d}c_{\mathrm{A}}/\mathrm{d}t &= k_1 \cdot c_{\mathrm{A}} + k_2 \cdot c_{\mathrm{D}} \cdot c_{\mathrm{A}} = k_1 \cdot c_{\mathrm{A}} \cdot (1 + k_2/k_1 \cdot c_{\mathrm{D}}), \\ \mathrm{d}c_{\mathrm{D}}/\mathrm{d}t &= k_1 \cdot c_{\mathrm{A}} - k_2 \cdot c_{\mathrm{A}} \cdot c_{\mathrm{D}} + k_3 \cdot c_{\mathrm{E}}, \qquad (5) \\ \mathrm{d}c_{\mathrm{E}}/\mathrm{d}t &= k_2 \cdot c_{\mathrm{A}} \cdot c_{\mathrm{D}} - k_3 \cdot c_{\mathrm{E}} - k_4 \cdot c_{\mathrm{E}}^2. \end{aligned}$$

Using Bodenstein's steady-state approximation (Sect. 4.3) after a short time the following equations hold:

$$\begin{aligned} \mathrm{d}c_{\mathrm{D}}/\mathrm{d}t &= k_1 \cdot c_{\mathrm{A}} - k_2 \cdot c_{\mathrm{A}} \cdot c_{\mathrm{D}} + k_3 \cdot c_{\mathrm{E}} \equiv 0, \\ \mathrm{d}c_{\mathrm{E}}/\mathrm{d}t &= k_2 \cdot c_{\mathrm{A}} \cdot c_{\mathrm{D}} - k_3 \cdot c_{\mathrm{E}} - k_4 \cdot c_{\mathrm{E}}^2 \equiv 0. \end{aligned} \quad (6)$$

The addition of both equations gives

$c_{\mathrm{E}} = (k_1/k_4)^{0.5} \cdot c_{\mathrm{A}}{}^{0.5}$. Substituting this into (6) yields $c_{\mathrm{E}} = k_1/k_2 + k_3/k_2 \cdot (k_1/k_4)^{0.5} \cdot c_{\mathrm{A}}{}^{-0.5}$. Combining this with (5) yields

$$-\mathrm{d}c_{\mathrm{A}}/\mathrm{d}t = k_1 \cdot c_{\mathrm{A}} \cdot \left(2 + k_3/(k_1 \cdot k_4)^{0.5} \cdot c_{\mathrm{A}}{}^{-0.5}\right).$$

In the case that k_1 and k_4 are significantly smaller than k_2 and k_3 (the prerequisite for quasi complete conversion of A to the products P1 and P2) the previous equation changes to

$$-\mathrm{d}c_{\mathrm{A}}/\mathrm{d}t = k_3 \cdot (k_1/k_4)^{0{,}5} \cdot c_{\mathrm{A}}{}^{0{,}5} \approx \mathrm{d}c_{(\mathrm{P1+P2})}/\mathrm{d}t$$

$$r = \mathrm{d}N_\mathrm{j}/\mathrm{d}t/v_\mathrm{j}/V = \mathrm{d}c_\mathrm{j}/\mathrm{d}t/v_\mathrm{j} = k \cdot {c_\mathrm{j}}^{0.5}. \tag{4.17}$$

The integration of Eq. (4.17) gives

$${c_\mathrm{j}}^{0.5} - {c_{\mathrm{j}(t=0)}}^{0.5} = {c_\mathrm{j}}^{0.5} - {c_\mathrm{j0}}^{0.5} \cdot v_\mathrm{j} \cdot k/2 \cdot t. \tag{4.18}$$

$$\text{At the point in time} \quad t_\mathrm{E} = -2 \cdot {c_\mathrm{j0}}^{0.5}/k/v_\mathrm{j} \tag{4.19}$$

all moles of reactant j are consumed. Combining (4.17), (4.18), (4.19) and (4.3) gives the temporal course of the thermal reaction power:

$$q(t) = k \cdot c^{0.5}_{\mathrm{j}(t=0)} \cdot V \cdot (1 - t/t_\mathrm{E}) \cdot (-\Delta H_\lambda) = k \cdot c^{0.5}_\mathrm{j0} \cdot V \cdot (1 - t/t_\mathrm{E}) \cdot (-\Delta H_\lambda).$$

q decreases (Fig. 4.2) from the starting value $q(t=0) = k \cdot c^{0.5}_\mathrm{j0} \cdot V \cdot (-\Delta H_\lambda)$ linearly with the slope

$$\kappa = -k \cdot c^{0.5}_\mathrm{j0} \cdot V \cdot (-\Delta H_\lambda)/t_\mathrm{E} = v_\mathrm{j} \cdot k \cdot V \cdot (-\Delta H_\lambda)/2.$$

The rate coefficient k and the heat of reaction $(-\Delta H_\lambda)$ yield, from the values κ and $q(t=0) = q_0$

$$k = \kappa/q_0/v_\mathrm{j} \cdot 2 \cdot c^{0.5}_\mathrm{j0}$$

and

$$(-\Delta H_\lambda) = v_\mathrm{j} \cdot q_0/\left(\kappa/2/c_\mathrm{j0}\right)/V$$

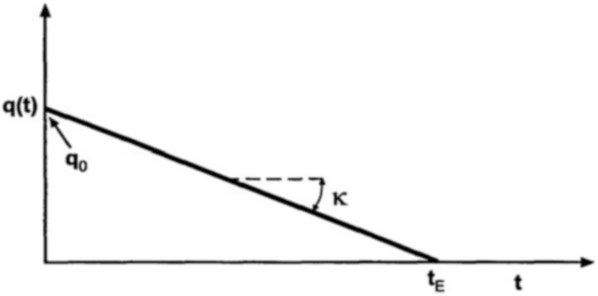

Fig. 4.2 Rate function of order 0.5; Isothermal, discontinuous, constant-volume reaction: $q = k \cdot {c_\mathrm{j0}}^{0.5} \cdot V \cdot (-\Delta H_\lambda) \cdot (1 - t/t_\mathrm{E})$

4.2.1.1.1.3 Reaction Function of Order 1

The rate of a chemical conversion with the stoichiometry $\nu_1 + \ldots + \nu_{j-1} + \nu_j + \ldots \rightarrow \ldots + \nu_{i-1} + \nu_i + \ldots$ must be proportional to the first power of the concentration of reactant j[12]:

$$r = dN_j/dt/\nu_j/V = dc_j/dt/\nu_j = k \cdot c_j.$$

The solution of the differential equation is

$$c_j = c_{j0} \cdot \mathrm{EXP}(\nu_j \cdot k \cdot t). \tag{4.20}$$

For the temporal course of the caloric reaction power q we obtain using (4.3)

$$q(t) = k \cdot c_{j0} \cdot V \cdot (-\Delta H_\lambda) \cdot \mathrm{EXP}(\nu_j \cdot k \cdot t). \tag{4.21}$$

Plotting[13] the natural logarithm of $q(t)$ versus time t (Fig. 4.3) gives a straight line,

$$\ln\{q(t)\} = \ln\{k \cdot c_{j0} \cdot V \cdot (-\Delta H_\lambda)\} + \nu_j \cdot k \cdot t = \ln\{\Phi\} + \kappa \cdot t,$$

with the slope $\kappa = \nu_j \cdot k$ and the point of intersection with the ordinate, $\ln\{\phi\}$, in which

$$\phi = q(t = 0) = q_0 = k \cdot c_{j0} \cdot V \cdot (-\Delta H_\lambda).$$

The rate coefficient k follows from the slope κ:

$$k = \kappa/\nu_j.$$

The heat of the reaction can be calculated using a point of intersection with the ordinate $\ln\{\phi\}$:

$$(-\Delta H_\lambda) = \phi/k/c_{j0}/V.$$

4.2.1.1.1.4 Rate Function of Order 2

The rate of a chemical conversion with the stoichiometry $\nu_1 + \ldots + \nu_{j-1} + \nu_j + \ldots \rightarrow \ldots + \nu_{i-1} + \nu_i \ldots + \ldots$ must be proportional to the square in concentration of

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[12] When j is the sole reactant and $\nu_j = -1$, the reaction can be an elementary one. However, it need not be so because a system of elementary reactions with the same overall stoichiometry can also yield an overall reaction rate of order 1: see the illustrated Rice–Herzfeld mechanism, however, with the terminating reaction $D + E \rightarrow BP_2$.

[13] In the case of negative q-values, $\ln\{|q(t)|\}$ must be plotted; the procedure for interpretation is similar.

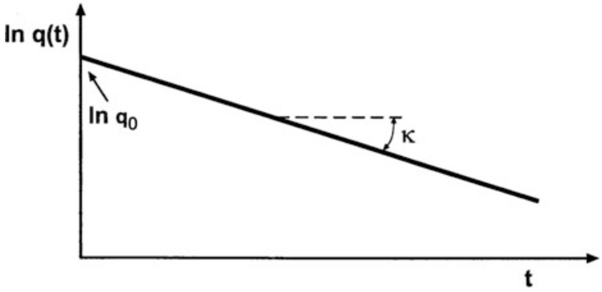

Fig. 4.3 Rate function of order 1; Isothermal, discontinuous, constant-volume reaction

$$q = k \cdot c_{j0} \cdot V \cdot (-\Delta H_\lambda) e^{v_j \cdot k \cdot t}$$

reactant j or to the product of two reactants j and $j + \sigma$ with equal starting concentrations and equal stoichiometric coefficients, $\left(c_{j0} = c_{(j+\sigma)0}, v_j = v_{j+\sigma}\right)$

$$r = \mathrm{d}N_j/\mathrm{d}t/v_j/V = \mathrm{d}c_j/\mathrm{d}t/v_j = k \cdot {c_j}^2. \tag{4.22}$$

Integration of the equation gives

$${c_j}^{-1} = {c_{j0}}^{-1} - v_j \cdot k \cdot t. \tag{4.23}$$

The temporal course of the thermal reaction power reads, according to (4.3), (4.22) and (4.23),[14]

$$\begin{aligned} q &= k \cdot {c_j}^2 \cdot V \cdot (-\Delta H_\lambda) \\ &\text{or} \\ |q|^{-1/2} &= [k \cdot V \cdot |(-\Delta H_\lambda)|]^{-1/2} \cdot {c_j}^{-1} \\ &= [k \cdot V \cdot |(-\Delta H_\lambda)|]^{-1/2} \cdot \left({c_{j0}}^{-1} - v_j \cdot k \cdot t\right) \\ &= [k \cdot V \cdot |(-\Delta H_\lambda)|]^{-1/2} \cdot {c_{j0}}^{-1} - [k \cdot V \cdot |(-\Delta H_\lambda)|]^{-1/2} \cdot v_j \cdot k \cdot t \\ &= [k \cdot V \cdot |(-\Delta H_\lambda)|]^{-1/2} \cdot {c_{j0}}^{-1} - [V \cdot |(-\Delta H_\lambda)|]^{-1/2} \cdot k^{1/2} \cdot v_j \cdot t. \end{aligned}$$

Combining this with (4.6) gives

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[14] If $v_j \neq v_{j+\sigma}$ and $c_{j0}/c_{(j+\sigma)0} = v_j/v_{j+\sigma}$ hold, then

$$\begin{aligned} {c_j}^{-1} - {c_{j0}}^{-1} &= v_{j+\sigma} \cdot k \cdot t \quad \text{and} \quad q^{-1/2} \\ &= \left[v_{j+\sigma}/v_j k \cdot V \cdot |(-\Delta H_\lambda)|\right]^{-1/2} \cdot {c_{j0}}^{-1} - [V \cdot |(-\Delta H_\lambda)|]^{-1/2} \cdot k^{1/2} \cdot v_{j+\sigma} \cdot t \end{aligned}$$

respectively

$$\begin{aligned} {c_{j+\sigma}}^{-1} &= {c_{(j+\sigma)0}}^{-1} - v_j \cdot k \cdot t \quad \text{and} \quad q^{-1/2} \\ &= \left[v_j/v_{j+\sigma} k \cdot V \cdot |(-\Delta H_\lambda)|\right]^{-1/2} \cdot c_{(j+\sigma)0}^{-1} - [V \cdot |(-\Delta H_\lambda)|]^{-1/2} \cdot k^{1/2} v_j \cdot t \end{aligned}$$

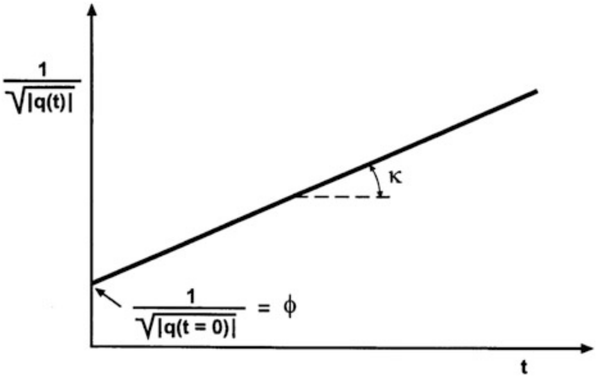

Fig. 4.4 Rate function of order 2; Isothermal, discontinuous, constant-volume reaction

$$|q|^{-1/2} = \left|k \cdot v_j \cdot Q_{j\infty} c_{j0}\right|^{-1/2} + \left|k \cdot v_j \cdot c_{j0}/Q_{j\infty}\right|^{-1/2} \cdot t$$

$$|q|^{-1/2} = \left[k \cdot \left|Q_{j\infty}\right| \cdot c_{j0} \cdot \left|v_j\right|\right]^{-1/2} + \left[c_{j0}/\left|Q_{j\infty}\right| \cdot k \cdot \left|v_j\right|\right]^{1/2} \cdot t. \tag{4.24}$$

Plotting $1/\sqrt{|q|}$ versus time (Fig. 4.4) gives as a result a straight line with

- Slope $\kappa = \left[c_{j0} \cdot k \cdot \left|v_j\right| / \left|Q_{j\infty}\right|\right]^{1/2}$
- Point of intersection with the ordinate $\phi = \left[k \cdot \left|v_j\right| \cdot \left|Q_{j\infty}\right| \cdot c_{j0}\right]^{-1/2}$.

With κ, ϕ and (4.6) we obtain the rate coefficient k and the absolute amount of heat of reaction $|-\Delta H_\lambda|$,

$$k = \kappa/\phi/c_{j0}/\left|v_j\right|$$

and

$$|-\Delta H_\lambda| = \left|v_j\right| \cdot \left(\kappa \cdot \phi \cdot V \cdot c_{j0}\right)^{-1},$$

with

$$(-\Delta H_\lambda) < 0 \text{ when } q < 0 \quad \text{and} \quad (-\Delta H_\lambda) > 0 \text{ when } q > 0.$$

4.2.1.1.1.5 Rate Function of Order n *(>0;≠1)*

The rate of a chemical reaction with the stoichiometry $v_1 + \cdots + v_{j-1} + v_j + \cdots \rightarrow \cdots + v_{i-1} + v_i + \cdots$ must be proportional to the power n (>0, but ≠1) in the concentration of reactant j

$$r = dN_j/dt/v_j/V = dc_j/dt/v_j = k \cdot c_j{}^n.$$

Integration of the equation for $n \neq 1$ leads to

$$c_{\mathrm{j}}{}^{1-n} = c_{\mathrm{j}0}{}^{1-n} + (1-n) \cdot v_{\mathrm{j}} \cdot k \cdot t. \tag{4.25}$$

From (4.3) and (4.25) follows the determining equation for the thermal reaction power

$$|q|^{(1-n)/n} = [k \cdot V \cdot |(-\Delta H_{\lambda})|]^{(1-n)/n} \cdot c_{\mathrm{j}}{}^{1-n}$$
$$= [k \cdot V \cdot |(-\Delta H_{\lambda})|]^{(1-n)/n} \cdot c_{\mathrm{j}0}{}^{(1-n)} + [k \cdot V \cdot |(-\Delta H_{\lambda})|]^{(1-n)/n} \cdot (1-n) \cdot v_{\mathrm{j}} \cdot k \cdot t.$$

Combining this with (4.6) and rearranging results in

$$|q|^{(1-n)/n} = \left[|v_{\mathrm{j}}| \cdot k \cdot |Q_{\mathrm{j}\infty}| \cdot c_{\mathrm{j}0}^{n-1}\right]^{(1-n)/n} + (n-1) \cdot \left[c_{\mathrm{j}0}{}^{n-1}/|Q_{\mathrm{j}\infty}|^{n-1} \cdot |v_{\mathrm{j}}| \cdot k\right]^{1/n} \cdot t.$$

Plotting $|q|^{(1-n)/n}$ versus time (Fig. 4.5) gives a straight line with

- Slope $\kappa = (n-1) \cdot \left[c_{\mathrm{j}0}{}^{n-1}/|Q_{\mathrm{j}\infty}|^{n-1} \cdot |v_{\mathrm{j}}| \cdot k\right]^{1/n}$
- Point of intersection with the ordinate $\phi = \left[|v_{\mathrm{j}}| \cdot \mathrm{k} \cdot |\mathrm{Q}_{\mathrm{j}\infty}| \cdot \mathrm{c}_{\mathrm{j}0}^{\mathrm{n}-1}\right]^{(1-\mathrm{n})/\mathrm{n}}$.

The combination of κ and ϕ with (4.6) yields the rate coefficient k and the absolute amount of the heat of the reaction $|-\Delta H_{\lambda}|$:

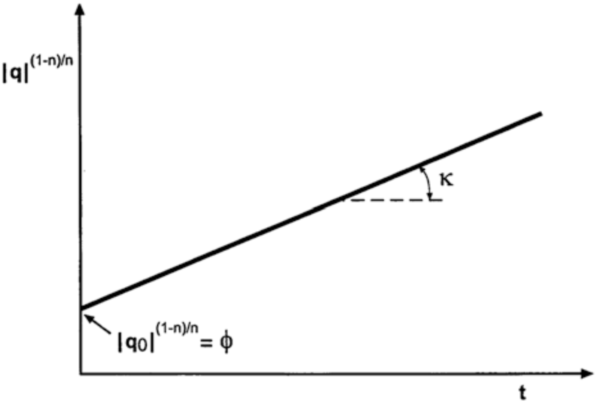

Fig. 4.5 Rate function of order n (>0; ≠1); Isothermal, discontinuous, constant-volume reaction

$$|q|^{(1-n)/n} = \left[|v_{\mathrm{j}}| \cdot k \cdot |Q_{\mathrm{j}\infty}| \cdot c_{\mathrm{j}0}{}^{n-1}\right]^{(1-n)/n} + (n-1)\left[c_{\mathrm{j}0}{}^{n-1} \cdot |v_{\mathrm{j}}| \cdot k \cdot |Q_{\mathrm{j}\infty}|^{n-1}\right]^{1/n} \cdot t$$

$$k = \kappa/\phi/{c_{j0}}^{n-1}/|\nu_j|/(n-1),$$

$$|-\Delta H_\lambda| = |\nu_j| \cdot (n-1) \cdot \left[V \cdot \kappa \cdot \phi^{1/(n-1)} \cdot c_{j0}\right]^{-1},$$

with

$$(-\Delta H_\lambda) < 0 \text{ when } q < 0 \quad \text{and} \quad (-\Delta H_\lambda) > 0 \text{ when } q > 0.$$

A comparison of the thermal reaction power q for conversions with rate orders n greater and smaller than 1 shows that q decreases down to zero for order $0 \leq n < 1$ within a finite time interval and for orders $n \geq 1$ after infinite time.

4.2.1.1.1.6 *Rate Function is a Product of Two Partial Orders 1, One Reactant in Surplus*

The rate of a chemical conversion with the stoichiometry $\nu_1 + \cdots + \nu_{j-1} + \nu_j + \cdots \rightarrow \cdots + \nu_{i-1} + \nu_i + \cdots$ must be proportional to the product of the concentrations of reactants j and j + σ with powers of value 1:

$$r = \mathrm{d}N_j/\mathrm{d}t/\nu_j/V = \mathrm{d}c_j/\mathrm{d}t/\nu_j = k \cdot c_j \cdot c_{j+\sigma}. \tag{4.26}$$

The stoichiometric coefficient of reactant j + σ is larger than that of reactant j. The reactant j + σ in comparison to reactant j is present in finite surplus.

We have

$$\left(c_{(j+\sigma)0} - c_{j0}\right)/c_{j0} = \delta \tag{4.27}$$

and

$$\nu_{j+\sigma}/\nu_j = \gamma,$$

hence, due to (4.4),

$$c_{j+\sigma} = c_{(j+\sigma)0} - \left(c_{j0} - c_j\right) \cdot \gamma. \tag{4.28}$$

By that and (4.26), the rate of change in the concentration c_j becomes

$$\mathrm{d}c_j/\mathrm{d}t = \nu_j \cdot k \cdot (1 + \delta - \gamma) \cdot c_{j0} \cdot c_j + \nu_j \cdot k \cdot \gamma \cdot {c_j}^2.$$

The solution of the equation reads[15]

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[15] Describing $\mathrm{EXP}\left[-\nu_j \cdot k \cdot (1 + \delta - \gamma) \cdot c_{j0} \cdot t\right]$ by means of series, we see that Eq. (4.29) with $\gamma = 1$ turns for the limiting case $\delta \rightarrow 0$ to the Eq. (4.23).

$$c_{\mathrm{j}} = c_{\mathrm{j}0} / \left[\{1 + \gamma/(1+\delta-\gamma)\} \cdot \mathrm{EXP}\left(-\nu_{\mathrm{j}} \cdot k \cdot (1+\delta-\gamma) \cdot c_{\mathrm{j}0}, \cdot t\right) - \gamma/\{(1+\delta-\gamma)\} \right]. \tag{4.29}$$

On the basis of (4.3), (4.6) and (4.26)–(4.29), we obtain as the result the thermal reaction power:[16]

$$\begin{aligned} q = {} & \nu_{\mathrm{j}} \cdot Q_{\mathrm{j}\infty} \cdot k \cdot (1+\delta-\gamma) \cdot c_{\mathrm{j}0} \cdot \{1+\gamma/(1+\delta-\gamma)\} \cdot \mathrm{EXP}\left[-\nu_{\mathrm{j}} \cdot k \cdot (1+\delta-\gamma) \cdot c_{\mathrm{j}0} \cdot t\right] / \\ & \left\{\gamma/(1+\delta-\gamma) - [1+\gamma/(1+\delta-\gamma)] \cdot \mathrm{EXP}\left[-\nu_{\mathrm{j}} \cdot k \cdot (1+\delta-\gamma) \cdot c_{\mathrm{j}0} \cdot t\right]\right\}^2. \end{aligned} \tag{4.30}$$

For $t \gg 0$ the term $\gamma/(1+\delta-\gamma)$ in the denominator can be neglected in comparison to the term $\left\{[1+\gamma/(1+\delta-\gamma)] \cdot \mathrm{EXP}\left[-\nu_{\mathrm{j}} \cdot k \cdot (1+\delta-\gamma) \cdot c_{\mathrm{j}0} \cdot t\right]\right\}^2$, with the result that the relation for $t \gg 0$ becomes

$$\begin{aligned} q(t \gg 0) = {} & \nu_{\mathrm{j}} \cdot Q_{\mathrm{j}\infty} \cdot k \cdot (1+\delta-\gamma)/\{1+\gamma/(1+\delta-\gamma)\} \cdot c_{\mathrm{j}0} \\ & \cdot \mathrm{EXP}\left[\nu_j \cdot k \cdot (1+\delta-\gamma) \cdot c_{\mathrm{j}0} \cdot t\right] \\ = {} & \nu_{\mathrm{j}} \cdot Q_{\mathrm{j}\infty} \cdot k \cdot (1+\delta-\gamma)^2/(1+\delta) \cdot c_{\mathrm{j}0} \cdot \mathrm{EXP}\left[\nu_{\mathrm{j}} \cdot k \cdot (1+\delta-\gamma) \cdot c_{\mathrm{j}0} \cdot t\right]. \end{aligned} \tag{4.31}$$

Plotting $\ln\{q\}$ versus time[17] (Fig. 4.6) gives a curve achieving a straight line with

- Slope

$$\kappa = \nu_{\mathrm{j}} \cdot k \cdot (1+\delta-\gamma) \cdot c_{\mathrm{j}0}, \tag{4.32}$$

- Point of intersection with the ordinate $\ln\{\phi\}$,
  with

$$\phi = \nu_{\mathrm{j}} \cdot Q_{\mathrm{j}\infty} \cdot k \cdot c_{\mathrm{j}0} \cdot (1+\delta-\gamma)^2/(1+\delta). \tag{4.33}$$

The combination of (4.32), (4.33) and (4.6) yields the relations for calculating the rate coefficient k and the heat of reaction $(-\Delta H_\lambda)$:

$$\begin{aligned} k &= \kappa/c_{\mathrm{j}0}/\nu_{\mathrm{j}}(1+\delta-\gamma) \\ -\Delta H_\lambda &= \phi \cdot \nu_{\mathrm{j}} \cdot (1+\delta) / \left[\kappa \cdot c_{\mathrm{j}0} \cdot (1+\delta-\gamma)\right]. \end{aligned}$$

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[16] Describing $\mathrm{EXP}\left[-\nu_{\mathrm{j}} \cdot k \cdot (1+\delta-\gamma) \cdot c_{\mathrm{j}0} \cdot t\right]$ by means of series, we see that Eq. (4.30) with $\gamma = 1$ turns for the limiting case $\delta \to 0$ to the Eq. (4.24).

[17] In the case of negative q-values, $\ln\{|q(t)|\}$ is must be plotted; the procedure of interpretation is similar.

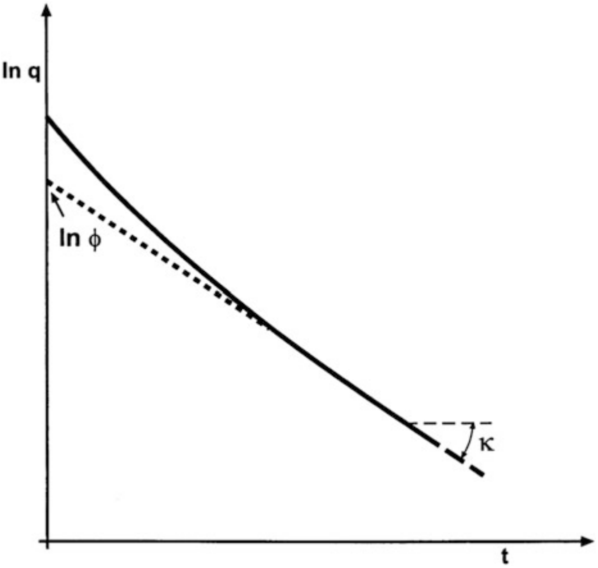

Fig. 4.6 Rate function: directly proportional to the product of the two reactants j and $j+\sigma$: $r = k \cdot c_{\mathrm{j}} \cdot c_{\mathrm{j}+\sigma}$; finite surplus of reactant $\mathrm{j}+\sigma$, different stoichiometric coefficients $\left(c_{(\mathrm{j}+\sigma)\mathrm{o}} - c_{\mathrm{j}0}\right)/c_{\mathrm{j}0} = \delta, \nu_{\mathrm{j}+\sigma}/\nu_{\mathrm{j}} = \gamma$; isothermal, discontinuous, constant-volume reaction

$$q = v \cdot Q_{\mathrm{j}\infty} \cdot k \cdot (1+\delta-\gamma) \cdot c_{\mathrm{j}0} \cdot \{1+\gamma/(1+\delta-\gamma)\} \cdot \mathrm{EXP}\left(-\nu_{\mathrm{j}} \cdot k \cdot (1+\delta-\gamma) \cdot c_{\mathrm{j}0} \cdot t\right)/ \\ \left\{\gamma/(1+\delta-\gamma) - [1+\gamma/(1+\delta-\gamma)] \cdot \mathrm{EXP}\left[-\nu_{\mathrm{j}} \cdot k \cdot (1+\delta-\gamma) \cdot c_{\mathrm{j}0} \cdot t\right]\right\}^2$$

4.2.1.1.2 System of Reactions Kinetically Characterized by Several Rate Functions

Two chemical conversions can be characterized by the same type of reaction rate, for instance, a reaction of order 1. Nevertheless, one conversion runs by a single elementary reaction, the other occurs via a multiplicity of simultaneous or consecutive elementary reactions—as has already been demonstrated. When the rates of the partial reactions are of similar orders of magnitude, ascertainable intermediate resultants are produced, and as a rule, it is not just the initial reactants that determine the course of conversion versus time.

For these complex reaction systems consisting of several elementary reactions ξ it follows that, owing to the superposition principle and relations (4.1), (4.4), and (4.11),

$$\mathrm{d}n_{\mathrm{j/j}} = \sum \nu_{(\mathrm{j/i})\xi} \cdot \mathrm{d}\lambda_{\xi}$$

respectively

$$\mathrm{d}n_{\mathrm{j/j}}/\mathrm{d}t/V = \sum \nu_{(\mathrm{j/i})\xi} \cdot r_{\xi} = \mathrm{d}c_{\mathrm{j/i}}/\mathrm{d}t + c_{\mathrm{j/i}}\mathrm{d}V/\mathrm{d}t/V.$$

With $V = \text{const}$ we obtain

$$\mathrm{d}c_{\mathrm{j/i}}/\mathrm{d}t = \sum v_{(\mathrm{j/i})\xi} \cdot r_\xi. \tag{4.34}$$

The rate of consumption respectively of formation $\mathrm{d}c_{\mathrm{j/i}}/\mathrm{d}t$ of reactants j respectively resultants i are a linear combination of the single rates of reaction r_ξ and the stoichiometric coefficients $v_{(\mathrm{j/i})\xi}$.

4.2.1.1.2.1 Two Coupled Parallel Reactions

4.2.1.1.2.1.1 Rate Functions of Order 0

The simplest, complex conversion consists in forming simultaneously two different products via two reactions starting from one reactant

$$\begin{aligned} &\mathrm{A} \xrightarrow{r_1,\,\Delta H_{\lambda 1}} \mathrm{B} \\ &\mathrm{A} \xrightarrow{r_2,\,\Delta H_{\lambda 2}} \mathrm{C} \end{aligned}$$

with

- The stoichiometric coefficients $v_{(\mathrm{j,i})\xi}$

$$v_{\mathrm{A1}} = -1, v_{\mathrm{A2}} = -1, v_{\mathrm{B1}} = 1, v_{\mathrm{B2}} = 0, v_{\mathrm{C1}} = 0, v_{\mathrm{C2}} = 1,$$

- The rate functions of order 0

$$r_1 = k_1 \quad \text{and} \quad r_2 = k_2.$$

According to (4.34), the rate of consumption in A and the rates of formation in B and C are

$$\begin{aligned} \mathrm{d}c_{\mathrm{A}}/\mathrm{d}t &= \sum v_{\mathrm{A}\xi} \cdot r_\xi = v_{\mathrm{A1}} \cdot r_1 + v_{\mathrm{A2}} \cdot r_2 = -(k_1 + k_2) \\ \mathrm{d}c_{\mathrm{B}}/\mathrm{d}t &= \sum v_{\mathrm{B}} \cdot r_\xi = r_1 = k_1 \\ \mathrm{d}c_{\mathrm{C}}/\mathrm{d}t &= \sum v_{\mathrm{C}} \cdot r_\xi = r_2 = k_2. \end{aligned}$$

The solution of the equation system is

$$\begin{aligned} c_{\mathrm{A}} &= c_{\mathrm{A0}} - (k_1 + k_2) \cdot t, \\ c_{\mathrm{B}} &= c_{\mathrm{B0}} + k_1 \cdot t, \\ c_{\mathrm{C}} &= c_{\mathrm{C0}} + k_2 \cdot t. \end{aligned} \tag{4.35}$$

The consumption in A as well as the formation in B and C are completed at time

$$t_{\mathrm{EA}} = c_{\mathrm{A0}}/(k_1 + k_2). \tag{4.36}$$

The formation in B and C occurs uniformly. At any time

$$(c_{\mathrm{B}} - c_{\mathrm{B0}})/(c_{\mathrm{C}} - c_{\mathrm{C0}}) = \left(c_{\mathrm{B}(t=\infty)} - c_{\mathrm{B0}}\right)/\left(c_{\mathrm{C}(t=\infty)} - c_{\mathrm{C0}}\right) = k_1/k_2 \tag{4.37}$$

is valid; moreover,

$$\begin{aligned}\left(c_{\mathrm{B}(t=\infty)} - c_{\mathrm{B0}}\right)/c_{\mathrm{A0}} = k_1/(k_1 + k_2), \left(c_{\mathrm{C}(t=\infty)} - c_{\mathrm{C0}}\right)/c_{\mathrm{A0}} \\ = k_2/(k_1 + k_2).\end{aligned} \tag{4.38}$$

$(-\Delta H_{\lambda 1})$ and $(-\Delta H_{\lambda 2})$ are the heats of production in B and C, respectively. With $(-\Delta H_{\lambda})$, the overall heat of consumption of A, we obtain for the thermal reaction power according to (4.7),

$$\begin{aligned} q &= [k_1 \cdot (-\Delta H_{\lambda 1}) + k_2 \cdot (-\Delta H_{\lambda 2})] \cdot V \\ &= (k_1 + k_2) \cdot V \cdot (-\Delta H_{\lambda}).\end{aligned} \tag{4.39}$$

The heat release takes place at a constant rate, $q(0 \leq t \leq t_{\mathrm{EA}}) = (k_1 + k_2) \cdot V \cdot (-\Delta H_{\lambda})$, up to the abrupt stop at time t_{EA} (Fig. 4.7). On the basis of the time t_{EA} of the end of heat release, the initial concentration c_{A0} of A and (4.36) yields for the sum of the rate coefficients

$$(k_1 + k_2) = c_{\mathrm{A0}}/t_{\mathrm{EA}}.$$

The rate coefficients k_1 and k_2 result from (4.37), (4.38), the final concentrations $c_{\mathrm{B}(t=\infty)}$ and $c_{\mathrm{C}(t=\infty)}$, and $(k_1 + k_2)$:

$$\begin{aligned} k_2 &= (k_1 + k_2)/\left[\left(c_{\mathrm{B}(t=\infty)} - c_{\mathrm{B0}}\right)/\left(c_{\mathrm{C}(t=\infty)} - c_{\mathrm{C0}}\right) + 1\right], \\ k_1 &= (k_1 + k_2) - (k_1 + k_2)/\left[\left(c_{\mathrm{B}(t=\infty)} - c_{\mathrm{B0}}\right)/\left(c_{\mathrm{C}(t=\infty)} - c_{\mathrm{C0}}\right) + 1\right].\end{aligned}$$

The overall heat of the reaction $(-\Delta H_{\lambda})$ follows from the value of the constant thermal reaction power $q(0 \leq t \leq t_{\mathrm{EA}})$ and the constant reaction volume V owing to (4.39)[18]

$$(-\Delta H_{\lambda}) = q(0 \leq t \leq t_{\mathrm{EA}})/(k_1 + k_2)/V.$$

Furthermore, with (4.39), we may apply

$$\begin{aligned}(-\Delta H_{\lambda}) &= k_1/(k_1 + k_2) \cdot (-\Delta H_{\lambda 1}) + k_2/(k_1 + k_2) \cdot (-\Delta H_{\lambda 2}) \\ &= \Omega_1 \cdot (-\Delta H_{\lambda 1}) + \Omega_2 \cdot (-\Delta H_{\lambda 2}).\end{aligned} \tag{4.40}$$

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[18] $(-\Delta H_{\lambda})$ results also from the total amount of heat released according to $(-\Delta H_{\lambda}) = \int q \cdot \mathrm{d}t/(C_{\mathrm{A0}} \cdot V)$.

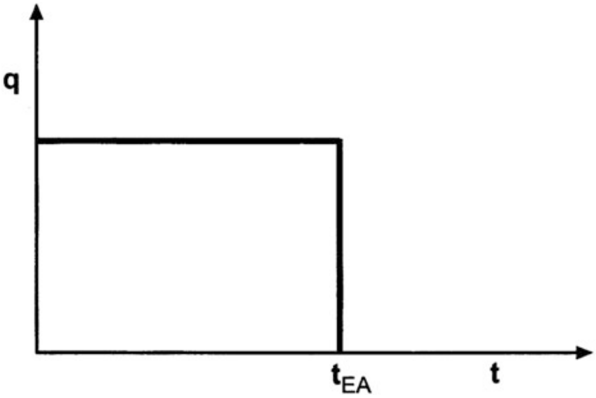

Fig. 4.7 Coupled parallel reactions $\begin{array}{l} A \xrightarrow{r_1,\, \Delta H_{\lambda 1}} B \\ A \xrightarrow{r_2,\, \Delta H_{\lambda 2}} C \end{array}$.
Rate functions of order 0; isothermal, discontinuous, constant-volume reactions

$$q = (k_1 + k_2) \cdot V \cdot (-\Delta H_\lambda)$$

An additional, independent thermal correlation of $(-\Delta H_{\lambda 1})$ $(-\Delta H_{\lambda 2})$ and $(-\Delta H_\lambda)$ does not exist, i.e. despite the knowledge of k_1, k_2 respectively Ω_1, Ω_2 and $(-\Delta H_\lambda)$, the heats of the reaction $(-\Delta H_{\lambda 1})$ and $(-\Delta H_{\lambda 2})$ cannot be found.

However, because of the uniform consumption in A respectively formation in B and C, knowledge of this is only of academic interest. At any time the relation of the single thermal reaction power is constant, and the course of the temporal rate of global heat release is formed by the kinetically balanced overall heat of the reaction $(-\Delta H_\lambda)$ according to (4.39). It is possible to determine single heats of a reaction only when the rates of formation in B or C are changed by specifically influencing catalysts. By two different values of reactivity, I and II, the following expressions are valid in this case:

$$\Delta H_\lambda(\mathrm{I}) = \Omega_1(\mathrm{I}) \cdot \Delta H_{\lambda 1} + \Omega_2(\mathrm{I}) \cdot \Delta H_{\lambda 2}$$
$$\Delta H_\lambda(\mathrm{II}) = \Omega_1(\mathrm{II}) \cdot \Delta H_{\lambda 1} + \Omega_2(\mathrm{II}) \cdot \Delta H_{\lambda 2}.$$

From the combination of the equations we obtain

$$\Delta H_{\lambda 2} = [\Delta H_\lambda(\mathrm{II}) - \Omega_1(\mathrm{II})/\Omega_1(\mathrm{I}) \cdot \Delta H_\lambda(\mathrm{I})]/[\Omega_2(\mathrm{II}) - \Omega_1(\mathrm{II})/\Omega_1(\mathrm{I}) \cdot \Omega_2(\mathrm{I})]$$

and

$$\Delta H_{\lambda 1} = \Delta H_\lambda(I) - \Omega_2(\mathrm{I})/\Omega_1(\mathrm{I}) \cdot \Delta H_{\lambda 2}.$$

An analogous procedure is also possible when the temperature dependency of the rate coefficients k_1 and k_2 differs but the dependency of the heats of reaction on temperature can be neglected.

If one of the reactions can be stopped by the addition of an inhibitor, $(-\Delta H_\lambda)$ corresponds to the heat of the active reaction; in this case, the other heat of the reaction can be elaborated by (4.39).

4.2.1.1.2.1.2 *Rate Functions of Order 1*

Starting from one reactant by two reactions, two products are formed:

$$\mathrm{A} \xrightarrow{r_1,\,\Delta H_{\lambda 1}} \mathrm{B}$$
$$\mathrm{A} \xrightarrow{\mathrm{r}_2,\,\Delta H_{\lambda 2}} \mathrm{C}$$

with

- The stoichiometric coefficients $v_{(\mathrm{j,i})\xi}$

$$v_{\mathrm{A1}} = -1, v_{\mathrm{A2}} = -1, v_{\mathrm{B1}} = 1, v_{\mathrm{B2}} = 0, v_{\mathrm{C1}} = 0, v_{\mathrm{C2}} = 1,$$

- The rate functions of order 1

$$r_1 = k_1 \cdot c_{\mathrm{A}} \quad \text{and} \quad r_2 = k_2 \cdot c_{\mathrm{A}}.$$

According to (D34), for the rate of consumption in A and the rates of formation in B and C we get

$$\begin{aligned}
\mathrm{d}c_{\mathrm{A}}/\mathrm{d}t &= \sum v_{\mathrm{A}\xi} \cdot r_\xi = v_{\mathrm{A1}} \cdot r_1 + v_{\mathrm{A2}} \cdot r_2 = -(k_1 + k_2) \cdot c_{\mathrm{A}},\\
\mathrm{d}c_{\mathrm{B}}/\mathrm{d}t &= \sum v_{\mathrm{B}} \cdot r_\xi = r_1 = k_1 \cdot c_{\mathrm{A}},\\
\mathrm{d}c_{\mathrm{C}}/\mathrm{d}t &= \sum v_{\mathrm{C}} \cdot r_\xi = r_2 = k_2 \cdot c_{\mathrm{A}}.
\end{aligned}$$

The solutions of the equations are as follows:

$$\begin{aligned}
c_{\mathrm{A}} &= c_{\mathrm{A0}} \cdot \mathrm{EXP}[-(k_1 + k_2) \cdot t],\\
c_{\mathrm{B}} &= c_{\mathrm{B0}} + k_1/(k_1 + k_2) \cdot c_{\mathrm{A0}} \cdot (1 - \mathrm{EXP}[-(k_1 + k_2) \cdot t]),\\
c_{\mathrm{C}} &= c_{\mathrm{C0}} + k_2/(k_1 + k_2) \cdot c_{\mathrm{A0}} \cdot (1 - \mathrm{EXP}[-(k_1 + k_2) \cdot t]).
\end{aligned} \tag{4.41}$$

The consumption in A and the formation in B and C occur uniformly. At any time

$$(c_{\mathrm{B}} - c_{\mathrm{B0}})/(c_{\mathrm{C}} - c_{\mathrm{C0}}) = \left(c_{\mathrm{B}(t=\infty)} - c_{\mathrm{B0}}\right)/\left(c_{\mathrm{C}(t=\infty)} - c_{\mathrm{C0}} = k_1/k_2 \right. \tag{4.42}$$

is valid; moreover,

$$\left(c_{\mathrm{B}(t=\infty)} - c_{\mathrm{B0}}\right)/c_{\mathrm{A0}} = k_1/(k_1 + k_2), \left(c_{\mathrm{C}(t=\infty)} - c_{\mathrm{C0}}\right)/c_{\mathrm{A0}} = k_2/(k_1 + k_2). \tag{4.43}$$

According to (4.7), the determining equation of the thermal reaction power holds:

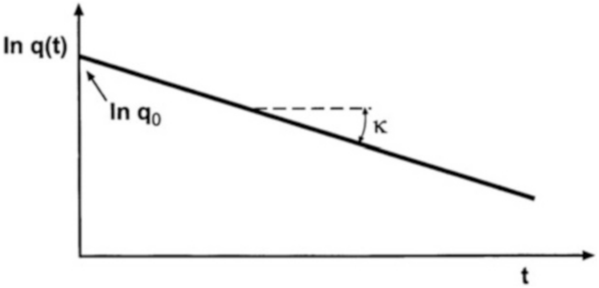

Fig. 4.8 Coupled parallel reactions, rate functions of order 1; isothermal, discontinuous, constant-volume reactions

$$q = (k_1 + k_2) \cdot c_{A0} \cdot V \cdot (-\Delta H_\lambda) \cdot \mathrm{EXP}\left[-(k_1 + k_2) \cdot t\right.$$

$$\begin{aligned} q &= \{k_1 \cdot (-\Delta H_{\lambda 1}) + k_2 \cdot (-\Delta H_{\lambda 2})\} \cdot c_{A0} \cdot V \cdot \mathrm{EXP}[-(k_1 + k_2) \cdot t] \\ &= (k_1 + k_2) \cdot c_{A0} \cdot V \cdot (-\Delta H_\lambda) \cdot \mathrm{EXP}[-(k_1 + k_2) \cdot t]. \end{aligned} \tag{4.44}$$

The plot of $\ln\{q\}$ versus time,[19] (Fig. 4.8) gives a straight line with a slope of $(k_1 + k_2)$ and the point of intersection with the ordinate $\ln\{q(t = 0)\} = \ln\{(k_1 + k_2) \cdot c_{A0} \cdot V \cdot (-\Delta H_\lambda)\}$. According to (4.42) and (4.43), from the slope $(k_1 + k_2)$ and the concentrations $c_{B(t=\infty)}$ and $c_{C(t=\infty)}$ result the rate coefficients k_1 and k_2

$$\begin{aligned} k_2 &= (k_1 + k_2)/\left[\left(c_{B(t=\infty)} - c_{B0}\right)/\left(c_{C(t=\infty)} - c_{C0}\right) + 1\right], \\ k_1 &= (k_1 + k_2) - (k_1 + k_2)/\left[\left(c_{B(t=\infty)} - c_{B0}\right)/\left(c_{C(t=\infty)} - c_{C0}\right) + 1\right]. \end{aligned}$$

From the point of intersection $\ln\{q(t = 0)\}$, the initial concentration c_{A0} and the reaction volume V follows the overall heat of the reaction[20]

$$(-\Delta H_\lambda) = q(t = 0)/(k_1 + k_2)/c_{A0}/V.$$

The overallheat of the reaction is due to (4.44):

$$\begin{aligned} (-\Delta H_\lambda) &= k_1/(k_1 + k_2) \cdot (-\Delta H_{\lambda 1}) + k_2/(k_1 + k_2) \cdot (-\Delta H_{\lambda 2}) \\ &= \Omega_1 \cdot (-\Delta H_{\lambda 1}) + \Omega_2 \cdot (-\Delta H_{\lambda 2}). \end{aligned} \tag{4.45}$$

As in the previous case, an additional independent thermal correlation of $(-\Delta H_{\lambda 1})$, $(-\Delta H_{\lambda 2})$ and $(-\Delta H_\lambda)$ does not exist. Because of that, the single heats of reactions $(-\Delta H_{\lambda 1})$ and $(-\Delta H_{\lambda 2})$ cannot be determined. However, because of the uniform

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[19] In the case of negative q-values $\ln\{|q(t)|\}$ must be plotted; the procedure of interpretation is similar.

[20] $(-\Delta H_\lambda)$ results also from the total amount of heat released according to $(-\Delta H_\lambda) = \int q \cdot \mathrm{d}t/(c_{A0} \cdot V)$.

consumption in A respectively production in B and C, knowing this is only of academic interest. At any time the relation between the single rates of heat production is constant and the temporal course of the measured heat release is formed by the kinetically balanced overall heat of the reaction $(-\Delta H_\lambda)$ according to (4.44). As in the previous case, the determination of the single reaction heats is only possible when the formation rates in B or C are changed by specifically influencing catalysts. For two different reaction activities I and II the following equations are valid:

$$\Delta H_\lambda(\mathrm{I}) = \Omega_1(\mathrm{I}) \cdot \Delta H_{\lambda 1} + \Omega_2(\mathrm{I}) \cdot \Delta H_{\lambda 2},$$
$$\Delta H_\lambda(\mathrm{II}) = \Omega_1(\mathrm{II}) \cdot \Delta H_{\lambda 1} + \Omega_2(\mathrm{II}) \cdot \Delta H_{\lambda 2}.$$

Combining the equations gives

$$\Delta H_{\lambda 2} = [\Delta H_\lambda(\mathrm{II}) - \Omega_1(\mathrm{II})/\Omega_1(\mathrm{I}) \cdot \Delta H_\lambda(\mathrm{I})]/[\Omega_2(\mathrm{II}) - \Omega_1(\mathrm{II})/\Omega_1(\mathrm{I}) \cdot \Omega_2(\mathrm{I})]$$

and

$$\Delta H_{\lambda 1} = \Delta H_\lambda(\mathrm{I}) - \Omega_2(\mathrm{I})/\Omega_1(\mathrm{I}) \cdot \Delta H_{\lambda 2}.$$

An analogous procedure is also possible when the temperature dependency of the rate coefficients k_1 and k_2 is different, and the dependency of the heats on temperature can be neglected. If one of the reactions can be stopped by the addition of an inhibitor, then $(-\Delta H_\lambda)$ corresponds to the heat of the active reaction; the other heat of the reaction is then determined by (4.45).

4.2.1.1.2.1.3 Rate Functions of Order 1 Respectively 2

The formation of two products starting from one reactant occurs by two reactions:

$$\mathrm{A} \xrightarrow{r_1,\, \Delta H_{\lambda 1}} \mathrm{B}$$
$$\mathrm{A} \xrightarrow{r_2,\, \Delta H_{\lambda 2}} \mathrm{C}$$

with

- The stoichiometric coefficients $v_{(\mathrm{j,i})\xi}$

$$v_{\mathrm{A}1} = -1, v_{\mathrm{A}2} = -2, v_{\mathrm{B}1} = 1, v_{\mathrm{B}2} = 0, v_{\mathrm{C}1} = 0, v_{\mathrm{C}2} = 1,$$

- The rate function of order 1 respectively 2

$$r_1 = k_1 \cdot c_\mathrm{A} \;\text{ and }\; r_2 = k_2 \cdot {c_\mathrm{A}}^2.$$

According to (4.34), the rates of consumption in A as well as formation in B and C are

$$\begin{aligned}
\mathrm{d}c_{\mathrm{A}}/\mathrm{d}t &= \sum \nu_{\mathrm{A}\xi} \cdot r_\xi = \nu_{\mathrm{A}1} \cdot r_1 + \nu_{\mathrm{A}2} \cdot r_2 = -k_1 \cdot c_{\mathrm{A}} - 2 \cdot k_2 \cdot {c_{\mathrm{A}}}^2,\\
\mathrm{d}c_{\mathrm{B}}/\mathrm{d}t &= \sum \nu_{\mathrm{B}} \cdot r_\xi = r_1 = k_1 \cdot c_{\mathrm{A}},\\
\mathrm{d}c_{\mathrm{C}}/\mathrm{d}t &= \sum \nu_{\mathrm{C}} \cdot r_\xi = r_2 = k_2 \cdot {c_{\mathrm{A}}}^2.
\end{aligned}$$

Using $2 \cdot k_2/k_1 = \backepsilon$ the solution to the equation system reads

$$\begin{gathered}
c_{\mathrm{A}} = 1/[({c_{\mathrm{A}0}}^{-1} + \backepsilon) \cdot \mathrm{EXP}(k_1 \cdot t) - \backepsilon],\\
c_{\mathrm{B}} = \backepsilon^{-1} \cdot \ln\left\{\left[\left(c_{\mathrm{A}0}^{-1} + \backepsilon\right) \cdot \mathrm{EXP}(k_1 \cdot t) - \backepsilon\right]/({c_{\mathrm{A}0}}^{-1} \cdot \mathrm{EXP}(k_1 \cdot t))\right\},\\
c_{\mathrm{C}} = \backepsilon^{-1} \cdot \left\{\ln\left[{c_{\mathrm{A}0}}^{-1} \cdot \mathrm{EXP}(k_1 \cdot t)/\left\{({c_{\mathrm{A}0}}^{-1} + \backepsilon) \cdot \mathrm{EXP}(k_1 \cdot t) - \backepsilon\right\}\right] + \backepsilon/{c_{\mathrm{A}0}}^{-1} - \backepsilon/\right.\\
\left.[({c_{\mathrm{A}0}}^{-1} + \backepsilon) \cdot \mathrm{EXP}(k_1 \cdot t) - \backepsilon]\right\}.
\end{gathered}$$

For this reason and with (4.7) the temporal course of the thermal reaction power becomes

$$\begin{aligned}
q &= [k_1 \cdot c_{\mathrm{A}} \cdot (-\Delta H_1) + k_2 \cdot {c_{\mathrm{A}}}^2 \cdot (-\Delta H_2)] \cdot V\\
&= k_1 \cdot (-\Delta H_1) \cdot V\big/\left\{({c_{\mathrm{A}0}}^{-1} + \backepsilon) \cdot \mathrm{EXP}(k_1 \cdot t) - \backepsilon\right\}\\
&\quad + k_2 \cdot (-\Delta H_2) \cdot V\big/\left\{({c_{\mathrm{A}0}}^{-1} + \backepsilon) \cdot \mathrm{EXP}(k_1 \cdot t) - \backepsilon\right\}^2.
\end{aligned} \tag{4.46}$$

For $t \gg 0$ the second term versus the first one can be neglected; the following result is obtained:

$$q_{(t \gg 0)} \cong c_{\mathrm{A}0} \cdot k_1^2 \cdot V \cdot (-\Delta H_1)/(k_1 + 2 \cdot k_2 \cdot c_{\mathrm{A}0}) \cdot \mathrm{EXP}(-k_1 \cdot t). \tag{4.47}$$

The plot of $\ln\{q\}$ versus time (Fig. 4.9) gives a curve turning in a straight line with slope κ and the point of intersection with the ordinate $\ln\{\phi\}$ in which[21]

$$\phi = \left\{\left[c_{\mathrm{A}0} \cdot k_1^2 \cdot V \cdot (-\Delta H_1)/(k_1 + 2 \cdot k_2 \cdot c_{\mathrm{A}0})\right]\right\}.$$

The rate coefficient k_1 corresponds to the slope κ:

$$k_1 = \kappa.$$

k_2, $\Delta H_{\lambda 1}$ and $\Delta H_{\lambda 2}$ can be evaluated by determining equations on the basis of quantities to be obtained from the measured thermal reaction power q:

- Specific intersection of ordinate $\ln\{\phi/V\} = \ln\{\phi_{\mathrm{s}}\}$,
- Specific initial value of thermal reaction power $q(t = 0)/V = q_{\mathrm{s}}(0)$,
- Specific total heat of reaction $\int_{t=0\to\infty} q \cdot \mathrm{d}t/V = Q_{\mathrm{s}}(\propto)$.

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[21] In the case of negative q-values, $\ln\{|q(t)|\}$ is plotted; the procedure of interpretation is similar.

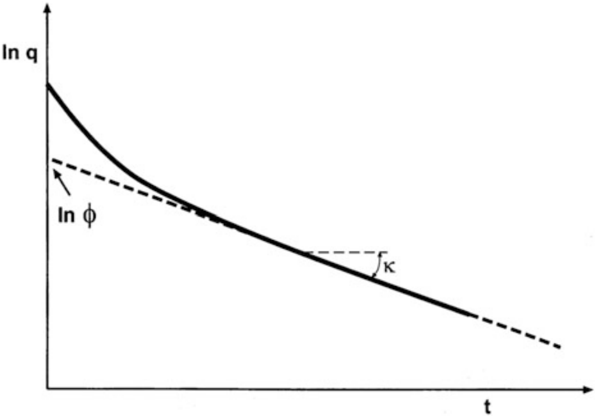

Fig. 4.9 Coupled parallel reactions; rate functions of order 1 respectively 2: isothermal, discontinuous, constant-volume reactions

$$q = \left[k_1 \cdot (-\Delta H_1)/\left\{\left(c_{A0}^{-1} + \backepsilon\right) \cdot \mathrm{EXP}(k_1 \cdot t) - \backepsilon\right\} + k_2 \cdot (-\Delta H_2)/\left\{\left(c_{A0}^{-1} + \backepsilon\right) \cdot \mathrm{EXP}(k_1 \cdot t) - \backepsilon\right\}^2\right] \cdot V$$

With (4.46) and (4.47) the following correlations appear:

$$\begin{aligned} q_s(0) &= k_1 \cdot c_{A0} \cdot (-\Delta H_1) + k_2 \cdot c_{A0}{}^2 \cdot (-\Delta H_2), \\ \phi_s &= c_{A0} \cdot k_1^2 \cdot (-\Delta H_1)/(k_1 + 2 \cdot k_2 \cdot c_{A0}), \\ Q_s(\propto) &= c_{B\infty} \cdot (-\Delta H_1) + c_{C\infty} \cdot (-\Delta H_2). \end{aligned} \tag{4.48}$$

For k_2, $\Delta H_{\lambda 1}$ and $\Delta H_{\lambda 2}$ it follows that

(a)

$$(-\Delta H_1) = (A + B + E)/2/D - \sqrt{\left[(A + B + E)^2/4/D^2 - F/D\right]},$$

with

$$\begin{aligned} A &= k_1 \cdot c_{A0}, \\ B &= k_1^2 \cdot c_{A0}{}^2/2/c_{C\propto} \cdot Q_s(\infty)/\phi_s, \\ C &= k_1 \cdot c_{A0}/2 \cdot Q_s(\infty), \\ D &= k_1{}^2 \cdot c_{A0}{}^2/2 \cdot c_{B\infty}/c_{C\infty}/\phi_s, \\ E &= k_1 \cdot c_{A0}/2 \cdot c_{B\infty}/c_{C\infty}, \\ F &= q_s(0) + k_1 \cdot c_{A0}/2 \cdot Q_s(\infty)^2; \end{aligned}$$

(b)

$$(-\Delta H_2) = [Q_s(\infty) - c_{B\infty} \cdot (-\Delta H_1)]/c_{C\infty};$$

(c)

$$k_2 = k_1{}^2 \cdot (-\Delta H_1)/2/\phi_s - k_1/c_{A0}/2.$$

4.2.1.1.2.1.4 Rate Functions Are the Product of Two Partial Orders 1

A coupled conversion consists of the formation of two different products starting from two reactants by two parallel reactions:

$$\begin{aligned} \mathrm{A} + \mathrm{B} &\xrightarrow{r_1,\, \Delta H_{\lambda 1}} \mathrm{C} \\ \mathrm{A} + \mathrm{B} &\xrightarrow{r_2,\, \Delta H_{\lambda 2}} \mathrm{D} \end{aligned}$$

with

- The stoichiometric coefficients $v_{(\mathrm{j,i})\xi}$

$$v_{\mathrm{A1}} = -1, v_{\mathrm{A2}} = -1, v_{\mathrm{B1}} = -1, v_{\mathrm{B2}} = -1, v_{\mathrm{C1}} = 1, v_{\mathrm{C2}} = 0, v_{\mathrm{D1}} = 0, v_{\mathrm{D2}} = 1,$$

- The rate functions: proportional to the product of two partial orders 1:

$$r_1 = k_1 \cdot c_{\mathrm{A}} \cdot c_{\mathrm{B}} \ \text{ und } \ r_2 = k_2 \cdot c_{\mathrm{A}} \cdot c_{\mathrm{B}}.$$

- Equal initial concentrations of reactants

$$c_{\mathrm{A0}} = c_{\mathrm{B0}}.$$

According to (4.34), the rates of consumption in A and B and the rates of formation in C and D are

$$\begin{aligned} \mathrm{d}c_{\mathrm{A}}/\mathrm{d}t &= \sum v_{\mathrm{A}\xi} \cdot r_\xi = -(k_1 + k_2) \cdot c_{\mathrm{A}} \cdot c_{\mathrm{B}}, \\ \mathrm{d}c_{\mathrm{B}}/\mathrm{d}t &= \sum v_{\mathrm{B}\xi} \cdot r_\xi = -(k_1 + k_2) \cdot c_{\mathrm{A}} \cdot c_{\mathrm{B}}, \\ \mathrm{d}c_{\mathrm{C}}/\mathrm{d}t &= \sum v_{\mathrm{C}\xi} \cdot r_\xi = k_1 \cdot c_{\mathrm{A}} \cdot c_{\mathrm{B}}, \\ \mathrm{d}c_{\mathrm{D}}/\mathrm{d}t &= \sum v_{\mathrm{D}\xi} \cdot r_\xi = k_2 \cdot c_{\mathrm{A}} \cdot c_{\mathrm{B}}. \end{aligned}$$

The solution of the equation system is

$$\begin{aligned} c_{\mathrm{A}} &= c_{\mathrm{B}} = c_{\mathrm{A0}}/[c_{\mathrm{A0}} \cdot (k_1 + k_2) \cdot t + 1], \\ c_{\mathrm{C}} &= k_1 \cdot c_{\mathrm{A0}}/(k_1 + k_2)/[c_{\mathrm{A0}} \cdot (k_1 + k_2) \cdot t + 1] + c_{\mathrm{C0}}, \\ c_{\mathrm{D}} &= k_2 \cdot c_{\mathrm{A0}}/(k_1 + k_2)/[c_{\mathrm{A0}} \cdot (k_1 + k_2) \cdot t + 1] + c_{\mathrm{D0}}. \end{aligned}$$

The consumption in A and B and the production in C and D occur uniformly. During the entire run of the conversion the following expressions are valid:

- $$c_{\mathrm{A}} = c_{\mathrm{B}}$$
- $$(c_{\mathrm{C}} - c_{\mathrm{C0}})/(c_{\mathrm{D}} - c_{\mathrm{D0}}) = \left(c_{\mathrm{C}(t=\infty)} - c_{\mathrm{C0}}\right)/\left(c_{\mathrm{D}(t=\infty)} - c_{\mathrm{D0}}\right) = k_1/k_2, \quad (4.49)$$

- $$\left(c_{C(t=\infty)}-c_{C0}\right)/c_{A0}=k_1/(k_1+k_2) \text{ and } \left(c_{D(t=\infty)}-c_{D0}\right)/c_{A0} = k_1/(k_1+k_2). \tag{4.50}$$

If $(-\Delta H_{\lambda 1})$ and $(-\Delta H_{\lambda 2})$ are the heats of formation in C and D and $(-\Delta H_{\lambda})$ is the overall heat of the reaction in relation to consumed A, then, according to (4.7), for the thermal reaction power, we obtain

$$\begin{aligned} q &= {c_{A0}}^2 \cdot [k_1 \cdot (-\Delta H_{\lambda 1}) + k_2 \cdot (-\Delta H_{\lambda 2})] \cdot V/[c_{A0} \cdot (k_1 + k_2) \cdot t + 1]^2 \\ &= {c_{A0}}^2 \cdot (k_1 + k_2) \cdot V \cdot (-\Delta H_{\lambda})/[c_{A0} \cdot (k_1 + k_2) \cdot t + 1]^2 \end{aligned} \tag{4.51}$$

respectively

$$q^{-1} = [c_{A0} \cdot (k_1 + k_2) \cdot t + 1]^2 / \left[{c_{A0}}^2 \cdot (k_1 + k_2) \cdot V \cdot (-\Delta H_{\lambda})\right]$$

or

$$\begin{aligned} |q|^{-1/2} &= 1/\sqrt{|q|} \\ &= \sqrt{[(k_1 + k_2)/(V \cdot |-\Delta H_{\lambda}|)]} \cdot t + 1/\sqrt{[{c_{A0}}^2 \cdot (k_1 + k_2) \cdot V \cdot |-\Delta H_{\lambda}|]}. \end{aligned}$$

Plotting $1/\sqrt{|q|}$ versus time (Fig. 4.10) leads to a straight line with

- Slope $\kappa = \sqrt{[(k_1 + k_2)/(V \cdot |-\Delta H_{\lambda}|)]}$,
- Point of intersection with the ordinate $\phi = 1/\sqrt{[{c_{A0}}^2 \cdot (k_1 + k_2) \cdot V \cdot |-\Delta H_{\lambda}|]}$.

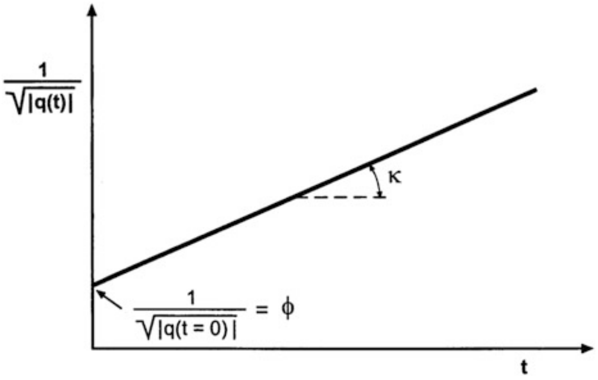

Fig. 4.10 Coupled parallel reactions $\begin{matrix} A + B \xrightarrow{r_1,\, \Delta H_{\lambda 1}} C \\ A + B \xrightarrow{r_2,\, \Delta H_{\lambda 2}} D \end{matrix}$. Overall enthalpy ΔH_{λ}, rate functions: product of two partial orders 1 $c_{AO} = c_{BO}$; isothermal, discontinuous, constant-volume reactions

$$|q|^{-1/2} = \sqrt{[(k_1 + k_2)/(V \cdot |-\Delta H_{\lambda}|)]} \cdot \mathrm{t} + 1/\sqrt{\left[c_{A0}^2 \cdot (k_1 + k_2) \cdot V \cdot |-\Delta H_{\lambda}|\right]}$$

From κ and ϕ result the sum of the rate coefficients k_1 and k_2 and the absolute amount of the overall heat of the reaction $(-\Delta H_\lambda)$:

$$\begin{aligned}
&k_1 + k_2 = \kappa/\phi/c_{A0},\\
&|-\Delta H_\lambda| = (\kappa \cdot \phi \cdot V \cdot c_{A0})^{-1},\\
&(-\Delta H_\lambda) < 0 \text{ when } q < 0 \quad \text{and} \quad (-\Delta H_\lambda) > 0 \text{ when } q > 0.
\end{aligned}$$

By means of the concentrations $c_{B(t=\infty)}$ and $c_{C(t=\infty)}$, as well as (4.49) and (4.50), the rate coefficients k_1 and k_2 are obtained:

$$\begin{aligned}
&k_2 = (k_1 + k_2)/\left[\left(c_{B(t=\infty)} - c_{B0}\right)/\left(c_{C(t=\infty)} - c_{C0}\right) + 1\right],\\
&k_1 = (k_1 + k_2) - (k_1 + k_2)/\left[\left(c_{B(t=\infty)} - c_{B0}\right)/\left(c_{C(t=\infty)} - c_{C0}\right) + 1\right].
\end{aligned}$$

The connection of the overall enthalpy of reaction with the single enthalpies of reaction reads, according to (4.51),

$$k_1 \cdot (-\Delta H_{\lambda 1}) + k_2 \cdot (-\Delta H_{\lambda 2}) = (k_1 + k_2) \cdot (-\Delta H_\lambda).$$

An additional independent correlation of $(-\Delta H_{\lambda 1})$, $(-\Delta H_{\lambda 2})$ and $(-\Delta H_\lambda)$ does not exist.

However, because of the uniform consumption in A respectively production in B and C, knowing that independent correlation does not exist, the knowledge of the single enthalpies is only of academic interest. At any time the relation of the single rates of heat release is constant, and the course of the total heat release is formed by the kinetically balanced overall heat of the reaction $(-\Delta H_\lambda)$ according to (4.51). The determination of the single heats of the reaction is only possible when the rates of formation in B or C are changed by specifically influencing the catalysts or inhibitors as well as by measurements under different temperatures, when the dependency of the rate coefficients k_1 and k_2 on the temperature are different and the dependency of the heats of reaction on the temperature can be neglected.

4.2.1.1.2.1.5 Rate Function is a Product of Two Partial Orders 1, One Component in Surplus

A coupled reaction occurs by the parallel formation of two products starting from two reactants by two reactions,

$$\begin{aligned}
&\mathrm{A + B} \xrightarrow{r_1,\,\Delta H_{\lambda 1}} \mathrm{C}\\
&\mathrm{A + B} \xrightarrow{r_2,\,\Delta H_{\lambda 2}} \mathrm{D}
\end{aligned}$$

with

- The stoichiometric coefficients $\nu_{(j,i)\xi}$:

$$v_{\mathrm{A1}} = -1, v_{\mathrm{A2}} = -1, v_{\mathrm{B1}} = -1, v_{\mathrm{B2}} = -1, v_{\mathrm{C1}} = 1, v_{\mathrm{C2}} = 0, v_{\mathrm{D1}} = 0, v_{\mathrm{D2}} = 1,$$

- The rate functions: proportional to the product of two partial orders 1

$$r_1 = k_1 \cdot c_{\mathrm{A}} \cdot c_{\mathrm{B}} \text{ and } r_2 = k_2 \cdot c_{\mathrm{A}} \cdot c_{\mathrm{B}}.$$

The component B is in surplus with respect to A,
It is

$$(c_{\mathrm{B0}} - c_{\mathrm{A0}})/c_{\mathrm{A0}} = \delta \tag{4.52}$$

$$c_{\mathrm{B}} = c_{\mathrm{B0}} - (c_{\mathrm{A0}} - c_{\mathrm{A}}). \tag{4.53}$$

According to (4.34) the rates of consumption in A and B and the rates of formation in C and D are

$$\mathrm{d}c_{\mathrm{A}}/\mathrm{d}t = \mathrm{d}c_{\mathrm{B}}/\mathrm{d}t = -(k_1 + k_2) \cdot \left[\delta \cdot c_{\mathrm{A0}} \cdot c_{\mathrm{A}} + {c_{\mathrm{A}}}^2\right], \tag{4.54}$$

$$\mathrm{d}c_{\mathrm{C}}/\mathrm{d}t = k_1 \cdot [\delta \cdot c_{\mathrm{A0}} \cdot c_{\mathrm{A}} + {c_{\mathrm{A}}}^2],$$
$$\mathrm{d}c_{\mathrm{D}}/\mathrm{d}t = k_2 \cdot [\delta \cdot c_{\mathrm{A0}} \cdot c_{\mathrm{A}} + {c_{\mathrm{A}}}^2].$$

Consumption in A and B and the formation in C and D occur uniformly, i.e. from (4.54) arise

$$\begin{aligned}(c_{\mathrm{C}} - c_{\mathrm{C0}})/(c_{\mathrm{A0}} - c_{\mathrm{A}}) = (c_{\mathrm{C}\infty} - c_{\mathrm{C}})/c_{\mathrm{A0}}\big) &= k_1/(k_1 + k_2),\\ (c_{\mathrm{D}} - c_{\mathrm{D0}})/(c_{\mathrm{A0}} - c_{\mathrm{A}}) = (c_{\mathrm{D}\infty} - c_{\mathrm{D}})/c_{\mathrm{A0}}\big) &= k_2/(k_1 + k_2),\\ (c_{\mathrm{C}} - c_{\mathrm{C0}})/(c_{\mathrm{D0}} - c_{\mathrm{D0}}) = (c_{\mathrm{C}\infty} - c_{\mathrm{C0}})/(c_{\mathrm{D}\infty} - c_{\mathrm{D0}}) &= k_1/k_2.\end{aligned} \tag{4.55}$$

The solution of Eq. (4.54) is

$$c_{\mathrm{A}} = c_{\mathrm{A0}}/[\{1 + 1/\delta\} \cdot \mathrm{EXP}((k_1 + k_2) \cdot \delta \cdot c_{\mathrm{A0}} \cdot t) - 1/\delta].$$

Using (4.3), (4.52), (4.53) and (4.54) leads to the temporal course of the thermal reaction power:

$$\begin{aligned}q = {c_{\mathrm{A0}}}^2 \cdot V \cdot (-\Delta H_\lambda) \cdot (k_1 + k_2) \cdot \delta \cdot \{1 + 1/\delta\}\\ \cdot \mathrm{EXP}[(k_1 + k_2) \cdot \delta \cdot c_{\mathrm{A0}} \cdot t]/\left\{1/\delta - (1 + 1/\delta) \cdot \mathrm{EXP}[(k_1 + k_2)] \cdot \delta \cdot c_{\mathrm{j0}} \cdot t\right\}^2.\end{aligned} \tag{4.56}$$

The term $1/\delta$ in the denominator, compared with the term $(1 + 1/\delta)\cdot$ $\mathrm{EXP}[(k_1 + k_2) \cdot \delta \cdot c_{\mathrm{A0}} \cdot t]$, can be neglected for $t \gg 0$ and the relation changes to

$$\begin{aligned}q(t \gg 0) &= {c_{\mathrm{A0}}}^2 \cdot V \cdot (-\Delta H_\lambda) \cdot (k_1 + k_2) \cdot \delta/(1 + 1/\delta) \cdot \mathrm{EXP}[-(k_1 + k_2) \cdot \delta \cdot c_{\mathrm{A0}} \cdot t]\\ &= {c_{\mathrm{A0}}}^2 \cdot V \cdot (-\Delta H_\lambda) \cdot (k_1 + k_2) \cdot \delta^2/(1 + \delta) \cdot \mathrm{EXP}[-(k_1 + k_2) \cdot \delta \cdot c_{\mathrm{A0}} \cdot t].\end{aligned}$$

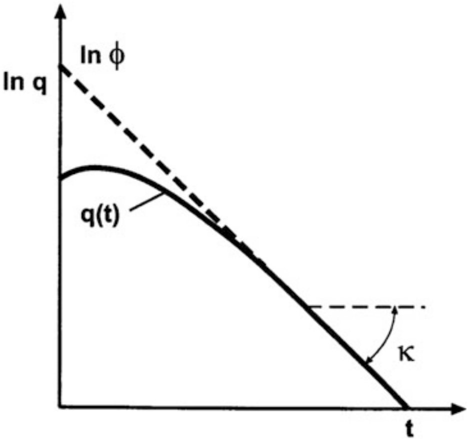

Fig. 4.11 Coupled parallel reactions $\begin{array}{l} \mathrm{A}+\mathrm{B}\xrightarrow{r_1,\,\Delta H_{\lambda 1}} C \\ \mathrm{A}+\mathrm{B}\xrightarrow{r_2,\,\Delta H_{\lambda 2}} \mathrm{D} \end{array}$. Overall enthalpy of reaction ΔH_λ, rate functions: product of two partial orders 1; isothermal, discontinuous, constant-volume reactions $(c_{\mathrm{B0}} - c_{\mathrm{A0}})/c_{\mathrm{A0}} = \delta$

$$q = c_{\mathrm{j0}}^2 \cdot V \cdot (-\Delta H_\lambda) \cdot (k_1 + k_2) \cdot \delta \cdot \{1 + 1/\delta\} \cdot \mathrm{EXP}\big[(k_1 + k_2) \cdot \delta \cdot c_{\mathrm{j0}} \cdot t\big] / \\ \big\{1/\delta - (1 + 1/\delta) \cdot \mathrm{EXP}\big[(k_1 + k_2) \cdot \delta \cdot c_{\mathrm{j0}} \cdot t\big]\big\}^2$$

Plotting $\ln\{q\}$ versus time[22] (Fig. 4.11) a curved line appears which changes to a straight line with

- Slope $\kappa = (k_1 + k_2) \cdot \delta \cdot c_{\mathrm{A0}}$
- Intersection of the ordinate $\ln\{\phi\}$
  with

$$\phi = c_{\mathrm{A0}}{}^2 \cdot V \cdot (-\Delta H_\lambda) \cdot (k_1 + k_2) \cdot \delta^2/(1 + \delta).$$

κ and ϕ give as a result the sum of the rate coefficients k_1 and k_2 as well as the heat of the reaction $(-\Delta H_\lambda)$:

$$\begin{aligned} (k_1 + k_2) &= \kappa/c_{\mathrm{A0}}/\delta \\ -\Delta H_\lambda &= \phi \cdot (1 + \delta)/[\kappa \cdot c_{\mathrm{A0}} \cdot V \cdot \delta]. \end{aligned}$$

From (4.55) and (4.56) and the concentrations $c_{\mathrm{C}\infty}$ and $c_{\mathrm{D}\infty}$ we obtain the rate coefficients k_2 and k_1:

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[22] In the case of negative q-values, $\ln\{|q(t)|\}$ is plotted; the procedure of interpretation is similar.

$$k_2 = (k_1 + k_2)/\left[\left(c_{\mathrm{B}(t=\infty)} - c_{\mathrm{B0}}\right)/\left(c_{\mathrm{C}(t=\infty)} - c_{\mathrm{C0}}\right) + 1\right],$$
$$k_1 = (k_1 + k_2) - (k_1 + k_2)/\left[\left(c_{\mathrm{B}(t=\infty)} - c_{\mathrm{B0}}\right)/\left(c_{\mathrm{C}(t=\infty)} - c_{\mathrm{C0}}\right) + 1\right].$$

From (4.54) follows the correlation of the overall heat of the reaction $(-\Delta H_\lambda)$ and the heats of reactions $(-\Delta H_{\lambda 1})$ and $(-\Delta H_{\lambda 2})$:

$$k_1 \cdot (-\Delta H_{\lambda 1}) + k_2 \cdot (-\Delta H_{\lambda 2}) = (k_1 + k_2) \cdot (-\Delta H_\lambda).$$

An additional independent correlation of $(-\Delta H_{\lambda 1})$, $(-\Delta H_{\lambda 2})$ and $(-\Delta H_\lambda)$ does not exist.

However, because of the uniform consumption in A respectively production in B and C, the knowledge of this is only of academic interest. At any time the relation between the single rates of heat release is constant, and the course of the total heat release is formed by the kinetically balanced overall heat of the reaction $(-\Delta H_\lambda)$ according to (4.56). The determination of the individual heats of reaction is only possible when the rates of formation in B or C are changed by specifically influencing the catalysts or inhibitors as well as by measurements under different temperatures, when the dependency of the rate coefficients k_1 and k_2 on the temperature are different and the dependency of the heats of the reaction on temperature can be neglected.

4.2.1.1.2.2 Two Non-coupled Parallel Reactions

4.2.1.1.2.2.1 Rate Functions of Order 0

The simplest non-coupled conversion consists of the following two reactions, which occur side by side without mutual influence:

$$\mathrm{A} \xrightarrow{r_1,\, \Delta H_{\lambda 1}} \mathrm{B}$$
$$\mathrm{C} \xrightarrow{r_2,\, \Delta H_{\lambda 2}} \mathrm{D}$$

with

- The stoichiometric coefficients $v_{(\mathrm{j,i})\xi}$

$$v_{\mathrm{A1}} = -1, v_{\mathrm{A2}} = 0, v_{\mathrm{B1}} = 1, v_{\mathrm{B2}} = 0, v_{\mathrm{C1}} = 0, v_{\mathrm{C2}} = -1, v_{\mathrm{D1}} = 0, v_{\mathrm{D2}} = 1,$$

- The rate functions of order 0

$$r_1 = k_1 \text{ und } r_2 = k_2.$$

According to (4.34), the rates of consumption in A and C are

$$\mathrm{d}c_\mathrm{A}/\mathrm{d}t = \sum v_{\mathrm{A}\xi} \cdot r_\xi = v_{\mathrm{A}1} \cdot r_1 = -k_1,$$

$$\mathrm{d}c_\mathrm{C}/\mathrm{d}t = \sum v_{\mathrm{C}\xi} \cdot r_\xi = v_{\mathrm{C}2} \cdot r_2 = -k_2.$$

The solutions of the equations are

$$c_\mathrm{A} = c_{\mathrm{A}0} - k_1 \cdot t,$$
$$c_\mathrm{C} = c_{\mathrm{C}0} - k_2 \cdot t.$$

The consumptions in A and C occur at constant rates and end abruptly at the points in time

$$t_\mathrm{EA} = c_{\mathrm{A}0}/k_1 \;\; and \;\; t_\mathrm{EC} = c_{\mathrm{C}0}/k_2. \tag{4.57}$$

The thermal reaction power is described by

$$q = q_1 + q_2 = k_1 \cdot V \cdot (-\Delta H_{\lambda 1}) + k_2 \cdot V \cdot (-\Delta H_{\lambda 2}). \tag{4.58}$$

The course of q versus time is just like the side profile of a two-level staircase (Fig. 4.12). Up to $t_{\mathrm{E}1}$ the constant rate of heat release comprises the thermal powers of the consumptions in A and C, i.e. $q = (q_1 + q_2)$; in the time after that up to the abrupt fall to zero at time $t_{\mathrm{E}2}$ q is given solely by the constant heat release of the continual conversion of the still existing amount of A or C, i.e. $q = q_{1 \text{ or } 2}$.

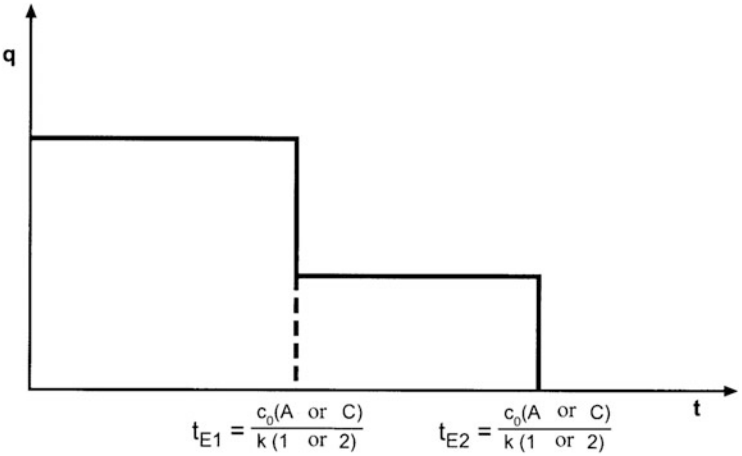

Fig. 4.12 Non-coupled parallel reactions $\begin{matrix} \mathrm{A} \xrightarrow{r_1,\, \Delta H_{\lambda 1}} \mathrm{B} \\ \mathrm{C} \xrightarrow{r_2,\, \Delta H_{\lambda 2}} \mathrm{D} \end{matrix}$. Rate-functions of order 0; isothermal, discontinuous, constant-volume reactions

$$q = q_1 + q_2 = k_1 \cdot V \cdot (-\Delta H_{\lambda 1}) + k_2 \cdot V \cdot (-\Delta H_{\lambda 2})$$

To determine the rate coefficients k_1 and k_2 as well as the heats of the reaction $(-\Delta H_{\lambda 1})$ and $(-\Delta H_{\lambda 2})$ a calorimetric investigation is performed first with equimolar use of A and C and, in addition, the times t_{E1} and t_{E2} of the step-like change in the constant heat release are recorded. The measurement is repeated using a surplus of one of the reactants. When t_{E1} remains unchanged and t_{E2} increases, the conversion of the used reactant is the slow reaction, $\{c_{\mathrm{slow},} k_{\mathrm{slow}}\}$.

When t_{E2} remains unchanged and t_{E1} increases, the conversion of this reactant is the quicker reaction, $\{c_{\mathrm{quick}}, k_{\mathrm{quick}}\}$.

k_{slow}, k_{quick} and $(\Delta H_\lambda)_{\mathrm{slow}}$, $(\Delta H_\lambda)_{\mathrm{quick}}$ yield, by means of (4.57, 4.58),

$$\begin{aligned}&k_{\mathrm{quick}} = c_{0\mathrm{quick}}/t_{\mathrm{E1}}\\ &(-\Delta H_\lambda)_{\mathrm{quick}} = [q(0 < t \le t_{\mathrm{E1}}) - q(t_{\mathrm{E1}} < t \le t_{\mathrm{E2}})]/k_{\mathrm{quick}}/V).\end{aligned}$$

$$\begin{aligned}&k_{\mathrm{slow}} = c_{0\mathrm{slow}}/t_{\mathrm{E2}}\\ &(-\Delta H_\lambda)_{\mathrm{slow}} = q(t_{\mathrm{E1}} < t \le t_{\mathrm{E2}})]/k_{\mathrm{slow}}/V.\end{aligned}$$

4.2.1.1.2.2.2 Rate Functions of Order 1

The non-coupled reaction consists of the following two conversions, which occur side by side without mutual influence:

$$\begin{aligned}&\mathrm{A} \xrightarrow{r_1,\, \Delta H_{\lambda 1}} \mathrm{B}\\ &\mathrm{C} \xrightarrow{r_2,\, \Delta H_{\lambda 2}} \mathrm{D}\end{aligned}$$

with

- The stoichiometric coefficients $v_{(\mathrm{j,i})\xi}$

$$v_{\mathrm{A1}} = -1, v_{\mathrm{A2}} = 0, v_{\mathrm{B1}} = 1, v_{\mathrm{B2}} = 0, v_{\mathrm{C1}} = 0, v_{\mathrm{C2}} = -1, v_{\mathrm{D1}} = 0, v_{\mathrm{D2}} = 1,$$

- The rate functions of order 1

$$r_1 = k_1 \cdot c_{\mathrm{A}} \text{ and } r_2 = k_2 \cdot c_{\mathrm{C}}.$$

According to (4.34), the rates of consumption in A and C are

$$\begin{aligned}\mathrm{d}c_{\mathrm{A}}/\mathrm{d}t &= \sum v_{\mathrm{A}\xi} \cdot r_\xi = v_{\mathrm{A1}} \cdot r_1 = -k_1 \cdot c_{\mathrm{A}},\\ \mathrm{d}c_{\mathrm{C}}/\mathrm{d}t &= \sum v_{\mathrm{C}\xi} \cdot r_\xi = v_{\mathrm{C2}} \cdot r_2 = -k_2 \cdot c_{\mathrm{C}}.\end{aligned}$$

The solution of the equations reads

$$\begin{aligned}c_{\mathrm{A}} &= c_{\mathrm{A0}} \cdot \mathrm{EXP}[-k_1 \cdot t],\\ c_{\mathrm{C}} &= c_{\mathrm{C0}} \cdot \mathrm{EXP}[-k_2 \cdot t].\end{aligned}$$

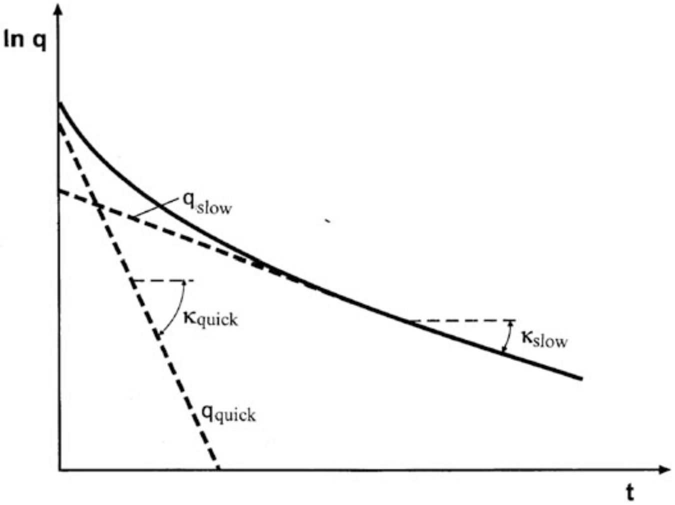

Fig. 4.13 Non-coupled parallel reactions $\begin{matrix} A \xrightarrow{r_1,\, \Delta H_{\lambda 1}} B \\ C \xrightarrow{r_2,\, \Delta H_{\lambda 2}} D \end{matrix}$. Rate functions of order 1, isothermal, discontinuous, constant-volume reactions

$$q = q_1 + q_2 = k_1 \cdot c_{A0} \cdot V \cdot (-\Delta H_{\lambda 1}) \cdot \mathrm{EXP}[-k_1 \cdot t] + k_2 \cdot c_{C0} \cdot V \cdot (-\Delta H_{\lambda 2}) \cdot \mathrm{EXP}[-k_2 \cdot t]$$

As temporal course of the thermal reaction power yields

$$\begin{aligned} q &= q_1 + q_2 \\ &= k_1 \cdot c_{A0} \cdot V \cdot (-\Delta H_{\lambda 1}) \cdot \mathrm{EXP}[-k_1 \cdot t] + k_2 \cdot c_{C0} \cdot V \cdot (-\Delta H_{\lambda 2}) \cdot \mathrm{EXP}[-k_2 \cdot t]. \end{aligned}$$

The plot of $\ln\{q\}$ versus time (Fig. 4.13) gives a curve which turns into a straight line for $t \gg 0$.[23] The slope of the straight line corresponds to the rate coefficient of the slow reaction, either k_1 or k_2.

From the point of intersection with the ordinate $\ln\{q_{1\mathrm{or}2}(t = 0)\}$ results the heat of the slow reaction

$$\left(-\Delta H_{\lambda(1\text{ or }2)}\right) = q_{(1\text{ or }2)}(t = 0) / \left(k_{(1\text{ or }2)} \cdot c_{(\mathrm{A\ or\ C})0} \cdot V\right).$$

The plot of $\ln\left\{q - q_{(1\text{ or }2)}\right\}$ versus time is a straight line whose slope corresponds to the rate coefficient of the quick reaction. From the point of intersection with the ordinate follows the heat of this reaction.

A second calorimetric measurement with changed initial concentration of one of the two reactants reveals the slow reaction: when the measured thermal reaction

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[23] In the case of negative q-values, $\ln\{|q(t)|\}$ must be plotted; the procedure of interpretation is analogous.

power is only increased in the initial part, the conversion of the used reactant is the quick reaction; when, in comparison with that, the whole course of the thermal reaction power is increased, the conversion of this reactant is the slow reaction.

With $k_1 = k_2 = k$ the expression of thermal reaction power changes into

$$q = k \cdot V \cdot [c_{A0} \cdot (-\Delta H_{\lambda 1}) + c_{C0} \cdot (-\Delta H_{\lambda 2})] \cdot \mathrm{EXP}[-k \cdot t].$$

In this case the plot $\ln\{q\}$[24] versus time is a straight line with slope k and point of intersection with the ordinate $\ln\{q(t = 0)\}$, in which

$$q(t = 0) = k \cdot V \cdot [c_{A0} \cdot (-\Delta H_{\lambda 1}) + c_{C0} \cdot (-\Delta H_{\lambda 2})].$$

From the integration of q over the total reaction time we obtain $\int_{t=0\to\infty} q \cdot \mathrm{d}t = Q_\infty = V \cdot [c_{A0} \cdot (-\Delta H_{\lambda 1}) + c_{C0} \cdot (-\Delta H_{\lambda 2})]$; this means that there is no additional, independent thermal correlation of $\Delta H_{\lambda 1}$ and $\Delta H_{\lambda 2}$. However, to quantify the thermal reaction power the heats of the single reaction must be known. These quantities can be determined by means of separately performed conversions. If it is not possible to obtain pure reactants A and C for this purpose, the conversion of the reaction mixture must be performed at a temperature in which k_1 and k_2 differ significantly due to the reaction's different dependency on temperature.

4.2.1.1.2.3 Consecutive Reaction, Two Stages

4.2.1.1.2.3.1 Rate Functions of Order 0

The simplest, consecutive reaction is the following formation of a product C, starting from reactant A, in two stages via an ascertainable intermediate product B:

$$\mathrm{A} \xrightarrow{r_1,\, \Delta H_{\lambda 1}} \mathrm{B} \xrightarrow{r_2,\, \Delta H_{\lambda 2}} \mathrm{C}$$

with

- The stoichiometric coefficients $\nu_{(j,i)\xi}$

$$\nu_{A1} = -1, \nu_{A2} = 0, \nu_{B1} = 1, \nu_{B2} = -1, \nu_{C1} = 0, \nu_{C2} = 1,$$

- The rate functions of order 0[25]

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[24] In the case of negative q-values, $\ln\{|q(t)|\}$ must be plotted; the procedure of interpretation is analogous.

[25] In view of an ascertainable consecutive reaction only $k_2 < k_1$ makes sense. For $k_2 \geq k_1$ C is immediately formed from A by a one-stage reaction.

$$r_1 = k_1 \text{ and } r_2 = k_2. \tag{4.59}$$

According to (4.34), the rates of consumption in A and change in B and formation in C are

$$\begin{aligned}
\mathrm{d}c_A/\mathrm{d}t &= \sum v_{A\xi} \cdot r_\xi = v_{A1} \cdot r_1 + v_{A2} \cdot r_2 = -k_1,\\
\mathrm{d}c_B/\mathrm{d}t &= \sum v_{B\xi} \cdot r_\xi = v_{B1} \cdot r_1 + v_{B2} \cdot r_2 = k_1 - k_2,\\
\mathrm{d}c_C/\mathrm{d}t &= \sum v_{C\xi} \cdot r_\xi = v_{C1} \cdot r_2 = k_2.
\end{aligned}$$

A is consumed after the time

$$t_{EA} = c_{A0}/k_1, \tag{4.60}$$

B is consumed after the time

$$t_{EB} = (c_{A0} + c_{B0})/k_2. \tag{4.61}$$

The temporal courses of the concentrations are described by

$$\begin{aligned}
c_A &= c_{A0} - k_1 \cdot t && \text{for } 0 \leq t \leq t_{EA},\\
c_B &= c_{B0} + (k_1 - k_2) \cdot t && \text{for } 0 \leq t \leq t_{EA},\\
c_B &= c_{B0(t=t_{EA})} - k_2 \cdot (t - t_{EA}) && \text{for } t_{EA} \leq t \leq t_{EB},\\
c_C &= c_{C0} + k_2 \cdot t && \text{for } 0 \leq t \leq t_{EB}.
\end{aligned}$$

The reactions $(-\Delta H_{\lambda1})$ and $(-\Delta H_{\lambda2})$ are the heats of formation in B respectively in C, it follows from (4.59), according to (4.7), that for the measurable thermal reaction power q

$$\begin{aligned}
q &= q_1 + q_2,\\
&= k_1 \cdot V \cdot (-\Delta H_{\lambda1}) + k_2 \cdot V \cdot (-\Delta H_{\lambda2}),
\end{aligned} \tag{4.62}$$

with

$$k_1 = 0 \text{ for } t > t_{EA}$$

and

$$k_1 = 0 \text{ and } k_2 = 0 \quad \text{for } t > t_{EB} > t_{EA}.$$

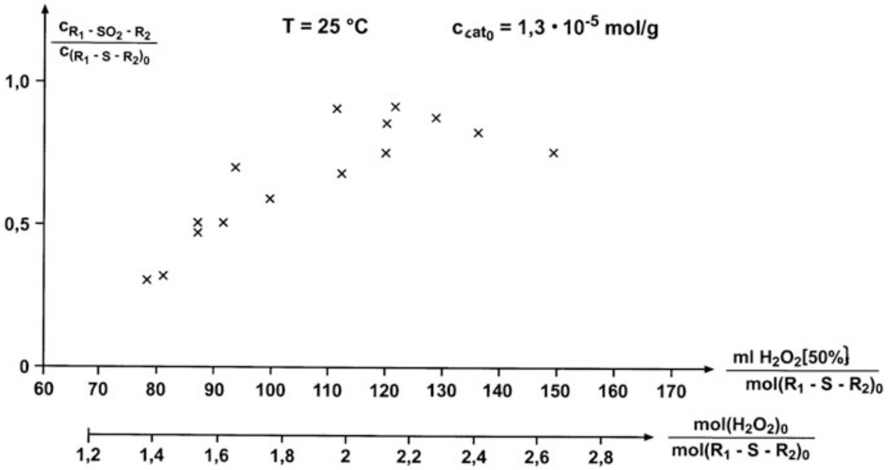

Fig. 4.14 Two-stage consecutive reaction $A \xrightarrow{r_1,\,\Delta H_{\lambda 1}} B \xrightarrow{r_2,\,\Delta H_{\lambda 2}} C$. Rate functions of order 0; isothermal, discontinuous, volume-constant reaction

$$q = q_1 + q_2 = k_1 \cdot V \cdot (-\Delta H_{\lambda 1}) + k_2 \cdot V \cdot (-\Delta H_{\lambda 2})$$

The measured thermal reaction power (Fig. 4.14) is constant up to an abruptly terraced change at time t_{EA}. In the time $t \le t_{EA}$ the thermal reaction power is composed of the rates of heat release due to the conversions of both A and B, $q = (q_1 + q_2)$; in the time $t_{EA} < t \le t_{EB}$, i.e. after the consumption in A up to the consumption in B, the measured thermal reaction power q corresponds only to the thermal reaction power due to the consumption in B, i.e. $q = q_2$.

From (4.61) we obtain k_2:

$$k_2 = (c_{A0} + c_{B0})/t_{EB}.$$

$(-\Delta H_{\lambda 2})$ follows according to

$$(-\Delta H_{\lambda 2}) = q(t_{EA} < t \le t_{EB})/(k_2 \cdot V).$$

Due to (4.60) the following relation is valid:

$$k_1 = c_{A0}/t_{EA}.$$

In accordance with (4.62), the following equation holds:

$$(-\Delta H_{\lambda 1}) = [q(0 < t \le t_{EA}) - q(t_{EA} < t \le t_{EB})]/(k_1 \cdot V).$$

4.2.1.1.2.3.2 Reaction Functions of Order 1

A consecutive reaction occurs by the formation of a product C from a reactant A in two stages via the ascertainable intermediate resultant B:

$$\mathrm{A} \xrightarrow{r_1,\, \Delta H_1} \mathrm{B} \xrightarrow{r_2,\, \Delta H_2} \mathrm{C}$$

with

- The stoichiometric coefficients $v_{(\mathrm{j,i})\xi}$

$$v_{\mathrm{A1}} = -1, v_{\mathrm{A2}} = 0, v_{\mathrm{B1}} = 1, v_{\mathrm{B2}} = -1, v_{\mathrm{C1}} = 0, v_{\mathrm{C2}} = 1;$$

- The rate functions of order 1

$$r_1 = k_1 \cdot c_{\mathrm{A}} \text{ and } r_2 = k_2 \cdot c_{\mathrm{B}}. \tag{4.63}$$

According to (4.34), the rates of change in A and B are

$$\begin{aligned} \mathrm{d}c_{\mathrm{A}}/\mathrm{d}t &= \sum v_{\mathrm{A}\xi} \cdot r_\xi = v_{\mathrm{A1}} \cdot r_1 = -k_1 \cdot c_{\mathrm{A}}, \\ \mathrm{d}c_{\mathrm{B}}/\mathrm{d}t &= \sum v_{\mathrm{B}\xi} \cdot r_\xi = v_{\mathrm{B1}} \cdot r_1 + v_{\mathrm{B2}} \cdot r_2 = k_1 \cdot c_{\mathrm{A}} - k_2 \cdot c_{\mathrm{B}}. \end{aligned}$$

With $c_{\mathrm{B0}} = 0$, the solution of the equation system is

$$\begin{aligned} c_{\mathrm{A}} &= c_{\mathrm{A0}} \cdot \mathrm{EXP}[-k_1 \cdot t], \\ c_{\mathrm{B}} &= k_1/(k_2 - k_1) \cdot c_{\mathrm{A0}} \cdot \{\mathrm{EXP}[-k_1 \cdot t] - \mathrm{EXP}[-k_2 \cdot t]\}. \end{aligned} \tag{4.64}$$

For the measurable thermal reaction power q it follows from (4.64) and (4.7) that

$$\begin{aligned} q &= q_1 + q_2 \\ &= k_1 \cdot (-\Delta H_{\lambda 1}) \cdot c_{\mathrm{A0}} \cdot V \cdot \mathrm{EXP}[-k_1 \cdot t] + k_1 \cdot k_2/(k_2 - k_1) \cdot c_{\mathrm{A0}} \cdot V \cdot (-\Delta H_{\lambda 2}) \cdot \\ &\quad (\mathrm{EXP}[-k_1 \cdot t] - \mathrm{EXP}[-k_2 \cdot t]) \\ &= \{k_1 \cdot (-\Delta H_{\lambda 1}) \cdot c_{\mathrm{A0}} \cdot V - k_1 \cdot k_2/(k_1 - k_2) \cdot c_{\mathrm{A0}} \cdot V \cdot (-\Delta H_{\lambda 2})\} \cdot \mathrm{EXP}[-k_1 \cdot t] + \\ &\quad \{k_1 \cdot k_2/(k_1 - k_2) \cdot c_{\mathrm{A0}} \cdot V \cdot (-\Delta H_{\lambda 2})\} \cdot \mathrm{EXP}[-k_2 \cdot t] \\ &= \alpha \cdot \mathrm{EXP}[-k_1 \cdot t] + \beta \cdot \mathrm{EXP}[-k_2 \cdot t]. \end{aligned} \tag{4.65}$$

Plotting $\ln\{q\}$ versus time[26] (Fig. 4.15) an initially curved line results which turns into a straight line $\ln\{q_{\mathrm{Slow}}\}$ whose slope indicates the rate coefficient of the

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[26] In the case of negative q-values, $\ln\{|q(t)|\}$ must be plotted; the procedure of interpretation is analogous.

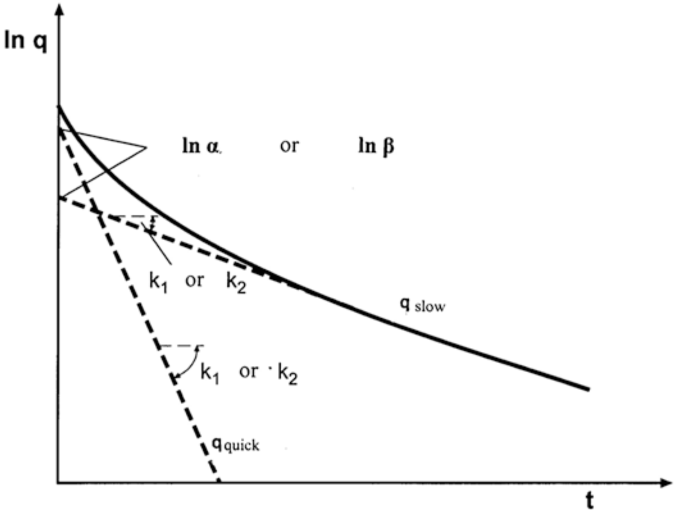

Fig. 4.15 Two-stage, consecutive reaction $A \xrightarrow{r_1, \Delta H_{\lambda 1}} B \xrightarrow{r_2, \Delta H_{\lambda 2}} C$. Rate functions of order 1; isothermal, discontinuous, constant-volume reaction $q = q_1 + q_2 = \alpha \cdot \mathrm{EXP}(-k_1 \cdot t) + \beta \cdot \mathrm{EXP}(-k_2 \cdot t)$

relatively slow reaction, i.e. either k_1 or k_2. The point of intersection with the ordinate $\ln\{q_{0\mathrm{Slow}}\}$ is either

$$\begin{gathered} \ln\{\alpha\} = \ln\{k_1 \cdot (-\Delta H_{\lambda 1}) \cdot c_{A0} V - k_1 \cdot k_2/(k_1 - k_2) \cdot c_{A0} \cdot (-\Delta H_{\lambda 2})\} \\ \text{or} \\ \ln\{\beta\} = \ln\{k_1 \cdot k_2/(k_1 - k_2) \cdot c_{A0} \cdot (-\Delta H_{\lambda 2})\}, \end{gathered} \tag{4.66}$$

depending on whether the first stage (formation of B, k_1) or the second stage (formation of C, k_2) is the relatively slow reaction. The plot of $\ln\{q - q_{\mathrm{Slow}}\}$ versus time gives a straight line $\ln\{q_{\mathrm{Quick}}\}$ with the point of intersection with the ordinate $\ln\{q_{0\mathrm{Quick}}\}$. The slope of the straight line corresponds to the rate coefficient of the relatively quick reaction.

Which of the reactions (4.1, 4.2) is relatively slow cannot be determined directly, only indirectly by thermodynamic assistance. To this end one of the two heats of reaction $(-\Delta H_{\lambda 1})$ or $(-\Delta H_{\lambda 2})$ is estimated based on the heats of formation,[27] calculated from the incremental method in tabular form. Then, by means of the two possibilities of (4.66), a test is conducted to determine which of the assumptions ($k_1 < k_2$ or $k_1 > k_2$) gives the smallest deviation between the calculated values (α respectively β) and the measured intersection values ($q_{0\mathrm{Slow}}$ respectivily $q_{0\mathrm{Quick}}$). Now, with the coordinated $\ln\{\alpha\}$, $\ln\{\beta\}$, $\ln\{q_{0\mathrm{Slow}}\}$ and $\ln\{q_{0\mathrm{Quick}}\}$ the precise

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[27] The second heat of reaction is determined on the basis of $\{(-\Delta H_{\lambda 1}) \cdot c_{A0} \cdot V + (-\Delta H_{\lambda 2}) \cdot c_{A0} \cdot V\} = \int_{t=0 \to \infty} q \cdot \mathrm{d}t$.

heats of reaction $(-\Delta H_{\lambda 1})$ respectively $(-\Delta H_{\lambda 2})$ can be calculated on the basis of (4.66).[28]

If $k_1 = k_2 = k$, then the following equation results from (4.65), using the rule of de l'Hospital:

$$\begin{aligned} q &= k \cdot (-\Delta H_{\lambda 1}) \cdot c_{A0} \cdot V \cdot \mathrm{EXP}[-k \cdot t] + k^2 \cdot (-\Delta H_{\lambda 2}) \cdot c_{A0} \cdot V \cdot t \cdot \mathrm{EXP}[-k \cdot t] \\ &= k \cdot \{(-\Delta H_{\lambda 1}) \cdot c_{A0} \cdot V + (-\Delta H_{\lambda 2}) \cdot c_{A0} \cdot V \cdot k \cdot t\} \cdot \mathrm{EXP}[-k \cdot t] \\ &= k \cdot \{\Phi_1 + \Phi_2 \cdot k \cdot t\} \cdot \mathrm{EXP}[-k \cdot t], \end{aligned}$$

with

$$(-\Delta H_{\lambda 1}) \cdot c_{A0} \cdot V = \Phi_1 \ \text{ and } \ (-\Delta H_{\lambda 2}) \cdot c_{A0} \cdot V = \Phi_2. \tag{4.67}$$

k, $(-\Delta H_{\lambda 1})$ and $(-\Delta H_{\lambda 1})$ are worked out as follows:

For the rate of the thermal reaction power q (Fig. 4.16) at $t = 0$ the following equation is valid:

$$q(0) = k \cdot \Phi_1. \tag{4.68}$$

The derivation of q with respect to time gives

$$\mathrm{d}q/\mathrm{d}t = \left(-k^2 \cdot \Phi_1 + k^2 \cdot \Phi_2 - k^3 \cdot \Phi_2 \cdot t\right) \cdot \mathrm{EXP}[-k \cdot t].$$

Setting this equal to zero yields the point in time t_{Extreme}, at which q passes the peak value

$$t_{\mathrm{Extreme}} = (\Phi_2 - \Phi_1)/\Phi_2/k. \tag{4.69}$$

In addition to that, the following equation is valid:

$$\Phi_1 + \Phi_2 = \int_{t=0\rightarrow\infty} q \cdot \mathrm{d}t. \tag{4.70}$$

From (4.68), (4.69) and (4.70) results a quadratic determining equation for Φ_1:

$$2 \cdot \Phi_1{}^2 + \left\{-q(0) \cdot t_{\mathrm{Extreme}} - \int_{t=0->\infty} q \cdot \mathrm{d}t\right\} \cdot \Phi_1 + q(0) \cdot t_{\mathrm{Extreme}} \cdot \int_{t=0\rightarrow\infty} q \cdot \mathrm{d}t = 0$$

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[28] For instance,

$$\ln\{q_{0\mathrm{Slow}}\} = \ln\{\alpha\} = \ln\{k_1 \cdot (-\Delta H_{\lambda 1}) \cdot c_{A0} \cdot V - k_1 \cdot k_2/(k_1 - k_2) \cdot c_{A0} \cdot (-\Delta H_{\lambda 2})\} \text{ when } k_1 < k_2$$

or

$$\ln\{q_{0\mathrm{Slow}}\} = \ln\{\beta\} = \ln\{k_1 \cdot k_2/(k_1 - k_2) \cdot c_{A0} \cdot (-\Delta H_{\lambda 2})\} \quad \text{when } k_2 < k_1.$$

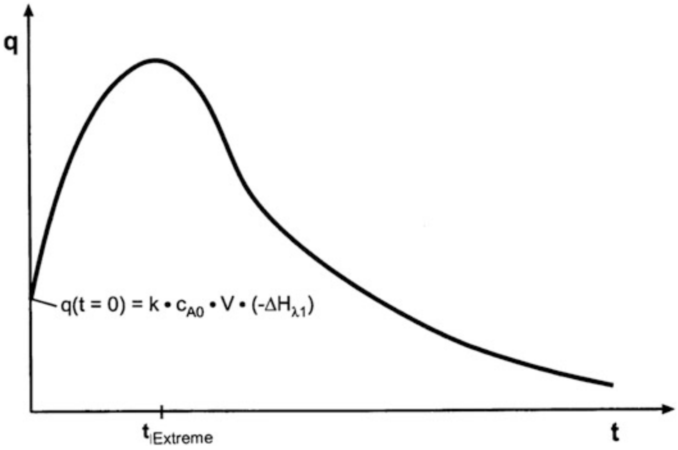

Fig. 4.16 Consecutive, two-stage reaction. Rate functions of order 1, isothermal, discontinuous, constant-volume reactions

$$q = k \cdot \{(-\Delta H_{\lambda 1}) \cdot c_{\mathrm{A0}} \cdot V + (-\Delta H_{\lambda 2}) \cdot c_{\mathrm{A0}} \cdot V \cdot k \cdot t\} \cdot \mathrm{EXP}[-k \cdot t]$$

with the solution

$$\Phi_1 = \left\{q(0) \cdot t_{\mathrm{Extreme}} + \int_{t=\rightarrow\infty} q \cdot \mathrm{d}t\right\}/4$$
$$+\sqrt{\left[\left\{q(0) \cdot t_{\mathrm{Extreme}} + \int_{t=0->\infty} q \cdot \mathrm{d}t\right\}^2/16 - \left\{q(0) \cdot t_{\mathrm{Extreme}} + \int_{t=0\rightarrow\infty} q \cdot \mathrm{d}t\right\}/2\right]}.$$

The values

$q(0)$	initial thermal reaction power
t_{Extreme}	time at which q passes the peak value
$\int_{t=0\rightarrow\infty} q \cdot \mathrm{d}t$	total amount of released heat

can be taken from the q-curve.

k is determined by (4.68), Φ_2 by (4.70) and $\Delta H_{\lambda 1}$ and $\Delta H_{\lambda 2}$ by (4.67).

$$k = q(0)/\Phi_1,$$
$$\Phi_2 = \int_{t=0\rightarrow\infty} q \cdot \mathrm{d}t - \Phi_1,$$
$$(-\Delta H_{\lambda 1}) = \Phi_1/(c_{\mathrm{A0}} \cdot V),$$
$$(-\Delta H_{\lambda 2}) = \Phi_2/(c_{\mathrm{A0}} \cdot V).$$

4.2.1.1.2.3.3 First Stage Irreversible: Rate Function of Order 1 Second Stage Reversible[29]: Rate Functions of Forward and Backward Reaction of Order 1

The two-stage, consecutive reaction consists of the irreversible formation of an ascertainable intermediate product B from a reactant A as well as the following reversible formation of the final product C:

$$\mathrm{A} \xrightarrow{r_1,\,\Delta H_{\lambda 1}} \mathrm{B} \underset{r_3,\,\Delta H_{\lambda 3}=-\Delta H_{\lambda 2}}{\overset{r_2,\,\Delta H_{\lambda 2}}{\rightleftarrows}} \mathrm{C}$$

with

- The stoichiometric coefficients $v_{(\mathrm{j,i})\xi}$

$$v_{\mathrm{A1}} = -1, v_{\mathrm{A2}} = 0, v_{\mathrm{A3}} = 0, v_{\mathrm{B1}} = 1, v_{\mathrm{B2}} = -1, v_{\mathrm{B3}} = 1, v_{\mathrm{C1}} = 0, v_{\mathrm{C2}} = 1, v_{\mathrm{C3}} = -1,$$

- The rate functions of order 1

$$r_1 = k_1 \cdot c_{\mathrm{A}},\ r_2 = k_2 \cdot c_{\mathrm{B}} \text{ and } r_3 = k_3 \cdot c_{\mathrm{C}}. \tag{4.71}$$

According to (4.34) the rates of change in A, B and C are

$$\begin{aligned}
\mathrm{d}c_{\mathrm{A}}/\mathrm{d}t &= \sum v_{\mathrm{A}\xi} \cdot r_\xi = v_{\mathrm{A1}} \cdot r_1 + v_{\mathrm{A2}} \cdot r_2 + v_{\mathrm{A3}} \cdot r_3 = -k_1 \cdot c_{\mathrm{A}},\\
\mathrm{d}c_{\mathrm{B}}/\mathrm{d}t &= \sum v_{\mathrm{B}\xi} \cdot r_\xi = v_{\mathrm{B1}} \cdot r_1 + v_{\mathrm{B2}} \cdot r_2 + v_{\mathrm{B3}} \cdot r_3 = k_1 \cdot c_{\mathrm{A}} - k_2 \cdot c_{\mathrm{B}} + k_3 \cdot c_{\mathrm{C}},\\
\mathrm{d}c_{\mathrm{C}}/\mathrm{d}t &= \sum v_{\mathrm{C}\xi} \cdot r_\xi = v_{\mathrm{C1}} \cdot r_1 + v_{\mathrm{C2}} \cdot r_2 + v_{\mathrm{C3}} \cdot r_3 = k_2 \cdot c_{\mathrm{B}} - k_3 \cdot c_{\mathrm{C}}.
\end{aligned}$$

The solution of the equation system for $c_{\mathrm{B0}} = 0$ and $c_{\mathrm{C0}} = 0$ reads

$$\begin{aligned}
c_{\mathrm{A}} &= c_{\mathrm{A0}} \cdot \mathrm{EXP}[-k_1 \cdot t],\\
c_{\mathrm{B}} &= c_{\mathrm{A0}} \cdot (1 - \mathrm{EXP}[-k_1 \cdot t]) - k_2 \cdot c_{\mathrm{A0}} \cdot \{1/(k_2 + k_3) - \mathrm{EXP}[-k_1 \cdot t]/(k_2 + k_3 - k_1)\\
&\quad + \mathrm{EXP}[-(k_2 + k_3) \cdot t] \cdot k_1/(k_2 + k_3 - k_1)/(k_2 + k_3)\},
\end{aligned} \tag{4.72}$$

$$\begin{aligned}
c_{\mathrm{C}} &= k_2 \cdot c_{\mathrm{A0}} \cdot \{1/(k_2 + k_3) - \mathrm{EXP}[-k_1 \cdot t]/(k_2 + k_3 - k_1)\\
&\quad + \mathrm{EXP}[-(k_2 + k_3) \cdot t] \cdot k_1/(k_2 + k_3 - k_1)/(k_2 + k_3)\}.
\end{aligned}$$

From that follow

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[29] See Sect. 4.2.1.1.2.7.

$$\begin{aligned} c_{\mathrm{B}\infty} &= c_{\mathrm{A}0} \cdot (1 - k_2/(k_2 + k_3)), \\ c_{\mathrm{C}\infty} &= k_2 \cdot c_{\mathrm{A}0} \cdot (k_2 + k_3), \\ c_{\mathrm{C}\infty}/c_{\mathrm{B}\propto} &= k_2/k_3. \end{aligned} \tag{4.73}$$

Due to (4.7), (4.71) and (4.72), the thermal reaction power is expressed by

$$\begin{aligned} q = \sum \left[r_\xi \cdot \left(-\Delta H_{\lambda\xi}\right)\right] \cdot V &= [r_1 \cdot (-\Delta H_{\lambda 1}) + r_2 \cdot (-\Delta H_{\lambda 2}) + r_3 \cdot (-\Delta H_{\lambda 3})] \cdot V \\ &\qquad \text{because of} (-\Delta H_{\lambda 3}) = -(-\Delta H_{\lambda 2}) \\ &= [r_1 \cdot (-\Delta H_{\lambda 1}) + r_2 \cdot (-\Delta H_{\lambda 2}) - r_3 \cdot (-\Delta H_{\lambda 2})] \cdot V \\ &= \big(\{c_{\mathrm{A}0} \cdot (-\Delta H_{\lambda 1}) \cdot k_1 - c_{\mathrm{A}0} \cdot (-\Delta H_{\lambda 2}) \cdot k_1 \cdot k_2/(k_1 - k_2 - k_3)\} \cdot \mathrm{EXP}[-k_1 t] \\ &\quad + c_{\mathrm{A}0} \cdot (-\Delta H_{\lambda 2}) \cdot \{(k_1 \cdot k_2)/(k_1 - k_2 - k_3)\} \cdot \mathrm{EXP}[-(k_2 + k_3)t]\big) \cdot V \\ &= q_1(t = 0) \cdot \mathrm{EXP}[-k_1 t] + q_2(t = 0) \cdot \mathrm{EXP}[-(k_2 + k_3)t]. \end{aligned} \tag{4.74}$$

The correlation (4.74) corresponds formally to the previously discussed two-stage, consecutive, irreversible reaction (4.65) and $k_3 = 0$ (4.74) changes to (4.65). Hence, the kinetic analysis takes place in a similar way. When $\ln\{q\}$ is plotted against time[30] (Fig. 4.17) yields a curved line turning into a straight line with the slope κ_2. In contrary to the totally irreversible two-stage, consecutive reaction (4.65) it can be assumed a priori that the following expression holds: $k_1 > (k_2 + k_3)$.[31] This means that the slope of the ending straight line κ_2 is the sum of the rate coefficients k_2 and k_3.

The plot of $\ln\{q(t) - q_2(t)\} = \ln\{q_1(t)\}$ against time gives a straight line which corresponds to the rate coefficient k_1.

From (4.73) and (4.74) we obtain

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[30] In the case of negative q-values, $\ln\{|q(t)|\}$ must be plotted; the procedure of interpretation runs analogously.

[31] When the equilibrium achieved between B and C is quicker than the consumption rate of A, the temporal course of the formation in B and C corresponds more or less to the course of a coupled parallel reaction, the plot of $\ln\{q\}$ over time yields in the case $(k_2 + k_3) \gg k_1$ over the total reaction time approximately a straight line with slope $\kappa = k_1$: in that case, (4.72) changes to

$$\begin{aligned} c_\mathrm{A} &= c_{\mathrm{A}0} \cdot \mathrm{EXP}[-k_1 \cdot t], \\ c_\mathrm{B} &\cong c_{\mathrm{A}0} \cdot \{1 - k_2/(k_2 + k_3)\} \cdot \{1 - \mathrm{EXP}[-k_1 \cdot t]\} = c_{\mathrm{A}0} \cdot k_3/(k_2 + k_3) \cdot \{1 - \mathrm{EXP}[-k_1 \cdot t]\}, \\ c_\mathrm{C} &\cong c_{\mathrm{A}0} \cdot k_2/(k_2 + k_3) \cdot \{1 - \mathrm{EXP}[-\, k_1 \cdot t]\}. \end{aligned} \tag{a}$$

This results in

$$c_\mathrm{B}/c_\mathrm{C} = c_{\mathrm{B}\propto}/c_{\mathrm{C}\propto} \cong k_3/k_2 \tag{b}$$

and

$$c_{\mathrm{B}\propto}/c_{\mathrm{A}0} \cong k_3/(k_2 + k_3), c_{\mathrm{C}\propto}/c_{\mathrm{A}0} \cong k_2/(k_2 + k_3). \tag{c}$$

Relations (a), (b) and (c) are in accordance with (4.41), (4.42) and (4.43).

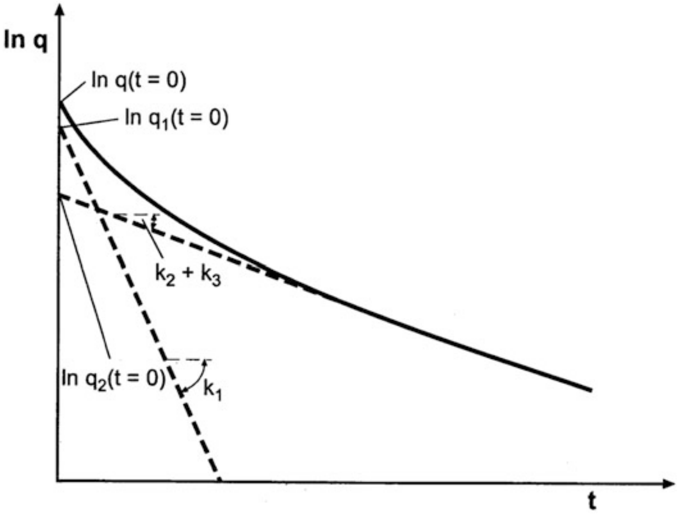

Fig. 4.17 $k_1 \neq k_2 + k_3$ Consecutive reaction consisting of an irreversible starting stage and a reversible, subsequent stage $\mathrm{A} \xrightarrow{r_1,\,\Delta H_{\lambda 1}} \mathrm{B} \underset{r_3,\,\Delta H_{\lambda 3}=-\Delta H_{\lambda 2}}{\overset{r_2,\,\Delta H_{\lambda 2}}{\rightleftarrows}} \mathrm{C}$. Rate-functions of order 1, $r_1 = k_1 \cdot c_\mathrm{A}$; $r_2 = k_2 \cdot c_\mathrm{B}$; $r_3 = k_3 \cdot c_\mathrm{C}$; isothermal, discontinuous, constant-volume reactions

$$q = q_1(t=0) \cdot \mathrm{EXP}[-k_1 \cdot t] + q_2(t=0) \cdot \mathrm{EXP}[-(k_2 + k_3) \cdot t]$$

$$\begin{aligned}
k_1 &= \kappa_1, \\
k_2 &= \kappa_2/(1 + c_{\mathrm{B}\infty}/c_{\mathrm{C}\infty}), \\
k_3 &= \kappa_2 - k_2, \\
(-\Delta H_{\lambda 2}) &= q_2(t=0)/c_{\mathrm{A}0}/V/\{k_1 \cdot k_2)/(k_1 - k_2 - k_3)\}, \\
(-\Delta H_{\lambda 1}) &= [q_1(t=0) + c_{\mathrm{A}0} \cdot V \cdot (-\Delta H_{\lambda 2}) \cdot k_1 \cdot k_2/(k_1 - k_2 - k_3)]/k_1/c_{\mathrm{A}0}/V \\
&= q(t=0)/k_1/c_{\mathrm{A}0}/V.
\end{aligned}$$

If $k_1 = (k_2 + k_3) = k$ it follows from (4.74) using the rule of de l'Hospital that

$$\begin{aligned}
q &= k \cdot (-\Delta H_{\lambda 1}) \cdot c_{\mathrm{A}0} \cdot V \cdot \mathrm{EXP}[-k \cdot t] + k \cdot k_2 \cdot (-\Delta H_{\lambda 2}) \cdot c_{\mathrm{A}0} \cdot V \cdot t \cdot \mathrm{EXP}[-k \cdot t] \\
&= k \cdot \{(-\Delta H_{\lambda 1}) \cdot c_{\mathrm{A}0} V + (-\Delta H_{\lambda 2}) \cdot c_{\mathrm{A}0} \cdot V \cdot k_2 \cdot t\} \cdot \mathrm{EXP}[-k \cdot t] \\
&= k \cdot \{\Phi_1 + \Phi_2 \cdot k_2 \cdot t\} \cdot \mathrm{EXP}[-k \cdot t],
\end{aligned}$$

in which

$$\Phi_1 = (-\Delta H_{\lambda 1}) \cdot c_{\mathrm{A}0} \cdot V \quad \text{and} \quad \Phi_2 = (-\Delta H_{\lambda 2}) \cdot c_{\mathrm{A}0} \cdot V. \qquad (4.75)$$

The course of the thermal reaction power against time (Fig. 4.18) is similar to the course of a two-stage, irreversible, consecutive reaction (Fig. 4.16) with rates of order 1 as well as equal rate coefficients, $k_1 = k_2$.

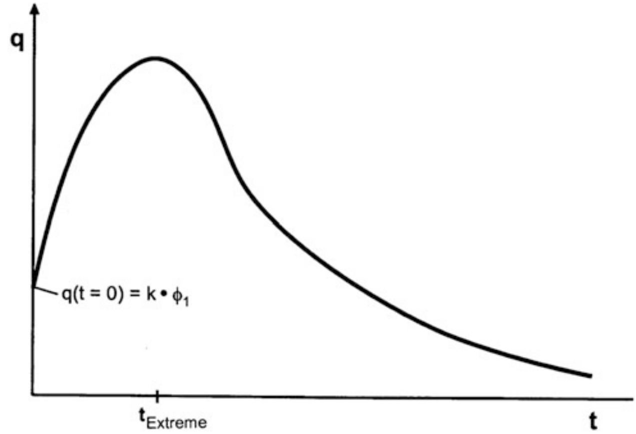

Fig. 4.18 Consecutive reaction consisting of a starting irreversible step and a reversible, subsequent step $A \xrightarrow{r_1,\, \Delta H_{\lambda 1}} B \underset{r_3,\, \Delta H_{\lambda 3} = -\Delta H_{\lambda 2}}{\overset{r_2,\, \Delta H_{\lambda 2}}{\rightleftarrows}} C$. Isothermal, discontinuous, constant-volume reactions

$$k_1 = k_2 + k_3 = k$$

$$q = k \cdot \{\Phi_1 + \Phi_2 \cdot k_2 \cdot t\} \cdot \mathrm{EXP}[-k \cdot t]$$

For the initial thermal reaction power at time $t = 0$ the following equation is valid:

$$q(0) = k \cdot \Phi_1. \tag{4.76}$$

The differentiation of q with respect to time yields

$$\mathrm{d}q/\mathrm{d}t = \left(-k^2 \cdot \Phi_1 + k \cdot k_2 \cdot \Phi_2 - k^2 \cdot k_2 \cdot \Phi_2 \cdot t\right) \cdot \mathrm{EXP}[-k_1 \cdot t].$$

Setting this equal to zero we obtain the time at which q passes the peak value:

$$t_{\mathrm{Extreme}} = 1/k - \Phi_1/\Phi_2/k_2. \tag{4.77}$$

Furthermore, we get

$$\Phi_1 + \Phi_{2-\mathrm{Equilibrium}} = \int_{t=0 \to \infty} q \cdot \mathrm{d}t, \tag{4.78}$$

with

$$\begin{aligned} \Phi_{2-\mathrm{Equilibrium}} &= V \cdot c_{\mathrm{B}\infty} \cdot (-\Delta H_{\lambda 2}), \\ &\quad \text{with regard to (4.73)} \\ &= V \cdot c_{\mathrm{A0}} \cdot (-\Delta H_{\lambda 2}) \cdot k_2/k. \end{aligned} \tag{4.79}$$

The combination of (4.76), (4.79) and (4.78), as well as rearrangement, gives

$$\begin{aligned}\Phi_1 = {} & \left\{ q(0)\cdot t_{\text{Extreme}} + \int_{t=0\to\infty} q\cdot \mathrm{d}t \right\}/4 \\ & + \sqrt{\left[\left\{ q(0)\cdot t_{\text{Extreme}} + \int_{t=0\to\infty} q\cdot \mathrm{d}t \right\}^2/16 - \left\{ q(0)\cdot t_{\text{Extreme}} + \int_{t=0\to\infty} q\cdot \mathrm{d}t \right\}/2 \right]}.\end{aligned}$$

The values

$q(0)$	initial thermal reaction power
t_{Extreme}	time at which q passes the peak value
$\int_{t=0\to\infty} q\cdot \mathrm{d}t$	total amount of released heat

can be found from the q-curve.

k is determined by (4.76), k_2 by (4.73), Φ_2 by (4.77), and $\Delta H_{\lambda 1}$ and $\Delta H_{\lambda 2}$ according to (4.75). This results in the following equations:

$$\begin{gathered} k = q(0)/\Phi_1, \\ k_2 = c_{\text{C}\infty}/c_{\text{A0}}\cdot k, \\ \Phi_2 = \Phi_1/k_2/(1/k - t_{\text{Extreme}}), \\ (-\Delta H_{\lambda 1}) = \Phi_1/(c_{\text{A0}}\cdot V), \\ (-\Delta H_{\lambda 2}) = \Phi_2/(c_{\text{A0}}\cdot V). \end{gathered}$$

4.2.1.1.2.4 Autocatalytic Reaction

4.2.1.1.2.4.1 Rate Function of Intrinsic Reaction of Order 0; Rate Function of Catalysed, Parallel Reaction of Order 0, Its Rate Coefficient Directly Proportional to Concentration of Product

The simplest, autocatalytic reaction follows a coupled conversion:

$$\begin{aligned} &\mathrm{A} \xrightarrow{r_1,\,\Delta H_{\lambda 1}} \mathrm{B} \quad \text{intrinsic} \\ &\mathrm{A} \xrightarrow{r_2,\,\Delta H_{\lambda 2}} \mathrm{B} \quad \text{catalytic} \end{aligned}$$

with

- The stoichiometric coefficients $v_{(\mathrm{j,i})\xi}$

$$v_{\text{A1}} = -1, v_{\text{A2}} = -1, v_{\text{B1}} = 1, v_{\text{B2}} = 1,$$

- The rate functions[32]

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[32] Or 1 and 2 conversely.

$$r_1 = k_1 \ \text{and} \ r_2 = F\{c_\text{B}\} = k_2 \cdot c_\text{B}.$$

The rate function of the first reaction, the intrinsic reaction, is of order 0. The rate of the second catalysed, parallel reaction is a function F of the concentration of the product B respectively of a by-product, formed in tiny amounts, which is directly proportional to B. Hence, the second reaction starts only in the presence or with the appearance of B or its by-product.

In the assumed case, $F = k_2 \cdot c_\text{B}$.

According to (4.34), we have

- The rate of consumption in A

$$\begin{aligned} \mathrm{d}c_\text{A}/\mathrm{d}t &= \sum v_{\text{A}\xi} \cdot r_\xi = v_{\text{A}1} \cdot r_1 + v_{\text{A}2} \cdot r_2 = -k_1 - k_2 \cdot c_\text{B} \\ &\qquad \text{due to the balance } c_\text{B} - c_\text{B0} = c_\text{A0} - c_\text{A} \\ &= -k_1 - k_2 \cdot (c_\text{A0} - c_\text{A} + c_\text{B0}) \\ &= -[k_1 + k_2 \cdot (c_\text{A0} + c_\text{B0})] + k_2 \cdot c_A. \end{aligned}$$

- The rate of formation in B is

$$\mathrm{d}c_\text{B}/\mathrm{d}t = \sum v_{\text{B}\xi} \cdot r_\xi = v_{\text{B}1} \cdot r_1 + v_{\text{B}2} \cdot r_2 = k_1 + k_2 \cdot c_\text{B}.$$

The solutions of the equations are

$$\begin{aligned} c_\text{A} &= [k_1 + k_2 \cdot (c_\text{A0} + c_\text{B0})]/k_2 - [k_1/k_2 + c_\text{B0}] \cdot \text{EXP}(k_2 \cdot t), \\ c_\text{B} &= -k_1/k_2 + [k_1/k_2 + c_\text{B0}] \cdot \text{EXP}(k_2 \cdot t). \end{aligned} \tag{4.80}$$

Equation (4.7) yields the following temporal course of the thermal reaction power:

$$\begin{aligned} q &= \sum q_\xi = q_1 + q_2 = r_1 \cdot V \cdot (-\Delta H_{\lambda 1}) + r_2 \cdot V \cdot (-\Delta H_{\lambda 2}) \\ &\qquad \text{because of } \Delta H_{\lambda 1} = \Delta H_{\lambda 2} = \Delta H_\lambda \\ &= (r_1 + r_2) \cdot V \cdot (-\Delta H_\lambda) = (k_1 + k_2 \cdot c_\text{B0}) \cdot V \cdot (-\Delta H_\lambda) \\ &= V \cdot (-\Delta H_\lambda) \cdot [k_1 + k_2 \cdot c_\text{B0}] \cdot \text{EXP}(k_2 \cdot t). \end{aligned}$$

Plotting $\ln\{q\}$[33] versus time (Fig. 4.19) gives a straight line with slope κ and the point of intersection with the ordinate $\ln\{\phi\}$, with $\phi = V \cdot (-\Delta H_\lambda) \cdot [k_1 + k_2 \cdot c_\text{B0}]$. The straight line ends abruptly at the time t_E, at which A is consumed. From (4.80) we obtain

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[33] In the case of negative q-values, $\ln\{|q(t)|\}$ must be plotted; the procedure of interpretation is analogous.

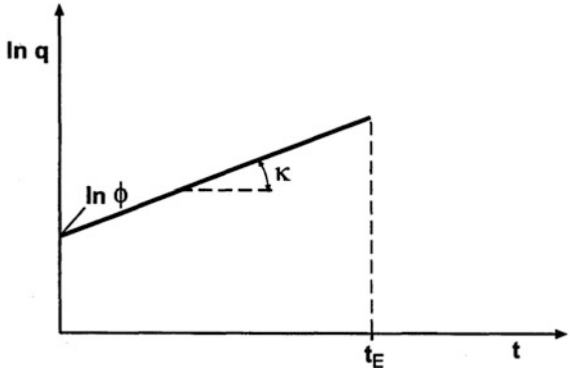

Fig. 4.19 Autocatalytic reaction $\begin{matrix} A \xrightarrow{r_1,\,\Delta H_{\lambda 1}} B \\ A \xrightarrow{r_1,\,\Delta H_{\lambda 2}} B \end{matrix}$

$r_1 = k_1; r_2 = f\{c_B\} = k_2 \cdot c_B$

isothermal, discontinuous, constant-volume reactions

$$q = V \cdot (-\Delta H_\lambda) \cdot [k_1 + k_2 \cdot c_{B0}] \cdot \mathrm{EXP}(k_2 \cdot t)$$

$$t_E = \ln\{[k_1 + k_2 \cdot (c_{A0} + c_{B0})]/[k_1 + k_2 \cdot c_{B0}]\}/k_2.$$

The heat of reaction is given by the amount of total heat $\int_{t=0 \to tE} q \cdot \mathrm{d}t$ released up to the time t_E:

$$(-\Delta H_\lambda) = \int_{t=0 \to tE} q \cdot \mathrm{d}t / c_{A0} / V.$$

The slope κ corresponds to the rate constant k_2:

$$k_2 = \kappa.$$

The rate constant k_1 is given by k_2, $(-\Delta H_\lambda)$ and $\{\phi\}$ according to

$$k_1 = \phi / V / (-\Delta H_\lambda) - k_2 \cdot (c_{A0} + c_{B0}).$$

4.2.1.1.2.4.2 Rate Function of Intrinsic Reaction of Order 1; Rate Function of Catalysed Parallel Reaction of Order 1, Its Rate Coefficient Directly Proportional to Concentration of Product

The scheme of the reaction is

$$\begin{matrix} A \xrightarrow{r_1,\,\Delta H_{\lambda 1}} B & \text{intrinsic} \\ A \xrightarrow{r_2,\,\Delta H_{\lambda 2}} B & \text{catalytic} \end{matrix}$$

with

- The stoichiometric coefficients $\nu_{(\mathrm{j,i})\xi}$

$$\nu_{\mathrm{A1}} = -1, \nu_{\mathrm{A2}} = -1, \nu_{\mathrm{B1}} = 1, \nu_{\mathrm{B2}} = 1,$$

- The rate functions

$$r_1 = k_1 \cdot c_{\mathrm{A}}, \quad r_2 = F\{c_{\mathrm{B}}\} \cdot c_{\mathrm{A}} = k_2 \cdot c_{\mathrm{B}} \cdot c_{\mathrm{A}}.$$

The rate function of the first, intrinsic reaction is of order 1, which also holds for the parallel reaction. However, its rate coefficient is a function F of the concentration of product B or of a negligibly tiny amount of a by-product which is formed by a parallel reaction directly proportional to B. Hence, the second reaction starts only in the presence or due to the appearance of B or of a by-product. We obtain $F = k_2 \cdot c_{\mathrm{B}}$.

According to (4.34), the rate of change in A reads

$$\begin{aligned} \mathrm{d}c_{\mathrm{A}}/\mathrm{d}t &= \sum \nu_{\mathrm{A}\xi} \cdot r_\xi = \nu_{\mathrm{A1}} \cdot r_1 + \nu_{\mathrm{A2}} \cdot r_2 = -k_1 \cdot c_{\mathrm{A}} - k_2 \cdot c_{\mathrm{B}} \cdot c_{\mathrm{A}} \\ &= -(k_1 + k_2 \cdot c_{\mathrm{B}}) \cdot c_{\mathrm{A}} \\ &= -[k_1 + k_2 \cdot (c_{\mathrm{A0}} - c_{\mathrm{A}} + c_{\mathrm{B0}})] \cdot c_{\mathrm{A}} \\ &= -[k_1 + k_2 \cdot (c_{\mathrm{A0}} + c_{\mathrm{B0}})] \cdot c_{\mathrm{A}} + k_2 \cdot {c_{\mathrm{A}}}^2. \end{aligned} \tag{4.81}$$

The solution of the equation is

$$c_{\mathrm{A}} = \{k_2/(k_1 + k_2(c_{\mathrm{A0}} + c_{\mathrm{B0}})) + [1/c_{\mathrm{A0}} - k_2/(k_1 + k_2(c_{\mathrm{A0}} + c_{\mathrm{B0}}))] \cdot \mathrm{EXP}[k_1 + k_2 \cdot (c_{\mathrm{A0}} + c_{\mathrm{B0}}) \cdot t]\}^{-1}. \tag{4.82}$$

With $k_1 + k_2 \cdot (c_{\mathrm{A0}} + c_{\mathrm{B0}}) = \alpha$ and $k_2 \cdot c_{\mathrm{A0}} = \beta$, and (4.7) results for the course of the thermal reaction power versus time the following equation:

$$\begin{aligned} q &= \sum q_\xi = q_1 + q_2 = r_1 \cdot V \cdot (-\Delta H_{\lambda 1}) + r_2 \cdot V \cdot (-\Delta H_{\lambda 2}) \\ &= \quad (r_1 + r_2) \cdot V \cdot (-\Delta H_\lambda) \\ &\quad \text{with } \Delta H_{\lambda 1} = \Delta H_{\lambda 2} = \Delta H_\lambda \\ &= \{c_{\mathrm{A0}} \cdot V \cdot (-\Delta H_\lambda) \cdot (1 - \beta/\alpha) \cdot \mathrm{EXP}(\alpha \cdot t)\}/\{\beta/\alpha + [1 - \beta/\alpha] \cdot \mathrm{EXP}(\alpha \cdot t)\}^2. \end{aligned} \tag{4.83}$$

For $t \gg 0$ it follows that

$$q(t \gg 0) = \alpha^2/\{\alpha - \beta\} \cdot c_{\mathrm{A0}} \cdot V \cdot (-\Delta H_\lambda) \cdot \mathrm{EXP}(-\alpha \cdot t). \tag{4.84}$$

Plotting $\ln\{q\}$ against time[34] (Fig. 4.20) gives a curved line turning into a straight line with slope α and the point of intersection with the ordinate $\ln\{\phi\}$

with

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[34] In the case of negative q-values, $\ln\{|q(t)|\}$ must be plotted; the procedure of interpretation is analogous.

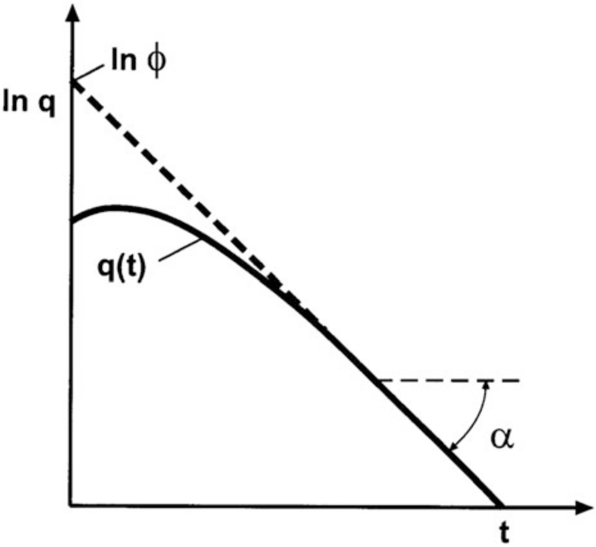

Fig. 4.20 Autocatalytic, parallel reactions;

$$A \xrightarrow{r_1,\,\Delta H_{\lambda 1}} B$$
$$A \xrightarrow{r_2,\,\Delta H_{\lambda 2}} B$$
$$\Delta H_{\lambda 1} = \Delta H_{\lambda 2} = \Delta H_\lambda$$
$$r_1 = k_2 \cdot c_A; \quad r_2 = f\{c_B\} \cdot c_A = k_2 \cdot c_B \cdot c_A$$

Isothermal, discontinuous, constant-volume reactions

$$q = \{c_{A0} \cdot V \cdot (-\Delta H_\lambda) \cdot (1 - \beta/\alpha) \cdot \mathrm{EXP}(\alpha \cdot t)\} / \{\beta/\alpha + [1 - \beta/\alpha] \cdot \mathrm{EXP}(\alpha \cdot t)\}^2.$$

$$\phi = \alpha^2/\{\alpha - \beta\} \cdot c_{A0} \cdot V \cdot (-\Delta H_\lambda).$$

From the point of intersection with the ordinate $\ln\{\phi\}$ we obtain the heat of the reaction

$$(-\Delta H_\lambda) = \phi \cdot \{\alpha - \beta\}/\alpha^2/c_{A0}/V. \tag{4.85}$$

From the slopes α_I and α_{II} of the two measured curves for $(c_{A0}+c_{B0})_I$ and $(c_{A0}+c_{B0})_{II}$ we obtain the rate coefficients

$$k_2 = (\alpha_I - \alpha_{II})/\left[(c_{A0} + c_{B0})_I - (c_{A0} + c_{B0})_{II}\right], \tag{4.86}$$

$$k_1 = \alpha_{II} - k_2 \cdot (c_{A0} + c_{B0})_{II}. \tag{4.87}$$

4.2.1.1.2.4.3 The Rate Function of an Intrinsic Reaction Is the Product of Two Partial Orders 1; The Rate Function of Catalysed, Parallel Reaction Is the Product of Two Partial Orders 1, Its Rate Coefficient Being Directly Proportional to the Concentration of the Product

The scheme of the reaction is

$$\begin{aligned} \mathrm{A} + \mathrm{B} &\xrightarrow{r_1,\, \Delta H_{\lambda 1}} \mathrm{C}, \\ \mathrm{A} + \mathrm{B} &\xrightarrow{r_2,\, \Delta H_{\lambda 2}} \mathrm{C}, \end{aligned}$$

with

- The stoichiometric coefficients $v_{(\mathrm{j,i})\xi}$

$$v_{\mathrm{A1}} = -1, v_{\mathrm{A2}} = -1, v_{\mathrm{B1}} = -1, v_{\mathrm{B2}} = -1, v_{\mathrm{C1}} = 1, v_{\mathrm{C2}} = 1,$$

- The rate functions

$$r_1 = k_1 \cdot c_{\mathrm{A}} \cdot c_{\mathrm{B}},\ r_2 = F\{c_{\mathrm{C}}\} \cdot c_{\mathrm{A}} \cdot c_{\mathrm{B}} = k_2 \cdot c_{\mathrm{C}} \cdot c_{\mathrm{A}} \cdot c_{\mathrm{B}}.$$

The rate function of the first, intrinsic reaction is directly proportional to the product of both reactants, and the rate function of the second reaction is, too. However, its rate coefficient is a function F of the concentration of product C or of a negligibly tiny amount of a by-product which is formed directly proportional to C by a parallel reaction. Hence, the second reaction starts only in the presence of or due to the appearance of C or its by-product. We have $F = k_2 \cdot c_{\mathrm{C}}$.

According to (4.34), the rate of change in A is

$$\begin{aligned} \mathrm{d}c_{\mathrm{A}}/\mathrm{d}t &= \sum v_{\mathrm{A}\xi} \cdot r_\xi = v_{\mathrm{A1}} \cdot r_1 + v_{\mathrm{A2}} \cdot r_2 = -k_1 \cdot c_{\mathrm{A}} \cdot c_{\mathrm{B}} - k_2 \cdot c_{\mathrm{C}} \cdot c_{\mathrm{A}} \cdot c_{\mathrm{B}} \\ &\qquad \text{because of} \\ &\qquad c_{\mathrm{B}} = c_{\mathrm{A}} - c_{\mathrm{A0}} + c_{\mathrm{B0}} \text{ and } c_{\mathrm{C}} = c_{\mathrm{A}} - c_{\mathrm{A0}} + c_{\mathrm{C0}} \\ &= \left(k_1 \cdot c_{\mathrm{B0}} - k_1 \cdot c_{\mathrm{A0}} - k_2 \cdot c_{\mathrm{A0}} \cdot c_{\mathrm{C0}} - k_2 \cdot {c_{\mathrm{A0}}}^2 + k_2 \cdot c_{\mathrm{B0}} \cdot c_{\mathrm{C0}} + k_2 \cdot c_{\mathrm{B0}} \cdot c_{\mathrm{A0}}\right) \\ &\quad \cdot c_{\mathrm{A}} + (k_1 + 2 \cdot k_2 \cdot c_{\mathrm{A0}} + k_2 \cdot c_{\mathrm{C0}} - k_2 \cdot c_{\mathrm{B0}}) \cdot {c_{\mathrm{A}}}^2 - k_2 \cdot {c_{\mathrm{A}}}^3. \end{aligned} \tag{4.88}$$

A solution of the differential equation in the explicit form $c_{\mathrm{j}} = f(t)$ does not exist. Nevertheless, a thermokinetic analysis on the basis of algebraic relations is possible with satisfactory approximation if there is

$$c_{\mathrm{B0}} \gg c_{\mathrm{A0}}, c_{\mathrm{C0}}.$$

For this condition, Eq. (4.88) achieves the simple form

$$\mathrm{d}c_{\mathrm{A}}/\mathrm{d}t = -\left[k_1' + k_2' \cdot (c_{\mathrm{A0}} + c_{\mathrm{C0}})\right] \cdot c_{\mathrm{A}} + k_2' \cdot {c_{\mathrm{A}}}^2,$$

with the constant, pseudo rate coefficients

$$k_1' = k_1 \cdot c_{B0} \text{ and } k_2' = k_2 \cdot c_{B0},$$

i.e. because B is in a large surplus compared with A and C, the concentration c_{B0} changes during a small conversion only to a low degree. Therefore Eq. (4.83) holds for the description of the temporal course of the thermal reaction power during the measurement. Hence, the determination of the pseudo rate coefficients k_1' and k_2' as well as the heats of the reaction $(-\Delta H_\lambda) = (-\Delta H_{\lambda 1}) = (-\Delta H_{\lambda 2})$ result by means of (4.83)–(4.85).

The actual rate coefficients k_1 and k_2 result from the analysis of a number of measurements. To this end, the measuring kettle is pre-filled with a large charge of B. Then small portions of component A are added n times successively, each time following the consumption of the prior portion. With good approximation for the single measurement (n) the following equations are valid:

- Volume of reaction:

$$V_n = V_{\text{batch of B0}} + \sum\nolimits_{n=1 \rightarrow n} \delta V_{\text{A-portion(n)}}$$

Initial concentrations:

- $c_{A0,n} = A_{\text{portion } n} / V_n$
- $c_{C0,n} = \left(C_{\text{Initial moles of series}} + \sum\nolimits_{n=1 \rightarrow n-1} A_{\text{portion(n)}} \right) / V_n$ **|for n=1:**
- $c_{B0,n} = \left(B_{\text{Initial moles of series}} - \sum\nolimits_{n=1 \rightarrow n-1} A_{\text{portion}(n)} \right) / V_n$ **|Summation term=0**.

Hence, k_{1n}' and k_{2n}' change from measurement to measurement owing to the number of

- Added $\delta V_{\text{A-portion}}$,
- Already formed mols C,
- Residual moles B.

Because of (4.82) the quantities $\alpha_n = k_{1n}' + k_{2n}' \cdot (c_{A0} + c_{C0})_n = k_1 \cdot c_{B0,n} + k_2 \cdot c_{B0,n} \cdot (c_{A0} + c_{C0})_n$ and $\beta_n = k_2' \cdot c_{A0,n} = k_2 \cdot c_{B0,n} \cdot c_{A0,n}$ differ for the single measurements, i.e. the slopes α_n and the points of intersection with the ordinate $\ln\{\phi_n\}$ of the extrapolated straight lines which result from the plot of $\ln\{q_n(t)\}$ for $t \gg 0$ (Fig. 4.21a). Plotting $\alpha_n / c_{B0,n}$ against $(c_{A0} + c_{C0})_n$ yields a straight line (Fig. 4.21b) whose slope corresponds to k_2, and the point of intersection with the ordinate corresponds to k_1.

Equation (4.85) gives the heat of the reaction for any point ϕ_n of intersection with the ordinate:

$$(-\Delta H_\lambda) = \phi_n \cdot \{\alpha - \beta\}_n / {\alpha_n}^2 / c_{A0,n} / V_n. \tag{4.89}$$

Whether we like it or not, because of the inevitable errors of measurement, the values of the heat of the reaction, calculated on the basis of the different ϕ_n, vary around the exact value.

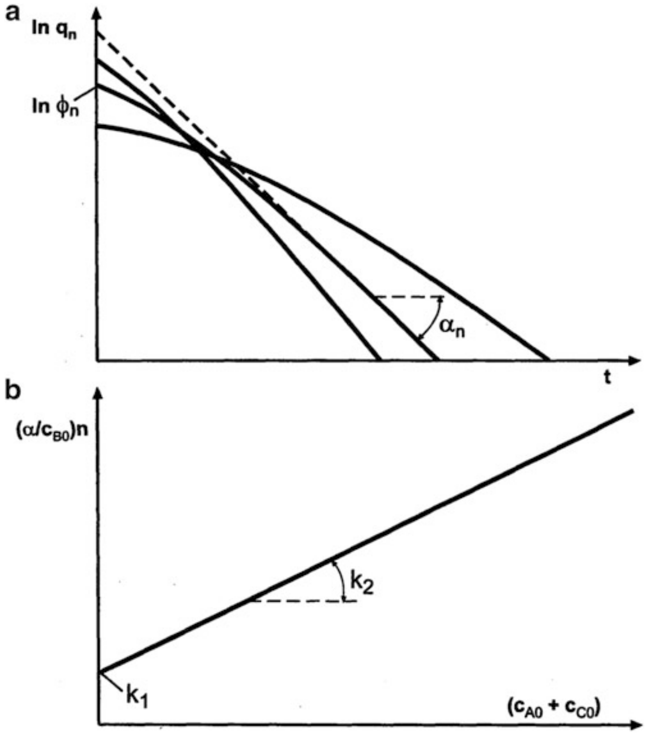

Fig. 4.21 Autocatalytic, parallel reactions

$$A + B \xrightarrow{r_1,\,\Delta H_{\lambda 1}} C$$
$$A + B \xrightarrow{r_2,\,\Delta H_{\lambda 2}} C$$
$$\Delta H_{\lambda 1} = \Delta H_{\lambda 2} = \Delta H_{\lambda}$$

Isothermal, discontinuous, constant-volume reactions

$$r_1 = k_1 \cdot c_A \cdot c_B; r_2 = f\{c_C\} \cdot c_A \cdot c_B = k_2 \cdot c_C \cdot c_B \cdot c_A$$
$$q_n = \{c_{A0,n} \cdot V_n \cdot (-\Delta H_\lambda) \cdot (1 - \beta_n/\alpha_n) \cdot \mathrm{EXP}(\alpha_n \cdot t)\}/\{\beta_n/\alpha_n + [1 - \beta_n/\alpha_n] \cdot \mathrm{EXP}(\alpha_n \cdot t)\}^2$$

4.2.1.1.2.5 Autocatalytic, Competing, Consecutive Reaction in Two Stages

4.2.1.1.2.5.1 Rate Function of Intrinsic Reaction of Both Stages of Order 0; Rate Function of Catalysed, Parallel Reactions of Order 0, Their Rate Coefficients Directly Proportional to Concentration of Product

The simplest, autocatalytic, competing, consecutive reaction consists of two successive conversions $A \to B + \varsigma$, $B + A \to C + \varsigma$, in which the first and the second conversion occur by both intrinsic and autocatalysed steps:

$$1)\quad A \xrightarrow{r_1,\,\Delta H_{\lambda I}} B + \varsigma \qquad 2)\quad A \xrightarrow{r_2(\varsigma),\,\Delta H_{\lambda I}} B + \varsigma \qquad \text{stage I}$$
$$3)\quad B + A \xrightarrow{r_3,\,\Delta H_{\lambda II}} B + \varsigma \qquad 4)\quad B + A \xrightarrow{r_4(\varsigma),\,\Delta H_{\lambda II}} C + \varsigma \qquad \text{stage II}$$

with

- The stoichiometric coefficients $v_{(\mathrm{j,i})\xi}$

$$\begin{aligned}&v_{\mathrm{A}1}=-1, v_{\mathrm{A}2}=-1, v_{\mathrm{A}3}=-1, v_{\mathrm{A}4}=-1,\\&v_{\mathrm{B}1}=1, v_{\mathrm{B}2}=1, v_{\mathrm{B}3}=-1, v_{\mathrm{B}4}=-1,\\&v_{\varsigma 1}=1, v_{\varsigma 2}=1, v_{\varsigma 3}=1, v_{\varsigma 4}=1,\\&v_{\mathrm{C}1}=0, v_{\mathrm{C}2}=0, v_{\mathrm{B}3}=1, v_{\mathrm{B}4}=1;\end{aligned}$$

- The rate functions

$$\begin{aligned}r_1=k_1 \text{ and } r_2=F\{c_\zeta\}=k_2\cdot c_\zeta,\\r_3=k_3 \text{ and } r_4=F\{c_\zeta\}=k_4\cdot c_\zeta.\end{aligned}\tag{4.90}$$

The rate functions for steps 1 and 3 are constants and for steps 2 and 4 linear functions F of the concentration of product ς. None of the rate functions depend explicitly on the concentrations of reactant A and the intermediate product B.

Owing to the rate functions, we have a kind of hybrid of a competing, consecutive reaction and a parallel reaction. Both stages start simultaneously at time $t=0$. Only the cases $k_1 > k_3$ and $k_2 > k_4$ make sense; otherwise A would react by a one-stage reaction to C and ς without producing the intermediate resultant B.

According to (4.34) we have

- The rate of consumption in A

$$\mathrm{d}c_\mathrm{A}/\mathrm{d}t=\sum v_{\mathrm{A}\xi}\cdot r_\xi=-(k_1+k_3)-(k_2+k_4)\cdot c_\varsigma$$

due to

mol balance $c_\zeta - c_{\zeta 0} = c_{\mathrm{A}0} - c_\mathrm{A}$ and with $(k_1+k_3)=\kappa_\mathrm{intrins}$ and $(k_2+k_4)=\kappa_\mathrm{autoc}$

$$\begin{aligned}&=-\kappa_\mathrm{intrins}-\kappa_\mathrm{autoc}\cdot(c_{\mathrm{A}0}-c_\mathrm{A}+c_{\varsigma 0})\\&=-[\kappa_\mathrm{intrins}+\kappa_\mathrm{autoc}\cdot(c_{\mathrm{A}0}+c_{\varsigma 0})]+\kappa_\mathrm{autoc}\cdot c_\mathrm{A},\end{aligned}\tag{4.91}$$

- The rate of formation in ς

$$\mathrm{d}c_\varsigma/\mathrm{d}t=\sum v_{\varsigma\xi}\cdot r_\xi=\kappa_\mathrm{intrins}+\kappa_\mathrm{autoc}\cdot c_\varsigma.$$

The solutions of the equations are

$$\begin{aligned}c_\mathrm{A}&=\left[\kappa_\mathrm{intrins}+\kappa_\mathrm{autoc}\cdot\left(c_{\mathrm{A}0}+c_{\zeta 0}\right)\right]/\kappa_\mathrm{autoc}-\left[\kappa_\mathrm{intrins}/\kappa_\mathrm{autoc}+c_{\zeta 0}\right]\cdot\mathrm{EXP}(\kappa_\mathrm{autoc}\cdot t),\\c_\zeta&=-\kappa_\mathrm{intrins}/\kappa_\mathrm{autoc}+\left[\kappa_\mathrm{intrins}/\kappa_\mathrm{autoc}+c_{\zeta 0}\right]\cdot\mathrm{EXP}(\kappa_\mathrm{autoc}\cdot t).\end{aligned}\tag{4.92}$$

Equations (4.7), (4.90), and (4.92) result in the temporal course of the thermal reaction power:

$$\begin{aligned} q_{(\mathrm{I+II})} &= \sum q_\xi = [r_1 + r_2]\cdot V \cdot (-\Delta H_{\lambda I}) + [r_3 + r_4]\cdot V \cdot (-\Delta H_{\lambda \mathrm{II}}) \\ &= \{\varphi_{\mathrm{I}} \cdot (-\Delta H_{\lambda \mathrm{I}}) + \varphi_{\mathrm{II}} \cdot (-\Delta H_{\lambda \mathrm{II}}) + [\psi_{\mathrm{I}} \cdot (-\Delta H_{\lambda \mathrm{I}}) + \psi_{\mathrm{II}} \cdot (-\Delta H_{\lambda \mathrm{II}})] \cdot \mathrm{EXP}(\kappa_{\mathrm{autoc}} \cdot t)\} \cdot V, \end{aligned} \tag{4.93}$$

with

- $\varphi_{\mathrm{I}} = k_1 - k_2 \cdot \kappa_{\mathrm{intrins}}/\kappa_{\mathrm{autoc}},\ \varphi_{\mathrm{II}} = k_3 - k_4 \cdot \kappa_{\mathrm{intrins}}/\kappa_{\mathrm{autoc}},$
- $\psi_{\mathrm{I}} = \mathrm{k}_2 \cdot \left(\kappa_{\mathrm{intrins}}/\kappa_{\mathrm{autoc}} + c_{\zeta 0}\right),\ \ \psi_{\mathrm{II}} = \mathrm{k}_4 \cdot \left(\kappa_{\mathrm{intrins}}/\kappa_{\mathrm{autoc}} + c_{\zeta 0}\right).$

Experience shows that the enthalpies of reaction $\Delta H_{\lambda \mathrm{I}}$ and $\Delta H_{\lambda \mathrm{II}}$ differ in order of magnitude by a factor of two to three at the most. In contrast, the rate coefficients k_2 and k_4 are larger than the rate coefficients k_1 and k_3 in order of magnitude by powers of ten (there is otherwise no ascertainable autocatalysis). Thus, we have

$$\varphi_{\mathrm{I}} \cdot (-\Delta H_{\lambda \mathrm{I}}) + \varphi_{\mathrm{II}} \cdot (-\Delta H_{\lambda \mathrm{II}}) \ll \psi_{\mathrm{I}} \cdot (-\Delta H_{\lambda \mathrm{I}}) + \psi_{\mathrm{II}} \cdot (-\Delta H_{\lambda \mathrm{II}}).$$

This means that the plot of $\ln\left\{q_{(\mathrm{I+II})}\right\}$ versus time (Fig. 4.22) turns at $t \gg 0$ into a straight line with a slope κ_{autoc} and the point of intersection with the ordinate $\ln\{\phi_{\mathrm{I+II}}\}$. $\phi_{\mathrm{I+II}}$ corresponds in praxis to $[\psi_{\mathrm{I}} \cdot (-\Delta H_{\lambda \mathrm{I}}) + \psi_{\mathrm{II}} \cdot (-\Delta H_{\lambda \mathrm{II}})] \cdot V$. When A is consumed at time $t_{\mathrm{E(I+II)}}$, the straight line ends abruptly. According to (4.92), we obtain

$$t_{\mathrm{E(I+II)}} = \ln\left[\left(\kappa_{\mathrm{intrins}} + \kappa_{\mathrm{autoc}} \cdot \left(c_{\mathrm{A0}} + c_{\zeta 0}\right)\right)/\left(\kappa_{\mathrm{intrins}} + \kappa_{\mathrm{autoc}} \cdot c_{\zeta 0}\right)\right]/\kappa_{\mathrm{autoc}}. \tag{4.94}$$

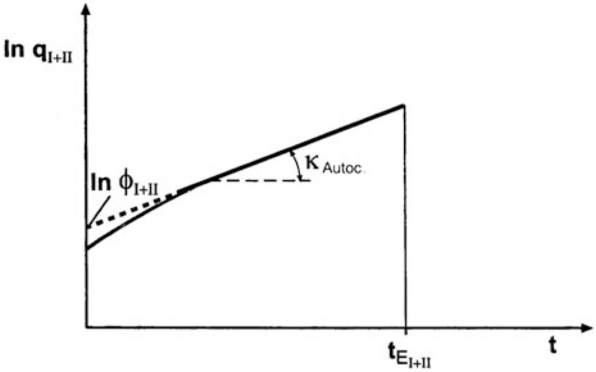

Fig. 4.22 Autocatalytic, competing, consecutive reaction in two stages:

$$\begin{array}{lll} \mathrm{A} \xrightarrow{r_1,\, \Delta H_{\lambda \mathrm{I}}} \mathrm{B} + \varsigma, & \mathrm{A} \xrightarrow{r_2(\varsigma),\, \Delta H_{\lambda \mathrm{I}}} \mathrm{B} + \varsigma & \text{stage I} \\ \mathrm{B} + \mathrm{A} \xrightarrow{r_3,\, \Delta H_{\lambda \mathrm{II}}} \mathrm{C} + \varsigma, & \mathrm{B} + \mathrm{A} \xrightarrow{r_4(\varsigma),\, \Delta H_{\lambda \mathrm{II}}} \mathrm{C} + \varsigma, & \text{stage II} \end{array}$$

$$r_1 = k_1; r_2 = f\left\{c_\varsigma\right\} = k_2 \cdot c_\varsigma$$
$$r_3 = k_3; r_4 = f\left\{c_\varsigma\right\} = k_4 \cdot c_\varsigma$$

The following relations apply:

$$\begin{aligned} q_{(\mathrm{I+II})}\left(t=0, c_{\zeta 0}=0\right) &= [k_1 \cdot (-\Delta H_{\lambda \mathrm{I}}) + k_3 \cdot (-\Delta H_{\lambda \mathrm{II}})] \cdot V, \\ q_{(\mathrm{I+II})}\left(t=0, c_{\zeta 0} \neq 0\right) &= [k_1 + k_2 \cdot \zeta_0 \cdot (-\Delta H_{\lambda \mathrm{I}}) + k_3 + k_4 \cdot \zeta_0(-\Delta H_{\lambda \mathrm{II}})] \cdot V, \\ \int q_{(\mathrm{I+II})} \mathrm{d}t &= \left\{\left[c_{\mathrm{B}(t \geq t\mathrm{E(I+II)})} + c_{\mathrm{C}(t \geq t\mathrm{E(I+II)})}\right] \cdot (-\Delta H_{\lambda \mathrm{I}}) + c_{\mathrm{C}(t \geq t\mathrm{E(I+II)})} \cdot (-\Delta H_{\lambda \mathrm{II}})\right\} \cdot V. \end{aligned} \tag{4.95}$$

The quantities k_1, k_2, k_3, k_4, $\Delta H_{\lambda \mathrm{I}}$ and $\Delta H_{\lambda \mathrm{II}}$ cannot be elaborated solely from relations (4.93), (4.94) and (4.95) of the reaction system I + II. The separate calorimetric investigation of the second stage II $(\mathrm{B} + \mathrm{A} \rightarrow \mathrm{C} + \varsigma)$ is needed in addition. This can be caused by the use of inhibitors with specific effects.

In that case it follows from (4.91), (4.92) and (4.93) due to $k_1 = 0$ and $k_2 = 0$ that

$$c_{\mathrm{A}} = \left[k_3 + k_4 \cdot \left(c_{\mathrm{A0}} + c_{\zeta 0}\right)\right] \Big/ k_4 - \left[k_3 + k_4 + c_{\zeta 0}\right] \cdot \mathrm{EXP}(k_4 \cdot t), \tag{4.96}$$

$$q_{(\mathrm{II})}(t) = \left(k_3 + k_4 \cdot c_{\zeta 0}\right) \cdot V \cdot \Delta H_{\lambda \mathrm{II}} \cdot \mathrm{EXP}[k_4 \cdot t].$$

Plotting $\ln\{q_{(\mathrm{II})}\}$ over time[35] (Fig. 4.23) gives a straight line with slope $\kappa_{\mathrm{II}} = k_4$ and the point of intersection with the ordinate $\ln\{\phi_{\mathrm{II}}\}$ with $\phi_{\mathrm{II}} = (k_3 + k_4 \cdot c_{\varsigma 0}) \cdot V \cdot \Delta H_{\lambda \mathrm{II}}$. When A is consumed, the straight line ends abruptly at time $t_{\mathrm{E(II)}} = \ln[(k_3 + k_4 \cdot (c_{\mathrm{A0}} + c_{\varsigma 0}))/(k_3 + k_4 \cdot c_{\varsigma 0})]/k_4$.

With the additional quantities κ_{II} and ϕ_{II} k_1, k_2, k_3, k_4, $\Delta H_{\lambda \mathrm{I}}$ and $\Delta H_{\lambda \mathrm{II}}$ can be found.

- The heat of reaction $(-\Delta H_{\lambda \mathrm{II}})$ is given from the total amount of heat released up to the time $t_{\mathrm{E(II)}}$ of the abrupt end of reaction

$$-\Delta H_{\lambda \mathrm{II}} = \int_{t=0 \rightarrow t\mathrm{E(II)}} q_{(\mathrm{II})} \cdot \mathrm{d}t / c_{\mathrm{A0}} / V.$$

- The rate constant k_4 corresponds to the slope κ_{II} of the straight line

$$k_4 = \kappa_{\mathrm{II}}.$$

- From the point of intersection $\ln\{\phi_{\mathrm{II}}\}$ and k_4 it follows that

$$k_3 = \phi_{\mathrm{II}} / V / (-\Delta H_{\lambda 2}) - k_4 \cdot c_{\zeta 0}.$$

- The rate coefficient k_2 is calculated due to (4.91) by means of κ_{autoc} (Fig. 4.22) and k_4:

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[35] In the case of negative q-values, $\ln\{|q(t)|\}$ must be plotted; the procedure for interpretation is analogous.

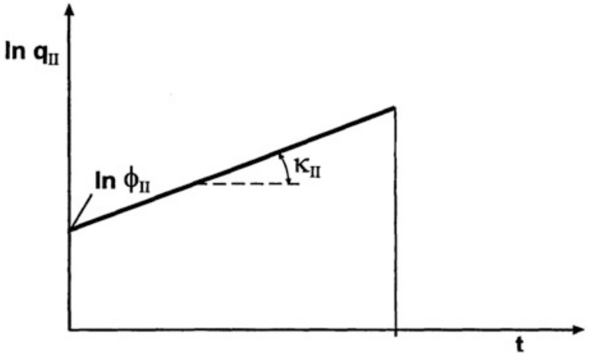

Fig. 4.23 Second stage of autocatalytic, consecutive reaction:

$$\begin{array}{lll} \mathrm{A} \xrightarrow{r_1,\,\Delta H_{\lambda \mathrm{I}}} \mathrm{B} + \varsigma, & \mathrm{A} \xrightarrow{r_2(\varsigma),\,\Delta H_{\lambda \mathrm{I}}} \mathrm{B} + \varsigma & \text{stage I} \\ \mathrm{B} + \mathrm{A} \xrightarrow{r_3,\,\Delta H_{\lambda \mathrm{II}}} \mathrm{C} + \varsigma, & \mathrm{B} + \mathrm{A} \xrightarrow{r_4(\varsigma),\,\Delta H_{\lambda \mathrm{II}}} \mathrm{C} + \varsigma & \text{stage II} \end{array}$$

$$k_2 = \kappa_{\mathrm{autoc}} - k_4.$$

- The rate coefficient k_1 results by means of κ_{autoc}, k_3 and $t_{\mathrm{E(I+II)}}$ according to (4.94):

$$k_1 = \left\{\kappa_{\mathrm{autoc}} \cdot \left[\left(c_{\mathrm{A}0} + c_{\zeta 0}\right) - c_{\zeta 0} \cdot \mathrm{EXP}\left(\kappa_{\mathrm{autoc}} \cdot t_{\mathrm{E(I+II)}}\right)\right]\right\} / \\ \left\{\mathrm{EXP}\left(\kappa_{\mathrm{autoc}} \cdot t_{\mathrm{E(I+II)}}\right) - 1\right\} - k_3.$$

- From (4.95) we obtain

$$(-\Delta H_{\lambda \mathrm{I}}) = \left[\left[\int_{t=0 \to t\mathrm{E(I+II)}} q_{\mathrm{(I+II)}} \cdot \mathrm{d}t - c_{\mathrm{C}(t \geq t\mathrm{E(I+II)})} \cdot (-\Delta H_{\lambda \mathrm{II}})\right] \right/ \\ \left[c_{\mathrm{B}(t \geq t\mathrm{E(I+II)})} + c_{\mathrm{C}(t \geq t\mathrm{E(I+II)})}\right] / V.$$

4.2.1.1.2.6 Rhythmic Reaction

The following system of conversion is discussed:

$$\begin{array}{ll} \mathrm{A} \xrightarrow{r_1,\,\Delta H_{\lambda 1}} \mathrm{B} & \mathrm{I} \\ \mathrm{B} \xrightarrow{r_2,\,\Delta H_{\lambda 2}} \mathrm{C} & \mathrm{II} \\ \mathrm{C} \xrightarrow{r_3,\,\Delta H_{\lambda 3}} \mathrm{D} & \mathrm{III} \end{array}$$

Reactant A converts via the intermediate products B and C to the final product D. The stoichiometric coefficients are

$$\nu_{A1} = -1, \nu_{A2} = 0, \nu_{A3} = 0; \nu_{B1} = 1, \nu_{B2} = -1, \nu_{B3} = 0;$$
$$\nu_{C1} = 0, \nu_{C2} = 1, \nu_{C3} = -1; \nu_{D1} = 0, \nu_{D2} = 0, \nu_{D3} = 1.$$

The rate functions are [32]

$$\begin{aligned} r_1 &= k_1(c_B) \cdot c_A = k_1 \cdot c_B \cdot c_A, \\ r_2 &= k_2(c_C) \cdot c_B = k_2 \cdot c_C \cdot c_B, \\ r_3 &= k_3 \cdot c_C. \end{aligned}$$

Because the rate coefficients of reactions I and II are directly proportional to the concentration of the corresponding product B respectively C, stages I and II are autocatalytic reactions, i.e. during the run of the conversion oscillations can be originated.[36] To start the reaction, B and C must exist at least in marginal amounts or be produced by intrinsic parallel reactions. Here the latter option is neglected simplifying the illustration of the conversion, which is in any case not simple but already, apart from that, a mathematically and analytically complex.

According to (4.34), the rates of change in A, B, C and D are

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[36] The second postulate of the classical thermodynamics of chemical equilibrium states or quasi-static progress via an infinite sequence of equilibrium states requires

- that in a closed reactor the chemical conversions of the overall stoichiometry $(. + A_i + . + . \rightarrow . + B_j + .)$ must be marked by a monotonous decrease in the free energy G of the reaction systems, at all reaction times $\Delta G(t) < 0$;
- that, as a consequence, the overall reaction for constant temperature and constant pressure achieves monotonously, i.e. without overstepping, exceeding, understepping or falling back, an equilibrium.

  Hence, during the conversion the concentrations of intermediate products pass their peak values or quickly achieve stationary values.

  A real chemical conversion takes place as non-quasi-static progress. The corresponding thermodynamics of non-equilibrium states or of non-quasi-static progress far from equilibrium[15] leads one to deduce that oscillations of the concentrations can occur when
- The mechanism of the reaction is sufficiently complex and

  the reactants of the reaction $(. + A_i + . \rightarrow + B_j + .)$ are incapable of reacting at a considerable velocity directly or by intermediate products to B_j, so that, instead of that, a process can occur via another complex but far quicker mechanism;

  for instance, a mechanism functions in such a way that within a sequence of succeeding steps at least one intermediate product acts as a catalyst or inhibitor one step ahead. The retrocoupling causes an acceleration or braking of the intermediate step by which oscillations can originate.
- The state of the reaction system is sufficiently far from thermodynamic equilibrium. The decrease in free energy supplies the driving force for the oscillations. By approaching the equilibrium state, the driving force respectively the amplitudes of the oscillations get closer to the value zero with the effect that all concentrations make their way to the equilibrium values more and more monotonously.
- The concentrations of educts and products do not oscillate, only the concentrations of certain intermediate resultants.

$$\begin{aligned}
\mathrm{d}c_\mathrm{A}/\mathrm{d}t &= \sum v_{\mathrm{A}\xi}\cdot r_\xi = -k_1\cdot c_\mathrm{B}\cdot c_\mathrm{A},\\
\mathrm{d}c_\mathrm{B}/\mathrm{d}t &= \sum v_{\mathrm{B}\xi}\cdot r_\xi = k_1\cdot c_\mathrm{B}\cdot c_\mathrm{A} - k_2\cdot c_\mathrm{C}\cdot c_\mathrm{B},\\
\mathrm{d}c_\mathrm{C}/\mathrm{d}t &= \sum v_{\mathrm{C}\xi}\cdot r_\xi = k_2\cdot c_\mathrm{C}\cdot c_\mathrm{B} - k_3\cdot c_\mathrm{C},\\
\mathrm{d}c_\mathrm{D}/\mathrm{d}t &= \sum v_{\mathrm{D}\xi}\cdot r_\xi = k_3\cdot c_\mathrm{C}.
\end{aligned}$$

A solution in the explicit form $c_{\mathrm{i/j}} = f_{\mathrm{i/j}}(t)$ does not exist, hence there is no function $q(t)$ of the thermal reaction power:

$$q = \sum q_\xi = q_1 + q_2 + q_3 = r_1\cdot V\cdot(-\Delta H_{\lambda 1}) + r_2\cdot V\cdot(-\Delta H_{\lambda 2}) + r_3\cdot V\cdot(-\Delta H_{\lambda 3}).$$

Because mathematical-analytical solutions do not exist, stages I–III must be investigated separately to elaborate the kinetic and thermal data k_i and $\Delta H_{\lambda\mathrm{I}}$; for instance,

- Reaction I without C; mode of evaluation: autocatalytic reaction, Sect. 4.2.1.1.2.4.1, results in k_1 and $\Delta H_{\lambda 1}$
- Reaction III without A and B; mode of evaluation: reaction of order 1, Sect. 4.2.1.1.1.3, results in k_3 and $\Delta H_{\lambda 3}$
- Reaction II and III without A; mode of evaluation: the initial value of the thermal reaction power $q(t = 0)$, $\Delta H_{\lambda 3}$ and the total amount of released heat result in k_2 and $\Delta H_{\lambda 2}$:

  1. From the total amount of released heat

  $$\int_{t=0\to\infty}(q)\cdot \mathrm{d}t = c_{\mathrm{B}0}\cdot(-\Delta H_{\lambda 2})\cdot V + (c_{\mathrm{B}0}+c_{\mathrm{C}0})\cdot(-\Delta H_{\lambda 3})\cdot V)$$

  we obtain

  $$-\Delta H_{\lambda 2} = \left[\int_{t=0\to\infty} q\cdot \mathrm{d}t - (c_{\mathrm{B}0}+c_{\mathrm{C}0})\cdot(-\Delta H_{\lambda 3})\cdot V\right]/c_{\mathrm{B}0}/V.$$

  2. From the initial value of the thermal reaction power

  $$q(t=0) = k_2\cdot c_{\mathrm{B}0}\cdot c_{\mathrm{C}0}\cdot V\cdot(-\Delta H_{\lambda 2}) + k_3\cdot c_{\mathrm{C}0}\cdot V\cdot(-\Delta H_{\lambda 3})$$

  we obtain

$$\begin{aligned}
k_2 &= [q(t=0) - k_3\cdot c_{\mathrm{C}0}\cdot V\cdot(-\Delta H_{\lambda 3})]/c_{\mathrm{B}0}/c_{\mathrm{C}0}/V/(-\Delta H_{\lambda 2})\\
&= [q(t=0) - k_3\cdot c_{\mathrm{C}0}\cdot V\cdot(-\Delta H_{\lambda 3})]/c_{\mathrm{C}0}/\left[\int_{t=0\to\infty} q\cdot \mathrm{d}t - (c_{\mathrm{B}0}+c_{\mathrm{C}0})\cdot(-\Delta H_{\lambda 3})\right]/V.
\end{aligned}$$

Figures 4.24 and 4.25 show examples of numeric calculations with assumed values k_ξ and $\Delta H_{\lambda\xi}$ and $c_{0(\mathrm{j/i})}$. It can be seen that the concentrations of the intermediate products B and C during their temporal decrease distinctively oscillate; the frequency and the amplitude of the oscillation diminish. Against that, reactant A decreases respectively the final product D increases more or less

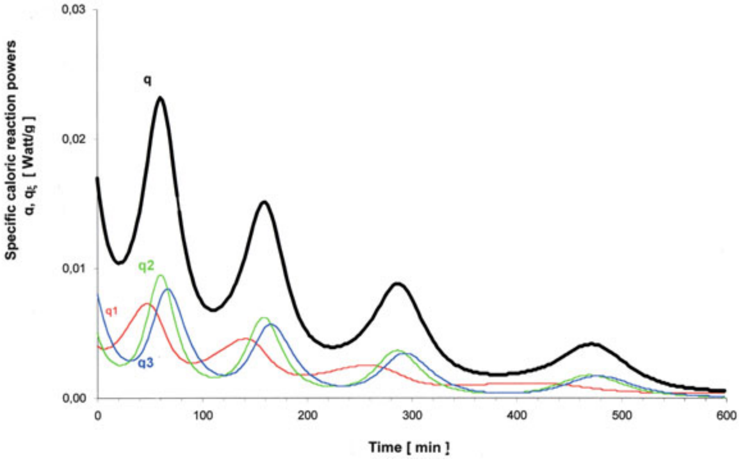

Fig. 4.24 Thermal reaction power of rhythmic reaction A→B→C→D; isothermal, discontinuous, constant-volume reaction

$r_1 = k_1(c_B) \cdot c_A = k_1 \cdot c_B \cdot c_A, \quad r_2 = k_2(c_C) \cdot c_B = k_2 \cdot c_C \cdot c_B, \quad r_3 = k_3 \cdot c_C$

$k_1 = 1 \;\; \text{ml/mol/s}\,, k_2 = 25 \;\; \text{ml/mol}/s\,, k_3 = 2 \times 10^{-3} \;\; \text{ml/mol/s}$

$c_{A0} = 1 \times 10^{-3}, \; c_{B0} = 5 \times 10^{-5}, c_{C0} = 5 \times 10^{-6}, c_{D0} = 0 \;\; \text{mol/ml}, \left(-\Delta H_{\lambda\xi}\right) = 80 \;\; \text{kJ/mol},$
$V = 1{,}000 \;\; \text{ml}$

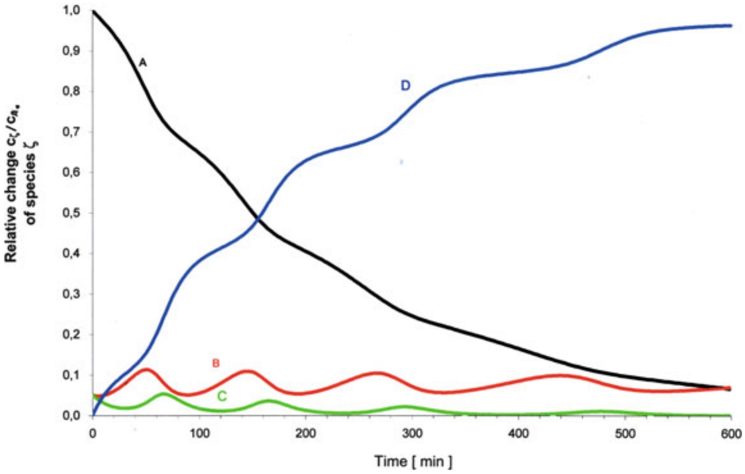

Fig. 4.25 Course of concentrations of rhythmic reaction A→B→C→D; isothermal, discontinuous, constant-volume reaction

$r_1 = k_1(c_B) \cdot c_A = k_1 \cdot c_B \cdot \; c_A, \quad r_2 = k_2(c_C) \cdot c_B = k_2 \cdot c_C \cdot c_B, \quad r_3 = k_3 \cdot c_C$

$k_1 = 1 \;\; \text{ml/mol/s}\,, k_2 = 25 \;\; \text{ml/mol/s}\,, k_3 = 2 \times 10^{-3} \;\; \text{ml/mol/s}$

$c_{A0} = 1 \times 10^{-3}, c_{B0} = 5 \times 10^{-5}, c_{C0} = 5 \times 10^{-6}, c_{D0} = 0 \;\; \text{mol/ml}, \; \left(-\Delta H_{\lambda\xi}\right) = 80 \;\; \text{kJ/mol},$
$V = 1{,}000 \;\; \text{ml}$

monotonously over time without a distinctive oscillation (always $\mathrm{d}A/\mathrm{d}t < 0$, always $\mathrm{d}D/\mathrm{d}t > 0$). The intensities of the oscillating thermal reaction powers q_1, q_2, q_3 as well as their superposition, the measurable thermal overall reaction power q, decay with decreasing frequency and amplitude.

4.2.1.1.2.7 Reversible Reaction

A reversible conversion differs from an irreversible conversion in that, besides the conversion of the reactants with respect to products according to the stoichiometry

$$v_{1\mathrm{I}} + v_{2\mathrm{I}} + v_{3\mathrm{I}} + \ldots \rightarrow v_{\zeta\mathrm{I}} + \ldots + v_{\mathrm{nI}} \quad \text{reaction I(forward reaction)},$$

simultaneously a retro-conversion of these products with respect to those reactants occurs according to the stoichiometry

$$v_{\zeta\mathrm{II}} + \ldots + v_{\mathrm{nII}} \rightarrow v_{1\mathrm{II}} + v_{2\mathrm{II}} + v_{3\mathrm{II}} \quad \text{reaction II(backward reaction)}.$$

Both reactions run over the same path due to the second law of thermodynamics. When the rate of the forward reaction and the rate of the backward reaction are equal, i.e. formation corresponds to consumption, the conversion has achieved equilibrium. For the stoichiometric coefficients the following equation is valid:

$$v_{\zeta\mathrm{II}} = -v_{\zeta\mathrm{I}} \quad (\zeta = 1, 2, \ldots, n, \ldots).$$

When the number of formula conversions are $\lambda_{\mathrm{I}}(t=0) = 0$, $\lambda_{\mathrm{II}}(t=0) = 0$, and the initial concentrations are $c_\zeta(t=0) = c_{\zeta 0}$,

we obtain due to (4.4) and (4.34) the relation

$$c_\zeta = c_{\zeta\mathrm{o}} + v_{\zeta\mathrm{I}} \cdot \lambda_{\mathrm{I}} + v_{\zeta\mathrm{II}} \cdot \lambda_{\mathrm{II}} = c_{\zeta\mathrm{o}} + v_{\zeta\mathrm{I}} \cdot (\lambda_{\mathrm{I}} - \lambda_{\mathrm{II}}) = c_{\zeta\mathrm{o}} + v_{\zeta\mathrm{I}} \cdot \lambda$$

with $\lambda = \lambda_{\mathrm{I}} - \lambda_{\mathrm{II}}$ as number of the overall formula conversion.

The reaction takes place uniformly, and we get

$$c_\zeta = c_{\zeta 0} + v_{\zeta\mathrm{I}}/v_{1\mathrm{I}} \cdot (c_1 - c_{10}) \quad (\zeta = 2, 3 \ldots, n).$$

For the purpose of simplifying arduous integrations for the thermokinetic analysis of reversible reactions, it is desirable to describe the reaction progress by means of the distance Θ_ζ of the concentration of component ζ from its concentration at equilibrium $c_{\zeta\infty}$ [35]. We have according to (4.4),

$$\begin{aligned} c_{10} + v_1 \cdot \lambda = c_1 = c_{1\infty} + \theta_1 \\ c_{\zeta 0} + v_\zeta \cdot \lambda = c_\zeta = c_{\zeta\infty} + \theta_\zeta \end{aligned} \tag{4.97}$$

with the simplified marking of the coefficients v, i.e.

$$\nu_1 \text{ instead of } \nu_{1\mathrm{I}} \quad \text{and} \quad \nu_\zeta \text{ instead of } \nu_{\zeta\mathrm{I}}.$$

Hence, we have

$$\begin{aligned}\lambda &= (c_{1\infty} - c_{10} + \theta_1)/\nu_1 = \left(c_{\zeta\infty} - c_{\zeta 0} + \theta_\zeta\right)/\nu_\zeta \\ &= (c_{1\infty} - c_{10})/\nu_1 + \theta_1/\nu_1 = \left(c_{\zeta\infty} - c_{\zeta 0}\right)/\nu_\zeta + \theta_\zeta/\nu_\zeta.\end{aligned}$$

In a state of equilibrium we have, by definition, $\theta_1 = \theta_\zeta = 0$, which yields

$$\lambda(t = \infty) = \lambda_\infty = (c_{1\infty} - c_{10})/\nu_1 = \left(c_{\zeta\infty} - c_{\zeta 0}\right)/\nu_\zeta$$

with the consequence that

$$\theta_1/\nu_1 = \theta_\zeta/\nu_\zeta \quad \text{or} \quad \theta_\zeta = \nu_\zeta/\nu_1 \cdot \theta_1.$$

At the start of the reaction at the moment $t = 0$ we have $\lambda = 0$; hence[37]

$$\theta_1(t = 0) = \nu_1/\nu_\zeta \cdot \left(c_\zeta(t = 0) - c_{\zeta\infty}\right) = c_1(t = 0) - c_{1\infty}, \tag{4.98}$$

i.e., due to $c_\zeta(t = 0) = c_{\zeta 0} = 0$,

$$\theta_1(t = 0) = -\nu_1/\nu_\zeta \cdot c_{\zeta\infty}.$$

Due to (4.97) we obtain

$$c_\zeta = c_{\zeta\infty} + \nu_\zeta/\nu_1 \cdot \theta_1. \tag{4.99}$$

4.2.1.1.2.7.1 Rate Functions of Forward and Backward Reaction of Order 1

The simplest reversible conversion occurs when two species in dilute solution change into each other via the following two elementary reactions I and II:

$$\mathrm{A} \underset{r_{II},\,\Delta H_{\lambda\mathrm{II}}}{\overset{r_I,\,\Delta H_{\lambda\mathrm{I}}}{\rightleftarrows}} \mathrm{B} \quad \begin{matrix}\mathrm{I}\\ \mathrm{II}\end{matrix}$$

With the stoichiometric coefficients $\nu_{(\mathrm{j,i})\xi}$ respectively rate functions r_ξ

$$\begin{aligned}\nu_{\mathrm{AI}} = -1, \nu_{\mathrm{BI}} = 1, \quad r_{\mathrm{I}} = k_1 \cdot c_{\mathrm{A}} \quad \mathrm{I}\\ \nu_{\mathrm{AII}} = 1, \nu_{\mathrm{BII}} = -1, \quad r_{\mathrm{II}} = k_2 \cdot c_{\mathrm{B}} \quad \mathrm{II}.\end{aligned}$$

---

[37] Example: $1\mathrm{A} \leftrightarrow 1\mathrm{B} + 2\mathrm{C}$,
with $c_{\mathrm{A0}} \neq 0,\quad c_{\mathrm{B0}} = 0,\quad c_{\mathrm{C0}} = 0:\quad \theta_1(t = 0) = c_{\mathrm{A0}} - c_{\mathrm{A}\infty} = -1/1 \cdot (0 - c_{\mathrm{B}\infty}) = -1/2 \cdot (0 - c_{\mathrm{C}\infty}) = c_{\mathrm{B}\infty} = c_{\mathrm{C}\infty}/2$
with $c_{\mathrm{A0}} = 0,\quad c_{\mathrm{B0}} \neq 0,\quad c_{\mathrm{C0}} \neq 0:\quad \theta_1(t = 0) = 0 - c_{\mathrm{A}\infty} = -1/1 \cdot (c_{\mathrm{B0}} - c_{\mathrm{B}\infty}) = -1/2 \cdot (c_{\mathrm{C0}} - c_{\mathrm{C}\infty}) = c_{\mathrm{B}\infty} - c_{\mathrm{B0}} = (c_{\mathrm{C}\infty} - c_{\mathrm{C0}})/2 = -c_{\mathrm{A}\infty}.$

We have according to (4.99) changing the marking of θ by $\theta_1 = \theta_A = \theta$,

$$c_A = c_{A\infty} + \theta \text{ and } c_B = c_{B\infty} - \theta. \tag{4.100}$$

Using (4.34) and (4.100) we get the rate of change in A

$$\begin{aligned} dc_A/dt &= \sum v_{(j,i)\xi} \cdot r_\xi = -k_1 \cdot c_A + k_2 \cdot c_B = d\theta/dt \\ &= -k_1 \cdot (c_{A\infty} + \theta) + k_2 \cdot (c_{B\infty} - \theta) \\ &= -k_1 \cdot c_{A\infty} + k_2 \cdot c_{B\infty} - (k_1 + k_2) \cdot \theta. \end{aligned}$$

At equilibrium of the reaction we have $\theta = 0$ and $d\theta/dt = 0$, hence

$$k_1 \cdot c_{A\infty} = k_2 \cdot c_{B\infty}, \tag{4.101}$$

and thus

$$d\theta/dt = -(k_1 + k_2) \cdot \theta$$

and[38]

$$\theta = \theta(t = 0) \cdot \mathrm{EXP}[-(k_1 + k_2) \cdot t]. \tag{4.102}$$

The thermal reaction power reads, according to (4.7),

$$q = \sum \left[r_\xi \cdot \left(-\Delta H_{\lambda\xi} \right) \right] \cdot V = [r_I \cdot (-\Delta H_{\lambda I}) + r_{II} \cdot (-\Delta H_{\lambda II})] \cdot V \tag{4.103}$$

$$\begin{aligned} &= [k_1 \cdot c_A \cdot (-\Delta H_{\lambda I})] + k_2 \cdot c_B \cdot (-\Delta H_{\lambda II}) \cdot V \text{ due to (4.99)} \\ &= [k_1 \cdot (c_{A\infty} + \theta) \cdot (-\Delta H_{\lambda I}) + k_2 \cdot (c_{B\infty} - \theta) \cdot (-\Delta H_{\lambda II})] \cdot V \\ &= [k_1 \cdot (c_{A\infty} + \theta) \cdot (-\Delta H_{\lambda I}) - k_2 \cdot (c_{B\infty} - \theta) \cdot (-\Delta H_{\lambda I})] \cdot V \\ &= [(k_1 \cdot c_{A\infty} - k_2 \cdot c_{B\infty}) \cdot (-\Delta H_{\lambda I}) + (k_1 + k_2) \cdot \theta \cdot (-\Delta H_{\lambda I})] \cdot V \\ &\quad \text{due to(4.101)} \\ &= [(k_1 + k_2) \cdot \theta \cdot (-\Delta H_{\lambda I})] \cdot V \text{ due to(4.102)} \\ &= (k_1 + k_2) \cdot (-\Delta H_{\lambda I}) \cdot V \cdot \theta_{(t=0)} \cdot \mathrm{EXP}[-(k_1 + k_2) \cdot t]. \end{aligned} \tag{4.104}$$

---

[38] Starting from A, i.e. $c_{A0} \neq 0$, $c_{B0} = 0$, it follows, with (4.102) and (4.98), that

$$c_A - c_{A\infty} = (c_{A0} - c_{A\infty}) \cdot \mathrm{EXP}[-(k_1 + k_2) \cdot t] = c_{B\infty} \cdot \mathrm{EXP}[-(k_1 + k_2) \cdot t].$$

Starting from B, i.e. $c_{B0} \neq 0$, $c_{A0} = 0$, it follows, with (4.102) and (4.98), that

$$c_B - c_{B\infty} = (c_{B0} - c_{B\infty}) \cdot \mathrm{EXP}[-(k_1 + k_2) \cdot t] = c_{A\infty} \cdot \mathrm{EXP}[-(k_1 + k_2) \cdot t],$$

4.2.1.1.2.7.1.1 Case (A→)

Starting from A, i.e. $c_{A0} \neq 0$ and $c_{B0} = 0$, according to (4.99) the following expression is valid:

$$\theta(t = 0) = c_{B\infty} = c_{A0} - c_{A\infty}. \tag{4.105}$$

By means of (4.104) the temporal course of the thermal reaction power reads

$$\begin{aligned} q_{(A\rightarrow)} &= (k_1 + k_2) \cdot c_{B\infty} \cdot V \cdot (-\Delta H_{\lambda I}) \cdot \mathrm{EXP}[-(k_1 + k_2) \cdot t] \\ &= (k_1 + k_2) \cdot (c_{A0} - c_{A\infty}) \cdot V \cdot (-\Delta H_{\lambda I}) \cdot \mathrm{EXP}[-(k_1 + k_2) \cdot t] \\ &\qquad \text{because of (4.101) and (4.105)} \\ &= k_1 \cdot c_{A0} \cdot V \cdot (-\Delta H_{\lambda I}) \cdot \mathrm{EXP}[-(k_1 + k_2) \cdot t] \\ &= q_{(A\rightarrow)0} \cdot \mathrm{EXP}[-(k_1 + k_2) \cdot t]. \end{aligned} \tag{4.106}$$

4.2.1.1.2.7.1.2 Case (B→)

Starting from B, i.e. $c_{A0} = 0$ and $c_{B0} \neq 0$, according to (4.99) we have

$$\theta(t = 0) = -c_{A\infty} = c_{B\infty} - c_{B0}, \tag{4.107}$$

and due to (4.104) we obtain

$$\begin{aligned} q_{(B\rightarrow)} &= -(k_1 + k_2) \cdot c_{A\infty} \cdot V \cdot (-\Delta H_{\lambda I}) \cdot \mathrm{EXP}[-(k_1 + k_2) \cdot t] \\ &= (k_1 + k_2) \cdot (c_{B\infty} - c_{B0}) \cdot V \cdot (-\Delta H_{\lambda I}) \cdot \mathrm{EXP}[-(k_1 + k_2) \cdot t] \\ &\qquad \text{because of (4.101) and (4.107)} \\ &= -k_2 \cdot c_{B0} \cdot V \cdot (-\Delta H_{\lambda I}) \cdot \mathrm{EXP}[-(k_1 + k_2) \cdot t] \\ &= q_{(B\rightarrow)0} \cdot \mathrm{EXP}[-(k_1 + k_2) \cdot t]. \end{aligned} \tag{4.108}$$

The plots of $\ln\left\{\left|q_{(A\rightarrow)}\right|\right\}$ and $\ln\left\{\left|q_{(B\rightarrow)}\right|\right\}$ versus time (Fig. 4.26) give in both cases a straight line with slope $\kappa = k_1 + k_2$.

We obtain k_1, k_2 and $(-\Delta H_{\lambda I}) = (-\Delta H_{\lambda II})$ as follows. According to (4.106) respectively (4.108), the thermal reaction power at the start of reactions q_0 is

$$q_{(A\rightarrow)0} = k_1 \cdot c_{A0} \cdot V(-\Delta H_{\lambda I}) \quad \text{respectively} \quad q_{(B\rightarrow)0} = -k_2 \cdot c_{B0} \cdot V \cdot (-\Delta H_{\lambda I}).$$

From κ and $q_{(A\rightarrow)0}$, $q_{(B\rightarrow)0}$ it follows that

$$\begin{gathered} k_2 = \kappa / \left[1 - c_{B0} \cdot q_{(A\rightarrow)0} / \left(c_{A0} \cdot q_{(B\rightarrow 0)}\right)\right], \\ k_1 = \kappa - k_2, \\ (-\Delta H_{\lambda I}) = -(-\Delta H_{\lambda II}) = q_{(A\rightarrow)0}/k_1/c_{A0} = -q_{(B\rightarrow)0}/k_2/c_{B0}. \end{gathered}$$

$(-\Delta H_{\lambda I})$ and $(-\Delta H_{\lambda II})$ result also from the amount of total released heat Q_∞, starting from A or B:

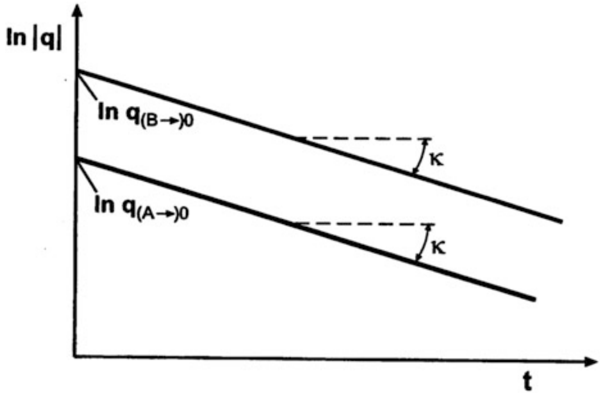

Fig. 4.26 Reversible reaction $\mathrm{A} \underset{r_{\mathrm{II}},\,\Delta H_{\lambda\mathrm{II}}}{\overset{r_I,\,\Delta H_{\lambda\mathrm{I}}}{\rightleftarrows}} \mathrm{B} \quad \begin{matrix}\mathrm{I} \\ \mathrm{II}\end{matrix};$

Isothermal, discontinuous, constant-volume reaction

$q_{(\mathrm{A}\rightarrow)} = q_{(\mathrm{A}\rightarrow)0} \cdot \mathrm{EXP}[-(k_1 + k_2) \cdot t]; q_{(\mathrm{B}\rightarrow)} = q_{(\mathrm{B}\rightarrow)0} \cdot \mathrm{EXP}[-(k_1 + k_2) \cdot t]$

- $$\begin{aligned} Q_{(\mathrm{A}\rightarrow)\infty} &= \int_{t=0\rightarrow\infty} q_{(\mathrm{A}\rightarrow)}\mathrm{d}t \\ &= \int_{t=0\rightarrow\infty} \{k_1 \cdot c_{\mathrm{A}0} \cdot V \cdot (-\Delta H_{\lambda\mathrm{I}}) \cdot \mathrm{EXP}[-(k_1 + k_2) \cdot t]\}\mathrm{d}t = k_1/\kappa \cdot c_{\mathrm{A}0} \cdot V \cdot (-\Delta H_{\lambda 1}) \end{aligned}$$

  and

- $$\begin{aligned} Q_{(\mathrm{B}\rightarrow)\infty} &= \int_{t=0\rightarrow\infty} q_{(\mathrm{B}\rightarrow)}\mathrm{d}t \\ &= \int_{t=0\rightarrow\infty} \{-k_2 \cdot c_{\mathrm{B}0} \cdot V \cdot (-\Delta H_{\lambda\mathrm{I}}) \cdot \mathrm{EXP}[-(k_1 + k_2) \cdot t]\}\mathrm{d}t = -k_2/\kappa \cdot c_{\mathrm{B}0} \cdot V \cdot (-\Delta H_{\lambda\mathrm{I}}), \end{aligned}$$

  hence

$$(-\Delta H_{\lambda\mathrm{I}}) = -(-\Delta H_{\lambda\mathrm{I}}) = Q_{(\mathrm{A}\rightarrow)\infty} \cdot \kappa/k_1 c_{\mathrm{A}0}/V = -Q_{(\mathrm{B}\rightarrow)\infty} \cdot \kappa/k_2/c_{\mathrm{B}0}/V.$$

4.2.1.1.2.7.2 The Rate Functions of a Forward Reaction of Order 1, Backward Reaction Is a Product of Two Partial Orders 1

Another simple reversible conversion occurs when three species in solution change into one another by two elementary reactions I and II:

$$\mathrm{A} \underset{r_{\mathrm{II}},\,\Delta H_{\lambda\mathrm{II}}}{\overset{r_{\mathrm{I}},\,\Delta H_{\lambda\mathrm{I}}}{\rightleftarrows}} \mathrm{B} + \mathrm{C} \quad \begin{matrix}\mathrm{I} \\ \mathrm{II}\end{matrix}$$

The stoichiometric coefficients $v_{(\mathrm{j,i})\xi}$ respectively the rate functions r_ξ

$$\begin{aligned} \nu_{\mathrm{AI}} &= -1, \nu_{\mathrm{BI}} = 1, \nu_{\mathrm{CI}} = 1; \quad & r_{\mathrm{I}} &= k_1 \cdot c_{\mathrm{A}}, \\ \nu_{\mathrm{AII}} &= 1, \nu_{\mathrm{BII}} = -1, \nu_{\mathrm{CII}} = -1; \quad & r_{\mathrm{II}} &= k_2 \cdot c_{\mathrm{B}} \cdot c_{\mathrm{C}}. \end{aligned}$$

According to (4.99) with $\theta_1 = \theta_{\mathrm{A}} = \theta$ the following expression is valid:

$$c_{\mathrm{A}} = c_{\mathrm{A}\infty} + \theta,\ c_{\mathrm{B}} = c_{\mathrm{B}\infty} - \theta \ \text{ and } \ c_{\mathrm{C}} = c_{\mathrm{C}\infty} - \theta. \tag{4.109}$$

The rate of change in A reads, due to (4.34),

$$\begin{aligned} \mathrm{d}c_{\mathrm{A}}/\mathrm{d}t &= \sum \nu_{\zeta\xi} \cdot r_{\xi} = -k_1 \cdot c_{\mathrm{A}} + k_2 \cdot c_{\mathrm{B}} \cdot c_{\mathrm{C}} \\ &= \mathrm{d}\theta/\mathrm{d}t = -k_1 \cdot (c_{\mathrm{A}\infty} + \theta) + k_2 \cdot (c_{\mathrm{B}\infty} - \theta) \cdot (c_{\mathrm{C}\infty} - \theta) \\ &= -k_1 \cdot c_{\mathrm{A}\infty} + k_2 \cdot c_{\mathrm{B}\infty} \cdot c_{\mathrm{C}\infty} - [k_1 + k_2 \cdot (c_{\mathrm{B}\infty} + c_{\mathrm{C}\infty})] \cdot \theta + k_2 \cdot \theta^2. \end{aligned}$$

In a state of equilibrium we have $\theta = 0$ and $\mathrm{d}\theta/\mathrm{d}t = 0$, hence

$$k_1 \cdot c_{\mathrm{A}\infty} = k_2 \cdot c_{\mathrm{B}\infty} \cdot c_{\mathrm{C}\infty}, \tag{4.110}$$

and therefore, with $\alpha = k_1 + k_2 \cdot (c_{\mathrm{B}\infty} + c_{\mathrm{C}\infty})$ and $\beta = k_2$,

$$\mathrm{d}\theta/\mathrm{d}t = -\alpha \cdot \theta + \beta \cdot \theta^2.$$

The solution of the equation reads[39]

$$\begin{aligned} \theta &= 1/\left\{\beta/\alpha + \left(1/\theta_{(t=0)} - \beta/\alpha\right) \cdot \mathrm{EXP}[\alpha \cdot t]\right\} \\ &= \alpha \cdot \theta_{(t=0)} \cdot \mathrm{EXP}[-\alpha \cdot t]/\left\{\alpha + \beta \cdot \theta_{(t=0)} \cdot \mathrm{EXP}[-\alpha \cdot t] - 1\right)\right\}. \end{aligned} \tag{4.111}$$

According to (4.7), the thermal reaction power becomes

---

[39] (a) Starting from A, so at $t = 0$ $c_{\mathrm{A0}} \neq 0$ and $c_{\mathrm{B0}} = c_{\mathrm{C0}} = 0$, we have $c_{\mathrm{B}\infty} = c_{\mathrm{C}\infty}$ and, due to (4.98), $\theta(t = 0) = c_{\mathrm{A0}} - c_{\mathrm{A}\infty} = c_{\mathrm{B}\infty} = c_{\mathrm{C}\infty}$. With that it follows from (4.109) and (4.111) that

$$\begin{aligned} c_{\mathrm{A}} &= c_{\mathrm{A}\infty} + (c_{\mathrm{A0}} - c_{\mathrm{A}\infty}) \cdot \alpha \cdot \mathrm{EXP}[-\alpha \cdot t]/\{\alpha + \beta \cdot (c_{\mathrm{A0}} - c_{\mathrm{A}\infty}) \cdot (\mathrm{EXP}[-\alpha \cdot t] - 1)\} \\ &= c_{\mathrm{A}\infty} + c_{\mathrm{B}\infty} \cdot \alpha \cdot \mathrm{EXP}[-\alpha \cdot t]/\left\{\alpha + \beta \cdot c_{\mathrm{B}\infty}\right) \cdot (\mathrm{EXP}[-\alpha \cdot t] - 1)\right\} \\ &= c_{\mathrm{A}\infty} + c_{\mathrm{C}\infty} \cdot \alpha \cdot \mathrm{EXP}[-\alpha \cdot t]/\left\{\alpha + \beta \cdot c_{\mathrm{C}\infty}\right) \cdot (\mathrm{EXP}[-\alpha \cdot t] - 1)\right\}. \end{aligned}$$

(b) Starting from B and C, so at $t = 0$ $c_{\mathrm{A0}} = 0$ and $c_{\mathrm{B0}} = c_{\mathrm{B0}} \neq 0$, we have $c_{\mathrm{B}\infty} = c_{\mathrm{C}\infty}$, and due to (4.98), $\theta(t = 0) = c_{\mathrm{B}\infty} - c_{\mathrm{B0}} = c_{\mathrm{C}\infty} - c_{\mathrm{C0}} = -c_{\mathrm{A}\infty}$. With that it follows from (4.109) and (4.111) that

$$\begin{aligned} c_{\mathrm{A}} &= c_{\mathrm{A}\infty} + (c_{\mathrm{B}\infty} - c_{\mathrm{B0}\infty}) \cdot \alpha \cdot \mathrm{EXP}[-\alpha \cdot t]/\{\alpha + \beta \cdot (c_{\mathrm{B}\infty} - c_{\mathrm{B0}}) \cdot (\mathrm{EXP}[-\alpha \cdot t] - 1)\} \\ &= c_{\mathrm{A}\infty} + (c_{\mathrm{C}\infty} - c_{\mathrm{C0}\infty}) \cdot \alpha \cdot \mathrm{EXP}[-\alpha \cdot t]/\left\{\alpha + \beta \cdot c_{\mathrm{C}\infty} - c_{\mathrm{C0}}\right) \cdot (\mathrm{EXP}[-\alpha \cdot t] - 1)\right\} \\ &= c_{\mathrm{A}\infty} - c_{\mathrm{A}\infty} \cdot \alpha \cdot \mathrm{EXP}[-\alpha \cdot t]/\left\{\alpha - \beta \cdot c_{\mathrm{A}\infty}\right) \cdot (\mathrm{EXP}[-\alpha \cdot t] - 1)\right\}. \end{aligned}$$

$$
\begin{aligned}
q &= \sum \left[r_\xi \cdot \left(-\Delta H_{\lambda\xi}\right)\right] \cdot V = \left[r_I \cdot \left(-\Delta H_{\lambda \mathrm{I}}\right) + r_{\mathrm{II}} \cdot \left(-\Delta H_{\lambda \mathrm{II}}\right)\right] \cdot V \\
&= \left[k_1 \cdot c_{\mathrm{A}} \cdot \left(-\Delta H_{\lambda \mathrm{I}}\right) + k_2 \cdot c_{\mathrm{B}} \cdot c_{\mathrm{B}} \cdot \left(-\Delta H_{\lambda \mathrm{II}}\right)\right] \cdot V \\
&\qquad \text{due to (4.109)} \\
&= \left[k_1 \cdot \left(c_{\mathrm{A}\infty} + \theta\right) \cdot \left(-\Delta H_{\lambda \mathrm{I}}\right) + k_2 \cdot \left(c_{\mathrm{B}\infty} - \theta\right) \cdot \left(c_{\mathrm{C}}\theta\right) \cdot \left(-\Delta H_{\lambda \mathrm{II}}\right)\right] \cdot V \\
&= \left[k_1 \cdot \left(c_{\mathrm{A}\infty} + \theta\right) \cdot \left(-\Delta H_{\lambda \mathrm{I}}\right) - k_2 \cdot \left(c_{\mathrm{B}\infty} - \theta\right) \cdot \left(c_{\mathrm{C}\infty} - \theta\right) \cdot \left(-\Delta H_{\lambda \mathrm{I}}\right)\right] \cdot V \\
&= \left[\left(k_1 \cdot c_{\mathrm{A}\infty} - k_2 \cdot c_{\mathrm{B}\infty} \cdot c_{\mathrm{C}\infty}\right) \cdot \left(-\Delta H_{\lambda \mathrm{I}}\right) + \left\{k_1 + k_2 \cdot \left(c_{\mathrm{B}\infty} + c_{\mathrm{C}\infty}\right) \cdot \theta + k_2 \cdot \theta^2\right\} \cdot \left(-\Delta H_{\lambda \mathrm{I}}\right)\right] \cdot V \\
&\qquad \text{due to (4.110)} \\
&= \left[\left\{k_1 + k_2 \cdot \left(c_{\mathrm{B}\infty} + c_{\mathrm{C}\infty}\right) \cdot \theta - k_2 \cdot \theta^2\right\} \cdot \left(-\Delta H_{\lambda \mathrm{I}}\right)\right] \cdot V, \\
&\qquad \text{with } \alpha = k_1 + k_2 \cdot \left(c_{\mathrm{B}\infty} + c_{\mathrm{C}\infty}\right) \text{ and } \beta = k_2 \qquad (4.112) \\
&= \left[\alpha \cdot \theta - \beta \cdot \theta^2\right\} \cdot \left(-\Delta H_{\lambda \mathrm{I}}\right)\Big] \cdot V \\
&\qquad \text{by means of (4.111),} \\
&= \alpha \cdot \left(-\Delta H_{\lambda \mathrm{I}}\right) \cdot V \cdot \left(1/\theta(t=0)\right) - \beta/\alpha\Big) \\
&\quad \cdot \mathrm{EXP}[\alpha \cdot t] / \left\{\beta/\alpha + \left(1/\theta(t=0) - \beta/\alpha\right) \cdot \mathrm{EXP}(\alpha \cdot t)\right\}^2.
\end{aligned}
\tag{4.113}
$$

For $t \gg 0$ we have $\beta/\alpha \ll (1/\theta(t=0) - \beta/\alpha) \cdot \mathrm{EXP}(\alpha \cdot t)$ and this yields

$$q(t \gg 0) = \alpha^2 \cdot \left(-\Delta H_{\lambda \mathrm{I}}\right) \cdot V \cdot \mathrm{EXP}[-\alpha \cdot t] / (\alpha/\theta(t=0) - \beta/\alpha). \tag{4.114}$$

Plotting the natural logarithm of the absolute amount of the thermal reaction power q versus time

- Starting from A: $\ln\left\{\left|q_{(\mathrm{A}\rightarrow)}\right|\right\}$
- Starting from B and C: $\ln\left\{\left|q_{(\mathrm{B}+\mathrm{C}\rightarrow)}\right|\right\}$

give curves which turn for times $t \gg 0$ into straight lines with the slope α

$$= k_1 + k_2 \cdot \left(c_{\mathrm{B}\infty} + c_{\mathrm{C}\infty}\right) \text{ (Fig. 4.27).}$$

4.2.1.1.2.7.2.1 Case (A→)

Starting from A, i.e. $c_{\mathrm{A}0} \neq 0$ and $c_{\mathrm{B}0} = c_{\mathrm{C}0} = 0$, the equation $c_{\mathrm{B}\infty} = c_{\mathrm{C}\infty}$ is valid, and according to (4.98),

$$\theta(t=0) = c_{\mathrm{A}0} - c_{\mathrm{A}\infty} = c_{\mathrm{B}\infty} = c_{\mathrm{C}\infty}. \tag{4.115}$$

Due to (4.112) it follows that

$$\alpha = k_1 + k_2 \cdot 2 \cdot c_{\mathrm{B}\infty} \text{ and } \beta = k_2. \tag{4.116}$$

The amount of heat released up to the achieved equilibrium is

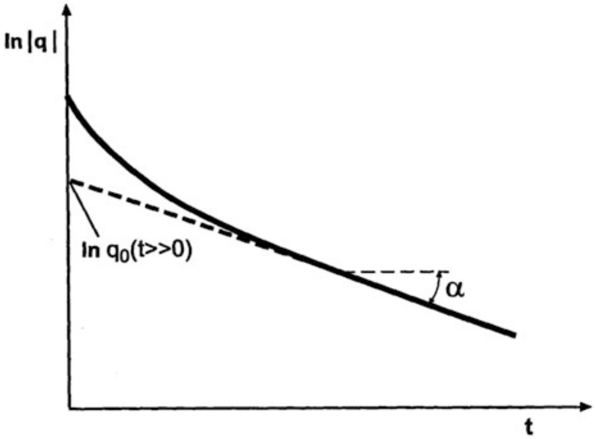

Fig. 4.27 Reversible reaction $\mathrm{A} \underset{r_{\mathrm{II}},\, \Delta H_{\lambda \mathrm{II}}}{\overset{r_I,\, \Delta H_{\lambda \mathrm{I}}}{\rightleftarrows}} \mathrm{B} + \mathrm{C} \quad \begin{matrix}\mathrm{I}\\ \mathrm{II}\end{matrix}$

$r_{\mathrm{I}} = k_1 \cdot c_{\mathrm{A}}, \quad r_{\mathrm{II}} = k_2 \cdot c_{\mathrm{B}} \cdot c_{\mathrm{C}}$

: isothermal, discontinuous, constant-volume reaction

$q = \alpha \cdot (-\Delta H_{\lambda \mathrm{I}}) \cdot V \cdot (1/\theta(t=0)) = \beta/\alpha) \cdot \mathrm{EXP}[\alpha \cdot t]/\{\beta/\alpha + (1/\theta(t=0) - \beta/\alpha) \cdot \mathrm{EXP}(\alpha \cdot t)\}^2$

$$Q_{(\mathrm{A}\to)\infty} = \int_{t=0\to\infty} q_{(\mathrm{A}\to)} \mathrm{d}t = V \cdot (-\Delta H_{\lambda \mathrm{I}}) \cdot \theta(t=0) = V \cdot (-\Delta H_{\lambda \mathrm{I}}) \cdot c_{\mathrm{B}\infty} \tag{4.117}$$

and the initial value of the thermal reaction power at $t=0$ according to (4.110), (4.113), (4.115), (4.116) and (4.117) is

$$q_{(\mathrm{A}\to)0} = (-\Delta H_{\lambda \mathrm{I}}) \cdot V \cdot k_1 \cdot c_{\mathrm{A}0} = Q_{(\mathrm{A}\to)\infty}/c_{\mathrm{B}\infty} \cdot k_1 \cdot c_{\mathrm{A}0}. \tag{4.118}$$

The rate coefficients k_1 and k_2 and the heats of reaction $(-\Delta H_{\lambda \mathrm{I}}) = -(-\Delta H_{\lambda \mathrm{II}})$ result from $q_{(\mathrm{A}\to)0}$, $Q_{(\mathrm{A}\to)\infty}$ and α as follows:
from (4.110), due to $c_{\mathrm{B}\infty} = c_{\mathrm{C}\infty}$ and $c_{\mathrm{A}0} - c_{\mathrm{A}\infty} = c_{\mathrm{B}\infty} = c_{\mathrm{C}\infty}$, we have

$$c_{\mathrm{B}\infty} = 0.5 \cdot \left[\sqrt{\left\{(k_1/k_2)^2 + 4 \cdot c_{\mathrm{A}0} \cdot k_1/k_2\right\}} - k_1/k_2\right];$$

combining with (4.116) gives as a result

$$k_2 = \left(\alpha^2 - k_1^2\right)/(4 \cdot c_{\mathrm{A}0} \cdot k_1); \tag{4.119}$$

from (4.116) and (4.118) it follows that

$$\alpha/k_1 = 1 + 2 \cdot Q_{(\mathrm{A}\to)\infty} \cdot k_2 \cdot c_{\mathrm{A}0}/q_{(\mathrm{A}\to)0}; \tag{4.120}$$

combining with (4.119) and (4.120) gives the rate coefficient k_1:

$$k_1 = q_{(\mathrm{A}\to)0}/Q_{(\mathrm{A}\to)\infty} - \sqrt{}\left\{\left(q_{(\mathrm{A}\to)0}/Q_{(\mathrm{A}\to)\infty}\right)^2 - 2 \cdot q_{(\mathrm{A}\to)0} \cdot \alpha/Q_{(\mathrm{A}\to)\infty} + \alpha^2\right\};$$

due to (4.117) the heat of the reaction is determined by

$$\begin{aligned}(-\Delta H_{\lambda\mathrm{I}}) &= Q_{(\mathrm{A}\to)\infty}/V/c_{\mathrm{B}\infty}\\ &\quad\text{combined with (4.120)}\\ &= Q_{(\mathrm{A}\to)\infty}/V \cdot 2/\left(\sqrt{\left\{(k_1/k_2)^2 + 4 \cdot c_{\mathrm{A}0} \cdot k_1/k_2\right\}} - k_1/k_2\right).\end{aligned}$$

4.2.1.1.2.7.2.2 Case (B+C→)

a) Starting from B and C with $c_{\mathrm{A}0} = 0$ and $c_{\mathrm{B}0} = c_{\mathrm{C}0}$ at $t = 0$ we have $c_{\mathrm{B}\infty} = c_{\mathrm{C}\infty}$, and according to (4.98),

$$\theta(t = 0) = c_{\mathrm{B}\infty} - c_{\mathrm{B}0} = c_{\mathrm{C}\infty} - c_{\mathrm{C}0} = -c_{\mathrm{A}\infty}. \tag{4.121}$$

Corresponding to (4.112) we have

$$\alpha = k_1 + k_2 \cdot 2 \cdot c_{\mathrm{B}\infty} \ \text{ and } \ \beta = k_2. \tag{4.116}$$

The amount of released heat in the time up to the establishment of equilibrium is

$$Q_{(\mathrm{B+C}\to)\infty} = \int_{t=0\to\infty} q_{(\mathrm{B+C}\to)}\mathrm{d}t = V \cdot (-\Delta H_{\lambda\mathrm{I}}) \cdot \theta(t = 0) = -V \cdot (-\Delta H_{\lambda\mathrm{I}}) \cdot C_{\mathrm{A}\infty} \tag{4.122}$$

and the initial thermal reaction power at $t = 0$ according to (4.110), (4.113), (4.116), (4.121) and (4.122) is

$$q_{(\mathrm{B+C}\to)0} = -(-\Delta H_{\lambda\mathrm{I}}) \cdot V \cdot k_2 {c_{\mathrm{B}0}}^2 - Q_{(\mathrm{B+C}\to)\infty}/c_{\mathrm{A}\infty} \cdot k_2 \cdot {c_{\mathrm{B}0}}^2. \tag{4.123}$$

The rate coefficients k_1 and k_2 and the heat of reaction $(-\Delta H_{\lambda\mathrm{I}}) = -(-\Delta H_{\lambda\mathrm{II}})$ result from $q_{(\mathrm{B+C}\to)0}$, $Q_{(\mathrm{B+C}\to)\infty}$ and α as follows:

The combination of (4.110), (4.120), (4.121), (4.122), and (4.123) leads to

$$H \cdot {k_1}^4 - M \cdot {k_1}^3 - N \cdot {k_1}^2 - O \cdot k_1 + p = 0$$

with

$$\begin{aligned}
&H = Q_{(\mathrm{B+C}\rightarrow)\infty},\\
&M = 4 \cdot q_{(\mathrm{B+C}\rightarrow)0},\\
&N = 2 \cdot Q_{(\mathrm{B+C}\rightarrow)\infty} \cdot \alpha^2 - 8 \cdot q_{(\mathrm{B+C}\rightarrow)0} \cdot \alpha,\\
&O = 4 \cdot q_{(\mathrm{B+C}\rightarrow)0} \cdot \alpha^2,\\
&P = Q_{(\mathrm{B+C}\rightarrow)\infty} \cdot \alpha^4;
\end{aligned}$$

k_1 results according to the method of zero position[40];
the combination of (4.110) and (4.116) gives

$$k_2 = \left(\alpha^2 - {k_1}^2\right)/(4 \cdot c_{\mathrm{A}0} \cdot k_1);$$

the heat of the reaction follows by means of (4.110), (4.121) and (4.122):

$$\begin{aligned}
&(-\Delta H_{\lambda \mathrm{I}}) = -(-\Delta H_{\lambda \mathrm{II}}) = Q_{(\mathrm{B+C}\rightarrow)\infty}/V/(c_{\mathrm{B}\infty} - c_{\mathrm{B}0})\\
&= Q_{(\mathrm{B+C}\rightarrow)\infty}/V/\left\{0.5 \cdot \left[\sqrt{\left\{(k_1/k_2)^2 + 4 \cdot c_{\mathrm{B}0} k_1/k_2\right\}} - k_1/k_2\right] - c_{\mathrm{B}0}\right\}.
\end{aligned}$$

b) Starting from B and C with $c_{\mathrm{A}0} = 0$, but $c_{\mathrm{B}0} \neq c_{\mathrm{C}0}$ at $t = 0$ we have

$$c_{\mathrm{B}\infty} \neq c_{\mathrm{C}\infty},$$

and according to (4.98),

$$\theta(t = 0) = c_{\mathrm{B}\infty} - c_{\mathrm{B}0} = c_{\mathrm{C}\infty} - c_{\mathrm{C}0} = -c_{\mathrm{A}\infty}. \tag{4.124}$$

Because of (4.112) and (4.123) we have

$$\alpha = k_1 + k_2 \cdot (c_{\mathrm{B}\infty} + c_{\mathrm{C}\infty}) = k_1 + k_2 \cdot (2 \cdot c_{\mathrm{B}\infty} + c_{\mathrm{C}0} - c_{\mathrm{B}0}) \text{ and } \beta = k_2. \tag{4.125}$$

The amount of heat released in the time up to achieving equilibrium is

$$Q_{(\mathrm{B+C}\rightarrow)\infty} = , \int q_{(\mathrm{B+C}\rightarrow)} \cdot \mathrm{d}t = V \cdot (-\Delta H_{\lambda \mathrm{I}}) \cdot \theta_{(t=0)} = -V \cdot (-\Delta H_{\lambda \mathrm{I}}) \cdot c_{\mathrm{A}\infty} \tag{4.126}$$

and the initial value of the thermal reaction power at $t = 0$ is, according to (4.110), (4.113), (4.116), (4.121), and (4.122),

$$q_{(\mathrm{B+C}\rightarrow)0} = -(-\Delta H_{\lambda \mathrm{I}}) \cdot V \cdot k_2 \cdot c_{\mathrm{B}0} \cdot c_{\mathrm{C}0} = Q_{(\mathrm{B+C}\rightarrow)\infty}/c_{\mathrm{A}\infty} \cdot k_2 \cdot c_{\mathrm{B}0} \cdot c_{\mathrm{C}0}. \tag{4.127}$$

The rate coefficients k_1 and k_2 and the heat of the reaction $(-\Delta H_{\lambda \mathrm{I}}) = -(-\Delta H_{\lambda \mathrm{II}})$ result from $q_{(\mathrm{B+C}\rightarrow)0}, Q_{(\mathrm{B+C}\rightarrow)\infty}$ and α as follows:
Combining (4.110) and (4.124) gives as result

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[40] By the use of the conventional methods of literature.

$$c_{\mathrm{B}\infty} = 0.5 \cdot \left\{ \sqrt{\left[(k_1/k_2 + c_{\mathrm{C}0} - c_{\mathrm{B}0})^2 + 4 \cdot k_1/k_2 \cdot c_{\mathrm{B}0} \right]} - k_1/k_2 - c_{\mathrm{C}0} + c_{\mathrm{B}0} \right\}. \tag{4.128}$$

Combining (4.125) and (4.128) yields for the slope α of the straight line of ln $q(t \gg 0)$, Fig. 4.21,

$$\alpha = \sqrt{\left[\{k_1 + k_2 \cdot (c_{\mathrm{C}0} - c_{\mathrm{B}0})\}^2 + 4 \cdot k_1 \cdot k_2 \cdot c_{\mathrm{B}0} \right]}$$

By rearrangement we oftain k_2 as a function $\boldsymbol{f_1}$ of α and k_1

$$k_2 = -0.5/O \cdot \left(P - \sqrt{\left[P^2 - 4 \cdot O \cdot N \right]} \right) = f_1\{\alpha, k_1\} \tag{4.129}$$

with

$$N = k_1^2 - \alpha^2,$$
$$P = 2 \cdot k_1 \cdot (c_{\mathrm{C}0} + c_{\mathrm{B}0}),$$
$$O = (c_{\mathrm{C}0} + c_{\mathrm{B}0})^2.$$

Substituting (4.129) into (4.128) yields $c_{\mathrm{B}\infty}$ as a function $\boldsymbol{f_2}$ of α and k_1:

$$c_{\mathrm{B}\infty} = \boldsymbol{f_2}\{\alpha, k_1\}. \tag{4.130}$$

From the combination of (4.127), (4.121) and (4.130) it follows that

$$0 = q_{(\mathrm{B+C}\rightarrow)0} - Q_{(\mathrm{B+C}\rightarrow)\infty} \cdot c_{\mathrm{B}0} \cdot c_{\mathrm{C}0} \cdot \boldsymbol{f_1}\{\alpha, k_1\}/(c_{\mathrm{B}0} - f_2\{\alpha, k_1\}). \tag{4.131}$$

Due to (4.131) we get k_1 according to the method of zero position, and k_2 can now be deduced from (4.129) respectively (4.125).

The combination of (4.124), (4.127) and (4.128) gives the heat of the reaction

$$\begin{aligned}(-\Delta H_{\lambda\mathrm{II}}) &= -(-\Delta H_{\lambda\mathrm{I}}) = -Q_{(\mathrm{B+C}\rightarrow)\infty}/V/c_{A\infty} = Q_{(\mathrm{B+C}\rightarrow)\infty}/V/(c_{\mathrm{B}\infty} - c_{\mathrm{B}0}) \\ &= Q_{(\mathrm{B+C}\rightarrow)\infty}/V/\Big(0.5 \cdot \Big\{ \sqrt{\left[k_1/k_2 + c_{\mathrm{C}0} - c_{\mathrm{B}0})^2 + 4 \cdot k_1/k_2 \cdot c_{\mathrm{B}0} \right]} \\ &\qquad -k_1/k_2 - c_{\mathrm{C}0} + c_{\mathrm{B}0} \Big\} - c_{\mathrm{B}0} \Big).\end{aligned}$$

4.2.1.2 Variable-Volume Reaction

The chemical conversion in a liquid reaction mixture can occasionally be accompanied by an evident change in volume, for instance using more or less diluted liquid reactants. This case represents (4.11), the correlation of the rate of reaction, the rate of change in concentration and the rate of change in volume

$$\nu_j \cdot r = dN_j/dt/V = dc_j/dt + c_j \cdot dV/dt/V. \qquad (4.132)$$

The change in volume of the reaction mixture as a consequence of chemical conversion is very complex. For simple conversions which do not run via consecutive reactions, in practise it is assumed in a first approximation that the reaction volume changes linearly to the fractional conversion[41] X of the component j dominating the reaction,[42]

$$V = V_0 \cdot (1 + \upsilon \cdot X) = V_0 \cdot \left(1 + \upsilon \cdot \left(N_{j0} - N_j\right)/N_{j0}\right), \qquad (4.133)$$

in which υ is the relative change in volume between the initial volume V_0 and the final volume $V_{X=1}$ with the complete conversion of the dominating component j:

$$\upsilon = (V_{X=1} - V_0)/V_0.$$

By differentiation of (4.133) there arises

$$(dV/dt)/V = \left(-\upsilon/c_{j0}/dN_j/dt\right)/V.$$

Combining this with (4.132) yields

$$dc_j/dt = \nu_j \cdot r + \nu_j \cdot \upsilon \cdot c_j/c_{j0} \cdot r = r \cdot \nu_j \cdot \left(1 + \upsilon \cdot c_j/c_{j0}\right). \qquad (4.134)$$

4.2.1.2.1 System of Reactions Kinetically Characterized by a Single Rate Function

4.2.1.2.1.1 Rate Function of Order 0

A reaction with a rate function of order 0, $r = k$, (4.134) leads to

$$\begin{aligned} dc_j/dt &= \nu_j \cdot r \cdot \left(1 + \upsilon \cdot c_j/c_{j0}\right) \\ &= \nu_j \cdot k \cdot \left(1 + \upsilon \cdot c_j/c_{j0}\right) \\ &= \nu_j \cdot k + \nu_j \cdot k \cdot \upsilon/c_{j0} \cdot c_j. \end{aligned}$$

The solution of the equation is[43]

$$c_j = \left[c_{j0} + c_{j0}/\upsilon\right] \cdot \mathrm{EXP}\left(\nu_j \cdot k \cdot \upsilon/c_{j0} \cdot t\right) - c_{j0}/\upsilon. \qquad (4.135)$$

In contrast to a constant-volume reaction, the concentration changes not linearly

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[41] Henceforth called simply conversion.

[42] For parallel and simultaneous reactions the single changes in volume must be added.

[43] The description of $\mathrm{EXP}\left[-\nu_j \cdot k \cdot \upsilon/c_{j0} \cdot t\right]$ by series gives for the limiting case $\upsilon \rightarrow 0$, Eq. (4.15).

but exponentially and the reaction is finished at the point in time $t_{\mathrm{E}} = -c_{\mathrm{j}0}/\nu_{\mathrm{j}}/k/\upsilon \cdot \ln(\upsilon + 1)$.[44] The combination of (4.133) and (4.135) gives as result the temporal course of the volume:

$$V = V_0 \cdot \mathrm{EXP}\left(-\nu_{\mathrm{j}} \cdot k \cdot \upsilon / c_{\mathrm{j}0} \cdot t\right)$$

and the temporal course of the thermal reaction power[45]

$$q = r \cdot (-\Delta H_\lambda) \cdot V = k \cdot (-\Delta H_\lambda) \cdot V_0 \cdot \mathrm{EXP}\left(-\nu_{\mathrm{j}} \cdot k \cdot \upsilon / c_{\mathrm{j}0} \cdot t\right). \qquad (4.136)$$

The calculated thermal reaction power of a variable-volume reaction of order 0 does not remain constant, in contrast to the constant-volume reaction of order 0, but changes exponentially. This results from the assumption that not the entire reaction rate $r_{\mathrm{entire}} = \mathrm{d}\lambda/\mathrm{d}t$ but the specific one $r_{\mathrm{specific}} = r_{\mathrm{entire}}/V = \mathrm{d}\lambda/\mathrm{d}t/V = r$ is constant over time.

4.2.1.2.1.2 Rate Function of Order 1

For a chemical conversion with a rate function of order 1, in accordance with (4.134), the following equation is valid:

$$\begin{aligned} \mathrm{d}c_{\mathrm{j}}/\mathrm{d}t &= \nu_{\mathrm{j}} \cdot r \cdot \left(1 + \upsilon \cdot c_{\mathrm{j}}/c_{\mathrm{j}0}\right) \\ &= \nu_{\mathrm{j}} \cdot k \cdot c_{\mathrm{j}} \cdot \left(1 + \upsilon \cdot c_{\mathrm{j}}/c_{\mathrm{j}0}\right) \\ &= \nu_{\mathrm{j}} \cdot k \cdot c_{\mathrm{j}} + \nu_{\mathrm{j}} \cdot k \cdot \upsilon / c_{\mathrm{j}0} \cdot {c_{\mathrm{j}}}^2. \end{aligned}$$

The solution of the equation reads[46]

$$c_{\mathrm{j}} = c_{\mathrm{j}0} \cdot \mathrm{EXP}\left(\nu_{\mathrm{j}} \cdot k \cdot t\right) / \left\{1 + \upsilon \cdot \left[1 - \mathrm{EXP}\left(\nu_{\mathrm{j}} \cdot k \cdot t\right)\right]\right\}.$$

Combining this with (4.133) gives the temporal change in the volume of the reaction mixture

$$V = V_0 \cdot \left\{1 + \upsilon \cdot \left[1 - \mathrm{EXP}\left(\nu_{\mathrm{j}} \cdot k \cdot t\right)\right]\right\}.$$

The temporal course of the thermal reaction power reads

$$q = r \cdot (-\Delta H_\lambda) \cdot V = k \cdot c_{\mathrm{j}} \cdot (-\Delta H_\lambda) \cdot V = k \cdot (-\Delta H_\lambda) \cdot c_{\mathrm{j}0} \cdot V_0 \cdot \mathrm{EXP}\left(\nu_{\mathrm{j}} \cdot k \cdot t\right).$$

A comparison of the results for a constant-volume conversion with variable-volume conversion, both with rate of order 1, shows

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[44] The description of $\ln[\upsilon + 1]$ by series gives for the limiting case $\upsilon \to 0$, Eq. (4.16).

[45] The description by series gives for the limiting case $\upsilon \to 0$, Eq. (4.14).

[46] The description by series gives for the limiting case $\upsilon \to 0$, Eq. (4.20).

- The temporal courses of the thermal reaction powers are equal [for assumption (4.133)],
- The temporal courses of the concentrations differ from each other:

$$\begin{aligned} c(t)_{V=\mathrm{const}} &> c(t)_{V\neq\mathrm{const}} \quad for\ \ \upsilon > 0, \\ c(t)_{V=\mathrm{const}} &< c(t)_{V\neq\mathrm{const}} \quad for\ \ \upsilon < 0. \end{aligned}$$

4.2.1.2.1.3 Rate Function of Order n

For a chemical process with a rate function of order $n(n > 0; \neq 1)$ we have, according to (4.133),

$$\begin{aligned} \mathrm{d}c_{\mathrm{j}}/\mathrm{d}t &= v_{\mathrm{j}} \cdot r \\ &= v_{\mathrm{j}} \cdot k \cdot c_{\mathrm{j}}{}^{n} \cdot \left(1 + \upsilon \cdot c_{\mathrm{j}} \cdot /c_{\mathrm{j}0}\right) \\ &= v_{j} \cdot k \cdot c_{\mathrm{j}}{}^{n} + v_{\mathrm{j}} \cdot k \cdot \upsilon/c_{\mathrm{j}0} \cdot c_{\mathrm{j}}{}^{n+1}. \end{aligned}$$

A solution of the equation in the explicit form $c_{\mathrm{j}} = f(t)$ does not exist and, therefore, no function $V = g(t)$ respectively $q = h(t)$.

4.2.2 Isothermal, Continuous Reaction

In contrast to the discontinuous run of a chemical conversion which gives for a quantity[47] a series of values over time, a continuous run gives only one value of the quantity. This raises the question of why a kinetic investigation should be conducted by the continuous run of a reaction. Experience has shown that

- The kinetics of certain reactions, especially copolymerization, is primarily worked out on the basis of continuous runs.
- The kinetics discovered by discontinuous runs can be examined with respect to correctness.
- Only in this way can principally exact enthalpies of reaction be determined.

In industrial practise, reaction kinetics are often elaborated on the basis of stereotypically planned, discontinuous runs. Therefore, results with respect to kinetics should be examined by means of experiments under changed operating conditions. Only in this way is it possible to detect whether the used simplifications are defensible or whether the discovered mechanism and the elicited rate function must be corrected.

One possibility proposes a isothermal, calorimetric investigation of continuous runs, in which the measuring kettle of the calorimeter functions as a totally mixed throughput reactor[48]: the inlet stream in the measuring kettle is nearly instantaneously mixed by a quickly agitating mixer. There are differences in either

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[47] Or several different quantities, for instance concentration, pressure or electric conductivity etc.

[48] See Sect. 2.2.1.

concentration temperature; the contents are completely mixed. Thus, the exit stream out of the measuring kettle has the same composition as the reaction mass within the kettle.[49] Because the composition is uniform at any moment in time, the balance concerns the total volume V of the measuring kettle.

The stoichiometry and the reaction rates of a system of reactions commonly reads as follows:

$$\begin{array}{rlll}
\ldots + \ldots + \ldots & + \ldots \rightarrow \ldots + \ldots & + \ldots + \ldots, & \\
v_{1,\xi-1} + \ldots + \ldots v_{\mathrm{j},\xi-1} \ldots & + \ldots \rightarrow \ldots + v_{\mathrm{i},\xi-1} & + \ldots + \ldots, & r_{\xi-1} \\
v_{1,\xi} + \ldots + \ldots v_{\mathrm{j},\xi} \ldots & + \ldots \rightarrow \ldots + v_{\mathrm{i},\xi} & + \ldots + \ldots, & r_{\xi} \\
v_{1,\xi+1} + \ldots + \ldots v_{\mathrm{j},\xi+1} \ldots & + \ldots \rightarrow \ldots + v_{\mathrm{i},\xi+1} & + \ldots + \ldots, & r_{\xi+1} \\
\ldots + \ldots + \ldots & + \ldots \rightarrow \ldots + & + \ldots + \ldots, &
\end{array}$$

The material balance for components i and j of the reaction mass reads

$$V \cdot \mathrm{d}c_{\mathrm{j,i}}/\mathrm{d}t = \mathrm{v}_{\mathrm{in}} \cdot c_{(\mathrm{j,i})0} - \mathrm{v}_{\mathrm{out}} \cdot c_{\mathrm{j,i}} + V \cdot \sum\nolimits_{\xi} \left(v_{(\mathrm{j,i})\xi} \cdot r_{\xi}\right),$$

with

• v_{in} respectively $\mathrm{v}_{\mathrm{out}}$	volumetric inflow respectively outflow of measuring kettle
• $c_{(\mathrm{j,i})\mathrm{o}}$ respectively $c_{\mathrm{j,i}}$	concentrations of reactants j and products i of inflow respectively within measuring kettle
• c_{l0} respectively c_1	concentration of component j = 1 of inflow respectively within measuring kettle
• $X_1 = (\mathrm{v}_{\mathrm{in}} \cdot c_{10} - \mathrm{v}_{\mathrm{out}} \cdot c_1)/(\mathrm{v}_{\mathrm{in}} \cdot c_{10})$	fractional conversion of component j = 1 of inflow respectively within measuring kettle
• λ_{ξ}	number of formula conversions, reaction ξ
• $\Delta H_{\lambda\xi}$	enthalpy of reaction ξ
• V	volume of measuring kettle
• $r_{\xi} = \mathrm{d}\lambda_{\xi}/\mathrm{d}t/V = \mathrm{d}N_{(\mathrm{j,i})\xi}/\mathrm{d}t/v_{(\mathrm{j,i})\xi}/V = \mathrm{d}c_{(\mathrm{j,i})\xi}/\mathrm{d}t/v_{(\mathrm{j,i})\xi}$	rate of reaction ξ

In steady state $\left(\mathrm{d}c_{\mathrm{j,i}}/\mathrm{d}t = 0\right)$ the fractional conversion of reaction component 1 is

$$X_1 = -V \cdot \sum\nolimits_{\xi} \left(v_{1\xi} \cdot r_{\xi}\right)/(\mathrm{v}_{\mathrm{in}} \cdot c_{10}). \tag{4.137}$$

For the thermal reaction power the following equation is valid according to (4.7):

---

[49] There is no connection between a continuously and a discontinuously operating calorimeter unless it is considered as representing the facts of a certain moment in time in a discontinuously operating calorimeter.

$$q = \left[\sum\nolimits_{\xi} r_{\xi} \cdot \left(-\Delta H_{\lambda\xi}\right)\right] \cdot V. \tag{4.138}$$

4.2.2.1 Constant-Volume Reaction

In what follows constant-volume reactions are assumed, i.e. $\mathrm{v}_{\mathrm{in}} = \mathrm{v}_{\mathrm{out}} = \mathrm{v}$.

4.2.2.1.1 System of Reactions Kinetically Characterized by a Single Rate Function

4.2.2.1.1.1 Rate Function of Order n

The rate of a chemical process with the stoichiometry $v_1 \ldots + v_{\mathrm{j}-1} + v_{\mathrm{j}} + \ldots \to \ldots + v_{\mathrm{i}-1} + v_{\mathrm{i}} + \ldots$ is a power function of the concentration of reactant 1:

$$r = k \cdot {c_1}^n.$$

From (4.138) and (4.137) it follows that

$$r = q/[V \cdot (-\Delta H_{\lambda})] \tag{4.139}$$

and

$$\begin{aligned} X_1 &= -V \cdot v_1 \cdot r/[\mathrm{v} \cdot c_{10}] \\ &\quad \text{with}\,(4.139) \\ &= -v_1 \cdot q/[\mathrm{v} \cdot c_{10} \cdot (-\Delta H_{\lambda})]. \end{aligned} \tag{4.140}$$

The rate function $r = k \cdot {c_1}^n$ can be transformed into a function based on the conversion X_1 [22]

$$r = k \cdot {c_1}^n = k \cdot {c_{10}}^n \cdot [1 - X_1]^n.$$

From that we obtain, using (4.139) and (4.140),

$$q/[V \cdot (-\Delta H_{\lambda})] = k \cdot {c_{10}}^n \cdot [1 + v_1 \cdot q/\{\mathrm{v} \cdot c_{10} \cdot (-\Delta H_{\lambda})\}]^n.$$

Taking logarithms gives as a result

$$\begin{aligned} \log\{q/(V \cdot (-\Delta H_{\lambda}))\} = \log\{k \cdot {c_{l0}}^n\} + n \\ \cdot \log\{1 + v_1 \cdot q/[\mathrm{v} \cdot c_{10} \cdot (-\Delta H_{\lambda})]\}. \end{aligned} \tag{4.141}$$

Equation (4.140) of the heat of reaction $(-\Delta H_{\lambda})$ for the continuous run of the reaction gives, by means of the fractional conversion X_1 and the thermal reaction power q,

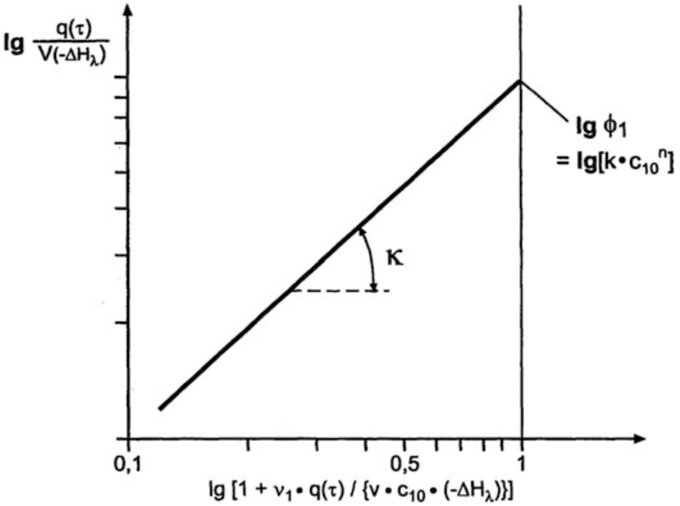

Fig. 4.28 Isothermal, continuous, constant-volume reaction: stoichiometry $v_1 + \ldots + v_{j-1} + v_j + \ldots \rightarrow \ldots + v_{i-1} + v_i + \ldots$; rate function $r = k \cdot c_1{}^{\mathrm{n}}$

$$-\Delta H_\lambda = -v_1 \cdot q / [\mathrm{v} \cdot c_{10} \cdot X_1].$$

Plotting $\log\{q(\tau)/[V \cdot (-\Delta H_\lambda)]\}$ versus $\log\{[1 + v_1 \cdot q(\tau)/\{\mathrm{v} \cdot c_{10} \cdot (-\Delta H_\lambda)\}]\}$ on the basis of measured results $q(\tau)$ by different residence times $\tau = V/\mathrm{v}$, i.e. different v but unchanged inlet concentration $c_{1\mathrm{o}}$ (Fig. 4.28) gives, due to (4.141), a straight line. Its slope κ corresponds to the order n of the reaction rate. The point of the interception with the ordinate $\log\{\Phi_1\}$ at the abscissa value 1 corresponds to log $\{k \cdot c_{10}{}^n\}$. The result is

$$n = \kappa$$
$$k = \Phi_1 / c_{10}{}^n.$$

4.2.2.1.1.2 *Rate Function: Product of Partial Orders* n *and* m

The rate function is the product of concentrations of reactants 1 and j with powers n and m:

$$r = k \cdot c_1{}^n \cdot c_j{}^m.$$

Because of the stoichiometric relation $(c_1 - c_{10})/v_1 = \left(c_\mathrm{j} - c_{\mathrm{j}0}\right)/v_\mathrm{j}$ in combination with the fractional conversion X_1 it follows that

$$r = k \cdot c_{10}{}^n \cdot c_{\mathrm{j}0}{}^m \cdot (1 - X_1)^n \cdot \left(1 - X_1 \cdot c_{10} \cdot v_\mathrm{j}/c_{\mathrm{j}0}/v_1\right)^m. \tag{4.142}$$

Using (4.139) and (4.140) we obtain

$$
\begin{aligned}
q/[V\cdot(-\Delta H_\lambda)] &= k\cdot c_{10}{}^{n}\cdot c_{j0}{}^{m}\cdot[1+v_1\cdot q/\{\mathrm{v}\cdot c_{10}\cdot(-\Delta H_\lambda)\}]^{n}\\
&\quad\cdot\left[1+v_1\cdot q/\{\mathrm{v}\cdot c_{10}\cdot(-\Delta H_\lambda)\}\cdot c_{10}\cdot v_{\mathrm{j}}/c_{\mathrm{j}0}/v_1\right]^{m}\\
&= k\cdot c_{10}{}^{n}\cdot c_{\mathrm{j}0}{}^{m}\cdot[1+v_1\cdot q/\{\mathrm{v}\cdot c_{10}\cdot(-\Delta H_\lambda)\}]^{n}\cdot\left[1+v_{\mathrm{j}}\cdot q/\left\{\mathrm{v}\cdot c_{\mathrm{j}0}\cdot(-\Delta H_\lambda)\right\}\right]^{m}.
\end{aligned}
$$

Taking logarithms gives

$$
\begin{aligned}
\log\{q/[V\cdot(-\Delta H_\lambda)]\} = \log\left\{k\cdot c_{10}{}^{n}\cdot c_{\mathrm{j}0}{}^{m}\right\}+&\\
n\cdot\log\{1+v_1\cdot q/[\mathrm{v}\cdot c_{10}\cdot(-\Delta H_\lambda)]\}+&\\
m\cdot\log\left\{1+v_{\mathrm{j}}\cdot q/\left[\mathrm{v}\cdot c_{\mathrm{j}0}\cdot(-\Delta H_\lambda)\right]\right\}.&
\end{aligned}
$$

To determine the partial order n, measurements with $c_{\mathrm{j}0}\gg c_{10}$ are carried out so that the last term compared with the next to last can be neglected. Plotting $q(\tau)/[V\cdot(-\Delta H_\lambda)]$ from measurements with different residence times $\tau=V/\mathrm{v}$ as well as unchanged inlet concentrations c_{10} and $c_{\mathrm{j}0}$ versus $[1+v_1\cdot q(\tau)/\{\mathrm{v}\cdot c_{10}\cdot(-\Delta H_\lambda)\}]$ (Fig. 4.29a) yields a straight line. Its slope κ_{n} gives the order n of the reaction rate regarding c_1:

$$n=\kappa_{\mathrm{n}}.$$

The heat of the reaction is known by means of the fractional conversion and the thermal reaction power according to (4.139):

$$-\Delta H_\lambda=-v_1\cdot q/[\mathrm{v}\cdot c_{10}\cdot X_1].$$

To determine the partial order m of the rate on the basis of now known partial order n, (4.142) is rearranged with the result that

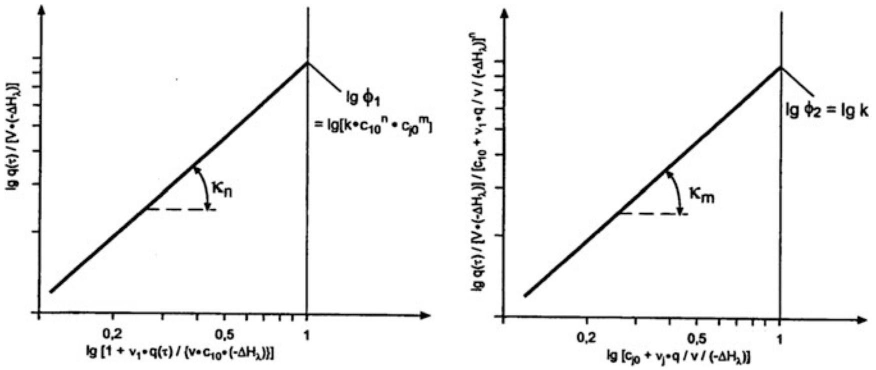

Fig. 4.29 Isothermal, continuous, constant-volume reaction: stoichiometry $v_1+\ldots+v_{\mathrm{j}-1}+v_{\mathrm{j}}+\ldots\rightarrow\ldots+v_{\mathrm{i}-1}+v_{\mathrm{i}}+\ldots$; rate function $r=k\cdot c_1{}^{\mathrm{n}}\cdot c_{\mathrm{j}}{}^{\mathrm{m}}$

$$r = k \cdot {c_{10}}^n \cdot (1 - X_1)^n \cdot \left(c_{\mathrm{j}0} - X_1 \cdot c_{10} \cdot v_{\mathrm{j}}/v_1\right)^m.$$

This gives

$$r/[c_{10} \cdot (1 - X_1)]^n = k \cdot \left[c_{\mathrm{j}0} - X_1 \cdot c_{10} \cdot v_{\mathrm{j}}/v_1\right]^m.$$

By means of (4.139) and (4.140) it follows that

$$q/[V \cdot (-\Delta H_\lambda)]/[c_{10} + v_1 \cdot q/\mathrm{v}/(-\Delta H_\lambda)]^n = k \cdot \left[c_{\mathrm{j}\,0} + v_{\mathrm{j}} \cdot q/\mathrm{v}/(-\Delta H_\lambda)\right]^m$$

or

$$\begin{aligned} &\log\{q/[V \cdot (-\Delta H_\lambda)]/c_{10} + v_1 \cdot q/\mathrm{v}/(-\Delta H_\lambda)^n\} \\ &\quad = \log\{k\} + m \cdot \log\left\{c_{\mathrm{j}\,0} + v_{\mathrm{j}} \cdot q/\mathrm{v}/(-\Delta H_\lambda)\right\}. \end{aligned}$$

To determine both the power m and the rate coefficient k, measurements with different residence times $\tau = V/\mathrm{v}$ must be carried out. Plotting log $\left\{q/[V \cdot (-\Delta H_\lambda)]\right.$ / $\left.\left[c_{10} + v_1 \cdot q/\mathrm{v}/(-\Delta H_\lambda)^n\right\}$ versus $\log\left\{\left[c_{\mathrm{j}0} + v_{\mathrm{j}} \cdot q(\tau)/\mathrm{v}/(-\Delta H_\lambda)\right]\right\}$ (Fig. 4.29b) gives a straight line. Its slope κ_{m} corresponds to the order m of the rate with respect to c_{j}, the ordinate value $\log\{\Phi_2\}$ at the abscissa value 1 corresponds to $\log\{k\}$. Therefore, we have

$$m = \kappa_{\mathrm{m}},$$
$$k = \Phi_2.$$

4.2.3 Non-isothermal, Discontinuous Reaction

Calorimetric investigations under non-isothermal conditions are usually carried out using a discontinuous measurement method. Such a method is concerned with

- Induced changes in temperature within the thermally open measuring kettle,
- Changes in temperature caused by the reaction itself within the measuring kettle opaque to heat,
- Changes in temperature caused by a reaction within a thermally open measuring kettle.

For the kinetic analysis of the thermal reaction power q of a reaction running under non-isothermal conditions, the following condition can be used as a base:

- The rate function r of a reaction under isothermal condition (4.1) is valid also for a run under non-isothermal conditions.[50,51], i.e.

---

[50] See Sect.4.1.

[51] A common assumption, but discussed in the literature of thermodynamics to this day, e.g. [33].

A change in temperature does not interfere with the power coefficients $|\nu j|$, only with the rate coefficient k due to the Arrhenius equation

$$\begin{aligned} \mathrm{d}\lambda/\mathrm{d}t/V = r = k(T) \cdot \left[\ldots \cdot \ldots \cdot c_{j-1}{}^{\nu j-1} \cdot c_j{}^{|\nu j|} \cdot \ldots \cdot \ldots\right] \\ = k_0 \cdot \mathrm{EXP}(-E/RT) \cdot \left[\ \ldots \cdot \ldots \cdot c_{j-1}{}^{\nu j-1} \cdot c_j{}^{\nu j} \cdot \ldots \cdot \ldots\right] \end{aligned} \tag{4.143}$$

- The relation between the rate of the stoichiometric formula conversion and the enthalpy of the reaction ΔH_λ is given by

$$\mathrm{d}\lambda/\mathrm{d}t = q/(-\Delta H_\lambda(T)). \tag{4.144}$$

- Analogously to (4.4) and (4.132) a change in the reaction volume is described by

$$\begin{aligned} V = V(T,X) = V(T(t=0)) \cdot [1 + \upsilon(T) \cdot X] \\ = V_0(T) \cdot [1 + \upsilon(T) \cdot \lambda/\lambda_\infty], \end{aligned} \tag{4.145}$$

with $\upsilon(T) = 0$ for a constant-volume reaction.

For sufficiently small changes in temperature the following can be used as base:

- $$V_0(T) \cong \mathrm{const} = V_0[T(t=0)] = V_0,$$
- $$\upsilon(T) \cong \mathrm{const} = \upsilon[T(t=0)] = \upsilon_0,$$
- $$\Delta H_\lambda(T) \cong \mathrm{const} = \Delta H_\lambda[T(t=0)] = \Delta H_{\lambda 0},$$

i.e. it can be sufficiently precisely assumed that

$$\mathrm{d}\lambda/\mathrm{d}t = q/(-\Delta H_{\lambda 0}), \tag{4.146}$$

$$V = V(T,X) = V(X) = V_0 \cdot (1 + \upsilon_0 \cdot \lambda/\lambda_\infty). \tag{4.147}$$

4.2.3.1 Constant-Volume Reaction

As a rule, for a reaction in solution the change in volume of the reaction mixture due to the reaction is negligibly small, i.e. $\upsilon_0 = 0$.

Hence, the following expressions are valid

$$V = \mathrm{const} = V_0,$$

$$\mathrm{d}\lambda/\mathrm{d}t = q/(-\Delta H_{\lambda 0}) = A(t), \tag{4.148}$$

$$(\lambda_\infty - \lambda) = \int_{t\to\infty} q \cdot \mathrm{d}t/(-\Delta H_{\lambda 0}) = B(t) \tag{4.149}$$

or

$$\lambda/\lambda_\infty = 1 - \int_{t\to\infty} q\cdot \mathrm{d}t/(-\Delta H_{\lambda 0})/\lambda_\infty, \tag{4.150}$$

$$\begin{aligned}(-\Delta H_{\lambda 0}) &= \int_{0\to\infty} q\cdot \mathrm{d}t/\lambda_\infty \\ &= -\nu_\mathrm{j}\cdot \int_{0\to\infty} q\cdot \mathrm{d}t/N_{\mathrm{j}0} \\ &= \nu_\mathrm{i}\cdot \int_{0\to\infty} q\cdot \mathrm{d}t/N_{\mathrm{i}\infty}\end{aligned} \tag{4.151}$$

due to (4.4):

$$\begin{gathered} N_\mathrm{j} - N_{\mathrm{j}0} = \nu_\mathrm{j}\cdot(\lambda-\lambda_0) \quad \text{and} \quad N_\mathrm{i} - N_{10} = \nu_\mathrm{i}\cdot(\lambda-\lambda_0) \\ \text{due to } \lambda_0 = 0,\ N_{\mathrm{j}\infty} = 0 \text{ and } N_{10} = 0 \\ = \quad \nu_\mathrm{j}\cdot\lambda \text{ and } N_\mathrm{i} = \nu_\mathrm{i}\cdot\lambda, \end{gathered}$$

hence

$$\lambda_\infty = N_{\mathrm{j}0}/-\nu_\mathrm{j} \text{ respectively } N_{\mathrm{i}\infty}/\nu_\mathrm{i}$$

and

$$N_\mathrm{j} = -\nu_\mathrm{j}\cdot\lambda_\infty + \nu_\mathrm{j}\cdot\lambda = -\nu_\mathrm{j}\cdot(\lambda_\infty - \lambda). \tag{4.152}$$

4.2.3.1.1 System of Reactions Kinetically Characterized by a Single Rate Function

4.2.3.1.1.1 Rate Function of Order n

The rate of a chemical conversion with the stoichiometry $\nu_1 + \ldots + \nu_{\mathrm{j}-1} + \nu_\mathrm{j} + \ldots \to \ldots + \nu_{\mathrm{i}-1} + \nu_\mathrm{i} + \ldots$ is proportional to the concentration of reactant j to the power n:

$$r = k\cdot c_\mathrm{j}{}^n.$$

According to (4.143) during the reaction run at any point of time t, the following expression is valid:

$$\mathrm{d}\lambda/\mathrm{d}t = A(t) = k_0\cdot \mathrm{EXP}(-E/RT)\cdot c_\mathrm{j}{}^n\cdot V_0.$$

The quotient of $\mathrm{d}\lambda/\mathrm{d}t$ for two arbitrary points in time t_1 and t_2 respectively for the relevant temperatures T_1 and T_2 is [13]

$$\begin{aligned} A_1/A_2 &= \left[\mathrm{EXP}(-E/RT)\cdot {N_\mathrm{j}}^n\right]_1 / \left[\mathrm{EXP}(-E/RT)\cdot {N_\mathrm{j}}^n\right]_2 \\ &\qquad \text{due to (4.152)} \\ &= [\mathrm{EXP}(-E/RT)\cdot(\lambda_\infty-\lambda)^n]_1/[\mathrm{EXP}(-E/RT)\cdot(\lambda_\infty-\lambda)^n]_2 \\ &\qquad \text{with (4.149)} \\ &= [\mathrm{EXP}(-E/RT)\cdot B(t)^n]_1/[\mathrm{EXP}(-E/RT)\cdot B(t)^n]_2. \end{aligned} \tag{4.153}$$

Taking natural logarithms of (4.153) gives as a result the linear relation[52]

$$\ln[A_1/A_2]/\ln[B_1/B_2] = n - E/R\cdot[1/T_1 - 1/T_2]/\ln[B_1/B_2]$$

or

$$y = n - E/R\cdot x \tag{4.154}$$

with

$$\begin{gathered} y = \ln[A_1/A_2]/\ln[B_1/B_2] \\ x = (1/T_1 - 1/T_2)/\ln[B_1/B_2] \cong 4\cdot(\delta T_2-\delta T_1)/(2T_\mathrm{S}+2\Delta T_0+\delta T_1+\delta T_2)^2/\ln[B_1/B_2]. \end{gathered}$$

The plot of y versus x gives a straight line (Fig. 4.29). Its slope κ corresponds to the activation temperature, and its intersection Φ with the ordinate gives the order of reaction

$$\begin{aligned} \kappa &= E/R, \\ \Phi &= n. \end{aligned}$$

Now, because of the known order n of the rate, the rate coefficient k is also determined due to (4.1), (4.143), and (4.152):

$$\begin{aligned} k &= V^{n-1}\cdot\left[-\nu_j\cdot(\lambda_\infty-\lambda)\right]^{-n}\cdot \mathrm{d}\lambda/\mathrm{d}t \\ &\qquad \text{with (4.148), (4.149)} \\ &= \left[-\nu_j\right]^{-n}\cdot {V_0}^{n-1}\cdot A(t)\cdot B(t)^{-n}. \end{aligned} \tag{4.155}$$

Because of the knowledge of k, the pre-exponential factor k_0 is also known due to the Arrhenius equation:

$$k = k_0\cdot\mathrm{EXP}(-E/RT).$$

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[52] $$\begin{aligned} 1/T_1 - 1/T_2 = (T_2-T_1)/(T_2\cdot T_1) \cong \Delta T_{21}/\overline{T}^2 &= \Delta T_{21}/[(T_1+T_2)/2]^2 = 4\cdot\Delta T_{21}/(T_S+\Delta T_0+\delta T_1+T_S+\Delta T_0+\delta T_2) \\ &= 4\cdot[(T_S+\Delta T_0+\delta T_2)-(T_S+\Delta T_0+\delta T_1)]/(2T_S+2\Delta T_0+\delta T_1+\delta T_2)^2 \\ &= 4\cdot(\delta T_2-\delta T_1)/(2T_S+2\Delta T_0+\delta T_1+\delta T_2)^2, \end{aligned}$$
in which $\delta T_1 = T(t_1)-T(t=0) = T(t_1)-T_0; \delta T_2 = T(t_2)-T(t=0) = T(t_2)-T_0; \Delta T_0 = T(t=0)-T_\mathrm{S} = T_0-T_\mathrm{S}$
(see Fig. 2.1; 2.26)

4.2.3.1.1.2 *The Rate Function Is a Product of Partial Orders* n *and* m

The rate function is

$$r = k \cdot c_{\mathrm{j}}{}^{n} \cdot c_{\mathrm{j+1}}{}^{m}.$$

Combining (4.143), (4.149), and (4.152) gives as a result

$$\begin{aligned}\mathrm{d}\lambda/\mathrm{d}t = A(t) &= k_0 \cdot \mathrm{EXP}(-E/RT) \cdot c_j{}^{n} \cdot c_{\mathrm{j-1}}{}^{m} \cdot V_0\\ &= k_0 \cdot \mathrm{EXP}(-E/RT) \cdot \left(-v_{\mathrm{j}} \cdot (\lambda_\infty - \lambda)/V_0\right)^{n} \cdot \left(-v_{\mathrm{j-1}} \cdot (\lambda_\infty - \lambda)/V_0\right)^{m} \cdot V_0\\ &= k_0 \cdot \mathrm{EXP}(-E/RT) \cdot (\lambda_\infty - \lambda)^{n+m} \cdot \left(-v_{\mathrm{j}}\right)^{n} \cdot \left(-v_{\mathrm{j+1}}\right)^{m} \cdot V_0{}^{-(n+m-1)}\\ &= k_0 \cdot \mathrm{EXP}(-E/RT) \cdot B(t)^{n+m} \cdot \left(-v_{\mathrm{j}}\right)^{n} \cdot \left(-v_{\mathrm{j-1}}\right)^{m} \cdot V_0^{-(n+m-1)}.\end{aligned}$$

We obtain the following result:[53]

$$\ln[A_1/A_2]/\ln[B_1/B_2] = (n+m) - E/R \cdot [1/T_1 - 1/T_2]/\ln[B_1/B_2]$$

respectively

$$y = (n+m) - E/R \cdot x,$$

with

$$\begin{aligned}y &= \ln[A_1/A_2]/\ln[B_1/B_2],\\ x &= (1/T_1 - 1/T_2)/\ln[B_1/B_2]\\ &\cong 4 \cdot (\delta T_2 - \delta T_1)/(2T_S + 2\Delta T_0 + \delta T_1 + \delta T_2)^2/\ln[B_1/B_2].\end{aligned}$$

The plot of y versus x gives a straight line whose slope κ corresponds to the activation temperature, and its intersection with the ordinate Φ gives the sum of the orders,

$$\begin{aligned}\kappa &= E/R,\\ \Phi &= n+m.\end{aligned}$$

To determine the partial orders n and m, a conversion must be carried out for example with a very large surplus of reactant j (or j + 1, depending on the usefulness) so that the process runs at a rate of

$$r = \mathrm{d}\lambda/\mathrm{d}t/V_0 = k \cdot c_j{}^{n} \cdot c_{j+1}{}^{m} = k \cdot \left\{c_j \cong \mathrm{const}\right\}^{n} \cdot c_{j+1}{}^{m} = k' \cdot c_{j+1}{}^{m}.$$

m is found out analogously to the procedure described earlier in Sect. 4.2.3.1.1.1. By means of the already known overall order $\Phi = (m+n)$ n is also determined.

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[53] See notice in Sect. 4.2.3.1.1.1.

Knowledge of the partial orders n and m allows for the calculation of the rate coefficient k analogously to the procedure described earlier in Sect. 4.2.3.1.1.1.

From

$$\begin{aligned} \mathrm{d}\lambda/\mathrm{d}t = A(t) &= k \cdot c_{\mathrm{j}}{}^{n} \cdot c_{\mathrm{j-1}}{}^{m} \cdot V_0 \\ &= k \cdot (\lambda_\infty - \lambda)^{n+m} \cdot \left(-v_{\mathrm{j}}\right)^{n} \cdot \left(-v_{\mathrm{j+1}}\right)^{m} \cdot V_0{}^{-(n\,+\,m-1)} \\ &= k \cdot B(t)^{n+m} \cdot \left(-v_{\mathrm{j}}\right)^{n} \cdot \left(-v_{\mathrm{j-1}}\right)^{m} \cdot V_0^{-(n\,+\,m-1)} \end{aligned}$$

it follows that

$$k = \left(-v_{\mathrm{j}}\right)^{-n} \cdot \left(-v_{\mathrm{j-1}}\right)^{-m} \cdot V_0^{(n+m-1)} \cdot A(t) \cdot B(t)^{-(n+m)}. \tag{4.156}$$

4.2.3.2 Variable-Volume Reaction

For a reaction in a concentrated liquid reaction mixture, for instance using barely diluted liquid reactants, the change in volume during the reaction can have an effect.

For $\upsilon_0 \neq 0$ the following expressions are valid

$$\mathrm{d}\lambda/\mathrm{d}t = q/(-\Delta H_{\lambda 0}), \tag{4.146}$$

$$(\lambda_\infty - \lambda) = \int_{t\to\infty} q \cdot \mathrm{d}t/(-\Delta H_{\lambda 0}), \tag{4.149}$$

$$\lambda/\lambda_\infty = 1 - \int_{t\to\infty} q \cdot \mathrm{d}t/(-\Delta H_{\lambda 0})/\lambda_\infty, \tag{4.150}$$

$$\begin{aligned} (-\Delta H_{\lambda 0}) &= \int_{0\to\infty} q \cdot \mathrm{d}t/\lambda_\infty \\ &\overset{\text{due to (4.152)}}{=} -v_{\mathrm{j}}/N_{\mathrm{j0}} \cdot \int_{0\to\infty} q \cdot \mathrm{d}t \\ &= v_{\mathrm{i}}/N_{\mathrm{i}\infty} \cdot \int_{0\to\infty} q \cdot \mathrm{d}t. \end{aligned} \tag{4.151}$$

For the variability of volume, the following equation is valid according to (4.150) using (4.147) as a base:

$$\begin{aligned} V &= V_0 \cdot (1 + \upsilon_0 \cdot \lambda/\lambda_\infty) \\ &= V_0 \cdot \left(1 + \upsilon_0 \cdot \left[1 - \int_{t\to\infty} q \cdot \mathrm{d}t/(-\Delta H_{\lambda 0})/\lambda_\infty\right]\right). \end{aligned} \tag{4.157}$$

From that, due to (4.146), (4.157), we obtain

$$\begin{aligned}\mathrm{d}\lambda/\mathrm{d}t/V &= q/(-\Delta H_0)\Big/\left\{V_0\cdot\left(1+\upsilon_0\cdot\left[1-\int_{t\to\infty} q\cdot\mathrm{d}t/(-\Delta H_{\lambda 0})/\lambda_\infty\right]\right)\right\}\\ &= -\nu_\mathrm{j}\cdot q\Big/\int_{0\to\infty} q\cdot\mathrm{d}t/N_{\mathrm{j}0}\Big/\left\{V_0\cdot\left(1+\upsilon_0\cdot\left[1-\int_{t\to\infty} q\cdot\mathrm{d}t\Big/\int_{0\to\infty} q\cdot\mathrm{d}t\right]\right)\right\}\\ &= A'(t).\end{aligned} \tag{4.158}$$

With (4.149), (4.151) and (4.157) we get

$$\begin{aligned}(\lambda_\infty-\lambda)/V &= (\lambda_\infty-\lambda)\Big/\left\{V_0\cdot\left(1+\upsilon_0\cdot\left[1-\int_{t\to\infty} q\cdot\mathrm{d}t/(-\Delta H_{\lambda 0})/\lambda_\infty\right]\right)\right\}\\ &= (\lambda_\infty-\lambda)\Big/\left\{V_0\cdot\left(1+\upsilon_0\cdot\left[1-\int_{t\to\infty} q\cdot\mathrm{d}t\Big/\int_{0\to\infty} q\cdot\mathrm{d}t\right]\right)\right\}\\ &= \int_{t\to\infty} q\cdot\mathrm{d}t/(\Delta H_{\lambda 0})\Big/\left\{V_0\cdot\left(1+\upsilon_0\cdot\left[1-\int_{t\to\infty} q\cdot\mathrm{d}t\Big/\int_{0\to\infty} q\cdot\mathrm{d}t\right]\right)\right\}\\ &= \lambda_\infty\cdot\int_{t\to\infty} q\cdot\mathrm{d}t\Big/\int_{0\to\infty} q\cdot\mathrm{d}t\Big/\left\{V_0\cdot\left(1+\upsilon_0\cdot\left[1-\int_{t\to\infty} q\cdot\mathrm{d}t\Big/\int_{0\to\infty} q\cdot\mathrm{d}t\right]\right)\right\}.\end{aligned}$$

This means that, due to (4.152),

$$\begin{aligned}N_\mathrm{j}/V &= N_{\mathrm{j}0}\cdot\int_{t\to\infty} q\cdot\mathrm{d}t\Big/\int_{0\to\infty} q\cdot\mathrm{d}t\Big/\left\{V_0\cdot\left(1+\upsilon_0\cdot\left[1-\int_{t\to\infty} q\cdot\mathrm{d}t\Big/\int_{0\to\infty} q\cdot\mathrm{d}t\right]\right)\right\}\\ &= B'(t).\end{aligned} \tag{4.159}$$

4.2.3.2.1 System of Reactions Kinetically Characterized by a Single Rate Function

4.2.3.2.1.1 Rate Function of Order n

The rate of a chemical conversion with the stoichiometry $\nu_1 + \ldots + \nu_{\mathrm{j}-1} + \nu_\mathrm{j} + \ldots \rightarrow \ldots + \nu_{\mathrm{i}-1} + \nu_\mathrm{i} + \ldots$ is proportional to the concentration of reactant j to the power n:

$$r = k\cdot c_j{}^n.$$

A change in the volume of the reaction mixture occurs during the chemical process. The procedure of the kinetic analysis is analogous to that carried out for the constant-volume reaction.

With (4.143) and (4.158) for any point in time we have

$$\mathrm{d}\lambda/\mathrm{d}t/V = A'(t) = k_0\cdot\mathrm{EXP}(-E/RT)\cdot c_\mathrm{j}{}^n.$$

The quotient of $\mathrm{d}\lambda/\mathrm{d}t/V$ for two times t_1 and t_2 (temperatures T_1 and T_2) reads

$$\begin{aligned} A_1'/A_2' &= \left[\mathrm{EXP}(-E/RT)\cdot\left[N_\mathrm{j}/V\right]^n\right]_1/\left[EXP(-E/RT)\cdot\left[N_\mathrm{j}/V\right]^n\right]_2 \\ &\qquad \text{because of (4.159)} \\ &= \left[EXP(-E/RT)\cdot B'\right]_1/\left[EXP(-E/RT)\cdot B'\right]_2. \end{aligned}$$

Taking logarithms yields the linear relation[54]

$$\ln\left[A_1'/A_2'\right]/\ln\left[B_1'/B_2'\right] = n - E/R\cdot[1/T_1 - 1/T_2]/\ln\left[B_1'/B_2'\right]$$

or

$$y = n - E/R\cdot x,$$

with

$$\begin{aligned} y &= \ln\left\{\left[A_1'/A_2'\right]\right\}/\ln\left\{\left[B_1'/B_2'\right]\right\}, \\ x &= (1/T_1 - 1/T_2)/\ln\left[B_1'/B_2'\right] \\ &\cong 4\cdot(\delta T_2 - \delta T_1)/(2T_\mathrm{S} + 2\Delta T_0 + \delta T_1 + \delta T_2)^2/\ln\left[B_1'/B_2'\right]. \end{aligned}$$

The plot of y versus x gives a straight line, analogously to Fig. 4.30. Its slope κ corresponds to the activation temperature; the intersection with the ordinate Φ gives the order of the rate

$$\begin{aligned} \kappa &= \mathrm{E/R}, \\ \Phi &= n. \end{aligned}$$

The kinetic interpretation of measured curves of reactions under non-isothermal conditions is clearly labour-intensive work and is especially very sensitive to measurement errors. Even small errors of the values q and T and the additive quantities C, kF, q_St and V will cause a perceptible and momentous change in the auxiliary quantities A and B and cause an important variance in the elaborated kinetic parameters k, n and E. For the sake of correctness it is advisable to choose such conditions of the reaction (temperature, concentration level)—if that is somehow possible—that the reaction runs at least for a large part of the total conversion under isothermal conditions. Errors that arise by extrapolating the curve q measured under isothermal conditions during the final run rearward to the non-isothermal initial phase (Fig. 2.31) are generally smaller than those caused by the described non-isothermal interpretation method.

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[54] See note in Sect. 4.2.3.1.1.1 and Fig. 5.18.

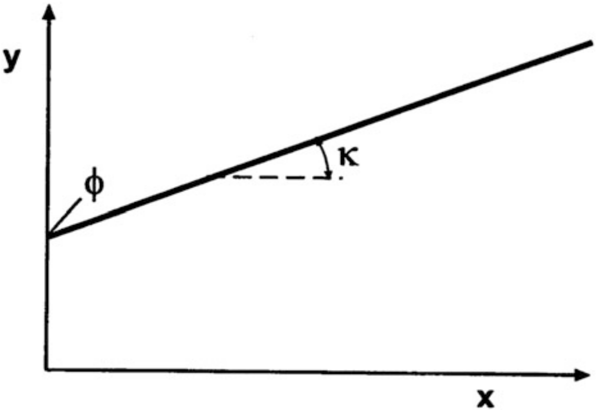

Fig. 4.30 Non-isothermal, discontinuous, volume-constant reaction: stoichiometry $\nu_1 + \ldots + \nu_{j-1} + \nu_j + \ldots \rightarrow \ldots + \nu_{i-1} + \nu_i + \ldots$; rate function $r = k \cdot c_j{}^n$

4.2.3.3 System of Reactions Kinetically Characterized by Several Rate Functions

It is evident that a non-isothermal kinetic analysis, even in the case of a simple reaction, is very labor intensive and especially prone to errors. It stands to reason that the analysis of a system of reactions is usually much more complex. A kinetic analysis on the basis of mathematical-analytical relations is usually impossible. A kinetic analysis is only practicable by an interactive procedure between numeric calculations and experimental results on the basis of common optimization methods.[55]

The most essential elements are as follows:

- Reaction mechanism, stoichiometries
- Rate function of single reactions ξ

$$r_\xi = k_{\xi 0} \cdot \mathrm{EXP}\left(-E_\xi/RT\right) \cdot \left[\ldots \cdot c_{j-1}{}^{\nu\xi j-1} \cdot c_j{}^{\nu\xi j} \cdot c_j{}^{\nu\xi j+1} \cdot \ldots\right]$$

- Generalized relation (4.143)

$$\mathrm{d}\lambda_\xi/\mathrm{d}t = q_\xi/\left(-\Delta H_{\lambda\xi}\right)$$

- Superposition of single thermal reaction powers (4.7)

$$q = \sum\nolimits_\xi \left[q_\xi\right].$$

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[55] See Sect. 4.3.

4.3 Elaboration of Rate Function and Enthalpy of Reaction on Basis of Electronic Data Processing (Numeric Evaluation)

The preceding treatment shows that the evaluation of kinetics on the basis of mathematical-analytical relations is rather difficult with just relatively simple reaction systems, even if the underlying curves are measured under isothermal conditions.[56] A neat mathematical treatment of complex reactions is mostly impossible due to analytically unsolvable systems of differential equations. Therefore, there has been no lack of attempts to make it easier to solve systems of kinetic differential equations using methods of approximation as follows.

- The concentrations of intermediate products are negligibly small,

$$\text{assumption}: c_{\text{intermediate-products}} = 0.$$

- Bodenstein hypothesis:
  The concentrations of intermediate products are negligibly small compared to the concentrations of reactants and products.

$$\text{First assumption(as previously)}: c_{\text{intermediate products}} = 0.$$

  Additionally, compared to the reactants and products, the temporal changes in the concentrations of intermediate products can be neglected.

$$\text{Second assumption}: \mathrm{d}c_{\text{intermediate-products}}/\mathrm{d}t = 0,$$

  i.e. Bodenstein's steady-state approximation.
- Method of quasi-stationary intermediate products.
  The second assumption $\left(\mathrm{d}c_{\text{intermediate-products}}/\mathrm{d}t = 0\right)$ of the Bodenstein hypothesis as a consequence of the first assumption $\left(c_{\text{intermediate-products}} = 0\right)$ is certainly plausible; but seen from a mathematical viewpoint the first assumption is neither a necessary nor a sufficient condition for justification of the second assumption. Therefore, for the method of quasi-stationary intermediate products the first assumption is disregarded and only quasi-stationary intermediate products are assumed,

$$\text{assumption}: \mathrm{d}c_{\text{intermediate-products}}/\mathrm{d}t = 0.$$

- The equilibrium approximation:

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[56] See Sect. 5.1.1.

for a reaction system including reversible stages it is assumed that the rates of the forward and backward stages are much larger than the rates of the irreversible stages:

assumption: equilibrium is achieved instantly.

The methods of approximation are mathematically very useful; nevertheless, the analysis of complex processes is labor intensive. In addition, the quality of the approximation can usually not be indicated. Therefore, in the age of electronic data processing it is more reliable, easier and more convenient to calculate the temporal course of both the concentrations and the thermal reaction power by means of computers. For this purpose we elaborate on the basis of both a presumed mechanism of the reaction and the relevant rate functions the relations for the rate of change in the concentration of each reactant, of each intermediate product and of each product as well as the corresponding functions of the thermal reaction power using (4.1), (4.3), (4.4), (4.7) and (4.9). The obtained system of equations is solved by numeric calculation. For this we need, in addition to the mathematical relations and their initial values, the orders of rates, the rate coefficients and the enthalpies of reactions (if necessary, estimated first). We obtain the temporal course of the concentrations of the participating species, the temporal course of the thermal reaction power of each stage and the temporal course of its superposition, i.e. the measurable thermal reaction power. The calculated results are compared with the measured quantities. In case of a deviation, the parameters of the rates and enthalpies as well as, if necessary, the reaction model itself are varied many times until the numeric and experimental results sufficiently correspond. Any further conformance between a new experiment and its calculation confirms the elaborated reaction kinetics, but it is not a mathematically definitive demonstration, such as the proof from n to $n + 1$.

The more complex the mechanism which is to be discussed for the interpretation of the recorded reaction courses, the larger the probability that the run of the reaction can be interpreted also by a somewhat different, complex mechanism, especially due to the restricted accuracy in measurement. The number of mechanisms which is compatible with the recorded data can be large. To be precise, after the calorimetric analysis, the measured data are not inconsistent with the assumed mechanism, rates and heats of the reaction.[57]

The more plentiful and variable experimental data can be compared with the numerical results, the more successful the thermokinetic analysis, i.e. the analysis is not only mathematically correct in a restricted frame but in addition physicochemically elaborated.

- In addition to the temporal courses of both the thermal reaction power and concentration of the reactants and products of the overall reaction, the courses of concentration as well as the thermal reaction powers of the appropriate partial reactions should be investigated.

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[57] The same goes for the elaboration of kinetics on the basis of classical chemical analysis.

- The use of ATR-IR spectroscopy is very helpful.
- Additional life signs of the chemical process should be measured, for instance changes in the heat-transfer coefficient ($k \cdot F$), changes in pressure, changes in electrical conductivity, changes in the viscosity of the reaction mixture. The addition of more reactants, intermediate products or other products during reaction run would yield very helpful information.
- Approximate data of similar reactions can be used for orientation.

Nowadays, electronic data processing makes it easier to discuss kinetic models. Meanwhile, various kinetic interpretations are included in standard software packages (parameter optimization by the gradient method or global search method), for instance sequential quadratic programming (SQP), general reduced gradient (GRG), simulated annealing (SA), evolution strategies and simplex algorithms [38, 39]. Indeed, the use of this software makes elaboration much easier; however, it may lead to making stereotypes and may encourage careless work. It has been said that all that glitters is not gold does not take into account that only a manifold, intensive and meticulous experimental investigation is the most important prerequisite for a thoroughly elaborated interpretation.

Conclusion

If the underlying reaction mechanism, the stoichiometry, the rate functions and the enthalpy of reaction are acceptable beyond a shadow of a doubt and the experimental quantities are correct, the elaboration of the reaction coefficients and enthalpies of reaction can take place automatically by numerical calculation. The available determination algorithms are in such a stage of development that a large number of the quantities can be elicited simultaneously. However, only in rare cases is the first, assumed reaction model correct.

Therefore, the elaboration of a precise kinetics is characterized by numerous actions, in which the mechanism, the stoichiometries, the rate functions and the enthalpies of reactions must be changed, and very often additional experiments are necessary, i.e. the initial way of proceeding very often needs to be changed.

In other words, as a rule, thermokinetic analysis is not brought to completion by carrying out only some measurements; it requires simultaneously intensive interpreation work (close interplay between measurements and interpretation).

Complex processes can be dissected neither by an a priori conception of experiments nor by an a priori scheme of interpretation, but principally only by means of knowledge, experience, instinctive feel for detection and intuition, just like the working out of chemical kinetics on the basis of conventional, analytical chemistry.

The general experience is that the interactive working method is the most successful procedure. For that the kinetic parameters are determined by the aforementioned routine software, in which however the optimizing procedure is controlled by the kineticist (optimization method on the basis of the flexible, sensitive, human intellect). The most important part of the elaboration is the experimenter because he has an overall knowledge of the chemical correlation, the message of the experiments, the chemical analysis and the accuracy of the individual measuring results.

4.4 Influence of Molecular Interaction on Thermal Reaction Power

Because of the increase in the concentrations in the reaction mixture, the mutual influence of all the species within the mixture (reactants, intermediate products, products, by-products and solvent) becomes more and more ascertainable. This occurrence affects the thermal reaction power because the interaction sets the tone for both the enthalpy and the rate of reaction.

To formulate the general rate function of heat release, it is convenient to represent the reactivity of mutually affected actual reactants in a concentrated mixture by virtual reactants without interacting with the surroundings. For that, in relations (4.9) and (4.10) the following replacements are made:

- The concentrations of the actual reactants $c_{\mathrm{j}} = N_{\mathrm{j}}/V$ by the concentrations of virtual reactants, i.e. a changed number of species j per unit volume, which represents without interaction the reactivity of the mutually affected real reactants j, called activities a_{j}, linked with the real concentrations c_{j} by $a_{\mathrm{j}} = f_{\mathrm{j}}(c_{\varepsilon}) \cdot c_{\mathrm{j}}$, in which the "correcting quantity" i.e. activity coefficient $f_{\mathrm{j}}(c_{\varepsilon})$ depends on the real concentrations c_{ε} of all components ε of the mixture and achieves a value of 1 when the mixture is ideally diluted;
- The molar enthalpies $\mathbf{H}_{\zeta}$ and the molar heat $\mathbf{C}_{\zeta}$ of the actual species ζ by the partial molar enthalpies $H_{\zeta} = \left(\delta H/\delta N_{\zeta}\right)_{\mathrm{p,T,N}\neq \mathrm{N}\zeta}$ respectively the partial molar heats $C_{\zeta} = \left(\delta H_{\zeta}/\delta T\right)_{\mathrm{p,N}}$, which also depend on the concentrations c_{ε} of all actual components ε, achieve in the ideally diluted mixture a value of $\mathbf{H}_{\zeta}$ respectively $\mathbf{C}_{\zeta}$.

Due to (4.1) and (4.4) the general rate function r and the enthalpy of reaction are[58,59]

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[58] For the technically oriented formal kinetics, characterized by the overall stoichiometry and the overall rate function, the powers in the rate equation usually do not agree with the stoichiometric coefficients v_{j}.

[59] Simple illustrative example:

In a concentrated mixture runs the elementary reaction 1A→.... The activity coefficient of reactant A does not change during the run, for example $f_{\mathrm{A}}(c_{\varepsilon}) = \mathrm{konst} = 0.5$. The rate of reaction is, according to (4.160), $r = k \cdot a_{\mathrm{A}} = k \cdot (f_{\mathrm{A}}(c_{\varepsilon}) \cdot c_{\mathrm{A,real}}) = k \cdot (0.5 \cdot c_{\mathrm{A,real}})$. This means that the mutual interaction acts as if in the actual mixture only half of the really present A moles originate without interaction the propelling force for the run of the reaction. The concentration of the virtual reactants corresponds to $0.5 \cdot c_{\mathrm{A,real}}$.

$$\begin{aligned} r = \mathrm{d}\lambda/\mathrm{d}t/V = \mathrm{d}N_\mathrm{j}/v_\mathrm{j}/\mathrm{d}t/V \quad &= k \cdot \left[\ldots\cdot\ldots\cdot a_{\mathrm{j}-1}{}^{v\mathrm{j}-1} \cdot a_\mathrm{j}{}^{|v\mathrm{j}|} \cdot\ldots\cdot\ldots\right] \\ &= k \cdot \left[\ldots\cdot\ldots\cdot f_{\mathrm{j}-1}(c_\varepsilon)^{|v\mathrm{j}-1|} \cdot c_{\mathrm{j}-1}{}^{v\mathrm{j}-1} \cdot f_\mathrm{j}(c_\varepsilon)^{|v\mathrm{j}|} \cdot c_\mathrm{j}{}^{|v\mathrm{j}|} \cdot\ldots\cdot\ldots\right] \\ = \left\{k \cdot \left[\ldots\cdot\ldots\cdot f_{\mathrm{j}-1}(c_\varepsilon)^{|v\mathrm{j}-1|} \cdot f_\mathrm{j}(c_\varepsilon)^{|v\mathrm{j}|} \cdot\ldots\cdot\ldots\right]\right\} &\cdot \left[\ldots\cdot\ldots\cdot c_{\mathrm{j}-1}{}^{v\mathrm{j}-1} \cdot c_\mathrm{j}{}^{|v\mathrm{j}|} \cdot\ldots\cdot\ldots\right] \\ &= k(c_\varepsilon) \cdot \left[\ldots\cdot\ldots\cdot c_{\mathrm{j}-1}{}^{v\mathrm{j}-1} \cdot c_\mathrm{j}{}^{|v\mathrm{j}|} \cdot\ldots\cdot\ldots\right] \end{aligned} \tag{4.160}$$

and

$$\Delta H_\lambda(c_\varepsilon) = \sum v_\zeta \cdot H_\zeta(c_\varepsilon). \tag{4.161}$$

The part $\left\{\ldots\cdot\ldots\cdot c_{\mathrm{j}-1}{}^{v\mathrm{j}-1} \cdot c_\mathrm{j}{}^{|v\mathrm{j}|} \cdot\ldots\cdot\ldots\right\}$ in the general rate function r corresponds to the one in an ideal diluted solution; the effect of mutual influence is represented exclusively by the part $\left[\ldots\cdot\ldots\cdot f_{\mathrm{j}-1}(c_\varepsilon)^{|v\mathrm{j}-1|} \cdot f_\mathrm{j}(c_\varepsilon)^{|v\mathrm{j}|} \cdot\ldots\cdot\ldots\right]$ which corresponds to the rate coefficient $k(c_\varepsilon)$. In the limiting case of an ideally diluted solution, all $f_\mathrm{j}(c_\varepsilon)$ achieve the value 1 and $k(c_\varepsilon)$ corresponds to the constant value k. Hence, the rate coefficient and the enthalpy of reaction are usually not constants but quantities whose values change because of the degree of interaction. This can already occur noticeably in very strong concentrated mixtures during the run of a chemical process owing to the change in the chemical composition.[60] However, these alterations are usually small compared with those by large jumps in the level of concentration; see an example of the change in enthalpy of reaction in [20], Table 4.1.

For a middle level of concentration, the interaction changes during the chemical reaction only slightly. Because of the unavoidable errors in measurements, it is, as a rule, impossible to detect clearly changes in both the rate coefficient and the enthalpy of reaction. For the complete run of a reaction, both a rate function with an average rate coefficient $\overline{k(c_\varepsilon)}$ and an average enthalpy of the reaction $\overline{\Delta H_\lambda(c_\varepsilon)}$ are usually worked out. With an alteration in the steps of the concentration level, the average values change stepwise.

During a chemical process in a strong concentrated solution, the rate coefficients and the enthalpies of reaction vary noticeably owing to the considerable change in the composition. The mutual influence changes to such a degree that the analysis of different reaction phases gives as a result plainly different average rate coefficients and average enthalpies of reaction.

It is no surprise that it is extremely difficult to determine the rate-function for the complete course of the reaction. Only for extremely rare cases it can be elaborated

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[60] Consequently, the enthalpy of reaction ΔH_λ and the rate coefficient k are to be taken no longer as a characteristic property of the combination of substances but as a measure of the thermodynamic state of the reaction mixture. Hence, to determine a defined reaction coefficient and a defined enthalpy of reaction, the composition of the reaction mixture is not allowed to change by the reaction. Strictly speaking, the measurements are to be carried out by a continuous run of the reaction (Sects. 2.2.1 and 4.2.2) or, in practise, also by a discontinuous run of the reaction in cases where only a small conversion occurs.

Table 4.1 Effect of concentration level in solutions of HCL and NaOH at 25 °C on neutralization enthalpy and on its temperature coefficient

[mol in liter H_2O]	$-\Delta H_\lambda$ [kcal/formula conversion]	$(\delta\Delta H_\lambda/\delta T)_p$ [cal/K/formula conversion]	[mol in liters H_2O]	$-\Delta H_\lambda$ [kcal/formula conversion]	$(\delta\Delta H_\lambda/\delta T)_p$ [cal/K/formula conversion]
$0^{\text{extrapolated}}$	13,320		10	17,130	
3	14,245	−53	11	17,655	
4	14,555		12	18,195	
5	14,915		13	18,735	
6	15,300		14	19,260	
7	15,715		15	19,825	
8	16,155		16	20,415	−42
9	16,630				

- On one hand the ideal[61] partial function $[\ldots\cdot\ldots\cdot c_j^{|vj|}\cdot\ldots\cdot\ldots]$ representing exclusively the motor of reaction, i.e. the real driving force on the reaction
- And on the other hand the related ideal partial function $[k\cdot\ldots\cdot\ldots\cdot f_j(c_\varepsilon)^{|vj|}\cdot\ldots\cdot\ldots]$ representing exclusively the mutual influence of all components ε on the reactants.

As a rule, the typical working procedure allows for sloppy and rather careless work when analyzing for the related characteristic dependencies, i.e. allows to include the real influence of the one or the other reactant on the function $[k\cdot\ldots\cdot\ldots\cdot f_j(c_\varepsilon)^{|vj|}\cdot\ldots\cdot\ldots]$ of the reaction coefficient $k(c_\varepsilon)$ falsely in the function $[\ldots\cdot\ldots\cdot c_j^{|vj|}\cdot\ldots\cdot\ldots]$ of the real reaction motor.

The result is a formal kinetics, characterized by

- A non-ideal function of the rate coefficient $k^{\#}(c_{\varepsilon\neq j})$ not representing the real effect of mutual influence of components
- Coupled with a non-ideal partial function $[\ldots\cdot\ldots\cdot c_j^{|vj\#|}\cdot\ldots\cdot\ldots]$ not representing the real driving force on the reaction

As an illustration serves the constant-volume elementary reaction $A \rightarrow B$. with

• Stoichiometric coefficients	$v_A = -1$ and $v_B = 1$
• Initial concentration of the product	$c_{B0} = 0$
• Mol balance	$c_{A0} = c_A + c_B$
• Rate function (4.160)	$r = k \cdot a_A^{\lvert v_A \rvert} = k \cdot a_A = k \cdot f_A(c_\varepsilon) \cdot c_A$
• Thermal reaction power (4.3)	$q = k \cdot f_A(c_\varepsilon) \cdot c_A \cdot (-\Delta H_\lambda(c_\varepsilon)) \cdot V.$

To illustrate activity a_A as simply as possible we assume

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[61] With respect to physicochemical criteria on the rate function of a elementary reaction (4.9) and (4.160) see Sect. 4.1.

- The activity $a_A = f_A(c_\varepsilon) \cdot c_A$ of reactant A decreases over the course of the reaction solely by the appearance of product B, and
  the relative decrease in the activity coefficient f_A from the initial value $f_{A0}(c_\varepsilon)$ is directly proportional to the product yield c_B/c_{A0}

$$\begin{aligned} f_A(c_\varepsilon) &= f_{A0}(c_\varepsilon) \cdot \{1 - ß(c_\varepsilon) \cdot c_B/c_{A0}\} = f_{A0}(c_\varepsilon) \cdot [1 - ß(c_\varepsilon) \cdot \{c_{A0} - c_A\}/c_{A0}] \\ &= f_{A0}(c_\varepsilon) \cdot [1 - ß(c_\varepsilon) + ß(c_\varepsilon) \cdot c_A/c_{A0}] \end{aligned}$$

  with $\beta(c_e)$ as the degree of interaction.
- The enthalpy of reaction $\Delta H_\lambda(c_\varepsilon)$ keeps unchanged during the course of the reaction $\Delta H_\lambda(c_\varepsilon) = \text{const} = \Delta H_\lambda$.

In the case of an ideally diluted solution, the degree of interaction $\beta(c_\varepsilon)$ is by definition zero and the activity coefficient $f_A(c_\varepsilon) = f_{A0}(c_\varepsilon \cong 0) = 1$. During the complete run of the reaction, the activity a_A corresponds to the real concentration c_A. Therefore, according to (4.160), we obtain the rate function

$$\begin{aligned} r &= k \cdot a_A \\ &= k \cdot f_A(c_\varepsilon) \cdot c_A = k \cdot f_{A0}(c_\varepsilon \cong 0) \cdot c_A = k \cdot 1 \cdot c_A = k \cdot c_A. \end{aligned}$$

The heat release takes place due to (4.3) at the rate

$$q = r \cdot (-\Delta H_\lambda(c_\varepsilon \cong 0)) \cdot V = k \cdot c_A \cdot (-\Delta H_\lambda) \cdot V.$$

The interpretation of $q(t)$ in accordance with Sect. 4.2.1.1.1.3 gives as a result that the reaction runs in the diluted mixture according to the reaction function of order 1. The rate coefficient k and the enthalpy of reaction ΔH_λ are constants.

In the case of a medium level of concentration, the degree of interaction is $\beta(c_\varepsilon) \neq 0$, but it is still small. Hence, because of (4.160), the reaction function reads

$$\begin{aligned} r &= k \cdot a_A \\ &= k \cdot f_A(c_\varepsilon) \cdot c_A = k \cdot f_{A0}(c_\varepsilon > 0) \cdot [1 - ß(c_\varepsilon) + ß(c_\varepsilon) \cdot c_A/c_{A0}] \cdot c_A. \end{aligned}$$

Corresponding to (4.3), for the thermal reaction power the following equation is valid:

$$\begin{aligned} q &= k \cdot f_{A0}(c_\varepsilon > 0) \cdot [1 - ß(c_\varepsilon) + ß(c_\varepsilon) \cdot c_A/c_{A0}] \cdot c_A \cdot (-\Delta H_\lambda(c_\varepsilon)) \cdot V \\ &= k \cdot f_{A0}(c_\varepsilon > 0) \cdot [1 - ß(c_\varepsilon) + ß(c_\varepsilon) \cdot c_A/c_{A0}] \cdot c_A \cdot (-\Delta H_\lambda) \cdot V. \end{aligned}$$

Because of $\beta(c_\varepsilon) \cong 0$ the change in the activity coefficient due to the change in the composition of the reaction is small during the run. Its effect both on the rate of reaction and heat release is in the framework of experimental error and not perceptible. The interpretation of $q(t)$ in accordance with Sect. 4.2.1.1.3 leads to a rate function of order 1,

$$r = k(c_\varepsilon) \cdot c_\mathrm{A},$$

however, with an average rate coefficient $k(c_\varepsilon) \cong k \cdot \overline{f_\mathrm{A}(c_\varepsilon)}$ as well as a constant enthalpy of reaction ΔH_λ.

In the case of a highly concentrated reaction mixture the degree of interaction $ß(c_\varepsilon)$ is clearly greater than zero. Therefore, the progress of the reaction affects the activity coefficient in an important way. For an uncomplicated illustration is assumed: $0 \ll ß(c_\varepsilon) = 1$.

Hence, the following reaction function is valid:

$$\begin{aligned} r &= k \cdot a_\mathrm{A} = k(c_\varepsilon) \cdot c_\mathrm{A} = k \cdot f_\mathrm{A}(c_\varepsilon) \cdot c_\mathrm{A} \\ &= k \cdot f_\mathrm{A0}(c_\varepsilon \gg 0) \cdot [1 - ß(c_\varepsilon) + ß(c_\varepsilon) \cdot c_\mathrm{A}/c_\mathrm{A0}] \cdot c_\mathrm{A} \\ &= \{k \cdot f_\mathrm{A0}(c_\varepsilon \gg 0) \cdot c_\mathrm{A}/c_\mathrm{A0}\} \cdot c_\mathrm{A}. \end{aligned}$$

According to (4.3) the thermal reaction power becomes

$$\begin{aligned} q = k(c_\varepsilon) \cdot c_\mathrm{A} \cdot (-\Delta H_\lambda(c_\varepsilon)) \cdot V &= \{k \cdot f_\mathrm{A0}(c_\varepsilon \gg 0) \cdot c_\mathrm{A}/c_\mathrm{A0}\} \cdot c_\mathrm{A} \cdot (-\Delta H_\lambda(c_\varepsilon)) \cdot V \\ &= \{k \cdot f_\mathrm{A0}(c_\varepsilon \gg 0) \cdot c_\mathrm{A}/c_\mathrm{A0}\} \cdot c_\mathrm{A} \cdot (-\Delta H_\lambda) \cdot V. \end{aligned} \tag{4.162}$$

An uncritical thermokinetic investigation of measured results holds the possibility of an elaborated kinetic interpretation with the result of a technically oriented, formal kinetics. For instance, if the reaction is carried out for several temperatures but for the sake of simplicity only for a single initial concentration c_A0, then the analysis according to Sect. 4.2.1.1.1.4 gives as a result that the reaction runs such that it corresponds to a rate function of order 2, the constant rate coefficient $k(c_\varepsilon)$ depends on the temperature, and the enthalpy of reaction ΔH_λ is constant.

However, additional experiments[62] with different initial concentration c_A0 reveal that

- Certainly, the rate of heat release q changes formally corresponding to a reaction rate of order 2,

  but the rate coefficient changes inversely to the initial concentration c_A0, contrary to a true rate function of order 2.
- The initial value q_0 of the thermal reaction power increases directly proportionally to c_A0

  1. In contrast to a reaction which runs in fact according to a rate function of order 2, whose q_0 changes quadratically with respect to the initial concentration c_A0, i.e. $q_0 = k \cdot {c_\mathrm{A0}}^2 \cdot \Delta H_\lambda \cdot V$.
  2. In accordance with a reaction which runs according to a rate function of order 1 whose q_0 changes directly proportionally to the concentration c_A0, i.e. $q_0 = k \cdot c_\mathrm{A0} \cdot \Delta H_\lambda \cdot V$.

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[62] Which give as results the same value ΔH_λ, within the framework of allowed errors.

Hence, the kinetic interpretation must take into account that the reaction of each experiment starts according to a reaction rate of order 1. This is in harmony with (4.160), according to which the powers of the partial function $[\ldots\cdot\ldots\cdot c_j^{|\nu j|}\cdot\ldots\cdot\ldots]$ of the rate function correspond to the positive value of the stoichiometric coefficients ν_j (in this example: $\left[\ldots\cdot\ldots\cdot c_\mathrm{j}^{|\nu\mathrm{j}|}\cdot\ldots\cdot\ldots\right] = \left[c_j^{|\nu\mathrm{A}|}\right] = [c_\mathrm{A}]^1$). The production of B however initiates the diminution of the activity of the molecules A, slowing down the process. According to (4.160), the decrease in activity can be described using the ideal function of the rate coefficient $k(c_\varepsilon) = \left\{k\cdot\left[f_\mathrm{A}(c_\varepsilon)^{|\nu\mathrm{A}|}\right]\right\} = \{k\cdot f_\mathrm{A}(c_\varepsilon)\}$. Assuming—using trial and error—a linear decrease in the activity coefficient versus the yield $c_\mathrm{B}/c_\mathrm{A0}$ of product B we obtain $f_\mathrm{A}(c_\varepsilon) = f_\mathrm{A0}(c_\varepsilon \gg 0)\cdot\ [1-ß\cdot c_\mathrm{B}/c_\mathrm{A0}] = f_\mathrm{A0}(c_\varepsilon \gg 0)\cdot[1-ß\cdot(c_\mathrm{A0}-c_\mathrm{A})/c_\mathrm{A0}]$. Combining this with the partial function $[c_\mathrm{A}]$ and assuming $\beta = 1$ we obtain rate function

$$r = \{k\cdot f_\mathrm{A0}(c_\varepsilon \gg 0)\cdot c_\mathrm{A}/c_\mathrm{A0}\}\cdot c_\mathrm{A},$$

with

- The ideal coefficient function $\left\{k\cdot\left[f_\mathrm{A}(c_\varepsilon)^{|\nu\mathrm{A}|}\right]\right\} = \{k\cdot f_\mathrm{A0}(c_\varepsilon \gg 0)\cdot c_\mathrm{A}/c_\mathrm{A0}\}$
- The ideal concentration function $c_\mathrm{A}^{|\nu\mathrm{A}|} = c_\mathrm{A}$

This elaborated rate function describes, together with $\Delta H_\lambda(c_\varepsilon) = \mathrm{const} = \Delta H_\lambda$, the measured curves q, i.e. q calculated accords with (4.162).

The arbitrary combination of the dependency of the coefficient function on the concentration c_A with the concentration function gives the rate function

$$r^\# = \{k\cdot f_\mathrm{A0}(c_\varepsilon \gg 0)/c_\mathrm{A0}\}\cdot {c_\mathrm{A}}^2 = k^\#\left(c_{\varepsilon\neq A}\right)\cdot {c_\mathrm{A}}^{|\nu A\#|},$$

with

- The non-ideal partial function $\left[{c_\mathrm{A}}^{|\nu\mathrm{A}\#|}\right] = {c_\mathrm{A}}^2$,
- The non-ideal partial function $k^\#\left(c_{\varepsilon\neq A}\right) = \{k\cdot f_\mathrm{A0}(c_\varepsilon \gg 0)/c_\mathrm{A0}\}$

with respect to the physicochemical criteria (4.9) and (4.160), an extremely unsatisfactory result.

Of course, from a mathematical point of view, r and $r^\#$ are identical, and both confirm, therefore, that

- The initial value of the thermal reaction power q_0 increases linearly by c_A0, i.e. $q_0 = \{r \text{ or } r^\#\}_0\cdot(-\Delta H_\lambda)\cdot V = \{k\cdot f_\mathrm{A0}(c_\varepsilon \gg 0)\cdot c_\mathrm{A0}\}\cdot(-\Delta H_\lambda)\cdot V$;
- The thermal reaction power q of a single experiment runs formally according to a rate of order 2, in which each rate coefficient decreases reciprocally to the initial concentration c_A0

$$q = \left\{r_\mathrm{oder} r^\#\right\}\cdot(-\Delta H_\lambda)\cdot V\ = \{k\cdot f_\mathrm{A0}(c_\varepsilon \gg 0)/c_\mathrm{A0}\}\cdot {c_A}^2\cdot(-\Delta H_\lambda)\cdot V.$$

Nevertheless,

- only the first expression of the rate function, r, is in accordance with the criteria of the general rate function of an elementary reaction (4.160);
- the second expression, $r^{\#}$, does not agree with it.
- In addition, there is always the simplest correlation between the ideal expression and other physicochemical relations, for instance the law of massaction.[63]

For the purpose of an uncomplicated illustration, some arbitrary assumptions were necessary because an exact thermokinetic analysis of strong concentrated reaction mixtures based on mathematical-analytical solutions is usually impossible, owing in particular to the really complex dependency of the reaction enthalpy on the concentration. As a rule, it is necessary to use a numeric procedure on the basis of routine software (parameter optimization by a gradient method or global search method). As already mentioned, its really potential application holds, however, the peril of an uncritical, stereotypical use, i.e. in using it one often forgets that only a manifold, intensive and meticulous experimental investigation allows for a mathematically and physicochemically thorough elaboration, i.e. to determine the ideal reaction function.

In many cases of technical practise, non-ideal reaction functions are elaborated from rarely varied experiments, so to speak, plain mathematical solutions. As a rule, such kinetics can be used only in a limited operating range (e.g., temperature, concentration, pressure, type of reactor).[64]

4.5 Estimating the Equilibrium Constant by Thermokinetic Measurements

It is generally known that the rates r_1 and r_2 of the forward and backward reaction of a reversible conversion system correspond at equilibrium to each other. Therefore, for an elementary conversion, for the equilibrium concentrations $(c_{\mathrm{j;i}})_{\mathrm{E}}$ due to (4.160) the following relation is obtained:

$$\left[\ldots \cdot c_{\mathrm{i}}^{|\nu\mathrm{i}|} \cdot \ldots\right]_{\mathrm{E}} \Big/ \left[\ldots \cdot c_{\mathrm{j}}^{|\nu\mathrm{j}|} \cdot \ldots\right]_{\mathrm{E}} = k_1(c_\varepsilon)_{\mathrm{E}} / k_2(c_\varepsilon)_{\mathrm{E}} = K_{\mathrm{K}}. \tag{4.163}$$

As has already been verified, $\mathrm{k}_1(\mathrm{c}_\varepsilon)_{\mathrm{E}}, \mathrm{k}_2(\mathrm{c}_\varepsilon)_{\mathrm{E}}$ and, hence, K_{K} are at higher concentration levels usually not constants but quantities which change from equilibrium

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[63] See Sect. 4.5.

[64] The question of the real mechanism and the ideal rate function is from a technical point of view usually less important. The most important consideration is whether the evaluated kinetics can predict the formation of the products and gives the optimal conditions for the process (technically oriented kinetics). Kinetics' precision (i.e. costs of elaboration) must be weighed against its benefits.

state to equilibrium state—depending on the initial concentrations $c_{\varepsilon o}$—continuously or for a stepwise alteration step by step.[65]

The law of mass-action of the thermodynamic theory states that the relation

$$\begin{aligned}&[\ldots \cdot a_i{}^{|vi|} \cdot \ldots]/[\ldots \cdot a_j{}^{|vi|} \cdot \ldots]\\ &= \left[\ldots \cdot f_i(c_\varepsilon)^{|vi|} \cdot c_i{}^{|vi|} \cdot \ldots\right] / \left[\ldots \cdot f_j(c_\varepsilon)^{|vj|} \cdot c_j{}^{|vj|} \cdot \ldots\right] \\ &= \left[\ldots \cdot f_i(c_\varepsilon)^{|vi|} \cdot \ldots\right] / \left[\ldots \cdot f_j(c_\varepsilon)^{|vj|} \cdot \ldots\right] \cdot \left[\ldots \cdot c_i{}^{|vi|} \cdot \ldots\right] / \left[\ldots \cdot c_j{}^{|vj|} \cdot \ldots\right]\end{aligned} \tag{4.164}$$

between the activities of the reactants $a_j = c_j \cdot f_j(c_\varepsilon)$, the products $a_i = c_i \cdot f_i(c_\varepsilon)$ and the stoichiometric coefficients $v_{j/i}$ the conversion achieve at equilibrium a constant value K_{Th}. The constant is a feature of the conversion in the reaction mixture. The quotient of (4.163) and (4.164) gives the correlation between the thermodynamic equilibrium constant K_{Th} and the kinetic equilibrium quantity K_K of a reversible elementary conversion

$$K_{Th} = K_K \cdot \left[\ldots \cdot f_i(c_\varepsilon)_E{}^{|vi|} \cdot \ldots\right] / \left[\ldots \cdot f_j(c_\varepsilon)_E{}^{|vj|} \cdot \ldots\right]. \tag{4.165}$$

If the rate coefficients $k(c_\varepsilon)_E$ on the basis of thermokinetic analysis are elaborated or K_K is determined by means of the concentrations in equilibrium $c_{j;i,E}$ due to (4.163), the thermodynamic equilibrium constant K_{Th} is determined by means of the activity coefficients $f_{j;i}(c_\varepsilon)_E$.

The following elementary, reversible conversion will help to clarify:

$$A + B \underset{r_2}{\overset{r_1}{\leftrightarrow}} C$$

with

- Stoichiometric coefficients
$$v_A = -1, v_B = -1 \text{ and } v_C = 1$$
- Mol balance
$$\begin{aligned}c_{A0} &= c_A + c_C\\ c_{B0} &= c_B + c_C\end{aligned}$$
- Ideal rate functions
$$\begin{aligned}r_1 &= k_1 \cdot a_A \cdot a_B = k_1(c_\varepsilon) \cdot c_A \cdot c_B\\ r_2 &= k_2 \cdot a_C = k_2(c_\varepsilon) \cdot c_C\end{aligned}$$
- Rate coefficients

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[65] With an ideally (practically large) diluted reaction mix all activity coefficients $f_{j,i}(c_\varepsilon)_E$ reach the limiting value 1, the rate coefficients $k_1(c_\varepsilon)_E$, $k_2(c_\varepsilon)_E$ the limiting values k_1, k_2 and the kinetic equilibrium quantity K_K the limiting, characteristic value k_1/k_2.

$$k_1(c_\varepsilon) = k_1 \cdot f_A(c_\varepsilon) \cdot f_B(c_\varepsilon)$$
$$k_2(c_\varepsilon) = k_2 \cdot f_C(c_\varepsilon)$$

- Thermodynamic equilibrium constant

$$K_{Th} = a_{CE}/(a_{AE} \cdot a_{BE}) = k_1/k_2$$

The activity coefficient $f_{j;i}(c_\varepsilon)$ is

- $f_A(c_\varepsilon) = f_{A0} \cdot (1 - c_C/c_{A0}) = f_{A0} \cdot c_A/c_{A0}$

(The activity of A decreases solely by the formation of C)

- $f_B(c_\varepsilon) = f_{B0}/(1 - c_C/c_{B0}) = f_{B0} \cdot c_{B0}/c_B,$

i.e. the activity of B increases solely by the formation of C

- $f_C(c_\varepsilon) = f_{C0} = const.$

(The activity of C itself remains unchanged.)

Due to (4.163), we obtain for the kinetic equilibrium quantity

$$K_K = k_1(c_\varepsilon)_E/k_2(c_\varepsilon)_E = k_1/k_2 \cdot c_{B0}/c_{A0} \cdot f_{A0} \cdot f_{B0}/f_{C0} \cdot (c_A/c_B)_E$$
$$\neq K_{Th} = k_1/k_2.$$

The value of the kinetic equilibrium quantity K_K differs from the thermodynamic equilibrium constant K_{Th} by the factor $c_{B0}/c_{A0} \cdot f_{A0} \cdot f_{B0}/f_{C0} \cdot (c_A/c_B)_E$, and, of course, according to (4.165) K_{Th} results from K_K by setting the available activity coefficients at equilibrium $f_{j;i}(c_\varepsilon)_E$:[66]

$$\begin{aligned} K_{Th} &= k_1(c_\varepsilon)_E/k_2(c_\varepsilon)_E \cdot \left[\ldots \cdot f_i(c_\varepsilon)_E{}^{|\nu i|} \cdot \ldots\right] / \left[\ldots \cdot f_j(c_\varepsilon)_E{}^{|\nu j|} \cdot \ldots\right] \\ &= K_K \cdot \left[\ldots \cdot f_i(c_\varepsilon)_E{}^{|\nu i|} \cdot \ldots\right] / \left[\ldots \cdot f_j(c_\varepsilon)_E{}^{|\nu j|} \cdot \ldots\right] \\ &= k_1/k_2 \cdot c_{B0}/c_{A0} \cdot f_{A0} \cdot f_{B0}/f_{C0} \cdot c_{AE}/c_{BE} \cdot f_{C0}/[f_{A0} \cdot (c_{AE}/c_{A0}) \cdot f_{B0} \cdot (c_{B0}/c_{BE})] \\ &= k_1/k_2. \end{aligned}$$

However, in practise, the activity coefficients $f_{j;i}(c_\varepsilon)_E$ are usually not available or cannot be determined with the necessary precision.[67] Hence, calorimetric and

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[66] In principle, a relation similar to (4.126) can also be established with the use of any non-ideal rate function $r^{\#}$—in which (see previous section) respective reactant concentrations c_ζ are transferred from the ideal partial function of the rate coefficient $k(c_\varepsilon)$ into the ideal partial function $\left[\ldots \cdot c_{j-1}{}^{|\nu j-1|} \cdot c_j{}^{|\nu j|} \cdot \ldots\right]$ of the concentrations really driving on the reaction—because r^- and $r^{\#}$ are identical from the mathematical point of view. However, the relations are more complex depending on the degree of change in the ideal form.

[67] Determination methods for systems of two or more components are known in the literature.

classical kinetic investigations for the determination of the thermodynamic equilibrium constant K_{Th} of concentrated reaction mixtures are useless, even in the case of elementary reactions. Only measurements in ideal (in practise, large, diluted) solutions enables the determination of K_{Th} via rate coefficients.

There are more difficulties, even in the case of diluted reaction mixtures, with respect to determining the equilibrium constant from an overall kinetics because the partial orders in the rate functions of the forward and backward reactions usually do not coincide with the positive values of the stoichiometric coefficients of the overall stoichiometry.

In such cases, one must first elaborate the system of reversible elementary reactions, which form the basis of the reversible overall process [19, 34]. If it becomes evident that one elementary reaction is dominant for the rate of the overall process, a "stoichiometric correction number" v can be stated. v is the number of stoichiometric conversions of this elementary reaction which are necessary for one stoichiometric conversion of the overall process. To calculate the thermodynamic constant K_{Th} of the overall reaction, the kinetic equilibrium quantity $K_{K\text{overall}} = (k_1/k_2)_{\text{overall}}$ (quotient of the rate coefficients of the overall forward and backward reactions) is raised to the power v:

$$(\mathrm{k}_1/\mathrm{k}_2)_{\text{overall}}{}^{v} = (\mathrm{K}_{\mathrm{K}\text{overall}})^{v} = \mathrm{K}_{\mathrm{Th}}.$$

If no elementary reaction predominates for the rate of the overall conversion, the stoichiometry of each elementary reaction ξ is multiplied by an integer factor v_ξ, so that the sum of these varied elementary stoichiometries corresponds to the overall stoichiometry, i.e. the intermediate products in the sum are eliminated. For the thermodynamic equilibrium constant it follows that

$$\begin{aligned} K_{Th} &= (k_{1\text{Forw}}/k_{1\text{Backw}})^{v_1} \cdot (k_{2\text{Forw}}/k_{2\text{Backw}})^{v_2} \cdot \ldots \cdot \left(k_{\xi\text{Forw}}/k_{\xi\text{Backw}}\right)^{v_\xi} \cdot \ldots \cdot \\ &= K_{Th1}{}^{v_1} \cdot K_{Th2}{}^{v_2} \cdot \ldots \cdot K_{Th\xi}{}^{v_\xi} \cdot \ldots \cdot \end{aligned}$$

It is evident that the amount of work involved in determining the thermodynamic constant K_{Th} via rate coefficients and its faultiness is considerable. Therefore, it is preferable to determine K_{Th} on the basis of measurement of the concentrations in sufficiently diluted reaction mass at equilibrium by means of classical chemical analysis according to of (4.164) with $f_\zeta(c_\varepsilon) = 1$.

Chapter 5
Examples of Thermokinetic Investigations

5.1 Isothermal, Discontinuous, Constant-Volume Reactions

5.1.1 *Reaction of a Sulphide with Hydrogen Peroxide*

As an example of the elaboration of a kinetics on the basis of

- Data of non-isothermal, discontinuous reactions
- Mathematical-analytical relations

the catalytic consecutive reaction of a substituted sulphide with hydrogen peroxide to sulpho acid is discussed:

$$\mathrm{R_1 - S - R_2 + 3H_2O_2 \rightarrow R_1' - R_2' - SO_3H - R_3'}.$$

The process takes place in three stages:
(1) from sulphide to sulphoxid, (2) to sulphone (3) to sulpho acid:

$$\mathrm{R_1 - S - R_2 \xrightarrow[H_2O_2,\,Cat]{r_1,\,\Delta H_1} R_1 - SO - R_2 \xrightarrow[H_2O_2,\,Cat]{r_2,\,\Delta H_2}}$$
$$\mathrm{R_1 - SO_2 - R_2 \xrightarrow[H_2O_2,\,Cat]{r_3,\,\Delta H_3} R_1' - R_2' - SO_3H - R_3'}.$$

W. Litz, *Bench Scale Calorimetry in Chemical Reaction Kinetics*,
DOI 10.1007/978-3-319-12532-9_5

The stoichiometric coefficients are

$$\begin{aligned}
&\nu_{\mathrm{R1-S-R2},1} = -1, \nu_{\mathrm{H2O2},1} = -1, \nu_{\mathrm{R1-SO-R2},1} = 1, \nu_{\mathrm{R1-SO2-R2},1} = 0,\\
&\qquad \nu_{\mathrm{R'1-R'2-SO3H-R'3},1} = 0,\\
&\nu_{\mathrm{R1-S-R2},2} = 0, \nu_{\mathrm{H2O2},2} = -1, \nu_{\mathrm{R1-SO-R2},2} = -1, \nu_{\mathrm{R1-SO2-R2},2} = 1,\\
&\qquad \nu_{\mathrm{R'1-R'2-SO3H-R'3},2} = 0,\\
&\nu_{\mathrm{R1-S-R2},3} = 0, \nu_{\mathrm{H2O2},3} = -1, \nu_{\mathrm{R1-SO-R2},3} = 0, \nu_{\mathrm{R1-SO2-R2},3} = -1,\\
&\qquad \nu_{\mathrm{R'1-R'2-SO3H-R'3},3} = 1.
\end{aligned} \tag{5.1}$$

It is known that acids (such as sulphuric acid, nitric acid) catalyse the first stage; the second and third stages require additionally the use of potassium permanganate or sodium molybdate as catalyst.

To conduct the kinetic investigation, the measuring kettle of the calorimeter is filled with a batch of sulphide, Na_2MoO_4, H_2O_2 and xylene because the industrial production is run under conditions of cooling by reflux. The batch is brought to reaction temperature and H_2O_2 is injected simultaneously at the start of the reaction.

Figure 5.1 shows, for $T = 50$ °C, the temporal course of the caloric reaction power after instantaneous addition of different amounts of H_2O_2 (50 %).

The conversion has the following appearance

- The characteristic course of the thermal reaction power is independent of the amount of the abruptly injected H_2O_2:

  after a certain time t_E of uniform decay, the caloric reaction power decreases relatively abruptly and in a short time interval reaches the value zero;
- The time t_E increases by the increased addition of H_2O_2;
- The typical reaction does not change by increasing the concentration by the reduction of the aqueous part in the batch;

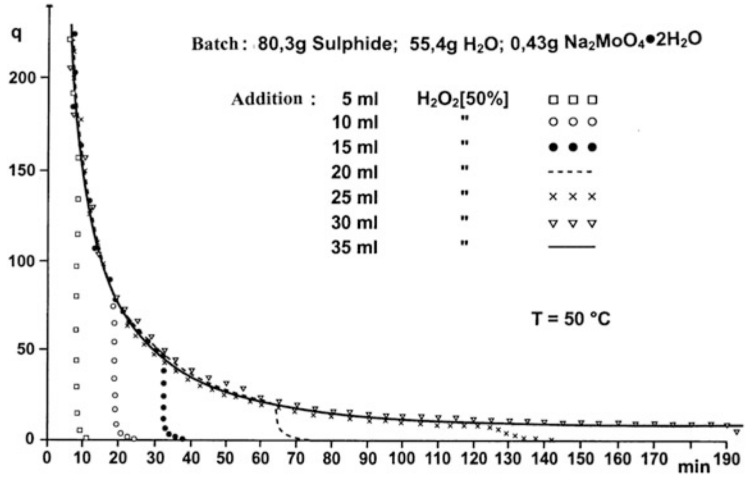

Fig. 5.1 Course of thermal reaction power q during oxidation of sulphide (95.5 % purity) for different amounts of dosed H_2O_2 (50 % purity)

- But the thermal reaction power increases; in contrast, the time interval up to the beginning of the almost abrupt decay of the rate of heat release diminishes.
- By the additional dose of H_2O_2 the phenomenon recurs, i.e. the thermal reaction power continues until it stops abruptly again after a time interval.
- When the added amount of H_2O_2 exceeds the stoichiometric amount for the total oxidation of the reaction system, the thermal reaction power no longer stops abruptly but decreases gradually to zero.
- When the first dosed amount of H_2O_2 exceeds the amount necessary for complete oxidation, the thermal reaction power diminishes, right away monotonously, to zero.
- The oxidation of sulphoxid or sulphon shows the same characteristic behaviour.

Obviously, the reaction steps are not elementary reactions, because the caloric reaction power respectively rate of reaction depends only on the concentration of sulphide, sulphoxid or sulphon but does not depend on the concentration of the reactant H_2O_2. Such a phenomenon occurs under special conditions when the catalyst first reacts reversibly with one of the reactants (Michaelis Menton mechanism); in the present case:

$$\mathrm{A} + \mathrm{Cat} \underset{r'_2,\,\Delta \mathrm{H}_{\lambda 2}}{\overset{r'_1,\,\Delta \mathrm{H}_{\lambda 1}}{\leftrightarrows}} \mathrm{A}\,\text{¤}\,\mathrm{Cat}$$

$$\mathrm{B} + \mathrm{A}\,\text{¤}\,\mathrm{Cat} \xrightarrow[r'_3,\,\Delta H_{\lambda 3}]{} \mathrm{C} + \mathrm{Cat}$$

with

$\mathrm{A} : H_2O_2$
B : sulphide, sulphoxid, sulphone
C : sulphoxid, sulphone, sulpho acid
Cat : sodium molybdate

Stoichiometric coefficients

$$\begin{aligned}
&\nu_{\mathrm{A1}} = -1, \nu_{\mathrm{Kat1}} = -1, \nu_{\mathrm{A\,¤\,Cat1}} = 1, \nu_{\mathrm{B1}} = 0, \nu_{\mathrm{C1}} = 0,\\
&\nu_{\mathrm{A2}} = 1, \nu_{\mathrm{Kat2}} = 1, \nu_{\mathrm{A\,¤\,Cat2}} = -1, \nu_{\mathrm{B2}} = 0, \nu_{\mathrm{C2}} = 0,\\
&\nu_{\mathrm{A3}} = 0, \nu_{\mathrm{Kat3}} = 1, \nu_{\mathrm{A\,¤\,Cat3}} = -1, \nu_{\mathrm{B3}} = -1, \nu_{\mathrm{C3}} = 1.
\end{aligned}$$

The intermediate product A¤Cat represents a, so to speak, activated H_2O_2; obviously, only in this state is a reaction with B for the production of C possible, by which the catalyst Cat returns to replenish the complex A¤Cat by means of the reservoir of A.

On the assumption that both the achievement of equilibrium and the following reaction occur by elementary steps, for the rate of change in the intermediate product A¤Cat and the rate of formation in the oxidized product C we obtain, corresponding to (4.9) and (4.34),

$$\begin{aligned} \mathrm{d}c_{\text{A ¤ Cat}}/\mathrm{d}t &= k_1^{'} \cdot c_{\mathrm{A}} \cdot c_{\mathrm{Cat}} - k_2^{'} \cdot c_{\text{A ¤ Cat}} - k_3^{'} \cdot c_{\text{A ¤ Cat}} \cdot c_{\mathrm{B}} \\ \mathrm{d}c_{\mathrm{C}}/\mathrm{d}t &= k_3^{'} \cdot c_{\text{A ¤ Cat}} \cdot c_{\mathrm{B}}. \end{aligned} \tag{5.2}$$

Because the catalyst and, consequently, the activated intermediate complex A¤Cat are present only in very small concentrations, naturally there is not much leeway for this to change, and after a short initial phase the following equation holds (Bodenstein hypothesis):

$$k_1^{'} \cdot c_{\mathrm{A}} \cdot c_{\mathrm{Cat}} - k_2^{'} \cdot c_{\text{A ¤ Cat}} - k_3^{'} \cdot c_{\text{A ¤ Cat}} \cdot c_{\mathrm{A}} = 0.$$

With the initial concentration of the catalyst c_{Cat_0} we obtain, according to the mol balance, $c_{\mathrm{Cat}} = c_{\mathrm{Cat}_0} - c_{\mathrm{A \div Cat}}$,

$$c_{\text{A ¤ Cat}} = \left[k_1^{'} \cdot c_{\mathrm{A}} \cdot c_{\mathrm{Cat}_0}\right] \Big/ \left[k_2^{'} + k_3^{'} \cdot c_{\mathrm{B}} + k_1^{'} \cdot c_{\mathrm{Cat}}\right].$$

A¤Cat does not fall into a state of congestion after the initial phase. Therefore, the rate of formation in the oxidized product C, the rates of consumption in reactants A and B and the rate of circulation in the intermediate complex A¤Cat correspond to one another. According to (5.2) the following equation is valid:

$$\begin{aligned} -\mathrm{d}c_{\mathrm{A}}/\mathrm{d}t &= -\mathrm{d}c_{\mathrm{B}}/\mathrm{d}t = \mathrm{d}c_{\mathrm{C}}/\mathrm{d}t \\ &= k_3^{'} \cdot k_1^{'} \cdot c_{\mathrm{Cat}_0} \cdot c_{\mathrm{A}} \cdot c_{\mathrm{B}} \Big/ \left[k_2^{'} + k_3^{'} \cdot c_{\mathrm{B}} + k_1^{'} \cdot c_{\mathrm{A}}\right]. \end{aligned} \tag{5.3}$$

If the conversion velocity of reactant B with the intermediate complex A¤Cat is essentially smaller than the velocity at which chemical equilibrium is achieved between A, Cat and A¤Cat, i.e. $k_3^{'} \ll k_2^{'} < k_1^{'}$, (5.3) changes to

$$-\mathrm{d}c_{\mathrm{A}}/\mathrm{d}t = -\mathrm{d}c_{\mathrm{B}}/\mathrm{d}t = \mathrm{d}c_{\mathrm{C}}/\mathrm{d}t = k_3^{'} \cdot c_{\mathrm{Cat}_0} \cdot c_{\mathrm{B}} \cdot \gamma$$

with

$$\gamma = k_1^{'}/k_2^{'} \cdot c_{\mathrm{A}} \Big/ \left[1 + k_1^{'}/k_2^{'} \cdot c_{\mathrm{A}}\right].$$

The factor γ is a function of c_{A}. γ sets the tone for the temporal course of the overall rate. Within the range of high concentration with $k_1^{'}/k_2^{'} \cdot c_{\mathrm{A}} \gg 1$ the factor γ is constant, i.e. $\cong 1$. The intermediate complex A¤Cat is present in the largest possible concentration ($\cong c_{\mathrm{Cat}_0}$). The reaction rate is only proportional to the concentration of B, and the reaction runs at a rate of order 1:

$$-\mathrm{d}c_{\mathrm{A}}/\mathrm{d}t = -\mathrm{d}c_{\mathrm{B}}/\mathrm{d}t = \mathrm{d}c_{\mathrm{C}}/\mathrm{d}t \cong \left[k_3^{'} \cdot c_{\mathrm{Cat}_0}\right] \cdot c_{\mathrm{B}} = k\{c_{\mathrm{Cat}_0}\} \cdot c_{\mathrm{B}} = r. \tag{5.4}$$

If the concentration of A during the conversion decreases to the range of small concentration with $k_1'/k_2' \cdot c_A \ll 1$, then the factor γ holds:

$$\gamma \cong k_1'/k_2' \cdot c_A.$$

The intermediate complex $A \div \mathrm{Cat}$ is not present now in practically unchanged concentration ($\cong c_{\mathrm{Cat}_0}$) but changes directly proportionally to c_A. We obtain the following results:

$$\begin{aligned} -\mathrm{d}c_A/\mathrm{d}t = -\mathrm{d}c_B/\mathrm{d}t = \mathrm{d}c_C/\mathrm{d}t &= \left(k_3' \cdot k_1'/k_2'\right) \cdot c_{\mathrm{Cat}_0} \cdot c_B \cdot c_A \\ &= k\{c_{\mathrm{Cat}_0}\} \cdot c_A \cdot c_B. \end{aligned} \tag{5.5}$$

The transition from the range with $\gamma \cong 1$, i.e. (5.4), to a range with $\gamma \cong k_1'/k_2' \cdot c_A$, i.e. (5.5), takes place more abruptly depending on the relation k_1'/k_2', i.e. the larger the thermodynamic equilibrium constant of the equilibrium between A, Cat and $A \div \mathrm{Cat}$, the more abrupt the transition.[1]

The course of the measured thermal reaction power versus time shows this occurrence in the form of a suddenly starting decay at t_{E1}, already reaching after a short time virtually the value zero at t_{E2} (Fig. 5.1). Hence, the transition of the reaction rate from (5.4) to (5.5) occurs immediately before the complete consumption of H_2O_2 at t_{E2}. Therefore, for simplification it is taken as a basis that the oxidation process runs according to the rate function (5.4) up to the complete conversion of H_2O_2 at the time t_E, for which the following expression holds: $t_{E1} < t_E < t_{E2}$, and t_E is determined according to $Q = \int_{t_{E1} \to t_{E2}} \left\{q_{(\text{measurement})}\right\} \mathrm{d}t = \int_{t_{E1} \to t_E} \left\{q_{(\text{due to 5.4})}\right\} \mathrm{d}t$.

The thermokinetic interpretation of the measured course of the thermal reaction power of the oxidation of sulphide via sulphoxid and sulphon up to sulpho acid is started on a trial basis according to the assumption of quasi-elementary steps, the stoichiometry and (5.1), (4.9), (4.34), with

$$\mathrm{d}c_{\mathrm{R1-S-R2}}/\mathrm{d}t = -r_1 = k_1 \cdot c_{\mathrm{R1-S-R2}}. \tag{5.6}$$

$$\mathrm{d}c_{\mathrm{R1-SO-R2}}/\mathrm{d}t = r_1 - r_2 = k_1 \cdot c_{\mathrm{R1-S-R2}} - k_2 \cdot c_{\mathrm{R1-SO-R2}}. \tag{5.7}$$

$$\mathrm{d}c_{\mathrm{R1-SO2-R2}}/\mathrm{d}t = r_2 - r_3 = k_2 \cdot c_{\mathrm{R1-SO-R2}} - k_3 \cdot c_{\mathrm{R1-SO2-R2}}. \tag{5.8}$$

$$\mathrm{d}c_{\mathrm{R'1-R'2-SO3H-R'3}}/\mathrm{d}t = r_3 = k_3 \cdot c_{\mathrm{R1-SO2-R2}}. \tag{5.9}$$

$$\begin{aligned} \mathrm{d}c_{\mathrm{H2O2}}/\mathrm{d}t &= -r_1 - r_2 - r_3 \\ &= -k_1 \cdot c_{\mathrm{R1-S-R2}} - k_2 \cdot c_{\mathrm{R1-SO-R2}} - k_3 \cdot c_{\mathrm{R1-SO2-R2}}. \end{aligned} \tag{5.10}$$

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[1] Compare, formally, the transition behaviour of the Langmuir adsorption isotherm.

The solution of the equation system (5.6), (5.7) and (5.8) gives

$$c_{\mathrm{R1-S-R2}}/(c_{\mathrm{R1-S-R2}})_0 = \mathrm{EXP}(-k_1 \cdot t) \tag{5.11}$$

$$c_{\mathrm{R1-SO-R2}}/(c_{\mathrm{R1-S-R2}})_0 = k_1/(k_2 - k_1) \cdot [\mathrm{EXP}(-k_1 \cdot t) - \mathrm{EXP}(-k_2 \cdot t)] \tag{5.12}$$

$$\begin{aligned} c_{\mathrm{R1-SO2-R2}}/(c_{\mathrm{R1-S-R2}})_0 = {} & k_1 \cdot k_2 \cdot (k_2 - k_1)^{-1} \cdot \Big[(k_2 - k_3)^{-1} \cdot \mathrm{EXP}(-k_2 \cdot t) \\ & -(k_1 - k_3)^{-1} \cdot \mathrm{EXP}(-k_1 \cdot t) + (k_2 - k_1) \\ & \cdot (k_1 - k_3)^{-1} \cdot (k_2 - k_3)^{-1} \cdot \mathrm{EXP}(-k_3 \cdot t)\Big] \\ = {} & k_1 \cdot k_2 \cdot (k_2 - k_1)^{-1} \cdot (k_1 - k_3)^{-1} \cdot (k_2 - k_3)^{-1} \\ & \cdot [(k_1 - k_3) \cdot \mathrm{EXP}(-k_2 \cdot t) - (k_2 - k_3) \\ & \cdot \mathrm{EXP}(-k_1 \cdot t) + (k_2 - k_1) \cdot \mathrm{EXP}(-k_3 \cdot t)]. \end{aligned} \tag{5.13}$$

The relative concentrations $c_{\mathrm{R1'-R2'SO3H-R3'}}/(c_{\mathrm{R1-S-R2}})_0$ and $c_{\mathrm{H2O2}}/(c_{\mathrm{R1-S-R2}})_0$ result from the mol balance in the following way:

- Integration of the sum of (5.6), (5.7), (5.8) and (5.9) gives

$$\begin{aligned} 0 = {} & \left[c_{\mathrm{R1-S-R2}} - (c_{\mathrm{R1-S-R2}})_0\right] + \left[c_{\mathrm{R1-SO-R2}} - (c_{\mathrm{R1-SO-R2}})_0\right] + \\ & + \left[c_{\mathrm{R1-SO2-R2}} - (c_{\mathrm{R1-SO2-R2}})_0\right] + \Big[c_{\mathrm{R1'-R2'-SO3H-R3'}} \\ & - \left(c_{\mathrm{R1'-R2'-SO3H-R3'}}\right)_0\Big]. \end{aligned}$$

or with (5.11), (5.12), (5.13) and

$$(c_{\mathrm{R1-SO-R2}})_0 = (c_{\mathrm{R1-SO2-R2}})_0 = \left(c_{\mathrm{R1'-R2'-SO3H-R3'}}\right)_0] = 0$$

it follows that

$$\begin{aligned} c_{\mathrm{R1'-R2'-SO3H-R3'}}/(c_{\mathrm{R1-S-R2}})_0 = {} & 1 + (k_2 - k_1)^{-1} \cdot [k_1 \cdot \mathrm{EXP}(-k_2 \cdot t) - k_2 \cdot \mathrm{EXP}(-k_1 \cdot t)] \\ & + k_1 \cdot k_2 \cdot (k_2 - k_1)^{-1} \cdot \big[(k_1 - k_3)^{-1} \cdot \mathrm{EXP}(-k_1 \cdot t) \\ & - (k_2 - k_3)^{-1} \cdot \mathrm{EXP}(-k_2 \cdot t) - (k_2 - k_1) \\ & \cdot (k_1 - k_3)^{-1} \cdot (k_2 - k_3)^{-1} \cdot \mathrm{EXP}(-k_3 \cdot t)\big] \\ = {} & 1 + (k_2 - k_1)^{-1} \cdot [k_1 \cdot \mathrm{EXP}(-k_2 \cdot t) \\ & - k_2 \cdot \mathrm{EXP}(-k_1 \cdot t)] - k_1 \cdot k_2 \cdot (k_2 - k_1) \\ & \cdot (k_1 - k_3)^{-1} \cdot (k_2 - k_3)^{-1} \cdot [(k_1 - k_3) \\ & \cdot \mathrm{EXP}(-k_2 \cdot t) - (k_2 - k_3) \cdot \mathrm{EXP}(-k_1 \cdot t) \\ & + (k_2 - k_1) \cdot \mathrm{EXP}(-k_3 \cdot t)]. \end{aligned} \tag{5.14}$$

- By the addition of (5.9) and (5.10), subtraction of (5.7) and 2·(5.6) and integration of the result we obtain

$$\begin{aligned}&\left[c_{\mathrm{H2O2}} - (c_{\mathrm{H2O2}})_0\right] + \left[c_{\mathrm{R1'-R2'-SO3H-R3'}} - \left(c_{\mathrm{R1'-R2'-SO3H-R1'}}\right)_0\right]\\&-\left[c_{\mathrm{R1-SO-R2}} - (c_{\mathrm{R1-SO-R2}})_0\right] - 2\cdot\left[c_{\mathrm{R1-S-R2}} - (c_{\mathrm{R1-S-R2}})_0\right] = 0\end{aligned}$$

or with (5.11), (5.12), (5.13) and $\left(c_{\mathrm{R1'-R2'-SO3H-R3'}}\right)_0 = (c_{\mathrm{R1-SO-R2}})_0 = 0$ it follows that

$$\begin{aligned}c_{\mathrm{H2O2}}/(c_{\mathrm{R1-S-R2}})_0 &= (c_{\mathrm{H2O2}})_0/(c_{\mathrm{R1-S-R2}})_0 - 3 + \left\{(k_1-k_2)^{-1}\cdot[k_1\cdot \mathrm{EXP}(-k_2\cdot t) - k_2\cdot \mathrm{EXP}(-k_1\cdot t)]\right.\\&\quad + k_1\cdot k_2\cdot (k_1-k_2)^{-1}\cdot(k_1-k_3)^{-1}\cdot(k_2-k_3)^{-1}\\&\quad \cdot\left[(k_2-k_3)\cdot \mathrm{EXP}(-k_1\cdot t) - (k_1-k_3)\cdot \mathrm{EXP}(-k_2\cdot t)\right.\\&\quad \left.\left. -(k_2-k_1)\cdot \mathrm{EXP}(-k_3\cdot t)\right]\right\} - k_1\cdot(k_1-k_2)^{-1}\\&\quad \cdot[\mathrm{EXP}(-k_1\cdot t) - \mathrm{EXP}(-k_2\cdot t)] + 2\cdot \mathrm{EXP}(-k_1\cdot t)\\&= \left[(c_{\mathrm{H2O2}})_0/(c_{\mathrm{R1-S-R2}})_0 - 3\right]\\&\quad + \left[2 + k_1\cdot k_2\cdot(k_1-k_2)^{-1}\cdot(k_1-k_3)^{-1} - k_1\cdot(k_1-k_2)^{-1} - k_2\cdot(k_1-k_2)^{-1}\right]\\&\quad \cdot \mathrm{EXP}(-k_1\cdot t) + \left[2\cdot k_1\cdot(k_1-k_2)^{-1} - k_1\cdot k_2\cdot(k_1-k_2)^{-1}\cdot(k_2-k_3)^{-1}\right]\\&\quad \cdot \mathrm{EXP}(-k_2\cdot t) + \left[k_1\cdot k_2\cdot(k_2-k_3)^{-1}\cdot(k_1-k_3)^{-1}\right]\cdot \mathrm{EXP}(-k_3\cdot t)\\&= \left[(c_{\mathrm{H2O2}})_0/(c_{\mathrm{R1-S-R2}})_0 - 3\right] + A_1\cdot \mathrm{EXP}(-k_1\cdot t) + A_2\cdot \mathrm{EXP}(-k_2\cdot t) + A_3\\&\quad \cdot \mathrm{EXP}(-k_3\cdot t)\\&= \left[(c_{\mathrm{H2O2}})_0/(c_{\mathrm{R1-S-R2}})_0 - 3\right] + F_1(t) + F_2(t) + F_3(t).\end{aligned} \tag{5.15}$$

The value 3 corresponds to the stoichiometric coefficient of hydrogen peroxide in the overall reaction $\mathrm{R_1 - S - R_2 + 3H_2O_2 \rightarrow R_1' - R_2' - SO_3H - R_3'}$. $\left[(c_{\mathrm{H2O2}})_0/(c_{\mathrm{R1-S-R2}})_0 - 3\right]$ represents the final, relative concentration of H_2O_2 after the complete oxidation of the batch. The concentration drops during the conversion monotonously to the final concentration according to (5.15). When the injected relative amount of the hydrogen peroxide exceeds the stoichiometric value 3, its final relative concentration is greater than zero: $\left\{(c_{\mathrm{H2O2}})_{\mathrm{E}}/(c_{\mathrm{R1-S-R2}})_0 > 0\right\}$. When the injected relative amount of the hydrogen peroxide is smaller than 3, $\left\{(c_{\mathrm{H2O2}})_0/(c_{\mathrm{R1-S-R2}})_0 < 3\right\}$, we obtain formally a negative final concentration: $\left\{(c_{\mathrm{H2O2}})_{\mathrm{E}}/(c_{\mathrm{R1-S-R2}})_0 < 0\right\}$. However, the concentration reaches a value of zero at time $t_{\mathrm{E}} < \infty$, i.e. the injected H_2O_2 is used up and the oxidation stops abruptly at time t_{E} (in reality: in the form of a curve sharply sloping to zero in shortest time).

Hence, the procedure for determining the rate coefficients k_1, k_2, k_3 is obvious:

The plot of $\ln\left\{3 - (c_{\mathrm{H2O2}})_0/(c_{\mathrm{R1-S-R2}})_0\right\}$ versus the measured points of time t_{E} of the ends of the reaction yields, according to (5.15), a curved line which turns into a straight line F_{slowest} (Fig. 5.2) whose slope corresponds to the rate coefficient of the slowest reaction, i.e. k_1, k_2 or k_3. The point of interception with the ordinate is either

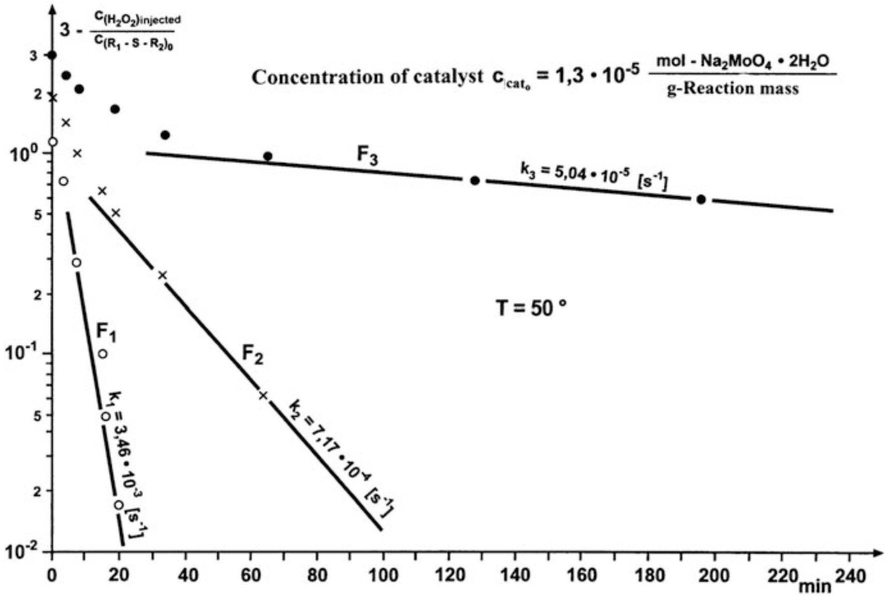

Fig. 5.2 Test of reaction model, determination of rate coefficients

$$\ln\{A_1\} = \ln\Big\{2 + k_1 \cdot k_2 \cdot (k_1 - k_2)^{-1} \cdot (k_1 - k_3)^{-1} - k_1 \cdot (k_1 - k_2)^{-1} - k_2 \cdot (k_1 - k_2)^{-1}\Big\}.$$

or

$$\ln\{A_2\} = \ln\Big\{2 \cdot k_1 \cdot (k_1 - k_2)^{-1} - k_1 \cdot k_2 \cdot (k_1 - k_2)^{-1} \cdot (k_2 - k_3)^{-1}\Big\} \tag{5.16}$$

or

$$\ln\{A_3\} = \Big\{k_1 \cdot k_2 \cdot (k_2 - k_3)^{-1} \cdot (k_1 - k_3)^{-1}\Big\},$$

depending on whether the first stage (formation of sulphoxid), the second stage (formation of sulphon) or the third stage (formation of sulpho acid) is the slowest step.

The plot of $\ln\big\{\big[3 - (c_{\mathrm{H2O2}})_0/(c_{\mathrm{R1-S-R2}})_0\big] - F_{\mathrm{slowest}}\big\}$ against t_{E} gives a curve which also turns into a straight line $F_{\mathrm{second\ slowest}}$ whose slope corresponds to the rate coefficient of the second slowest step. The slope can be k_1, k_2 or k_3 and the point of intersection with the ordinate can be

$$\ln\{A_1\} = \ln\Big\{2 + k_1 \cdot k_2 \cdot (k_1 - k_2)^{-1} \cdot (k_1 - k_3)^{-1} - k_1 \cdot (k_1 - k_2)^{-1} - k_2 \cdot (k_1 - k_2)^{-1}\Big\}.$$

or

$$\ln\{A_2\} = \ln\left\{2 \cdot k_1 \cdot (k_1 - k_2)^{-1} - k_1 \cdot k_2 \cdot (k_1 - k_2)^{-1} \cdot (k_2 - k_3)^{-1}\right\}$$

or

$$\ln\{A_3\} = \left\{k_1 \cdot k_2 \cdot (k_2 - k_3)^{-1} \cdot (k_1 - k_3)^{-1}\right\}.$$

Also, the plot of $\ln\left\{\left[3 - (c_{\mathrm{H2O2}})_0/(c_{\mathrm{R1-S-R2}})_0\right] - F_{\mathrm{slowest}} - F_{\mathrm{second\ slowest}}\right\}$ against t_{E} gives a straight line F_{quick}. Its slope corresponds to the rate coefficient of the quickest step, i.e. k_1 or k_2 or k_3. The point of intersection with the ordinate is either

$$\ln\{A_1\} = \ln\left\{2 + k_1 \cdot k_2 \cdot (k_1 - k_2)^{-1} \cdot (k_1 - k_3)^{-1} - k_1 \cdot (k_1 - k_2)^{-1} - k_2 \cdot (k_1 - k_2)^{-1}\right\}.$$

or

$$\ln\{A_2\} = \ln\left\{2 \cdot k_1 \cdot (k_1 - k_2)^{-1} - k_1 \cdot k_2 \cdot (k_1 - k_2)^{-1} \cdot (k_2 - k_3)^{-1}\right\}$$

or

$$\ln\{A_3\} = \left\{k_1 \cdot k_2 \cdot (k_2 - k_3)^{-1} \cdot (k_1 - k_3)^{-1}\right\}.$$

It is impossible to recognize directly the slowest, second slowest or quick reaction stage. This takes place indirectly. For that, an assumption on is made a trial basis assigning k_1, k_2 and k_3 to the slopes of the three straight lines F. By that is made simultaneously the assignment of $\ln A_1$, $\ln A_2$ and $\ln A_3$ to the corresponding points of the intersection of the straight lines with the ordinate. Then it is tested whether the calculated $\ln A_i$ and the measured intersection points coincide. If not, a second, different assignment is made, and so on. At most six different assumptions are checked.

Figures 5.2 and 5.3 show the plots of $\ln\left\{3 - (c_{\mathrm{H2O2}})_0/(c_{\mathrm{R1-S-R2}})_0\right\}$ versus t_{E} for the measured data at temperatures $T = 25$ °C and $T = 50$ °C. The result of the trial-and-error procedure gives $k_1 \gg k_2 > k_3$.

Now, on the basis of the known rate coefficients k_1, k_2 and k_3, the heats of reaction can be determined as follows. Due to (4.7), (4.34), (5.4), (5.11), (5.12) and (5.13), the determining equation of the thermal reaction power reads

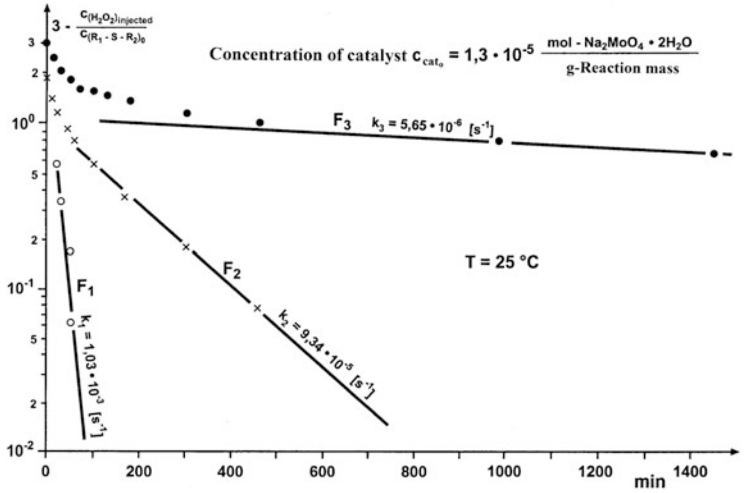

Fig. 5.3 Examination of reaction model, determination of rate coefficients *k*

$$
\begin{aligned}
q &= q_1 + q_2 + q_3 \\
&= r_1 \cdot (-\Delta H_{\lambda 1}) \cdot V + r_2 \cdot (-\Delta H_{\lambda 2}) \cdot V + r_3 \cdot (-\Delta H_{\lambda 3}) \cdot V \\
&= k_1 \cdot c_{\text{R1-S-R2}} \cdot (-\Delta H_{\lambda 1}) \cdot V + k_2 \cdot c_{\text{R1-SO-R2}} \cdot (-\Delta H_{\lambda 2}) \cdot V + k_3 \cdot c_{\text{R1-SO2-R2}} \\
&\quad \cdot (-\Delta H_{\lambda 3}) \cdot V \\
&= k_1 \cdot (c_{\text{R1-S-R2}})_0 \cdot V \cdot (-\Delta H_{\lambda 1}) \cdot \text{EXP}(-k_1 \cdot t) \\
&\quad + k_2 \cdot k_1 \cdot (k_2 - k_1)^{-1} \cdot (c_{\text{R1-S-R2}})_0 \cdot V \cdot (-\Delta H_{\lambda 2}) \cdot [\text{EXP}(-k_1 \cdot t) - \text{EXP}(-k_2 \cdot t)] \\
&\quad + k_1 \cdot k_2 \cdot k_3 \cdot (k_2 - k_1)^{-1} \cdot (k_1 - k_3)^{-1} \cdot (k_2 - k_3)^{-1} \cdot (c_{\text{R1-S-R2}})_0 \cdot V \cdot (-\Delta H_{\lambda 3}) \\
&\quad \cdot [(k_1 - k_3) \cdot \text{EXP}(-k_2 \cdot t) - (k_2 - k_3) \cdot \text{EXP}(-k_1 \cdot t) + (k_2 - k_1) \cdot \text{EXP}(-k_3 \cdot t)] \\
&= k_1 \cdot (-\Delta H_{\lambda 1}) + k_2 \cdot k_1 \cdot (k_2 - k_1)^{-1} \cdot (-\Delta H_{\lambda 2}) - k_1 \cdot k_2 \cdot k_3 \cdot (k_2 - k_1)^{-1} \cdot \\
&\quad (k_1 - k_3)^{-1} \cdot (-\Delta H_{\lambda 3}) \cdot (c_{\text{R1-S-R2}})_0 \cdot V \cdot \text{EXP}(-k_1 \cdot t) \\
&\quad + k_1 \cdot k_2 \cdot k_3 \cdot (k_2 - k_1)^{-1} \cdot (k_2 - k_3)^{-1} \cdot (-\Delta H_{\lambda 3}) - k_2 \cdot k_1 \cdot (k_2 - k_1)^{-1} \cdot \\
&\quad (-\Delta H_{\lambda 2}) \cdot (c_{\text{R1-S-R2}})_0 \cdot V \cdot \text{EXP}(-k_2 \cdot t) \\
&\quad + k_1 \cdot k_2 \cdot k_3 \cdot (k_1 - k_3)^{-1} \cdot (k_2 - k_3)^{-1} \cdot (-\Delta H_{\lambda 3}) \cdot (c_{\text{R1-S-R2}})_0 \cdot V \cdot \text{EXP}(-k_3 \cdot t) \\
&= B_1 \cdot \text{EXP}(-k_1 \cdot t) \; + \; B_2 \cdot \text{EXP}(-k_2 \cdot t) \; + \; B_3 \cdot \text{EXP}(-k_3 \cdot t) \\
&= \boldsymbol{I}_1(t) + \boldsymbol{I}_2(t) + \boldsymbol{I}_3(t).
\end{aligned}
\tag{5.17}
$$

Plotting $\ln\{q\}$ versus time *t* (Fig. 5.4) yields a curved line which turns into a straight line. Its slope gives the value of the rate coefficient of the slowest stage, i.e. k_3 as determined. Hence, the straight line represents $\ln\{I_3(t)\}$ and the point of its intercept with the ordinate is, according to (5.17),

$$
\begin{aligned}
\ln\{B_3\} \;=\; & \ln\big\{\big(k_1 \cdot k_2 \cdot k_3 \cdot (k_1 - k_3)^{-1} \cdot (k_2 - k_3)^{-1} \cdot (-\Delta H_{\lambda 3}) \\
& \cdot (c_{\text{R1-S-R2}})_0 \cdot V\big\}.
\end{aligned}
$$

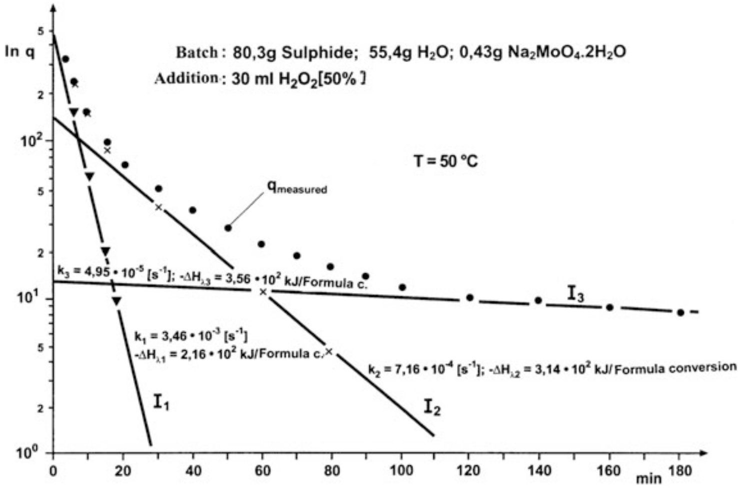

Fig. 5.4 Determination of enthalpies of reaction from course of thermal reaction power

The plot of $\ln\{(q - I_3)\}$ against time t gives a curve ending as a straight line whose slope corresponds to the rate coefficients of the second slowest reaction, i.e. k_2. Therefore, the straight line tallies with $\ln\{I_2(t)\}$ and the point of its intercept with the ordinate is in accordance with (5.17)

$$\begin{aligned}\ln\{B_2\} = \ln\Big\{ \Big[& k_1 \cdot k_2 \cdot k_3 \cdot (k_2 - k_1)^{-1} \cdot (k_2 - k_3)^{-1} \cdot (-\Delta H_{\lambda 3}) \\ & - k_2 \cdot k_1 \cdot (k_2 - k_1)^{-1} \cdot (-\Delta H_{\lambda 2}) \Big] \cdot (c_{\mathrm{R1-S-R2}})_0 \cdot V \Big\}.\end{aligned}$$

From the plot of $\ln\{(q - I_3 - I_2)\}$ versus t we get a straight line. Its slope corresponds with the rate coefficient of the quick stage, i.e. k_1, as determined previously. The ordinate intercept is, according to (5.17),

$$\begin{aligned}\ln\{B_1\} = \ln\big\{ \big[& k_1 \cdot (-\Delta H_{\lambda 1}) + k_2 \cdot k_1 \cdot (k_2 - k_1)^{-1} \cdot (-\Delta H_{\lambda 2}) \\ & - k_1 \cdot k_2 \cdot k_3 \cdot (k_2 - k_1)^{-1} \cdot (k_1 - k_3)^{-1} \cdot (-\Delta H_{\lambda 3}) \big] \cdot (c_{\mathrm{R1-S-R2}})_0 \cdot V \big\}.\end{aligned}$$

Using the relations B_3, B_2 and B_1 as well as the rate coefficients k_1, k_2 and k_3 we calculate the enthalpies of reaction:

$$\begin{aligned}(-\Delta H_{\lambda 1}) &= 216 \ \text{kJ/formula conversion}, \\ (-\Delta H_{\lambda 2}) &= 314 \ \text{kJ/formula conversion}, \\ (-\Delta H_{\lambda 3}) &= 356 \ \text{kJ/formula conversion}.\end{aligned}$$

Checking whether the linear dependence of the rate coefficients on the concentration of catalyst c_{Cat_0} is valid – as the first elementary hypothesis of the catalytic

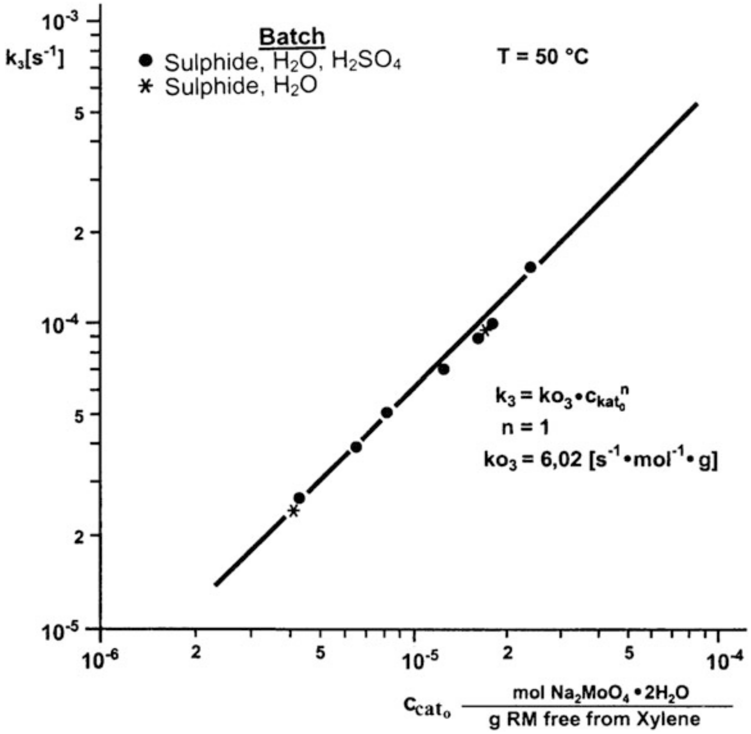

Fig. 5.5 Dependency of rate coefficient k_3 on concentration of catalyst c_{Cat_0}

elementary mechanism entails – the oxidation is carried out at different concentrations of the catalyst. Figures 5.5, 5.6, 5.7 and 5.8 show that the linear dependence applies only for the formation in sulpho acid. For the formation in sulphoxid respectively sulphon acid the dependencies of the rate coefficients on c_{Cat_0} have the powers 1.1 respectively 1.5.

Obviously, the reaction rates are overall rates which describe the dynamics of the oxidation sufficiently, see footnote[11] in 4.2.1.1.1.2.

Figures 5.5, 5.6, 5.7 and 5.8 show furthermore that the addition of either sulphuric acid or xylene does not have any effect on the value of the rate coefficients. They are only a function of the temperature and concentration of the catalyst. The Arrhenius equation (Fig. 5.9) describes the temperature dependency. Hence,

$$\begin{aligned} k_1 &= ko_1(T)\cdot c_{\mathrm{Cat}_0}^{1.1} = kH_1\cdot \mathrm{EXP}(-E_1/RT)\cdot c_{\mathrm{Cat}_0}^{1.1}, \\ k_2 &= ko_2(T)\cdot c_{\mathrm{Cat}_0}^{1.5} = kH_2\cdot \mathrm{EXP}(-E_2/RT)\cdot c_{\mathrm{Cat}_0}^{1.5}, \\ k_3 &= ko_3(T)\cdot c_{\mathrm{Cat}_0} = kH_3\cdot \mathrm{EXP}(-E_3/RT)\cdot c_{\mathrm{Cat}_0}, \end{aligned} \tag{5.18}$$

with

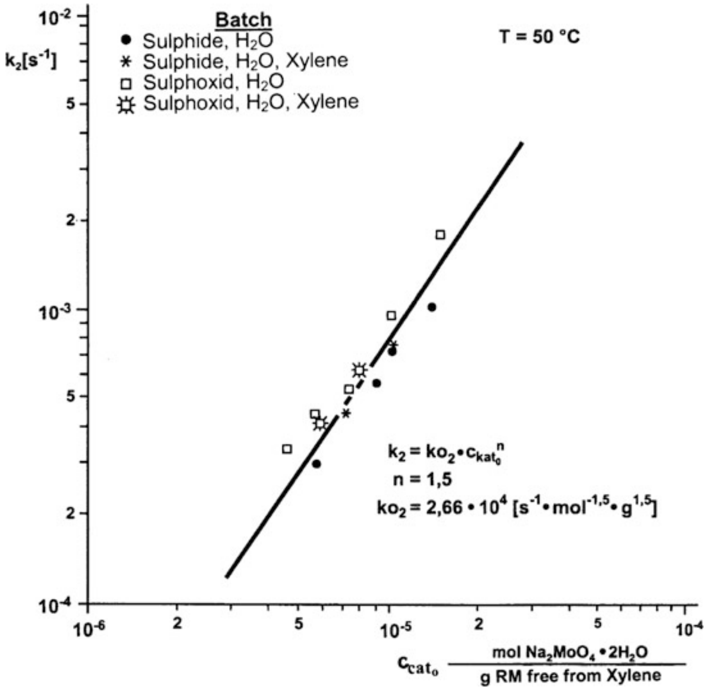

Fig. 5.6 Dependency of rate coefficient k_2 on concentration of catalyst c_{Cat_0}

$$
\begin{aligned}
kH_1 &= 2.05 \times 10^9 \left[\mathrm{s}^{-1}\ \mathrm{mol}^{-1.1}\ \mathrm{g}^{1.1}\right], E_1 = 38.78\ \mathrm{kJ/mol}, \\
kH_2 &= 5.45 \times 10^{14}\left[\mathrm{s}^{-1}\mathrm{mol}^{-1.5}\ \mathrm{g}^{1.5}\right], E_2 = 63.76\ \mathrm{kJ/mol}, \\
kH_3 &= 1.29 \times 10^{12}\left[\mathrm{s}^{-1}\mathrm{mol}^{-1}\ \mathrm{g}^{1}\right], E_3 = 70.04\ \mathrm{kJ/mol}.
\end{aligned}
$$

The different values of the activity energy E_1, E_2 and E_3 causes the rate of formation in the desired product sulphon to increase by increasing the temperature at a rate which is greater than the rate of sulphon formation, so that the greatest possible yield of sulfphon is reduced by increasing the temperature. Admittedly, the maximum yield is not only affected by the temperature but also by the amount of added catalyst, because of the different dependencies of the rates of formation and consumption on the concentration of the catalyst. By increasing the concentration of the catalyst, the rate of formation in sulphon increases more than the rate of its consumption. For a given temperature and used amount of catalyst the maximum yield is reached at an optimal time t_{opt}.

For a discontinuous conversion the optimal reaction time t_{opt} batch is found by differentiating (5.13) and setting to zero

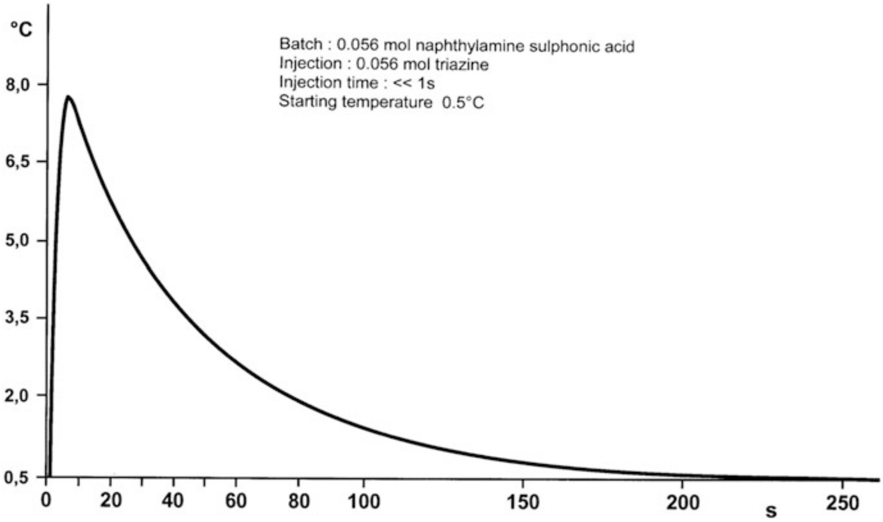

Fig. 5.7 Dependency of rate coefficient k_1 on concentration of catalyst c_{Cat_0}

$$\begin{aligned} & k_1 \cdot (k_2 - k_3) \cdot \mathrm{EXP}\left[(k_3 - k_1) \cdot t_{\mathrm{opt}}\right] - k_2 \cdot (k_1 - k_3) \\ & \quad \cdot \mathrm{EXP}\left[(k_3 - k_2) \cdot t_{\mathrm{opt}}\right] \\ & \quad = k_3 \cdot (k_2 - k_1). \end{aligned} \tag{5.19}$$

Rearrangement of the relation to the explicit expression $t_{\mathrm{opt}} = f_2(k_1, k_2, k_3)$ is not possible. Nevertheless, because of the elaborated kinetic fact that $k_1 \gg k_2$, k_3, a direct calculation with sufficient accuracy is possible; $k_1 \gg k_2$, k_3 means that the formation of sulphoxid from sulphide occurs – compared with the following relatively slow reactions to sulphon and sulpho acid – almost instantly (Fig. 5.10). Because of that, the exact equation (5.19) shrinks in good approximation to

$$-k_2 \cdot k_1 \cdot \mathrm{EXP}\left[(k_3 - k_2) \cdot t_{\mathrm{opt}}\mathrm{batch} \cong -k_3 \cdot k_1.\right.$$

Corresponding to the slowness of the consecutive stages, no distinct peak exists; rather, there is an elongated maximum. Hence, its temporal position is sufficiently precisely determined by

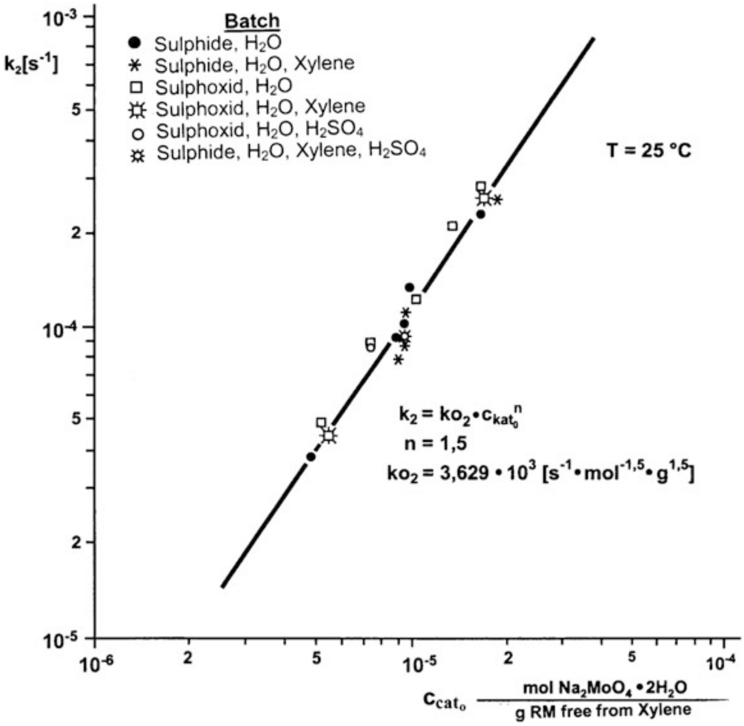

Fig. 5.8 Dependency of rate coefficient k_2 on concentration of catalyst c_{Cat_0}

$$t_{\mathrm{opt}}\mathrm{batch} = \ln(k_3/k_2)/(k_3 - k_2). \tag{5.20}$$

The combination of (5.18) and (5.20) gives t_{opt} batch as a function of the temperature and concentration of the catalyst:

$$\begin{aligned} t_{\mathrm{opt}}\mathrm{batch} &= kH_3/kH_2 \cdot \mathrm{EXP}[(E_2 - E_3)/RT] \\ &\quad \cdot c_{\mathrm{Cat}_0}^{-0.5} \Big/ \left(kH_3 \cdot \mathrm{EXP}[-E_3/RT] \cdot c_{\mathrm{Cat}_0} - kH_2 \cdot \mathrm{EXP}[-E_2/RT] \cdot c_{\mathrm{Cat}_0}^{1.5} \right). \end{aligned} \tag{5.21}$$

Combining (5.13), (5.20) and (5.21) and considering $k_1 \gg k_2$, k_3 yields the maximum concentration of the desired product sulphon as a function of temperature and amount of catalyst:

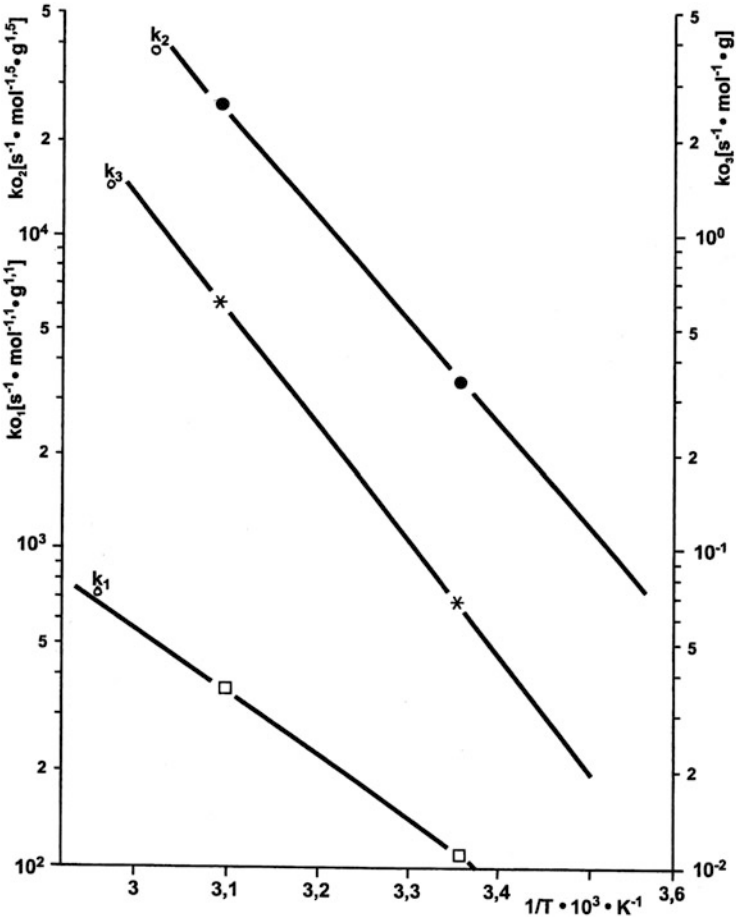

Fig. 5.9 Dependency on temperature of rate coefficients ko_1, ko_2 and ko_3 according to Arrhenius relation

$$\begin{aligned}
&\left[c_{\mathrm{R1-SO2-R2}}/\left(c_{\mathrm{R1-S-R2}}\right)_0\right]_{\max} = S_{\max} \\
&= k_2/(k_3-k_2)\cdot\left\{\mathrm{EXP}\left[k_2\cdot t_{\mathrm{opt}}\mathrm{batch}\right]-\mathrm{EXP}\left[k_3\cdot t_{\mathrm{opt}}\mathrm{batch}\right]\right\} \\
&= k_2/(k_3-k_2)\cdot\left[(k_3/k_2)^{-k_2/(k_3-k_2)}-(k_3/k_2)^{-k_3/(k_3-k_2)}\right] \\
&= (k_2/k_3)^{k_3/(k_3-k_2)} \\
&= \left\{kH_2/kH_3\cdot\mathrm{EXP}[(E_3-E_2)/RT]\cdot c_{\mathrm{Cat_0}}{}^{0.5}\right\}^{1/\left(1-kH_2/kH_3\cdot\mathrm{EXP}[(E_3-E_2)/RT]\cdot c_{\mathrm{Cat_0}}{}^{0.5}\right)}.
\end{aligned} \tag{5.22}$$

It is advisable to determine the dosage of H_2O_2 according to the amount which is consumed at the optimal oxidation time t_{opt} batch. This amount $(H_2O_2)_{\mathrm{oOptimum}}$ can

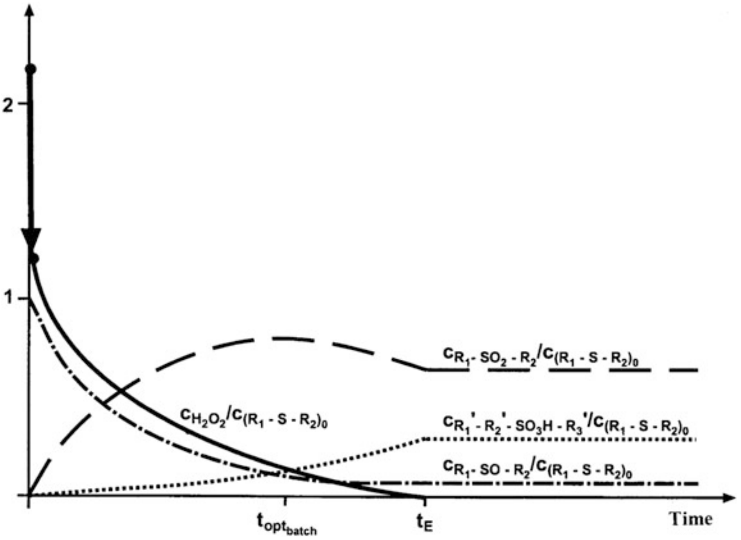

Fig. 5.10 Fundamental course of relative concentrations versus time after instantaneous dosage of H_2O_2 in a batch of R1–S–R2, by which $(c_{H2O2})_0/(c_{R1-S-R2})_0 < 3$, an isothermal, discontinuous conversion, constant-volume reaction

be calculated by setting (5.15) to zero, resolving to $(c_{H2O2})_0/(c_{R1-S-R2})_0$ using (5.22) and considering $k_1 \gg k_2, k_3$. The result is

$(c_{H2O2})_{0\text{Optimum}}/(c_{R1-S-R2})_0 = 3 - 2 \cdot \text{EXP}\left[-k_2 \cdot t_{\text{opt}}\text{batch}\right] - k_2/(k_2 - k_3) \cdot \left\{\text{EXP}\left[-k_3 \cdot t_{\text{opt}}\text{batch}\right] - \text{EXP}\left[-k_2 \cdot t_{\text{opt}}\text{batch}\right]\right\} = 3 - 2 \cdot \text{EXP}\left[-k_2 \cdot t_{\text{opt}}\text{batch}\right] -S_{\max}$. The dosage of H_2O_2 at the constant rate v instead of injection increases the optimal reaction time t_{opt}. At the beginning of the total dosing time t_{Dos} the inflowing H_2O_2 oxidizes during the time $\delta t_{\text{d0s}} = V \cdot (c_{R1-S-R2})_0/(v \cdot \rho_{H2O2}/M_{H2O2})$ virtually only the batch of sulphide to sulphoxid because of $k_1 \gg k_2, k_3$. Practically, only at that point in time do consecutive oxidations start (Fig. 5.11). The following expression is valid:

$$t_{\text{opt}}\text{batch} \ll t_{\text{opt}}\text{semibatch} < \left(t_{\text{opt}}\text{batch} + t_{\text{dos}}\right).$$

The rule of thumb gives a well-founded

$$t_{\text{opt}}\text{semibatch} \cong \left(t_{\text{opt}}\text{batch} + \delta t_{\text{dos}}\right).$$

Figure 5.12 shows for a batch process the temporal courses of

- The maximum concentration of sulphon R_1–SO_2–R_2
- The relevant amount of residual sulphide R_1–S–R_2
- The optimal reaction time
- The optimal amount of H_2O_2

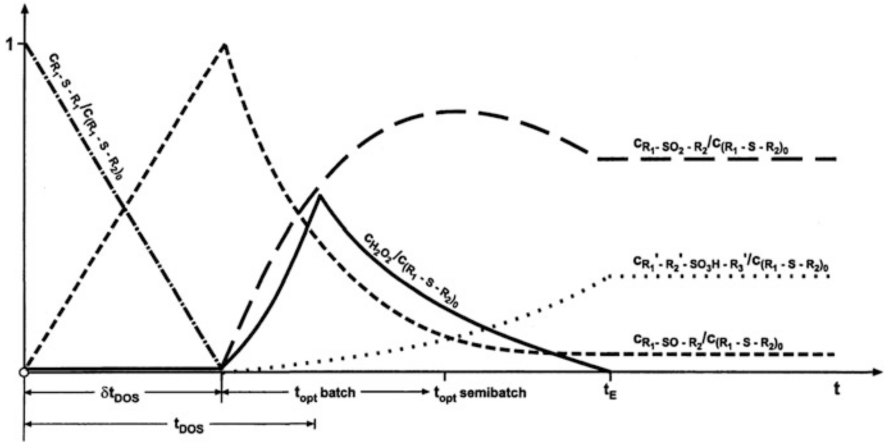

Fig. 5.11 Fundamental course of relative concentrations versus time for constant, continuous dosing of H_2O_2 in a batch of R1–S–R2, by which $(c_{H2O2})_0/(c_{R1\text{–}S\text{–}R2})_0 < 3$, in time interval t_{Dos}

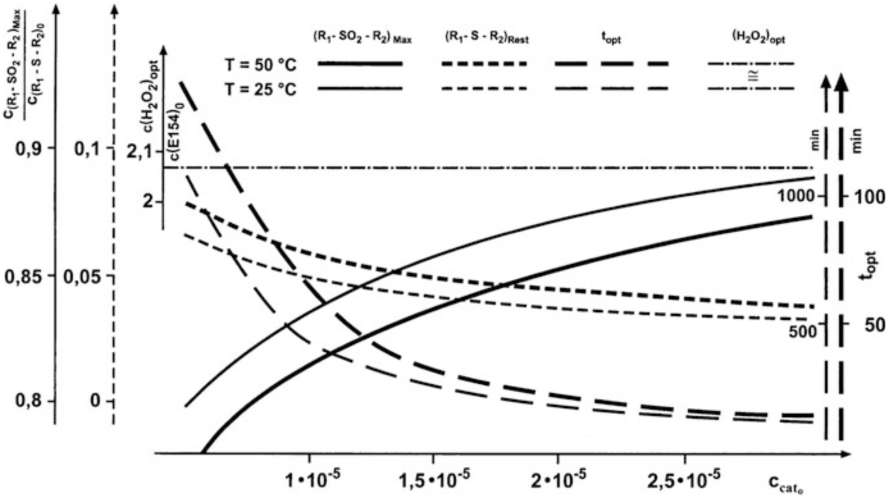

Fig. 5.12 Isothermal batch process, 25 and 50 °C, maximum concentration of sulphon $c_{R1\text{–}SO2\text{–}R2}/(c_{R1\text{–}S\text{–}R2})_0$, associated optimal reaction time t_{opt}, residual concentration of sulphide $c_{R1\text{–}S\text{–}R2}/(c_{R1\text{–}S\text{–}R2})_0$ and optimal dosage $(c_{H2O2})_0/(c_{R1\text{–}S\text{–}R2})_0$ depending on concentration of catalyst c_{Cat_0}

depending on the amount of catalyst used at temperatures of 25 and 50 °C.

Figures 5.13 and 5.14 present for both temperatures the analytically found concentrations of sulphon after consumption of H_2O_2 depending on the dosed amount of H_2O_2. Because of the scattered analyses, the optimal dosage of H_2O_2 cannot be determined exactly. Nevertheless, despite the scattered values it can be seen that the experimental results slightly exceed the optimum value calculated according to (5.13) and indicated in Fig. 5.12. The difference increases even with

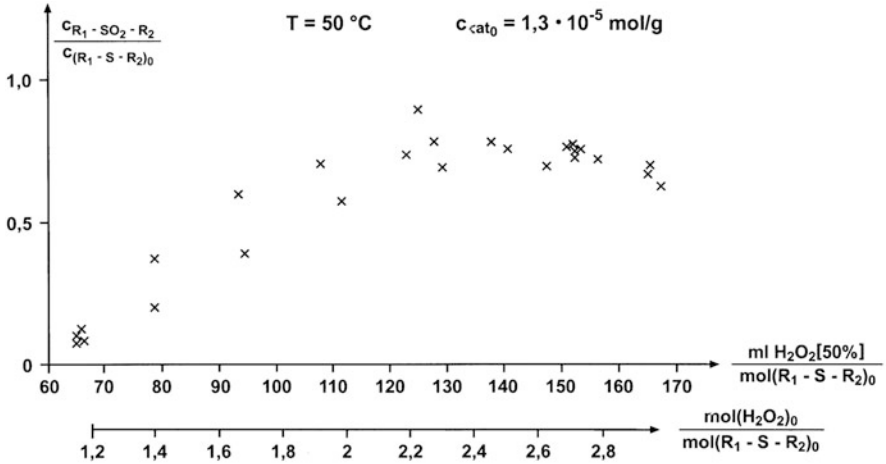

Fig. 5.13 Measured concentration $R_1 - S - R_2/(R_1 - S - R_2)_0$ depending on added amount of H_2O_2[50 %], $T = 50°$

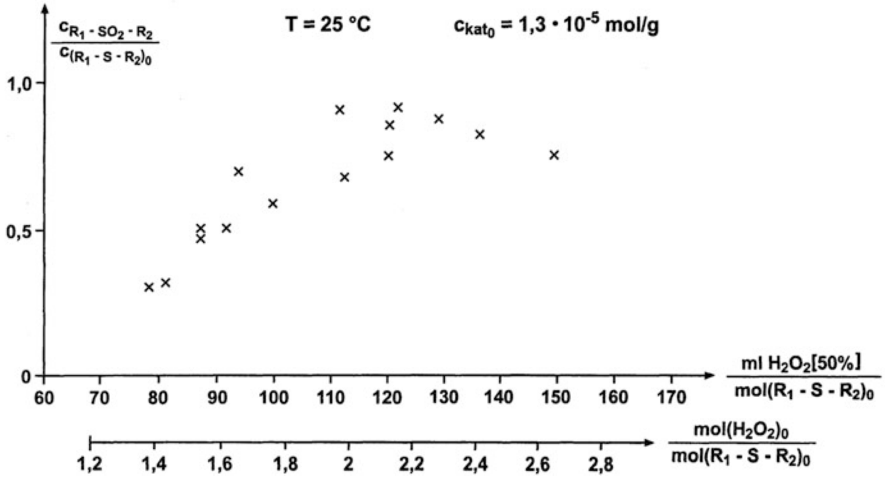

Fig. 5.14 Measured concentration $R_1 - S - R_2/(R_1 - S - R_2)_0$ depending on added amount of H_2O_2[50 %], $T = 25°$

the temperature. There is very good reason to suppose that the increased use of H_2O_2 is caused by the decomposition of H_2O_2, by which oxygen is released. Impurities in substances in the reaction mass (sulphide, xylene) and on the surface of the measuring-kettle wall give rise to the catalysis of the initially very small intrinsic decomposition of H_2O_2. The mingling of H_2O_2 in the filling leads to a slight increase in the pressure in the measuring kettle. Based on the rate of pressure increase, a mean formation of approximately 5×10^{-6} resp. 1×10^{-6} moles H_2O_2/s at 50 °C rsp. 25 °C is found.

5.1.2 Belousow–Zhabotinski Reaction in a Closed Reactor

One of the most interesting results of the thermodynamics of irreversible processes (thermodynamics far from equilibrium) is the realization that reaction systems in open or closed reactors under special premises are able to oscillate.[2] One of the early discovered, popular and intensively investigated reactions is the Belousow–Zhabotinski reaction. The overall process is the oxidation of malonic acid by means of bromate in sulphuric aqueous solution in the presence of the catalyst cerium:

$$2BrO_3^- + 3CH_2(COOH)_2 + 2H^+ \xrightarrow{Ce/H_2O/H_2SO_4} 2BrCH(COOH)_2 + 3CO_2 + 4H_2O.$$

During the discontinuous conversion in a closed reactor under conditions of oscillation, the reactants and the products do not perform damped oscillations, but the catalyst alternates in the time after an inducing and a finishing phase of the overall reaction rhythmically between two degrees of oxidation via certain intermediate reactions. Detailed detective work revealed that all in all 20 intermediate reactions run [12].

The course of conversion has already been photometrically, polarographically and barometrically recorded. The polarographic measurement, almost free of inertia, has revealed a sawtooth-shaped oscillation. Calorimetric investigation has been carried out until now only in micro calorimeters by differential thermal analysis DTA (non-isothermal) and by differential-scanning-calorimetry DSC (quasi-isothermal). The calorimetric inertia of the control systems is too large to enable the system to record correctly sawtooth-shaped oscillations, i.e. relatively abrupt changes in reaction power. The characteristic course can only be distortedly recorded.

The author has therefore tried to measure the thermal reaction power as well as the change in pressure due to CO_2 produced in the bench scale calorimeter TKR under virtually isothermal conditions. The level of the pH-value, prerequisite for the start of oscillations, is produced by an injection of strong concentrated sulphuric acid into the batch, which is already brought to the set temperature of the reaction. The unavoidable stroke of heat due to the abruptly released large amount of heat of dilution cannot be compensated completely, even despite having pre-chilled sulphuric acid and electric heating power p_2 temporarily reduced to zero (Fig. 5.15). The result is a large jump in temperature within the reaction mixture, so that the set temperature respectively the equilibrium of control is achieved relatively late.

During this time the induction phase of the oscillation has already finished, i.e. the oscillation is already started.

During the further, isothermal progress of the reaction the amplitude of the oscillations (recognizable by periodical cut-ins along the course of the measured thermal reaction power) increases from approximately 5 W up to approximately

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[2] See Sect. 4.2.1.1.2.6.

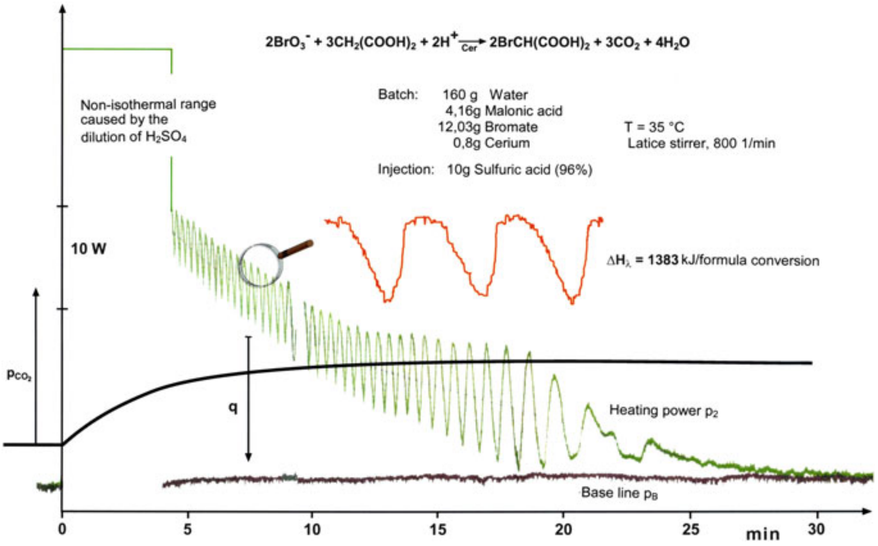

Fig. 5.15 Temporal course of thermal reaction power of Belousow–Zhabotinski reaction in a closed reactor under virtually isothermal conditions

about 10 W and then towards the end of the conversion decreases to zero. The time of oscillation increases instantly – also in the beginning phase of the descending amplitude. The slow motion reveals that the characteristic oscillation shape is similar to the usual sawtooth. From the area between the baseline p_B and the curve of the heating power p_2, both extrapolated rearwards towards the time zero, yields by approximation an overall heat of reaction of

$$-\Delta H_\lambda \cong 1{,}383 \text{ kJ/formula conversion.}$$

The overall heat of reaction per mol oxidized malonic acid is

$$\begin{aligned}-\Delta H_{\text{malonic acid}} &= (-\Delta H_\lambda)/|\nu_{\text{malonic acid}}| = (-\Delta H_\lambda)/|-3| \\ &\cong 461 \text{ kJ/mol}_{\text{malonic acid}}.\end{aligned}$$

5.1.3 *Reaction of Formic Acid with Hexamethylene-Diisocynate*

As an example of the elaboration of a reaction kinetic

- from the data of an isothermal, discontinuous conversion
- on the basis of numerical calculation

is discussed the initial phase of the multiple-stage, consecutive reaction of the aliphatic diisocynate hexamethylene-diisocyanate H and formic acid A to a variety of products P_ξ:

$$H + A \xrightarrow{NCO} P_1 \xrightarrow{NCO/P_\xi} P_2 \xrightarrow{NCO/P_\xi} P_\xi \rightarrow \ldots$$

For the thermokinetic measurement, the batch of hexamethylene-diisocyanate is brought to the reaction temperature 90 °C and a small amount of formic acid (p.a.) instantly injected to start the reaction. The injection causes an instantaneous, large heat stroke, and the pressure rises slightly. Then follows a monotonous decrease in the thermal reaction power accompanied by a slow increase in pressure. The same goes for the instant addition of larger amounts or for the successive addition of small amounts. Continuous, constant dosing causes a quick and linear temperature increase and a slow increase in the pressure. At the end of dosing the increase in temperature stops abruptly and at this moment the temperature starts to decay.

The analysis of the produced gas shows for all cases a mixture of CO_2 and CO. The relation of the components in samples of gas, taken during the further course of the reaction, changes favourably for CO.

From the heat stroke in the initial phase the quantity 59 kJ/mol_A results as heat from the process. The value is much larger than the value of a usual physicochemical process (e.g. heat of mixture).

With the purpose of reducing the dynamics of the obviously initial chemical processes, which at high temperatures evidently run almost instantly, and to have a dampening effect on the subsequent consecutive reactions the temperature is reduced to 0 °C and lower. Figure 5.16, for instance, shows the positive results. It can be seen that the thermal reaction power at first decreases monotonously, then increases, passing a peak, and then decreases again, approaching almost zero. The initial change in pressure after the injection of A is negligibly small. However, during the phase of increase in the thermal reaction power the pressure now increases quickly to achieve, after an S-shaped course, a nearly constant (i.e. minimally changing) run. In the analysis of the formed gas, a mixture of CO_2 and CO with far more than 90 % CO_2 is detected. Thus, it is assumed that during the initial phase and in particular during the following relatively short-term increase in the renewed heat release no or only an unimportant part of the injected formic acid decomposes.

A numeric method then gives a satisfying validation of the experimental results only when the following reaction mechanism is assumed. Hexamethylene-diisocyanate H and formic acid A first form the additive compound H¤A, which arranges by a further reversible step a ring R, stabilized by a hydrogen-bridge linkage.[3] The additive compound H¤A is unstable and forms, separating CO_2, the first product P_1 and in consecutive reactions a variety of products P_ξ, in Fig. 5.16 summarily denoted by

---

[3] In principle, the existence of the hydrogen-bridge linkage can be proved by infrared spectroscopy. At the time of the calorimetric investigation there existed only the method of IR illumination of cells. However, the IR beam was absorbed totally despite the fact that extremely thin fluid layers were used. Today the proof can easily be carried out by the attenuated total reflection infrared spectroscopy, ATR-IR method, quod sit perficiendum.

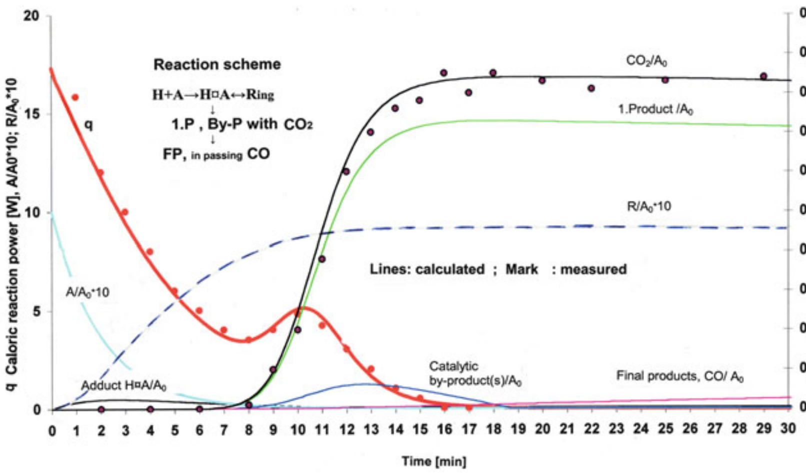

Fig. 5.16 Thermal reaction power q and relation CO_2/A_0 during reaction of hexamethylene-diisocyanate (H) and formic acid (A) p.a. 5.81 g F; 171 g H, i.e. in large excess; $T = 0$ °C; rpm = 1,500 – $\Delta H_{\lambda \text{reaction step}(n)} = 18/21/92/92$ kJ/formula conversion isothermal, discontinuous conversion. H ¤ A means additive compound of H and A

FP. However, this variety arises perceptibly only at reaction temperatures above 50 °C by consecutive reactions with the surplus hexamethylene-diisocynate. There also occur side reactions of subsequent products, separating CO.

The formation of the first product P_1 obviously occurs by autocatalysis, an usual occurrence in the chemistry of isocyanides (i.e. formation of urethane). For this formation, a relatively short-lived by-product BP is assumed with catalysing properties:

$$\begin{tikzcd}
H + A \arrow[r, "r1{,}\Delta H\lambda 1"] & H¤A \arrow[r, leftrightarrow, "r2{,}\Delta H\lambda 2", "r_3{,}\Delta H_{\lambda 3}"'] \arrow[d, shift right=2, "r_4{,}\ r_{5(BP)}"'] \arrow[d, phantom, shift left=4, "\Delta H_{\lambda 4/5/6/7}"] & R^{(ing)} \arrow[d, "r_6{,}r_{7(BP)}"] \\
 & P_1{,}CO_2 \arrow[d, "r_{f1}"', "\text{with, without H}"] & BP^{(catalysing)} \arrow[dl, "r_8"] \\
 & P_2{,}CO_2{,}CO \arrow[d, "r_{ff}"', "\text{with/ without H}"] & \\
 & P_{EP}{,}CO &
\end{tikzcd}$$

The stoichiometric coefficients are

$$\begin{aligned}
\nu_{\mathrm{A1}} &= -1\,, \nu_{\mathrm{A2}} = 0, \nu_{\mathrm{A3}} = 0, \nu_{\mathrm{A4}} = 0, \nu_{\mathrm{A5}} = 0, \nu_{\mathrm{A6}} = 0, \nu_{\mathrm{A7}} = 0, \nu_{\mathrm{A8}} = 0,\\
\nu_{\mathrm{Af1}} &= 0\,, \ldots, \nu_{\mathrm{Aff}} = ?(0 \text{ at } T = 0)\\
\nu_{\mathrm{H¤A}} &= 1\,, \nu_{\mathrm{H¤A2}} = -1, \nu_{\mathrm{H¤A3}} = 1, \nu_{\mathrm{H¤A4}} = -1, \nu_{\mathrm{H¤A5}} = -1,\\
\nu_{\mathrm{H¤A6}} &= 1, \nu_{\mathrm{H¤A7}} = -1, \nu_{\mathrm{H¤A8}} = -1, \nu_{\mathrm{H¤Af1}} = 0, \ldots, \nu_{\mathrm{Aff}} = ?(0 \text{ at } T = 0)\\
\nu_{\mathrm{R1}} &= 0, \nu_{\mathrm{R2}} = 1, \nu_{\mathrm{R3}} = -1, \nu_{\mathrm{R4}} = 0, \nu_{\mathrm{R5}} = 0, \nu_{\mathrm{R6}} = 0, \nu_{\mathrm{R7}} = 0, \nu_{\mathrm{R8}} = 0,\\
\nu_{\mathrm{Rf1}} &= 0, \ldots, \nu_{\mathrm{Rff}} = ?(0 \text{ at } T = 0)\\
\nu_{\mathrm{P11}} &= 0, \nu_{\mathrm{P12}} = 0, \nu_{\mathrm{P13}} = 0, \nu_{\mathrm{P14}} = 1, \nu_{\mathrm{P15}} = 1, \nu_{\mathrm{P16}} = 0, \nu_{\mathrm{P17}} = 0,\\
\nu_{\mathrm{P18}} &= 0, \nu_{\mathrm{P1f1}} = -1, \ldots, \nu_{\mathrm{B1ff}} = ?(0 \text{ at } T = 0)\\
\nu_{\mathrm{BP1}} &= 0, \nu_{\mathrm{BP2}} = 0, \nu_{\mathrm{BP3}} = 0, \nu_{\mathrm{BP4}} = 0, \nu_{\mathrm{BP5}} = 0, \nu_{\mathrm{BP6}} = 1, \nu_{\mathrm{BP7}} = 1,\\
\nu_{\mathrm{BP8}} &= -1, \nu_{\mathrm{BPf1}} = 0\,, \ldots, \nu_{\mathrm{BPff}} = ?(0 \text{ at } T = 0)\\
\nu_{\mathrm{H1}} &= -1, \nu_{\mathrm{H2}} = 0, \nu_{\mathrm{H3}} = 0, \nu_{\mathrm{H4}} = 0, \nu_{\mathrm{H5}} = 0, \nu_{\mathrm{H6}} = 0, \nu_{\mathrm{H7}} = 0, \nu_{\mathrm{H8}} = 0,\\
\nu_{\mathrm{Hf1}} &= 0, \ldots, \nu_{\mathrm{Hff}} = ?(0 \text{ at } T = 0).
\end{aligned}$$

According to (4.34), the rates of change in concentration are

$$\begin{aligned}
\mathrm{d}c_{\mathrm{F}}/\mathrm{d}t &= -\,r_1,\\
\mathrm{d}c_{\mathrm{H¤F}}/\mathrm{d}t &= r_1 -\; r_2 +\; r_3 -\; r_4 -\; r_5 -\; r_6 -\; r_7,\\
\mathrm{d}c_{\mathrm{R}}/\mathrm{d}t &= r_2 -\; r_3,\\
\mathrm{d}c_{\mathrm{P1}}/\mathrm{d}t &= r_4 +\; r_5 -\; r_{\mathrm{f1}}(\cong 0 \text{ at } 0\ ^\circ\mathrm{C}),\\
\mathrm{d}c_{\mathrm{BP}}/\mathrm{d}t &= r_6 +\; r_7 -\; r_8,\\
\mathrm{d}c_{\mathrm{H}}/\mathrm{d}t &= -\,r_1 - \{r_{\mathrm{f1}} + \textstyle\sum r_{\mathrm{ff}}\}(\cong 0 \text{ at } 0\ ^\circ\mathrm{C}),\\
\mathrm{d}c_{\mathrm{EP}}/\mathrm{d}t &= r_8 + \{r_{\mathrm{f1}} + \textstyle\sum r_{\mathrm{ff}}\}(\cong 0 \text{ at } 0^\circ\mathrm{C}).
\end{aligned}$$

Only the following expressions of the rate functions fit sufficiently the experimental results:

$$\begin{aligned}
&r_1 = k_1^{'} \cdot c_{\mathrm{H}}(\cong \text{const at } T = 0) \cdot c_{\mathrm{A}},\; r_2 = k_2 \cdot c_{\mathrm{H¤A}},\; r_3 = k_3 \cdot c_{\mathrm{R}},\; r_4 = k_4 \cdot c_{\mathrm{H¤A}},\\
&\quad r_5 = k_5^{'} \cdot c_{\mathrm{H¤A}} \cdot c_{\mathrm{NP}},\; r_6 = k_6 \cdot c_{\mathrm{H¤A}},\; r_7 = k_7^{'} \cdot c_{\mathrm{H¤A}} \cdot c_{\mathrm{BP}},\; r_8 = k_8 \cdot c_{\mathrm{BP}}, r_8\\
&\qquad = k_8 \cdot c_{\mathrm{BP}},\; r_{\mathrm{f1}}, r_{\mathrm{ff}} = ?(\cong 0 \text{ at } 0\ ^\circ C),
\end{aligned}$$

with

$$\begin{aligned}
k_5^{'} &= k_5/(c_{\mathrm{A}} + c_{\mathrm{H¤A}} + c_{\mathrm{R}} + c_{\mathrm{P1}} + c_{\mathrm{BP}} + c_{\mathrm{EP}}) \quad \text{respectively}\\
k_7^{'} &= k_7/(c_{\mathrm{A}} + c_{\mathrm{H¤A}} + c_{\mathrm{R}} + c_{\mathrm{P1}} + c_{\mathrm{BP}} + c_{\mathrm{EP}}).
\end{aligned}$$

Figure 5.16 shows optimally fitted curves of a measurement at 0 °C using $k_1{}' \cdot c_{\mathrm{H0}} = k_1$, $r_{\mathrm{f1}} = k_{\mathrm{f1}} \cdot c_{\mathrm{P1}}$, $r_{\mathrm{ff}} = 0$ and the following rate coefficients and heats of reaction:

$$\begin{array}{llll}
k_1 & = 8.33\times10^{-3}\ \mathrm{s}^{-1} & -\Delta H_{\lambda_1} = & 16.4\ \mathrm{kJ/formula\ conversion,}\\
k_2 & = 4.63\times10^{-3}\ \mathrm{s}^{-1} & -\Delta H_{\lambda_2} = & 20.9\ \mathrm{kJ/formula\ conversion,}\\
k_3 & = 4.63\times10^{-6}\ \mathrm{s}^{-1} & -\Delta H_{\lambda_3} = & -20.9\ \mathrm{kJ/formula\ conversion,}\\
k_4 & = 1.68\times10^{-11}\ \mathrm{s}^{-1} & -\Delta H_{\lambda_4} = & 92.1\ \mathrm{kJ/formula\ conversion,}\\
k_5 & = 1.01\ \mathrm{s}^{-1} & -\Delta H_{\lambda_5} = & 92.1\ \mathrm{kJ/formula\ conversion,}\\
k_6 & = 1.28\times10^{-13}\ \mathrm{s}^{-1} & -\Delta H_{\lambda_6} = & 92.1\ \mathrm{kJ/formula\ conversion,}\\
k_7 & = 1.39\times10^{-1}\ \mathrm{s}^{-1} & -\Delta H_{\lambda_7} = & 92.1\ \mathrm{kJ/formula\ conversion,}\\
k_8 & = 3E-4\ \mathrm{s}^{-1} & -\Delta H_{\lambda_8} = & -\,,\\
k_{\mathrm{f1}} & \cong 1E-6\ \mathrm{s}^{-1} & -\Delta H_{\lambda_{\mathrm{f1}}} = & -\,.
\end{array}$$

An ascending temperature increases the rates of the reactions as well as the catalysis. The activation temperature *E*/*R* of the intrinsic initial steps is approximately 10,000 K.

The catalysis is sensitive to foreign substances and impurities. For instance, the increase of the tiny residual concentration of oxalic acid in the usually available formic acid (p.a.) by the addition of a small amount of this acid stops the catalysis; in contrast, the addition of acetic acid, which is also present in the remained impurity of the formic acid (p.a.), does not show any effect. The catalytic process changes when the fluid residue of the distillation of formic acid (p.a.) instead of formic acid (p.a.) is used. In that case, the course of the caloric reaction power shows two, three or more consecutive wave lines and simultaneously in the course of the pressure CO_2/CO three or more successive stair lines depending on the duration of the distillation of the usually available formic acid (p.a.).

If one uses monoisocyanate (e.g. phenyl-isocyanate) instead of the aliphatic diisocyanate, catalysis does not take place, just as with toluidine-diisocyanate. In contrast, the use of isophorone-diisocyanate shows catalysis.

5.2 Non-isothermal, Discontinuous, Constant-Volume Reaction

5.2.1 Reaction of an Amine Hydrochloride and an Alkali Nitrite

As an example of a kinetic analysis of a quick reaction

- From the data of a non-isothermal, discontinuous conversion
- On the basis of mathematical-analytical relations

the irreversible conversion of an amino hydrochloride **A** and an alkali nitrite **B** in hydrochloric, aqueous solution to a heterocyclic resultant **F** is discussed.

By a first step the salt **C** is formed (as well as the by-products D and E)

$$\mathrm{A}+\mathrm{B}\xrightarrow[\mathrm{H_2O,HCl}]{r_1,\Delta\mathrm{H}_{\lambda 1}}\mathrm{C}+\ \mathrm{D}\ +\ \mathrm{E},$$

with

$$\text{stoichiometric coefficients}\quad \nu_{\mathrm{A1}}=-1,\nu_{\mathrm{B1}}=-1,\nu_{\mathrm{C1}}=1,\nu_{\mathrm{D1}}=2,\nu_{\mathrm{E1}}=1.$$

In a second step the intramolecular closure of the intermediate product **C** to the desired heterocyclic, final product **F** (as well as the production of by-product G) takes place:

$$\mathrm{C}\xrightarrow{r_2,\Delta H_2}\mathrm{F}+\mathrm{G},$$

with

$$\text{stoichiometric coefficients}\quad \nu_{\mathrm{C2}}=-1,\nu_{\mathrm{F2}}=-1,\nu_{\mathrm{F2}},\nu_{\mathrm{G2}}=1.$$

It is known that the conversion runs too quickly to perform a calorimetric investigation under isothermal conditions. Hence, the investigation must be carried out using the isoperibolic procedure.

To carry out the investigation, a batch of amino hydrochloride in the measuring kettle is brought to a reaction temperature of 50 °C and a pH-value of 0.7. To start the reaction, the stoichiometric amount of aqueous alkali nitrite at 50 °C is injected in a time interval of less than 2 s. Figure 5.17 shows the temporal course of the natural logarithm of the difference between the measured and the initial temperature $(T_2 - T_{20})$ after the start of injection. The reaction in the solution increases immediately upon dosing, achieves a maximum at the end of dosing and then decreases monotonously. The temperature decay slows down after about 10 s for a short time. Visual control of the process reveals the precipitation of solid matter. The brief slowing down of the temperature decay occurs obviously by the heat release due to the sudden, short-term precipitation in the already supersaturated reaction mixture. Then the subsequent precipitation takes place synchronously with the continuing conversion. The analysis of the solid matter shows that it is the desired heterocyclic product **F**.

For a comparison with the measured reaction curve, Fig. 5.17 presents in addition the curve of the temperature decay which is the result of a short-term heating up of the mixture following completion of the conversion by the electric heater to the maximum temperature $T_{2\mathrm{Max}}$ and then of its switch-off.

Elaboration of the thermokinetic data takes place according to

- The procedure of results of non-isothermal reactions (Sect. 4.2.3.1.1).
- The determination of the enthalpy of reaction, heat capacity and specific heat is given in Chap. 6.

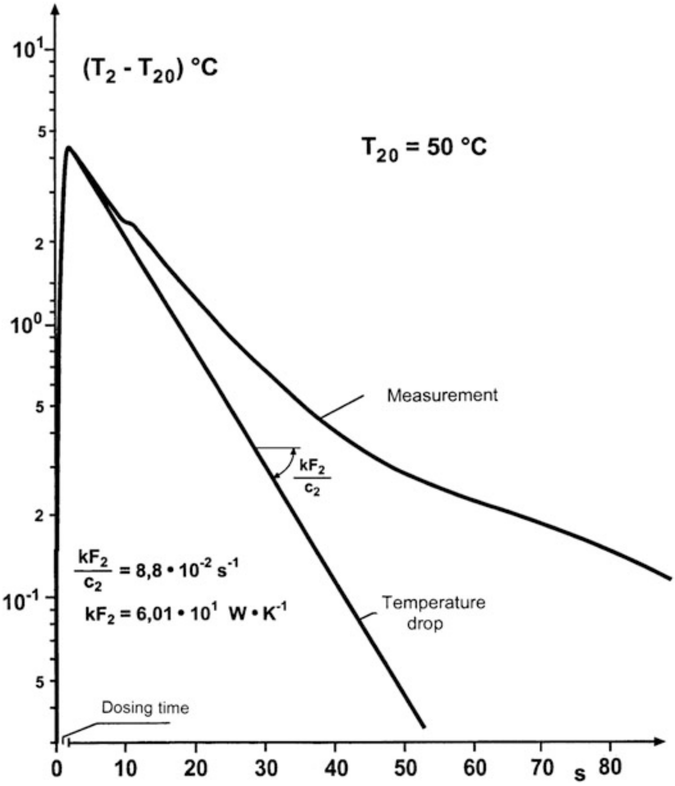

Fig. 5.17 Temporal course of difference between measured and initial temperature $(T_2 - T_{20})$ during heterocyclic reaction. Batch: 140 g aqueous solution of amine hydrochloride A. Dosage: 10 g aqueous solution of alkali nitrite B. Equal number of mol: 4.5×10^{-2}; $\mathrm{pH} = 0.7$

The instant increase in temperature by the start of the dosage of alkali nitrite and the instant cessation at the end of dosing shows that the formation of the salt **C** occurs instantly; hence we have

$$r_2 = r_{\text{ring-closure}} \ll r_{\text{salt-formation}} = r_1 \cong \infty.$$

From the temperature difference $(T_{2\mathrm{Max}} - T_{20})$, the effective heat capacity C_2 and the used number of mols N_0 amine hydrochloride yields the overall heat $(-\Delta H_{\lambda 1})$ of the formation of **C** (sum of the heat of physicochemical mixing and the heat of the desired reaction) according to[4]

---

[4] For determination of the effective heat capacity C_2 and the heat transfer coefficient $(k{\cdot}F)_2$ see Chap. 6.

$$\begin{aligned}-\Delta H_{\lambda 1} &= C_2 \cdot (T_{2\mathrm{Max}} - T_{20})/N_0 \\ &= 87 \cdot (1 \pm 0.02)\ \text{kJ/formula conversion.}\end{aligned}$$

The sum of the heats of ring closure and of the accompanying precipitation $-(\Delta H_{\lambda 2} + \Delta H_{\lambda \mathrm{Pr}}) = \int_{t\ \text{Dosing end} \to \infty} q \cdot \mathrm{d}t/N_0$ results from the difference in the total amount of heat released $\int_{0\to\infty} (T_2 - T_{20}) \cdot \mathrm{d}t \cdot kF_2$ and the amount of heat released $(-\Delta H_{\lambda 1}) \cdot N_0$ by the formation of salt **C:**

$$\begin{aligned}-(\Delta H_{\lambda 2} + \Delta H_{\lambda \mathrm{Pr}}) &= \int_{0\to\infty} (T_2 - T_{20}) \cdot \mathrm{d}t \cdot kF_2/N_0 - (-\Delta H_{\lambda 1}) \\ &= \int_{0\to\infty} (T_2 - T_{20}) \cdot \mathrm{d}t \cdot kF_2/N_0 - 87\ \text{kJ/formula conversion} \\ &= 39.3 \cdot (1 \pm 0.03)\ \text{kJ/formula conversion.}\end{aligned}$$

The temporal course of the total thermal reaction power $q = q_1 + q_2 + q_F$ during the formation of ***C***, the ring closure and the accompanying precipitation results analogously in (2.14), i.e. from the data $(T_2 - T_S), \mathrm{d}(T_2 - T_S)/\mathrm{d}t, q_{\mathrm{St2}}$ as well as $(k \cdot F)_2$ and C_2, respectively from the recorded data $(T_2 - T_{20}), \mathrm{d}(T_2 - T_{20})/\mathrm{d}t$ as well as $(k \cdot F)_2$ and C_2 because, due to the large degree of dilution, it can be assumed that $q_{\mathrm{St2}} = \text{const}$, thus $q_{\mathrm{St2}} = (k \cdot F)_2 \cdot (T_{20} - T_S)$.[5]

For $t > t_{\text{end of dosage}}$ we have $q_1(t) = 0$, hence $q = q_2 + q_F$. By means of q, $(\Delta H_{\lambda 2} + \Delta H_{\lambda \mathrm{Pr}})$, (4.148) and (4.149) the auxiliaries $A(t)$ and $B(t)$ respectively y and x are calculated. Plotting y against x allows us to determine the rate order n of the ring closure and its activation energy E due to (4.154):

$$\ln\{A_1/A_2\}/\ln\{B_1/B_2\} = n - E/R \cdot [1/T_{21} - 1/T_{22}]/\ln\{B_1/B_2\}$$

or

$$y = n - E/R \cdot x.$$

Figure 5.18 shows plot y versus x. From the slope of the fitted curve results the activation temperature E/R, i.e.

$$E = 94.1\ \text{kJ/mol.}$$

From its intersection with the ordinate we get

$$n = 0.9.$$

---

[5] With $q_{\mathrm{Mi}} = 0$: (2.16 and 2.25) $\equiv\ C_2 \cdot \mathrm{d}(T_2 - T_{20})/\mathrm{d}t = q - (k \cdot F)_2 \cdot (T_2 - T_{20})$.

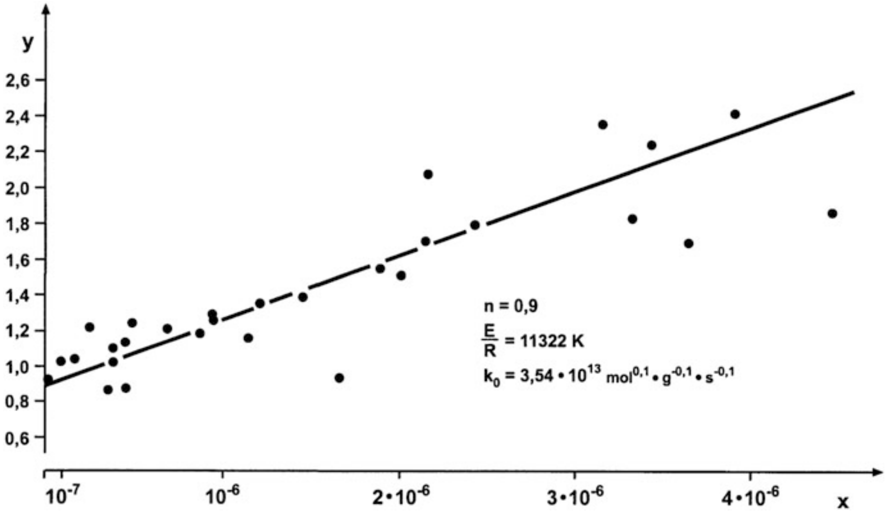

Fig. 5.18 Plot $Y = n - E/R \cdot X$ and fitted curve

The recorded data $T_2(t)$, $A(t)$ and $B(t)$ give, due to (4.155), the rate coefficients $k(T_{2(t)})$, for instance $k_2\left(T_{2(t=25\ \mathrm{s})}\right) = k_2(51\ °\mathrm{C}) = 2.36\ \mathrm{mol}^{0.1}\ \mathrm{g}^{-0.1}\ \mathrm{s}^{-1}$, and from that, according to the Arrhenius relation, we get the pre-exponential factor

$$ko_2 = 3.54 \times 10^{13}\ \mathrm{mol}^{0.1}\ \mathrm{g}^{-0.1}\ \mathrm{s}^{-1}.$$

Hence, the overall rate function of the ring closure reads

$$r = k_2 \cdot c_\mathrm{C}^n = ko_2 \cdot \mathrm{EXP}(-94,100/R \cdot T) \cdot c_\mathrm{C}^{0.9}.$$

5.2.2 Reaction of a Substituted Triazine with a Substituted Naphthylamine Sulphonic Acid in Water

An example of the working out of the kinetics of a very quick reaction

- From the data of non-isothermal, discontinuous runs
- On the basis of mathematical-analytical relations

the irreversible reaction of a substituted triazine A and a substituted naphthylamine sulphonic acid B in aqueous solution is discussed. The reaction system is

$$\mathrm{A} + \mathrm{B} \xrightarrow[(\mathrm{H_2O})]{r_1,\, \Delta H_1} \mathrm{C} + \mathrm{D},$$

with

$$\text{stoichiometric coefficients}\, \nu_{\mathrm{A1}} = -1, \nu_{\mathrm{B1}} = -1, \nu_{\mathrm{C1}} = 1, \nu_{\mathrm{D1}} = 1.$$

Triazine reacts also with water. Hence, besides the desired conversion, the following parasitic reaction runs:

$$\mathrm{A} + \mathrm{H_2O} \overset{r_1,\Delta H_1}{\underset{(\mathrm{H_2O})}{\rightarrow}} \mathrm{F} + \mathrm{D},$$

with

$$\text{stoichiometric coefficients}\, \nu_{\mathrm{A2}} = -1, \nu_{\mathrm{H2O2}} = -1, \nu_{\mathrm{F2}} = 1, \nu_{\mathrm{D2}} = 1.$$

It is known that the conversion runs very quickly, but it is unknown whether the reaction runs within the time interval of a minute or only of some seconds. This knowledge is important for technical production with regard to both chemical engineering and security. In addition, the enthalpy of reaction is unknown and therefore must be measured.

The investigation is carried out under isoperibolic conditions as follows.

- The batch in the measuring kettle consists of an aqueous solution of naphthylamine sulphonic acid **B** or pure water.
- The batch is brought to the temperature of reaction T_0.
- Triazine **A** at temperature T_0 is instantly injected (duration of injection $\ll$1 s) to start the conversion.
- The course of the temperature versus time is recorded.

Figure 5.19 gives an example of a characteristic run of the temperature. The soon-to-appeare temperature maximum after the injection of A confirms the unusual speed of the conversion. The course of the distorted signal of the temperature by the sensor must be antidistorted, i.e. (2.22) and (2.24) must be applied to make it possible for a kinetic interpretation to be done.

The desired reaction and the parasitic reaction are coupled parallel reactions. It is assumed in a first assumption that both reactions run according to a rate function of order 1 with respect to A. Hence, due to (4.44), for the thermal reaction power we get

$$q(t) = k \cdot c_{\mathrm{A0}} \cdot V \cdot (-\Delta H_{\lambda}) \cdot \mathrm{EXP}[-k \cdot t], \tag{5.23}$$

with $k = \left(\overline{k_1 + k_2}\right)_{T_{\mathrm{start}} \to T_{\mathrm{max}}}$ because of the relatively small temperature increase.

The combination of (2.24) and (5.23) gives as a result the rate of change in the real temperature T_2 in the reaction mixture:

$$\mathrm{d}(T_2 - T_{20})/\mathrm{d}t \;=\; a \cdot \mathrm{EXP}[-k \cdot t] \;-\; b \cdot (T_2 - T_{20}), \tag{5.24}$$

with

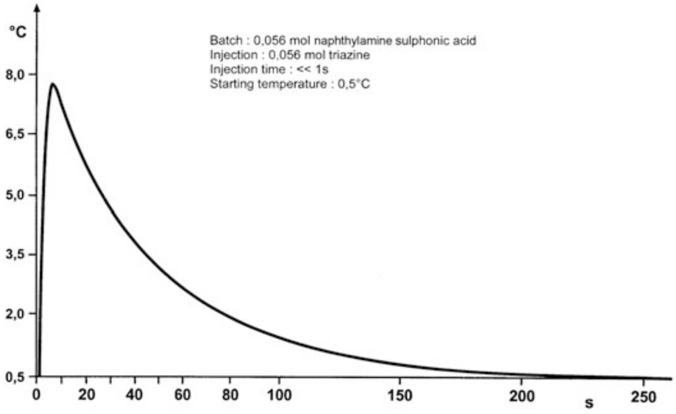

Fig. 5.19 Temporal course of signal T_{2F} of temperature sensor after injection of triazine A in aqueous solution of naphthylamine sulphonic acid B, non-isothermal, isoperibolic, discontinuous reaction

$$a = k \cdot c_{A0} \cdot V \cdot (-\Delta H_\lambda)/C_2, b = kF_2/C_2.$$

The solution of (5.24) is

$$T_2 = a/(k-b) \cdot \{\mathrm{EXP}[-b \cdot t] - \mathrm{EXP}[-k \cdot t]\} + T_{20}. \tag{5.25}$$

Substitution of (5.25) into (2.22) and solving the equation gives as a result the equation for the temporal course of the signal T_F by the temperature sensor:

$$\begin{aligned} T_F = &\beta \cdot a/(k-b) \cdot \{\mathrm{EXP}[-b \cdot t]/(\beta - b) - \mathrm{EXP}[-k \cdot t]/(\beta - k) \\ &-\{1/(\beta - b) - 1/(\beta - k)\} \cdot \mathrm{EXP}[-\beta \cdot t]\} + T_{20} \end{aligned} \tag{5.26}$$

T_F passes a maximum value at the time $t_{F\max}$, where the differentiation of T_F equals zero,

$$\begin{aligned} 0 = &(\beta - b)/(\beta - k) \cdot \{k \cdot \mathrm{EXP}[-k \cdot t_{F\max}] - \beta \cdot \mathrm{EXP}[-\beta \cdot t_{F\max}]\} + \beta \\ &\cdot \mathrm{EXP}[-\beta \cdot t_{F\max}] - b \cdot \mathrm{EXP}[-b \cdot t_{F\max}]. \end{aligned} \tag{5.27}$$

This relation is used for the evaluation of the rate coefficient k, for instance by means of the conventional zero-position method.

Knowledge of the necessary quantity of b and β arises in the following way. By the injection of a small amount of reacted mixture (taken beforehand from the reacted mixture and brought to a temperature $T > T_{20}$) in the reacted mixture, the temperature T_{20} jumps quasi-instantly to the temperature T_{2M} and then decreases due to heat outflow to achieve T_{20} again (Fig. 5.20).

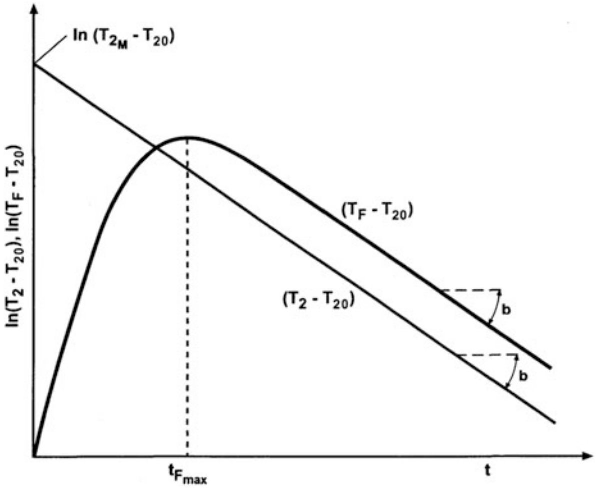

Fig. 5.20 Temporal course of difference
- $T_2 - T_{20}$ of real temperature T_2 in reacted mixture after abrupt temperature jump from $T_2 = T_{20}$ to $T_2 = T_{2M}$ at time $t = 0$ by injection of reacted mass
- $T_F - T_{20}$ of signal T_F of temperature sensor, non-isothermal, isoperibolic, discontinuous reaction

The solution of (2.24) gives, according to the present conditions, the temporal course of the real temperature decay in the reaction mixture:

$$T_2 = (T_{2M} - T_{20}) \cdot \mathrm{EXP}(-b \cdot t) + T_{20}. \tag{5.28}$$

Combining (5.28) and (2.22) and solving the resulting differential equation gives as a result the course of the temperature signal of the sensor:

$$T_F = \beta \cdot (T_{2M} - T_{20})/(\beta - b) \cdot (\mathrm{EXP}[-b \cdot t] - \mathrm{EXP}[-\beta \cdot t]) + T_{20}\,. \tag{5.29}$$

The sensor signal reaches its maximum at the time t_{Fmax} and then decreases monotonously to T_{20}. Because $\beta \gg b$, the logarithmic plot of T_F versus time turns for $t \gg 0$ into a straight line, where

$$\kappa = b.$$

Differentiating (5.29), setting to zero and rearranging results in

$$t_{\mathrm{Fmax}} = \ln\{\beta/b\}/(\beta - b).$$

From that follows β, for instance using the conventional zero-position method.

By means of (5.27), from experiments with different $A_0 = B_0$ the average overall rate results:

$$k = 1.52 \times (1 \pm 0.27)\ \mathrm{s}^{-1}.$$

Some conversions of pure water and triazine A give an average rate coefficient of the parasitic parallel reaction:

$$k_2 = 0.11 \times (1 \pm 0.3)\ \mathrm{s}^{-1}.$$

Thus, according to (4.41), the rate coefficient of the desired reaction is

$$k_1 = 1.41 \times (1 \pm 0.27)\ \mathrm{s}^{-1}.$$

Hence, the parasitic reaction runs approximately 13 times slower than the desired one.

The value of the overall heat of reaction is determined[6]:

$$(-\Delta H_\lambda) = 135 \times (1 \pm 0.15)\ \mathrm{kJ/formula\ \ conversion}.$$

The heat of the parasitic reaction results by means of the injection of triazine in pure water:

$$(-\Delta H_{\lambda 2}) = 341 \times (1 \pm 0.08)\ \mathrm{kJ/formula\ \ conversion}.$$

Corresponding to (4.45), the heat of reaction of the desired conversion can be calculated by means of k, k_1, k_2, $(-\Delta H_\lambda)$ and $(-\Delta H_{\lambda 2})$. We obtain

$$(-\Delta H_{\lambda 1}) = 119 \times (1 \pm 0.15)\ \mathrm{kJ/formula\ \ conversion}.$$

Figure 5.21 presents a calculated and measured T-curve.

The conformance of experiment with calculation is sufficient in view of the fact that

- For simplification the temperature dependency of the rate coefficient is not correctly considered (Arrhenius equation).
- Instead, a rate coefficient averaged over the temperature interval is used.
- Only the reaction time t_{Rt} needs to be estimated for a quasi-complete conversion.

The rule of thumb for the determination of the reaction time t_{Rt} reads for a rate of order 1

Reaction time for quasi-complete conversion $t_{\mathrm{Rt}} \cong 6 \cdot$ half-life $\iota_{1/2}$.

This yields in the case at hand

$$t_{\mathrm{Rt}} \cong 6 \cdot \iota_{1/2} = 6 \cdot \ln\{2\}/k = 2.74\ \mathrm{s}.$$

Hence, after approximately 3 to 4 s the reaction is practically finished.

When the desired and parasitic reactions run according to a rate function of order 2, the thermal reaction power is due to (4.51):

---

[6] See Sect. 6.1.2.

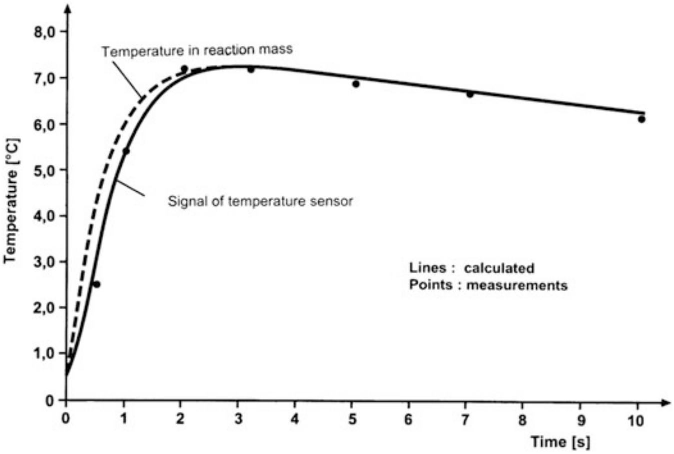

Fig. 5.21 Conversion of triazine A and naphthylamine sulphonic acid B in aqueous solution:
$A + B \rightarrow C + D$
$A + H_2O \rightarrow F + D$
$r_1 = k_1 * c_A, r_2 = k_2 * c_A$
$A0 = B0 = 0.056\,\text{mol},\ T_0 = 0.5\ \text{°C}$
Rate coefficient $k = \left(\overline{k_1 + k_2}\right)_{T\text{start}\rightarrow T\text{max}} = 1.31/\text{s},\ \beta = 5.522/\text{s},\ b = 2.255 \times 10^{-2}/\text{s}$
Overall reaction heat$(-\Delta H_\lambda) = 135$ kJ/formula conversion, $C_2 = 1{,}050$ J/K
non-isothermal, polytropic, discontinuous reaction

$$q(t) = c_{A0}{}^2 \cdot (k_1 + k_2) \cdot V \cdot (-\Delta H_\lambda)/[c_{A0} \cdot (k_1 + k_2) \cdot t \cdot 1]^2 \tag{5.30}$$

From the combination of (2.24) and (5.29) we obtain the change rate in the temperature T_2 of the reaction mixture:

$$\mathrm{d}(T_2 - T_{20})/\mathrm{d}t = \mathrm{e}/(\mathrm{d} \cdot t + 1)^2 - b \cdot (T_2 - T_{20}),$$

with

$$\begin{gathered}\left(\overline{k_1 + k_2}\right)_{T\text{start}\rightarrow T\text{max}} = k,\ d = c_{A0} \cdot k,\ e = c_{A0}{}^2 \cdot k \cdot V \cdot (-\Delta H_\lambda)/C_2, \\ b = (k \cdot F)_2/C_2.\end{gathered} \tag{5.31}$$

When in contrast against that the parasitic reaction runs according to a rate function of order 1 (for instance, due to the large excess of water) the thermal reaction power is, according to (4.46), with $\backepsilon = 2 \cdot k_2/k_1$,

$$\begin{aligned} q = \Big[& k_1 \cdot (-\Delta H_1) \cdot V/\left\{\left(c_{A0}{}^{-1} + \backepsilon\right) \cdot \mathrm{EXP}(k_1 \cdot t) - \backepsilon\right\}^2 \\ & + k_2 \cdot (-\Delta H_2) \cdot V/\left\{\left(c_{A0}{}^{-1} + \backepsilon\right) \cdot \mathrm{EXP}(k_1 \cdot t) - \backepsilon\right\}\Big]. \end{aligned} \tag{5.32}$$

The combination of (2.24) and (5.32) gives the change rate in temperature T_2:

$$\mathrm{d}(T_2 - T_{20})/\mathrm{d}t = \left[k_1 \cdot d_1/\{e \cdot \mathrm{EXP}(k_1 \cdot t) - \backepsilon\}^2 + k_2 \cdot d_2/\{e \cdot \mathrm{EXP}(k_1 \cdot t) - \backepsilon\}\right] - b \cdot (T_2 - T_{20}), \tag{5.33}$$

with

$$\overline{(k_1)_{T\mathrm{start}\to T\mathrm{max}}} = k_1,\ \overline{(k_2)_{T\mathrm{start}\to T\mathrm{max}}} = k_2,\ d_1 = (-\Delta H_1) \cdot V/C_2,\ d_2 = (-\Delta H_2) \cdot V/C_2,\ e = c_{\mathrm{A0}}^{-1} + \backepsilon,\ b = k \cdot F_2/C_2.$$

Analytical solutions of Eqs. (5.31) and (5.33) in the explicit form $T_2 = f(t)$ respectively of the combination of (5.31) and (5.33) with (2.22) in the explicit form $T_{2\mathrm{F}}(t)$, i.e. the signals of the temperature sensor, do not exist. Only numerical solutions of the equations are possible. Hence, the working-out procedure for k_i consists in numerical fitting of the measured curves of $T_{2\mathrm{F}}$.

Figure 5.22 shows for example a comparison of the measured and computed temperature signal $T_{2\mathrm{F}}$ on the assumption of the following rate functions:

(a) Both the desired and parasitic reaction of order 1
(b) Desired and parasitic reaction of order 2
(c) Desired reaction of order 2 and parasitic reaction of order 1

The best fit gives the assumption of order 1 for both reactions.

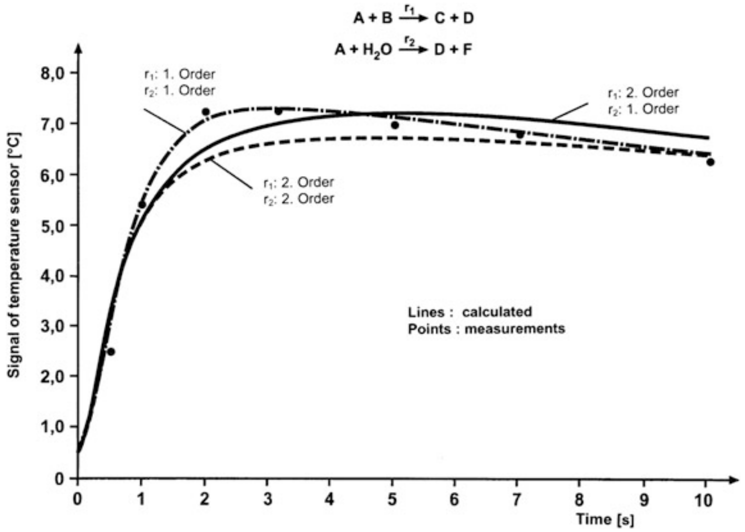

Fig. 5.22 Comparison of sensor signal $T_{2\mathrm{F}}$ versus time for different rate orders of conversion, triazine A and naphthylamine sulphonic acid B, in aqueous solution, non-isothermal, discontinuous reaction, isoperibolic condition, $\mathrm{A}_0 = \mathrm{B}_0$

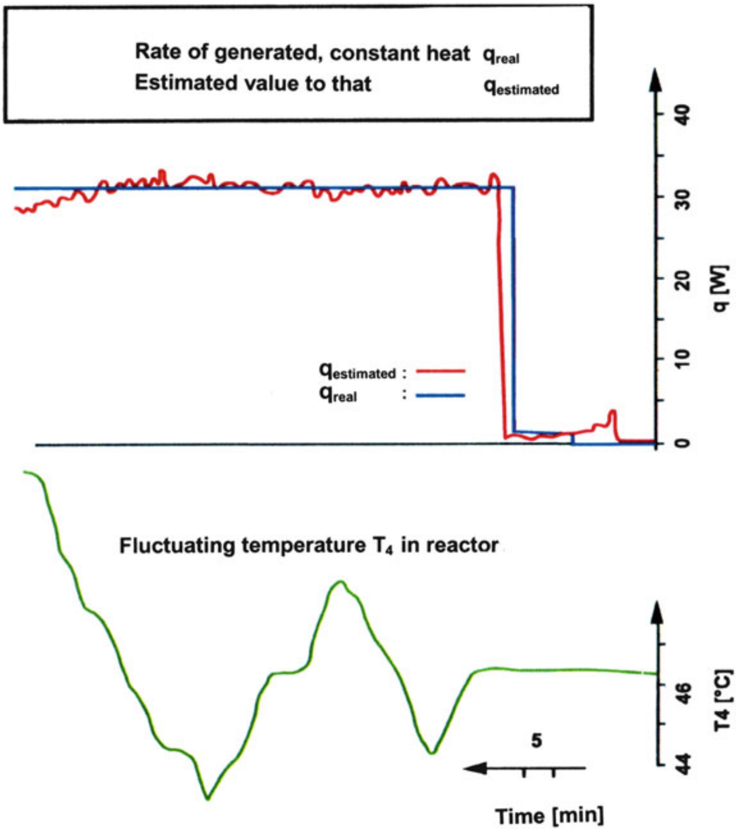

Fig. 5.23 Test of functionality of the sensor. Constant electric heating power q_{real} and its online estimated value $q_{estimated}$. The temperature T in the virtual tank reactor alternates

5.3 Measurements of Online Calorimeter (Sensor)

The run of a reaction is simulated to ensure the functionality of the online calorimeter. To that end the measuring kettle is

- Supplied with an additional electric heater of the same design as described in Sect. 2.1.1;
- Placed in the external circulation of a thermostat, which is filled with silicone oil.

An induced change in temperature in the thermostat simulates the temperature fluctuations T_4 within the technical tank reactor; the working heater in the measuring kettle simulates the thermal reaction power within the tank reactor.

The heater works initially at a constant rate of heat release q while the temperature T_4 of the thermostat (virtual tank reactor) fluctuates (Fig. 5.23).

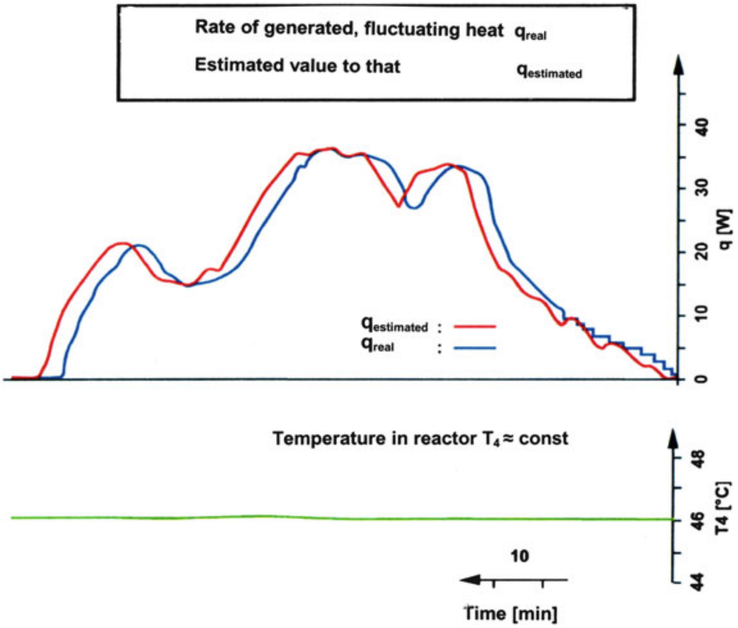

Fig. 5.24 Test of functionality of the sensor. Constant electric heating power q_{real} and its online estimated value $q_{estimated}$. The temperature T in the virtual tank reactor alternates

The illustration shows the conformity of the actual rate of heat release to the estimated one. The estimated line appears with a time lag of approximately 3 min due to the chosen finite estimation time of the Kalman–Bucy filter.

Figures 5.24 and 5.25 show the courses of a fluctuating electric heating power q and their estimated courses for a

- Constant
- Induced fluctuating

temperature T_4 of the thermostat (virtual tank reactor).

To measure the thermal reaction power q of a real reaction, the online calorimeter is placed in the circulation of an ideally mixed batch reactor with 15 L volume. In the batch reactor is installed an electric heater of the same design as described in Sect. 2.1.1.

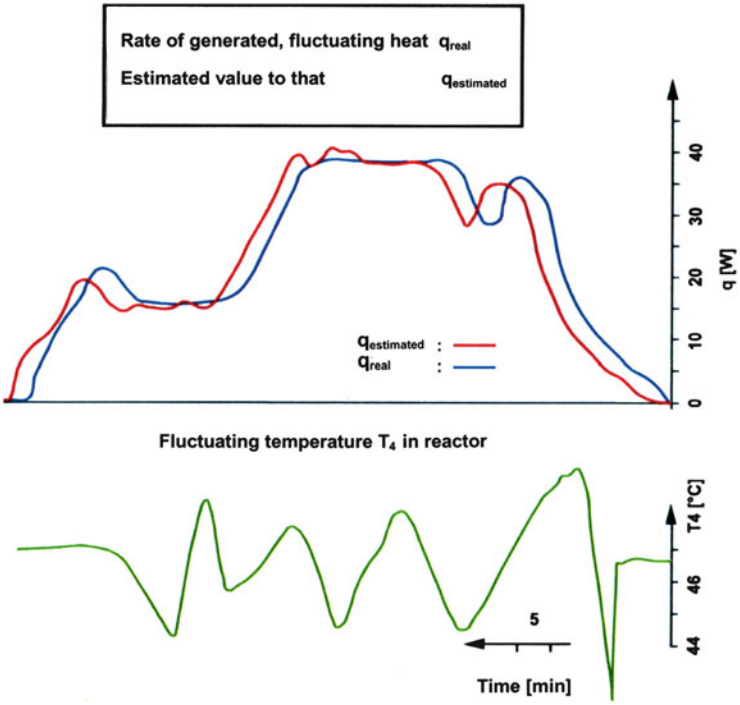

Fig. 5.25 Test of functionality of the sensor. Constant electric heating power q_{real} and its online estimated value $q_{\mathrm{estimated}}$. The temperature T in the virtual tank reactor alternates

The reaction is the alcoholysis of acetic acid anhydride by methanol. Pyridine catalyses the conversion. For the start of the reaction, methanol is dosed as quickly as possible in a batch of acetic anhydride, which is mixed with some added acetic acid as acting accelerator for solving. By the injection of pyridine at an advanced state of conversion, the reaction velocity is once more abruptly enlarged. Then the conversion ends in a relatively short amount of time. The temperature fluctuations in the batch reactor are induced during the conversion by means of the installed electric heater. Figure 5.26 shows the courses of thermal reaction power q and the accompanying induced change in temperature within the batch reactor.

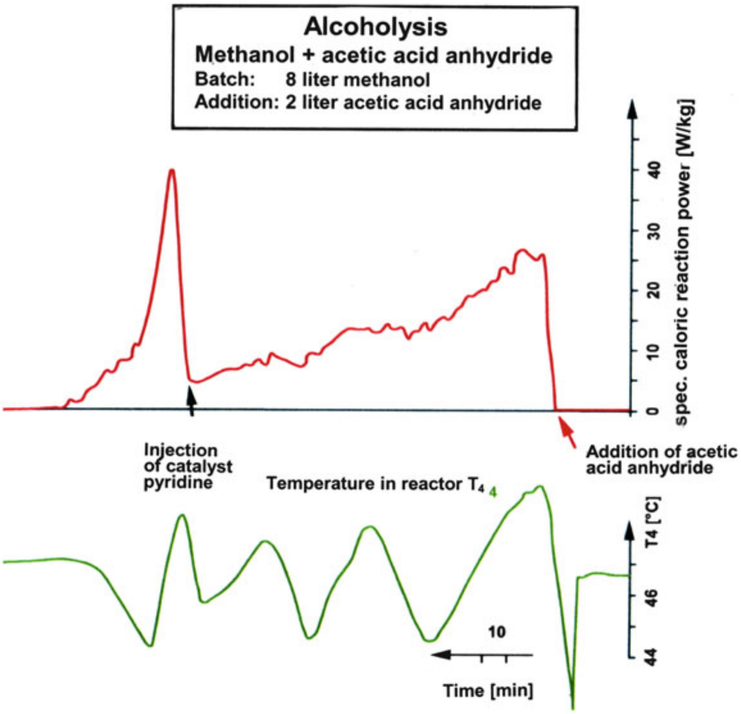

Fig. 5.26 Online measurement of the thermal reaction power *q* by the sensor during the reaction of methanol and acetic acid anhydride in a tank reactor. The alternating temperature in the reactor is induced

Part II
Practical Information and Applications

Chapter 6

Use of the Described Calorimeters to Determine Additional Relevant Quantities in Chemical Engineering

6.1 Determining the Heat of Dilution, Solution, Mixture, Precipitation and Reaction

The following heats of physicochemical processes can be determined by means of both isothermal and non-isothermal measuring modes using the previously described apparatus.

- Gross heat of reaction, i.e. heat of reaction mixed with heat of dilution, mixture, solution, precipitation or neutralization
- Heat of mixture
- Heat of solution
- Heat of dilution

6.1.1 Isothermal Measurements

The substance of filling in the measuring kettle should be chosen according to the aim of the measurement, for instance either a pure solvent, a solution of one of the components to be mixed or a solution of a basic part of reactants. The batch should be brought to the temperature T_{20}. To start the measurement, the completing component with mass G, specific heat c_p and temperature T_I is injected instantly at time $t = 0$ in the batch at temperature T_{20}.

The injection releases the physical heat $Q_{physical} = G \cdot c_p \cdot (T_I - T_{20})$ almost instantly. The release of $Q_{physicochemical}$ during the subsequent physicochemical process—with the exception of a chemical reaction—usually occurs extremely

W. Litz, *Bench Scale Calorimetry in Chemical Reaction Kinetics*,
DOI 10.1007/978-3-319-12532-9_6

quickly. Because of the inertia of the control system, the initial effect cannot be compensated by an instant change in the electric heating power p_2, i.e. the present, controlled equilibrium cannot be maintained at once. Hence, in the initial phase the temperature T_2 ($t \geq 0$) becomes unequal T_{20}.

In the time during which equilibrium of control is again established, the heat flow from the measuring kettle into the intermediate thermostat $(k{\cdot}F)_2{\cdot}[T_2 - T_1]$ is different compared to the heat flow prior to the injection $(k \cdot F)_2 \cdot [T_{20} - T_1]$. Because most of the heat stroke within the measuring kettle is usually compensated, the dynamics of the changed heat flow out of the measuring kettle is dampened to such a degree that the equilibrium of control in the intermediate thermostat is maintained ($T_1 = \text{const}$).

Hence, the heat balance of the intermediate thermostat reads

$$0 = [T_2 - T_1] \cdot (k \cdot F)_2 + p_1 + p_{\mathrm{St1}} - (T_1 - T_{\mathrm{S}}) \cdot (k \cdot F)_1 \quad \text{for } t \geq 0;$$

against that, the heat balance of the measuring kettle is expanded with the accumulation term $C_2{\cdot}\mathrm{d}T_2/\mathrm{d}t$:

$$C_2 \cdot \mathrm{d}T_2/\mathrm{d}t = q_{\text{physicochemical}} + q_{\text{physical}} + p_2 + p_{\mathrm{St2}} - (k \cdot F)_2 \cdot [T_2 - T_1] \quad \text{for } t \geq 0.$$

Combining both relations yields

$$q_{\text{physicochemical}} + q_{\text{physical}} = C_2 \cdot \mathrm{d}(T_2 - T_1)/\mathrm{d}t - (p_1 + p_2 + p_{\mathrm{St2}} + p_{\mathrm{St1}}) + (T_1 - T_{\mathrm{S}}) \cdot (k \cdot F)_1.$$

Prior to injection ($t < 0$) we have

$$0 = 0 - (p_1 + p_2 + p_{\mathrm{St2}} + p_{\mathrm{St1}}) + (T_1 - T_{\mathrm{S}}) \cdot (k \cdot F)_1,$$

hence

$$(T_1 - T_{\mathrm{S}}) \cdot (k \cdot F)_1 = (p_1 + p_2 + p_{\mathrm{St2}} + p_{\mathrm{St1}})_{t<0}.$$

Thus, the equation for the rate of heat release reads[1]

---

[1] Because the liquid within the intermediate thermostat remains unchanged.

$$
\begin{aligned}
q_{\text{physicochemical}} + q_{\text{physical}} &= C_2 \cdot \mathrm{d}(T_2 - T_1)/\mathrm{d}t - (p_1 + p_2 + p_{\text{St2}} + p_{\text{St1}}) \\
&\quad + (p_1 + p_2 + p_{\text{St2}} + p_{\text{St1}})_{t<0}\,, \\
&\text{due to } p_{\text{St1}} = \text{const} = p_{\text{St1}}(t<0) \text{ and } p_{\text{M2}} = p_{\text{St2}} + \text{const}_{\text{MStL2}} \\
&= C_2 \cdot \mathrm{d}(T_2 - T_1)/\mathrm{d}t - (p_1 + p_2 + p_{\text{M2}}) + (p_1 + p_2 + p_{\text{M2}})_{t<0} \\
&= C_2 \cdot \mathrm{d}(T_2 - T_1)/\mathrm{d}t + p_0 - p \\
&\quad \text{with } (p_1 + p_2 + p_{\text{M2}})_{t<0} = p_0 \text{ and } (p_1 + p_2 + p_{\text{M2}}) = p.
\end{aligned}
$$

By integration the amount of heat released is $Q = Q_{\text{physicochemical}} + Q_{\text{physical}}$[2]

$$
\begin{aligned}
Q = \int_{0\to\infty} \left[q_{\text{physicochemical}} + q_{\text{physical}}\right] \cdot \mathrm{d}t &= C_2 \cdot \left[(T_{2\infty} - T_1) - (T_{20} - T_1)\right] \\
&\quad + \int_{0\to\infty} [p_0 - p] \cdot \mathrm{d}t \\
&\quad \text{due to } T_{20} = T_{2\infty} \\
&= \int_{0\to\infty} [p_0 - p] \cdot \mathrm{d}t.
\end{aligned}
$$

6.1.2 Non-isothermal Measurement

An abrupt start to a large release of heat and its frequent and intensive fluctuation in the measuring kettle also causes in the intermediate thermostat a prolonged disturbance in the controlled equilibrium due to the thermal inertia.

In such a case it is reasonable

- To operate without an intermediate thermostat
- To switch off the compensation control in the measuring kettle
- To impose isoperibolic conditions

The measuring kettle is filled with a substance depending on the aim of the measurement: a pure solvent, a solution of one constituent for a mixture or a solution of the majority of the reactionless basic reactants for a chemical reaction. After thermal equilibrium is achieved at temperature $T_2 = T_{2\text{v}} = p_{\text{R2v}}/(kF)_{2\text{v}} + T_{\text{S}}$, the complementary substance of mass G, specific heat c_{p} and temperature T_{I} is injected instantly at time $t = 0$. Because of the physical heat input $Q_{\text{physical}} = G \cdot c_{\text{p}} \cdot (T_{\text{I}} - T_{2\text{v}})$ and the following physicochemical process, the temperature T_2 changes abruptly. But owing to heat exchange with the surrounding base thermostat at temperature T_{S} and the relatively small amount of injected mass, the temperature reaches ultimately a final value of $T_{2(t=\infty)} = T_{2\infty} \cong T_{2\text{v}}$, i.e. approximately the initial value of the batch.

---

[2] Again, this situation is valid only when the control of equilibrium in the intermediate thermostat is maintained.

To determine the physicochemical part, $Q_{\text{physicochemical}}$ see Sect. 6.2.

According to (2.16), the heat balance of the measuring kettle is

$$\begin{aligned} C_2 \cdot \mathrm{d}T_2/\mathrm{d}t &= q_{\text{physicochemical}} + q_{\text{physical}} + p_{\text{St2}} - (kF)_2 \cdot (T_2 - T_{\text{S}}) \quad \text{for } t \geq 0, \\ 0 &= p_{\text{St2v}} - (k \cdot F)_{2\text{v}} \cdot (T_{2\text{v}} - T_{\text{S}}) \quad \text{for } t < 0. \end{aligned}$$

Because of the small amount of injected mass, $p_{\text{St2}} \cong p_{\text{St2v}}$ and $(k{\cdot}F)_2 \cong (k{\cdot}F)_{2\text{v}}$ are valid, and the combination of both relations gives

$$\begin{gathered} C_2 \cdot \mathrm{d}T_2/\mathrm{d}t = q_{\text{physicochemical}} + q_{\text{physical}} - (k \cdot F)_{2\text{v}} \cdot (T_2 - T_{2\text{v}}), \\ \text{respectively} \\ C_2 \cdot \mathrm{d}(T_2 - T_{2\text{v}})/\mathrm{d}t = q_{\text{physicochemical}} + q_{\text{physical}} - (k \cdot F)_{2\text{v}} \cdot (T_2 - T_{2\text{v}}), \\ \text{or} \\ \text{with } (T_2 - T_{2\text{v}}) = \Delta T_{\text{v}} \\ C_2 \cdot \mathrm{d}\Delta T_{\text{v}}/\mathrm{d}t = q_{\text{physicochemical}} + q_{\text{physical}} - (k \cdot F)_{2\text{v}} \cdot \Delta T, \\ \text{respectively} \\ C_2 \cdot \mathrm{d}\Delta T_{\text{v}} = \left(q_{\text{physicochemical}} + q_{\text{physical}}\right) \cdot \mathrm{d}t - (k \cdot F)_{2\text{v}} \cdot \Delta T_{\text{v}} \cdot \mathrm{d}t. \end{gathered} \tag{6.1}$$

Because of $\Delta T_{\text{v}(t=0)} = \Delta T_{\text{v}(t=\infty)} = 0$, the integration yields

$$\begin{aligned} \int_{t=0\to\infty} \left[\left(q_{\text{physicochemical}} + q_{\text{physical}}\right) \cdot \mathrm{d}t\right] &= Q_{\text{physicochemical}} + Q_{\text{physical}} \\ &= (k \cdot F)_{2\text{v}} \cdot \int_{t=0\to\infty} [\Delta T_{\text{v}} \cdot \mathrm{d}t], \end{aligned}$$

which means that the released total amount of physical and physicochemical heat Q is directly proportional to the area between the measured curve T_2 and the horizontal baseline, i.e. the initial temperature $T_{2\text{v}} = p_{\text{St2v}}/(k{\cdot}F)_{2\text{v}} + T_{\text{S}}$ (Fig. 6.1). The proportionality factor is the value of the heat transfer coefficient $(k{\cdot}F)_{2\text{v}}$. To determine $(k{\cdot}F)_{2\text{v}}$, different and constant powers p_2 of the electric heater in the measuring kettle are set, and the corresponding equilibrium temperatures T_2 are recorded. Because of (2.1), for all different combinations of μ and ν, the following equation is valid

$$(k \cdot F)_{2\text{v}} = \left(p_{2\mu} - p_{2\nu}\right) / \left(T_{2\mu} - T_{2\nu}\right). \tag{6.2}$$

The physicochemical heat is determined by the equation

$$\begin{aligned} Q_{\text{physicochemical}} &= (k \cdot F)_{2\text{v}} \cdot \int_{t=0\to\infty} [\Delta T_{\text{v}} \cdot \mathrm{d}t] - Q_{\text{physical}} \\ &= (k \cdot F)_{2\text{v}} \cdot \int_{t=0\to\infty} [\Delta T_{\text{v}} \cdot \mathrm{d}t] - G \cdot c_{\text{p}} \cdot (T_{\text{I}} - T_{2\text{v}}). \end{aligned} \tag{6.3}$$

The final temperature $T_{2\infty}$ can differ somewhat from the initial temperature $T_{2\text{v}}$ (Fig. 6.1)

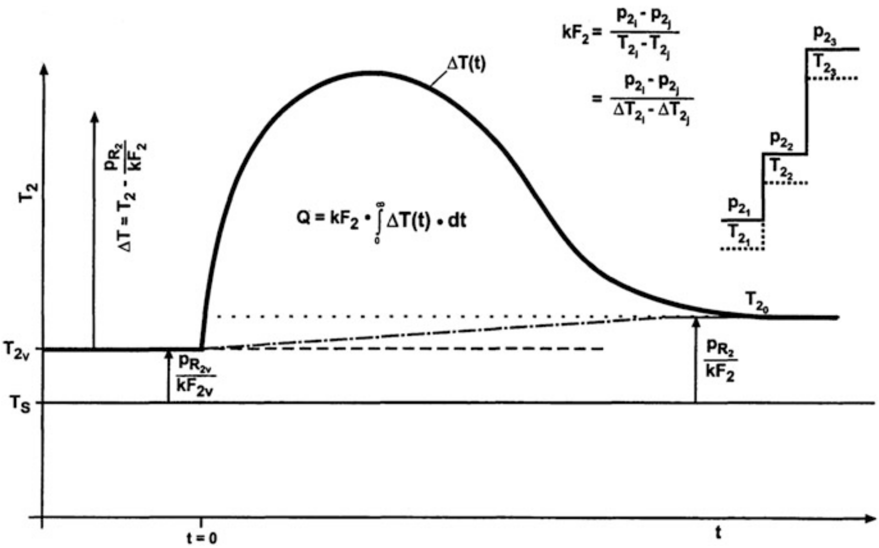

Fig. 6.1 Determining heat tones from temperature curve after injection of substance at temperature T_I into a batch of temperature T_{2v}, isoperibolic conditions

- When the heat transfer coefficient and the stirring power change noticeably during the chemical process. For a not too large difference, the connection line between T_{2v} and $T_{2\infty}$ can be used approximately as the baseline and $(k \cdot F_{2v} + k \cdot F_{2\infty})/2$ as the proportionality factor $(k{\cdot}F)_2$, in which $(k{\cdot}F)_{2v}$ and $(k \cdot F)_{2\infty}$ are determined prior to and after measurement, as described earlier.
- If a large amount of substance is injected, so that the stirring power respectively the heat-transfer coefficient jumps abruptly from p_{St2v} respectively $(k{\cdot}F)_{2v}$ to varied values $p_{St2\infty}$ respectively $(k \cdot F)_{2\infty}$[3], the baseline results approximately by means of rearward extrapolation $(t \rightarrow t = 0)$, i.e. starting from $T_{2\infty}$ in direction T_{2v}.

Occasionally it is necessary to determine a small $Q_{\text{physicochemical}}$ by the subtraction of large numerical values worked out according to (6.3). Such a situation cannot be weakened at will by the avoidance of producing the physical heat Q_{physical}, i.e. setting $T_I = T_{2v}$, because commercial temperature sensors usually have only a degree of measuring accuracy within 0.3↔1 %.

Therefore, sometimes it is necessary to obtain the exact equality of T_I and T_{2v} by physical means. In particular is the case where the generally small heat of a mixture Q_{Mi} must be determined. For such a problem it is advisable to install in the stirring shaft a closed chamber with the liquid batch flowing around it in the measuring

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[3] For the test: when the injected volume is extracted after the end of the measurement, the approximate initial temperature adjustment, i.e. T_{2v}, should return.

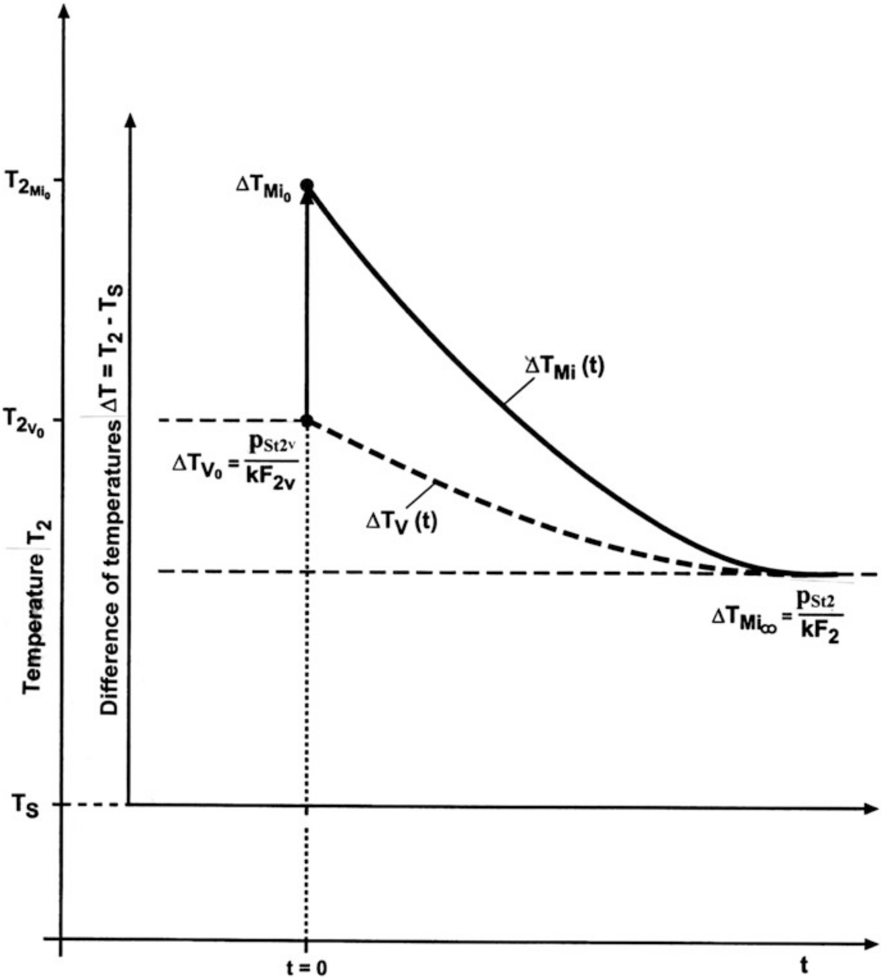

Fig. 6.2 Determining heat of mixture by non-isothermal, isoperibolic measurement

kettle (Fig. 3.3). The chamber is filled with the substance to be investigated. After thermal equilibrium is achieved, the filling in the chamber and the batch in the measuring kettle have the same temperature $T_{2v} = p_{St2v}/(k{\cdot}F)_{2v} + T_s$. Quickly pulling up the cylindrical jacket of the chamber, its content is mixed with the liquid batch of the measuring kettle within a very short time because of the large centrifugal and shearing forces. Simultaneously, the heat of the mixture Q_{Mi} is abruptly released. For that reason a temperature jump occurs from $T_{2v(t<0)} = T_{2v_0}$ to $T_{2Mi(t=0)} = T_{2Mi_0}$, in which $T_{2Mi(t=0)} = T_{2v(t<0)} + Q_{Mi}/C_2$ (Fig. 6.2). Using $T - T_S = \Delta T$ the equation used to determine the heat of the mixture reads

$$Q_{\mathrm{Mi}} = \left(\Delta T_{2\mathrm{Mi}(t=0)} - \Delta T_{2\mathrm{v}(t<0)}\right) \cdot C_2 = \left(\Delta T_{\mathrm{Mi}_0} - \Delta T_{\mathrm{v}_0}\right) \cdot C_2. \tag{6.4}$$

To calculate Q_{Mi}, we must know the accurate heat capacity of the mixture C_2. The usual method used to determine it is labour intensive and prone to error. Hence, for the exact estimation of Q_{Mi} another way is preferred:

By mixing the relatively large content in the chamber with the batch in the measuring kettle, the initial values of the physical quantities p_{St2v}, $(k{\cdot}F)_{2\mathrm{v}}$ and $C_{2\mathrm{v}}$ are suddenly changed to new values p_{St2}, $(k{\cdot}F)_2$ and C_2. The steady state, characterized by a steady heat flow out of the measuring kettle, is disturbed but appears again because of the changed heat flow following injection.

In case that the mixing of the content in the chamber with the filling in the measuring kettle would not release heat, the present balanced temperature difference $T_{2\mathrm{v}_0} - T_{\mathrm{S}} = \Delta T_{\mathrm{v}_0}$ alters because of the changed stirring power and the changed heat flow according to (2.11):

$$C_2 \cdot \mathrm{d}\Delta T_{\mathrm{v}}(t)/\mathrm{d}t = p_{\mathrm{St2}} - (k \cdot F)_2 \cdot \Delta T_{\mathrm{v}}(t).$$

The solution of the differential equation gives the decay of the still present temperature difference ΔT_{v_0} to the new value $\Delta T_{\mathrm{v}_\infty} = p_{\mathrm{St2}}/(kF)_2$ according to

$$\Delta T_{\mathrm{v}}(t) - p_{\mathrm{St2}}/kF_2 = \left[\Delta T_{\mathrm{v}_0} - p_{\mathrm{St2}}/(k \cdot F)_2\right] \cdot \mathrm{EXP}(-(k \cdot F_2)/C_2 \cdot t). \tag{6.5}$$

However, the really released heat of the mixture first causes an instant jump in the temperature from $T_{2\mathrm{v}_0}$ to $T_{2\mathrm{Mi}_0}$ respectively an instant change in the present temperature difference $T_{2\mathrm{v}_0} - T_{\mathrm{S}} = \Delta T_{\mathrm{v}_0}$ to $T_{2\mathrm{Mi}_0} - T_{\mathrm{S}} = \Delta T_{\mathrm{Mi}_0}$ (Fig. 6.2), which then decreases analogously to (6.5)

$$\Delta T_{\mathrm{Mi}}(t) - p_{\mathrm{St2}}/kF_2 = \left[\Delta T_{\mathrm{Mi}_0} - p_{\mathrm{St2}}/(k \cdot F)_2\right] \cdot \mathrm{EXP}(-k \cdot F_2/C_2 \cdot t). \tag{6.6}$$

The product of the area between the measuring curve $\Delta T_{\mathrm{Mi}}(t)$ and the baseline $\Delta T_{\mathrm{v}}(t)$ and the heat-transfer coefficient $(k{\cdot}F)_2$ gives as a result the desired heat of the mixture,

$$Q_{\mathrm{Mi}} = (k \cdot F)_2 \cdot \int_{0\to\infty} [\Delta T_{\mathrm{Mi}}(t) - \Delta T_{\mathrm{v}}(t)] \cdot \mathrm{d}t,$$

because it follows due to (6.5) and (6.6) that

$$\begin{aligned}(k \cdot F)_2 \cdot \int_{0\to\infty} [\Delta T_{\mathrm{Mi}}(t) - \Delta T_{\mathrm{v}}(t)] \cdot \mathrm{d}t &= (k \cdot F)_2 \cdot \int_{0\to\infty} [(\Delta T_{\mathrm{Mi}_0} - \Delta T_{\mathrm{v}_0}) \\ &\cdot \mathrm{EXP}\left(-(k \cdot F)_2/C_2 \cdot t\right)] \cdot \mathrm{d}t = \left(\Delta T_{\mathrm{Mi}_0} - \Delta T_{\mathrm{v}_0}\right) \cdot C_2 = Q_{\mathrm{Mi}}. \\ &\qquad\qquad\qquad \text{according to (6.4)}\end{aligned}$$

The course of the baseline $\Delta T_{\mathrm{v}}(t)$ can be found

- Either by calculation according to (6.5), because $(k{\cdot}F)_2/C_2$ can be worked out by the already measured decrease in $\Delta T_{\mathrm{Mi}}(t)$ over time[4]:

  Using a natural logarithmic plot of $\Delta T_{\mathrm{Mi}}(t) - q_{\mathrm{R2}}/(k{\cdot}F_2) = \Delta T_{\mathrm{Mi}}(t) - \Delta T_{\mathrm{Mi}}(t = \infty)$ versus time, which gives a straight line with a slope of $(k{\cdot}F)_2/C_2$,

  $$(k \cdot F_2)/C_2 = [\ln\{\Delta T_{\mathrm{Mi}}(t_1) - \Delta T_{\mathrm{Mi}}(t = \infty)\} - \ln\{\Delta T_{\mathrm{Mi}}(t_2) - \Delta T_{\mathrm{Mi}}(t = \infty)\}]/[t_2 - t_1].$$

- Or by measuring the decrease in $\Delta T_{\mathrm{v}}(t)$ after $\Delta T_{\mathrm{Mi}}(t)$ is recorded:

  to that end, the temperature of the filling in the measuring kettle is increased, for instance up to ΔT_{v_0}, by a short-term action of the electric heater, which is then switched off.

  $(k{\cdot}F)_2$ is found according to (6.2), as previously described.

6.2 Determining Specific Heat of Filling in Measuring Kettle

There exist three possibilities to determine the heat capacity C_2 respectively the specific heat c_{p} of filling within the measuring kettle

1. The measuring kettle is filled with the substances to be measured and brought to the temperature T_{20}. In addition, an injection syringe is filled with the mass G of the same substance and brought to the temperature $T_{\mathrm{I}} \neq T_{20}$. Because the substances in the measuring kettle and the syringe are identical, the injection does not release any heat of the mixture. Hence, according to (6.1) we have

   $$G \cdot c_{\mathrm{p}} \cdot (T_{\mathrm{I}} - T_{20}) = (k \cdot F)_2 \cdot \int_{t = 0 \to \infty} [\Delta T \cdot \mathrm{d}t]$$

   or

   $$c_{\mathrm{p}} = (k \cdot F)_2 \cdot \int_{t = 0 \to \infty} [\Delta T \cdot \mathrm{d}t]/G/(T_{\mathrm{I}} - T_{20}).$$

   $(k{\cdot}F)_2$ is found according to (6.2), as described previously.
2. The filling G in the measuring kettle is brought to the temperature T_2 by the short-term action of the electric heater, and then the temperature decrease $T_2(t) - T_{20} = \Delta T(t)$ is recorded. Because of (6.1) and $(q_{\mathrm{physicochemical}} + q_{\mathrm{physical}}) = 0$, the reaction runs corresponding to

   $$\Delta T(t) = \Delta T(t = 0) \cdot \mathrm{EXP}\big(-(k \cdot F)_2/C_2 \cdot t\big).$$

---

[4] $\Delta T_{\mathrm{v}}(t = \infty) = \Delta T_{\mathrm{Mi}}(t = \infty) = q_{\mathrm{R2}}/(k \cdot F)_2$ is valid.

Plotting $\ln\{\Delta T(t)\}$ versus time gives as a result a straight line with the slope $(k{\cdot}F)_2/C_2$

$$(k \cdot F)_2/C_2 \; = \; [\ln\{\Delta T(t_1)\} - \ln\{\Delta T(t_2)\}]/[t_2 - t_1]. \tag{6.7}$$

$(k{\cdot}F)_2$ can be obtained as described earlier by (6.2).

Between the specific heat c_p and the effective heat capacity C_2, the relation $c_p = (C_2 - C_{Mt})/G$ holds. Combining this with (6.7) we obtain

$$c_p = (C_2 - C_{Mt})/G = \left[(t_2 - t_1) \cdot (k \cdot F)_2/[\ln\{\Delta T(t_1)\} - \ln\{\Delta T(t_2)\}] - C_{Mt}\right]/G.$$

C_{Mt} is, so to speak, an apparatus constant, which can be determined from the heat capacity $C_{RM} = G{\cdot}c_p$ of a filling G with a known specific heat c_p and of the measured corresponding effective heat capacity C_2 (Sect. 2.5.1).

3. The filling in the measuring kettle is subject to a controlled temperature rise at a constant rate $\mathrm{d}T_2/\mathrm{d}t = \beta$. The start of the temperature program causes an abrupt jump in the electric heating power p_2 according to (2.10) by $\Delta p_2(t=0) = C_2{\cdot}\beta$.

   Considering point 2 gives

$$c_p = (C_2 - C_{Mt})/G = \Delta p_2(t = 0)/\beta/G.$$

6.3 Determining the Stirrer Power Within the Filling of the Measuring Kettle

According to (2.3), there exists between the stirring power p_{St2} in the measuring kettle and the power p_{M2} of the driving electromotor (provided the loss within the motor and in the bearing unit of the stirrer remains constant during the measurement) the linear relation

$$p_{St2} \; = \; p_{M2} \; - \; \mathrm{const}_{MStL2}.$$

The motor power p_{M2} for a stirrer rotating without load in an empty measuring kettle corresponds to the value const_{MStL} because the stirring resistance in the gas of an empty measuring kettle is negligibly small. Hence, the stirring power p_{St2} of the stirrer rotating with a load in a measuring kettle filled with reaction mixture is given by the difference of the motor powers for the stirrer rotating with a load and without a load:

$$p_{St2} \; = \; p_{M2(\text{on load})} \; - \; p_{M2(\text{without load})}.$$

In the case of DC disk-armature motors, due to (2.8), the following equation is valid[5]:

---

[5] To determine $I_{(\text{without load})}$, the filling is removed from the measuring kettle to the greatest possible extent. If possible, this must be done at an unchanged rotational speed of the stirrer, for instance by sucking out the filling without stopping the motor, because stopping and restarting the motor usually causes a slight change in torque loss, which hinders the determination of small stirring powers; in any case, the result of the measurement would be of questionable merit.

$$\begin{aligned} p_{\mathrm{St2}} &= d \cdot I_{(\text{on load})} \cdot 2\pi \cdot N \ - \ d \cdot I_{(\text{without load})} \cdot 2\pi \cdot N \\ &= \left(I_{(\text{on load})} \ - \ I_{(\text{without load})}\right) \cdot d_{\text{Torque}} \cdot 2\pi \cdot N. \end{aligned} \tag{6.8}$$

Using the torque factor d_{Torque} in pondcentimeter per ampere [pcm/A], the electric current strength I in amperes [A] and the rotating speed in revolutions N per minute [min^{-1}] gives the value of the stirring power p_{St2} in mechanical units (pcm/min). The transformation into a more practical electric unit (Watts) reads[6]

$$p_{\mathrm{St2}} = \left(I_{(\text{with load})} - I_{(\text{without load})}\right) \cdot d_{\text{Torque}} \cdot N/97{,}465 \ [\mathrm{W}].$$

In the case of a DC disk-armature motor, there exists, according to (2.7), between the mechanical torque factor d_{Torque} [pcm/A] and the electromotive factor k_{Motor} [V/min^{-1}][7] the linear relation d_{Torque} [pcm/A] = 97,465·k_{Motor} [V/min^{-1}]. Hence, p_{St2} can be expressed as a function of k_{Motor} [V/min^{-1}], I [A] and N [min^{-1}][8]:

$$\begin{gathered} p_{\mathrm{St2}} = \left(I_{(\text{on load})} - I_{(\text{without load})}\right) \cdot k_{\text{Motor}} \cdot N[\mathrm{W}] \\ \text{or} \\ \text{due to (2.6), i.e with } U_{\text{Tacho}}[\mathrm{V}] \text{ and } k_{\text{Tacho}}\left[\mathrm{V}/\mathrm{min}^{-1}\right] \\ = \left(I_{(\text{on load})} - I_{(\text{without load})}\right) \cdot k_{\text{Motor}} \cdot U_{\text{Tacho}}/k_{\text{Tacho}}[\mathrm{W}]. \end{gathered} \tag{6.9}$$

6.4 Determining Fractional Conversion of a One-Step Reaction

In the case of an irreversible one-step reaction (reaction without an ascertainable intermediate product), the fractional conversion X is given by the quotient of the released amount of heat $Q = \int_{0 \to t} q \cdot \mathrm{d}t$ from the start of the reaction up to time t and the total amount of heat released: $Q_{\infty} = \int_{0 \to \infty} q \cdot \mathrm{d}t$ (Fig. 6.3).

By definition we have $X = (N_{\mathrm{j}}(t = 0) - N_{\mathrm{j}})/N_{\mathrm{j}}(t = 0)$. On the basis of (4.2), (4.3) and (4.4) we obtain

---

[6] $\Psi[\mathrm{pcm}]\left[\mathrm{min}^{-1} \cdot 2\pi\right] \equiv \Psi[\mathrm{pcm/min}] \cdot 6.28 \equiv \Psi/10^3/10^2/60 \cdot 6.28\,[\mathrm{kpm/s}] \equiv \Psi/6/10^6 \cdot 6.28/0.102\ [\mathrm{W}] \equiv \Psi/97{,}465\ [\mathrm{W}]$.

[7] k_{Motor} [V/min^{-1}] generated electric voltage U_{Motor} of the DC disc-armature motor running without a load at one revolution per minute.

[8] k_{Tacho} [V/min^{-1}] is the generated electric voltage U_{Tacho} of the DC disk-armature tachogenerator running at one revolution per minute.

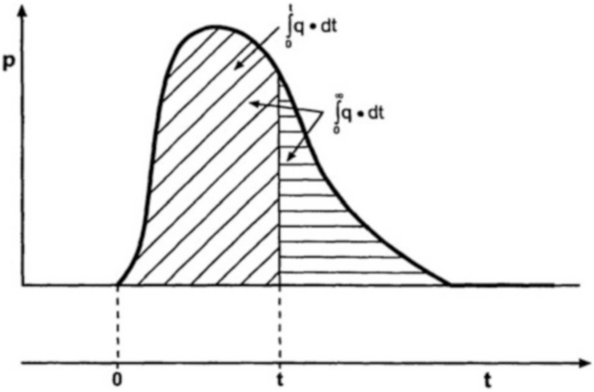

Fig. 6.3 Determining fractional conversion of one-step reaction fractional conversion ≡ released partial/released total amount of heat $X = \int_{0 \to t} q \cdot \mathrm{d}t / \int_{0 \to \infty} q \cdot \mathrm{d}t$

$$\begin{aligned}
\int_{0 \to t} q \cdot \mathrm{d}t / \int_{0 \to \infty} q \cdot \mathrm{d}t &= \int_{0 \to t} [r \cdot V \cdot (-\Delta H_\lambda)] \cdot \mathrm{d}t / \int_{0 \to \infty} [r \cdot V \cdot (-\Delta H_\lambda)] \cdot \mathrm{d}t \\
&= \int_{0 \to \mathrm{t}} [\mathrm{d}\lambda/\mathrm{d}t] \cdot \mathrm{d}t / \int_{0 \to \infty} [\mathrm{d}\lambda/\mathrm{d}t] \cdot \mathrm{d}t \\
&= \int_{\mathrm{Nj,0} \to \mathrm{Njt}} \mathrm{d}N_\mathrm{j} / \int_{\mathrm{Nj,0} \to \mathrm{Nj\infty}} \mathrm{d}N_\mathrm{j} \\
&= \left(N_\mathrm{jt} - N_\mathrm{j,0}\right) / \left(N_{\mathrm{j}\infty} - N_\mathrm{j,0}\right) \\
&\qquad \text{because of } N_{\mathrm{j}\infty} = 0 \\
&= \left(N_\mathrm{j,0} - N_\mathrm{jt}\right) / N_\mathrm{j,0}.
\end{aligned}$$

6.5 Determination of Heat Transfer Coefficient of Measuring Kettle

The heat balances (2.1) and (2.27) of the calorimeter for discontinuous and continuous reactions lead to the equations determining the heat-transfer coefficient $(k{\cdot}F)_2$ for heat flow from the measuring kettle to the intermediate thermostat:

$$(k \cdot F)_2 = [q + p_2 + p_{\mathrm{St2}}]/\Delta T_2$$

and

$$(k \cdot F)_2 = [(q + q_{\mathrm{Mi}}) + p_2 + p_{\mathrm{St2}}]/\Delta T_2.$$

The substitution of q respectively $(q + q_{\mathrm{Mi}})$ by (2.3), (2.4) respectively (2.27) gives[9]

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[9] See Sect. 6.3.

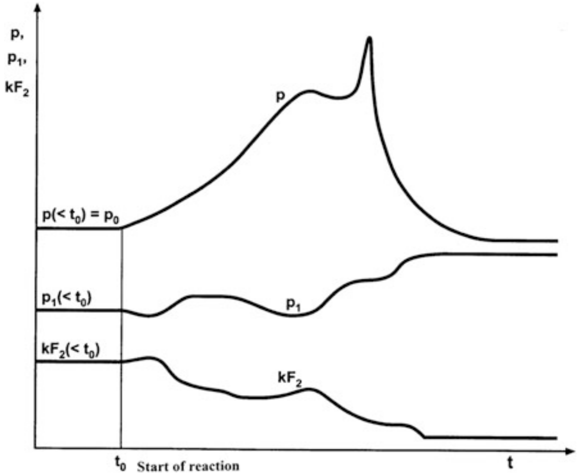

Fig. 6.4 Determining heat-transfer coefficient $(k{\cdot}F)_2$ measuring kettle → intermediate thermostat on basis of total thermal power p_0 prior to start of reaction, temporal course of electric heating power p_1 of intermediate thermostat after start of a discontinuous reaction and motor power $p_{\text{M2(without load)}}$

$$
\begin{aligned}
(k \cdot F)_2 &= [p_0 - p + p_2 + p_{\text{M2}} - \text{const}_{\text{MStL2}}]/\Delta T_2 \\
&\quad \text{due to } p = p_2 + p_1 + p_{\text{M2}} \\
&= [p_0 - p_1 - \text{const}_{\text{MStL2}}]/\Delta T_2 \\
&\qquad\qquad \text{with}(6.8) \\
&= \left[p_0 - p_1 - p_{\text{M2(without load)}}\right]/\Delta T_2 \\
&= \left[p_0 - p_1 - d_{\text{torque}} \cdot I_{\text{(without load)}} \cdot 2\pi \cdot N\right]/\Delta T_2 \\
&\qquad\quad \text{alike } (6.9) \\
&= \left[p_0 - p_1 - I_{\text{(without load)}} \cdot k_{\text{Motor}} \cdot U_{\text{Tacho}}/k_{\text{Tacho}}\right]/\Delta T_2.
\end{aligned}
$$

Figure 6.4 shows as an example the course of the heat-transfer coefficient $(k{\cdot}F)_2$ versus time during a discontinuously running reaction.

The specific heat-transfer coefficient k can be evaluated when the area F_2 of the heat transfer is known. F_2 corresponds to the area of the measuring-kettle wall being wetted by the reaction mixture.

- For a moderately stirred reaction mixture F_2, is given by the geometry of the measuring kettle respectively the volume of its filling.
- For a turbulently stirred reaction mixture, F_2 corresponds to the total area of the measuring kettle, i.e. cover, sidewall and bottom.

This yields

$$k = \left[p_0 - p_1 - I_{\text{(without load)}} \cdot k_{\text{Motor}} \cdot U_{\text{Tacho}}/k_{\text{Tacho}}\right]/\Delta T_2/F_2.$$

6.6 Determining the Heat Transfer from the Batch Within a Tank Reactor to Its Coolant Medium

In the chemical industry, heat must be transferred to allow for the safe use of tank reactors. Hence, it is very important to elaborate the attributes of heat transfer from a technical reactor. To this end, the application of the bench scale calorimeter proves advantageous.

The difficulties and the risk of scaling up the heat-transfer coefficient from a small to a large reactor increase dramatically from the increased size of the reactor because the content of the reactor increases by a power of three, but the area for heat transmission grows only by a power of two.

Instead of using a complex system of differential equations, often coupled with a somewhat dubious degree of accuracy, especially with regard to the used values of parameters, it is useful to scale up in accordance with the similitude theory with dimensionless groups [8, 37].

It is generally known that the total resistance $1/k$ per unit area of reactor wall against heat flow from the *r*eaction mixture into the medium of the cooling jacket is composed of the inside resistance $1/\alpha_{\mathrm{Rm}}$ against the transfer of heat from the reaction mixture to the reactor wall, the resistance $d_{\mathrm{Rw}}/\lambda_{\mathrm{Rw}}$ against the thermal conduction within the *r*eactor wall, and the outside resistance $1/\alpha_{\mathrm{c}}$ against the transfer of heat from the reactor wall to the medium of the *c*ooling jacket [51]:

$$1/k = 1/\alpha_{\mathrm{Rm}} + d_{\mathrm{Rw}}/\lambda_{\mathrm{Rw}} + 1/\alpha_{\mathrm{c}}. \tag{6.10}$$

The outside transfer resistance $1/\alpha_{\mathrm{c}}$ of a reactor is a function of the nature of the outside surface of the reactor wall, the properties of the coolant and its flow rate. The conductivity resistance $d_{\mathrm{Rw}}/\lambda_{\mathrm{Rw}}$ depends on the thickness of the reactor wall and its material. The temperature dependency is relatively small.

When a defined coolant flows at constant velocity through the jacket of a reactor filled with a reaction mixture, besides the resistance against the conduction of heat within the wall, the resistance against the transfer of heat out of the wall into the coolant is also constant. Hence, both can be combined into a total resistance $1/\alpha_{\mathrm{Tc}}$, which depends only on the temperature of the medium in the cooling jacket.

From (6.10) we obtain

$$1/k = 1/\alpha_{\mathrm{Rm}} + 1/\alpha_{\mathrm{Tc}}. \tag{6.11}$$

$1/\alpha_{\mathrm{Tc}}$ is inferred from the information of the manufacturer.

The inside resistance of heat transfer $1/\alpha_{\mathrm{Rm}}$ depends on the properties of the reaction mixture, the composition of the inner surface of the reactor, the design of the stirrer and its rotational speed. According to the similitude theory, the characteristic of the heat transfer reads [52, 53]

Table 6.1 Constant c of heat-transfer characteristic $\mathrm{Nu} = c \cdot \mathrm{Re}^{2/3} \cdot \mathrm{Pr}^{1/3} \cdot (\eta/\eta_{\mathrm{Wall}})^{0.14}$ for standardized reactors and standardized types of stirrer [52, 53] DIN 28136, ASME Code Section Vffl

Stirrer type	c	Range of validity
Plate	0.54	$16<\mathrm{Re}>4.6 \times 10^4$
Anchor	0.35	$70<\mathrm{Re}>6 \times 10^5$
Impeller	0.33	$9<\mathrm{Re}>5.5 \times 10^4$
Lattice	0.47	$12<\mathrm{Re}>3 \times 10^5$

$$\mathrm{Nu} = c \cdot \mathrm{Re}^{2/3} \cdot \mathrm{Pr}^{1/3} \cdot (\eta/\eta_{\mathrm{Wall}})^{0.14}, \tag{6.12}$$

with

$\mathrm{Nu} = \alpha_{\mathrm{Rm}} \cdot D_{\mathrm{R}}/\lambda_{\mathrm{Rm}}$	dimensionless Nussel characteristic
$\mathrm{Re} = N \cdot d_{\mathrm{St}}{}^2 \cdot \rho/\eta$	dimensionless Reynolds characteristic
$\mathrm{Pr} = \eta \cdot c_{\mathrm{p}}/\lambda_{\mathrm{Rm}}$	dimensionless Prandtl characteristic
$\eta/\eta_{\mathrm{Wall}}$	dimensionless viscosity
c	constant, depending on the type of stirrer, the conditions of the reactor and the heat exchange area (see Table 6.1)

From this we obtain

$$\begin{aligned}\alpha_{\mathrm{Rm}} &= c \cdot \left\{d_{\mathrm{St}}{}^{4/3}/D_{\mathrm{R}}/g^{1/3} \cdot N^{2/3}\right\} \cdot \left\{\lambda_{\mathrm{Rm}}{}^{2/3} \cdot \rho^{2/3} \cdot c_{\mathrm{p}}{}^{1/3} \cdot g^{1/3} \cdot (\eta/\eta_{\mathrm{Wall}})^{0.14}\right\}\\ &= c \cdot \left\{d_{\mathrm{St}}{}^{4/3}/D_{\mathrm{R}} \cdot \lambda_{\mathrm{Rm}}{}^{2/3} \cdot \rho^{2/3} \cdot c_{\mathrm{p}}{}^{1/3} \cdot g^{1/3} \cdot (\eta/\eta_{\mathrm{Wall}})^{0.14}\right\} \cdot N^{2/3}\\ &= \mathrm{A} \cdot N^{2/3}.\end{aligned} \tag{6.13}$$

The quantity A depends only on the properties of the reaction mixture, the characteristic diameter D_{R} of the reactor and the characteristic diameter d_{St} of the stirrer. For a given filled reactor the quantity A varies only by changes in temperature.

The combination of (6.11) and (6.13) yields

$$1/k = 1/\alpha_{\mathrm{Rm}} + 1/\alpha_{\mathrm{Tc}} = 1/A \cdot N^{-2/3} + 1/\alpha_{\mathrm{Tc}}. \tag{6.14}$$

According to (6.14), the quantities A, α_{Rm} and α_{Tc} can be found when k is measured for different rotations N of the stirrer per unit of time. Plotting $1/k$ versus $N^{-2/3}$ (Fig. 6.5) gives a straight line whose slope corresponds to $1/A$ and whose intercept with the ordinate corresponds to the total outside resistance of heat transition $1/\alpha_{\mathrm{Tc}}$, so that $1/\alpha_{\mathrm{Rm}}$ is determined.

For the quotient of the specific inside heat-transfer coefficients $\alpha_{\mathrm{Rm}\mathbf{TR}}$ of a tank reactor and α_{RmMK} the measuring kettle of a calorimeter, due to (6.13), is as follows:

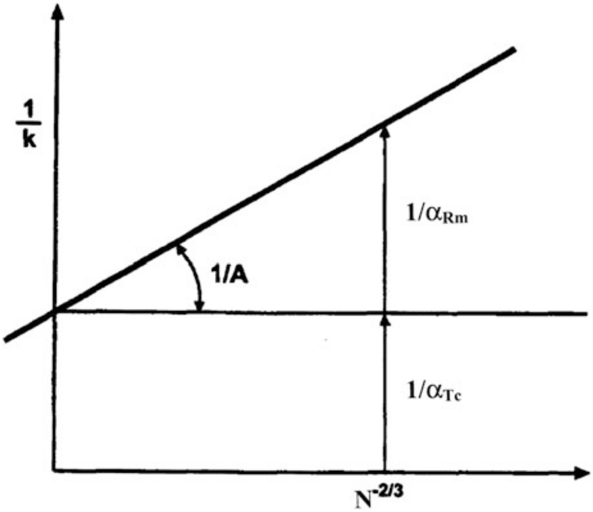

Fig. 6.5 Determining inside resistance of heat transfer of reactor $1/\alpha_{Rm}$ by plot of total resistance against heat transfer $1/k$ versus rotations of stirrer per unit of time N raised to power $-2/3$

$$\alpha_{RmTR}/\alpha_{RmMK} = c_{TR}/c_{MK} \cdot (N_{TR}/N_{MK})^{2/3} \cdot (D_{MK}/D_{TR}) \cdot (d_{StTR}/d_{StMK})^{4/3} \cdot \left\{(\eta/\eta_{wall})_{TR}/(\eta/\eta_{wall})_{MK}\right\}^{0.14}.$$

Therefore, the strategy for scaling up is obvious:

Choose a measuring kettle, similar in the sense of similitude theory to the tank reactor (and vice versa), so that the constants c of the heat-transfer characteristic correspond to each other:

$$c_{TK} = c_{MK}.$$

Hence, the following equation is valid:

$$\alpha_{RmTR} = \alpha_{RmMK} \cdot (N_{TR}/N_{MK})^{2/3} \cdot (D_{MK}/D_{TR}) \cdot (d_{RTR}/d_{RMK})^{4/3} \cdot \left\{(\eta/\eta_{wall})_{TR}/(\eta/\eta_{wall})_{MK}\right\}^{0.14}.$$

Considering

$$d_{StMK}/D_{MK} = d_{StTR}/D_{TR}$$

we obtain

$$\begin{aligned}\alpha_{RmTR} &= \alpha_{RmMK} \cdot (N_{TR}/N_{MK})^{2/3} \cdot (d_{StTR}/d_{StMK})^{1/3} \cdot \left\{(\eta/\eta_{Wall})_{TR}/(\eta/\eta_{Wall})_{MK}\right\}^{0.14} \\ &= \alpha_{RmMK} \cdot (N_{TR}/N_{MK})^{2/3} \cdot (D_{TR}/D_{MK})^{1/3} \cdot \left\{(\eta/\eta_{Wall})_{TR}/(\eta/\eta_{Wall})_{MK}\right\}^{0.14}.\end{aligned}$$

In contrast to the tank reactor, the temperature difference between the reaction mixture within the measuring kettle and the layer on the measuring-kettle wall is relatively small. Thus it can be assumed that $\eta_{\mathrm{MK}} \cong \eta_{\mathrm{wallMK}}$, i.e. in practise $(\eta/\eta_{\mathrm{wall}})_{\mathrm{MK}}{}^{0.14} = 1$.

Hence, the equation for the specific heat-transfer coefficient α_{RmTR} of the tank reactor reads

$$\begin{aligned}\alpha_{\mathrm{RmTR}} &\cong \alpha_{\mathrm{RmMK}} \cdot (N_{\mathrm{TR}}/N_{\mathrm{MK}})^{2/3} \cdot (d_{\mathrm{StTR}}/d_{\mathrm{StMK}})^{1/3} \cdot (\eta/\eta_{\mathrm{wall}})_{\mathrm{TR}}{}^{0.14}\\ &\cong \alpha_{\mathrm{RmMK}} \cdot (N_{\mathrm{TR}}/N_{\mathrm{MK}})^{2/3} \cdot (D_{\mathrm{StTR}}/D_{\mathrm{StMK}})^{1/3} \cdot (\eta/\eta_{\mathrm{wall}})_{\mathrm{TR}}{}^{0.14}.\end{aligned}$$

Conclusion

- The use of the bench scale calorimeter enables the determination of the inside resistance of heat transfer $1/\alpha_{\mathrm{RmTR}}$ of a similar tank reactor
- The outside resistance of heat transfer $1/\alpha_{\mathrm{TcTR}}$ out of the tank reactor can be inferred from the information of the manufacturer.

Consequently, the total resistance $1/k_{\mathrm{TK}}$ against heat flow from the reaction mixture via the tank wall into the coolant can be calculated according to (6.14).

6.7 Calorimetric Investigation of Incrustation of Foreign Matter on Superheated Metal (Fouling)

The calorimeter can help in

- Determining the conditions for the deposit of material on superheated surfaces (fouling), for instance on a heating installation in a reactor or on the evaporator of a rectifying column
- Elaborating the dynamics of an overlaying.

To this end, the calorimeter works without the use of an intermediate thermostat. In the measuring kettle, filled with a solution to be investigated, is installed a pipe coil through which a fluid of high temperature can be pumped (Fig. 6.6). Due to the high temperature at the surface of the pipe coil an incrustation of foreign material can start. If it does, the heat transfer coefficient $(k{\cdot}F)_{\mathrm{H}}$ of the pipe changes, and as a consequence, the heat flow into the measuring kettle changes as well. The change in heat flow is compensated by a variation in the heating power p_2 of the controlled electric heater.

The heat balance of the measuring kettle in controlled thermal equilibrium reads,

$$\begin{aligned}p_2 &= (T_2 - T_0) \cdot (k \cdot F)_2 - p_{\mathrm{St2}} - (T_{\mathrm{H}} - T_2) \cdot (k \cdot F)_{\mathrm{H}}\\ &= \Delta T_2 \cdot (k \cdot F)_2 - p_{\mathrm{St2}} - \Delta T_{\mathrm{H}} \cdot (k \cdot F)_{\mathrm{H}}\end{aligned}$$

We obtain

- Prior to the start of the passage of the superheated fluid at temperature T_{H} through the pipe coil at time $t = 0$, with $T_{\mathrm{H}}(<0) = T_2, p_{\mathrm{St2}} = \text{const}, \ \Delta T_2 \cdot (k \cdot F_2) = \text{const}$

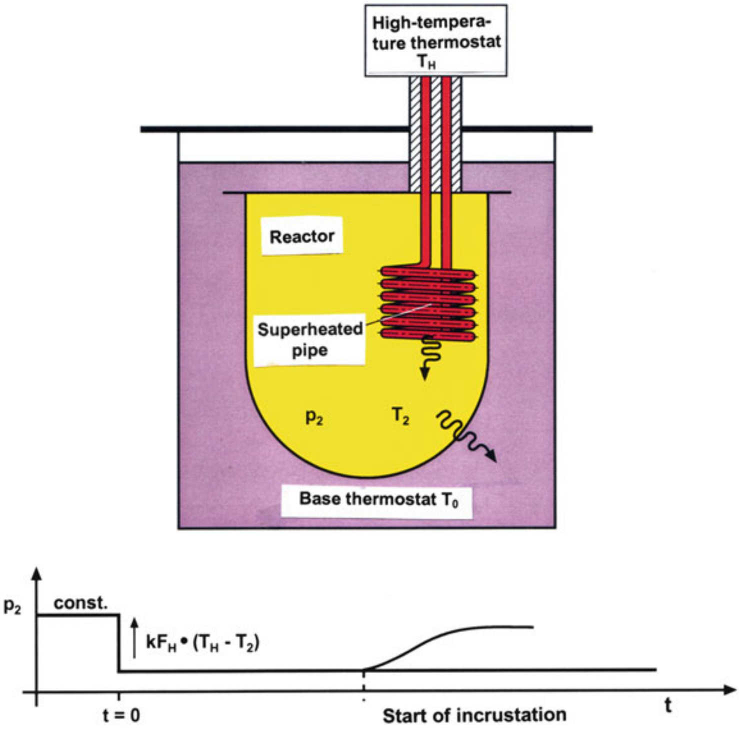

Fig. 6.6 Equipment for the investigation of
- Conditions for incrustation (fouling) on a superheated surface
- Dynamics of this occurrence

$$p_2(t < 0) \;=\; \Delta T_2 \cdot (k \cdot F)_2(t < 0) - p_{\mathrm{St2}}(t < 0) \;=\; \text{const.} \tag{6.15}$$

- During the passage of the fluid,

$$\begin{aligned}
p_2(t) &= \Delta T_2 \cdot (k \cdot F)_2(t) \;-\; p_{\mathrm{St2}}(t) \;-\; \Delta T_{\mathrm{H}} \cdot (k \cdot F)_{\mathrm{H}}(t)\\
&= \Delta T_2 \cdot \left[(k \cdot F)_2(t < 0) \;+\; \delta(k \cdot F)_2(t)\right] - \left[p_{\mathrm{St2}}(t < 0) \;+\; \delta p_{\mathrm{St2}}(t)\right] \;-\; \Delta T_{\mathrm{H}} \cdot (k \cdot F)_{\mathrm{H}}(t)\\
&= \Delta T_2 \cdot (k \cdot F)_2(t < 0) \;+\; \Delta T_2 \cdot \delta(k \cdot F)_2(t) - p_{\mathrm{St2}}(t < 0) \;-\; \delta p_{\mathrm{St2}}(t) \;-\; \Delta T_{\mathrm{H}} \cdot (k \cdot F)_{\mathrm{H}}(t)\\
&\quad \text{due to (6.15)}\\
&= \text{const} \;+\; \Delta T_2 \cdot \delta(k \cdot F)_2(t) \;-\; \delta p_{\mathrm{St2}}(t) \;-\; \Delta T_{\mathrm{H}} \cdot (k \cdot F)_{\mathrm{H}}(t)
\end{aligned}$$

or

$$p_2(t) \;+\; \delta p_{\mathrm{St2}}(t) \;-\; \Delta T_2 \cdot \delta(k \cdot F_2)(t) \;=\; \text{const} - \Delta T_{\mathrm{H}} \cdot (k \cdot F)_{\mathrm{H}}(t). \tag{6.16}$$

The incrustation of material on the pipe coil causes the material to disappear from the solution in the measuring kettle. However, usually this does not cause an discernible change in the consistency, i.e. $\delta p_{\mathrm{St2}}(t) \cong 0$ and $\delta(k{\cdot}F)_2(t) \cong 0$. Hence, this yields

$$(k \;\cdot\; F)_{\mathrm{H}}(t) = (\text{const} - p_2(t))/\Delta T_{\mathrm{H}}.$$

The change in p_2 indicates the onset of fouling and the amount of change is a measure of the thickness respectively mass of fouling (Fig. 6.6).

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 ($k \cdot F$).

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DOI 10.1007/978-3-319-12532-9_7

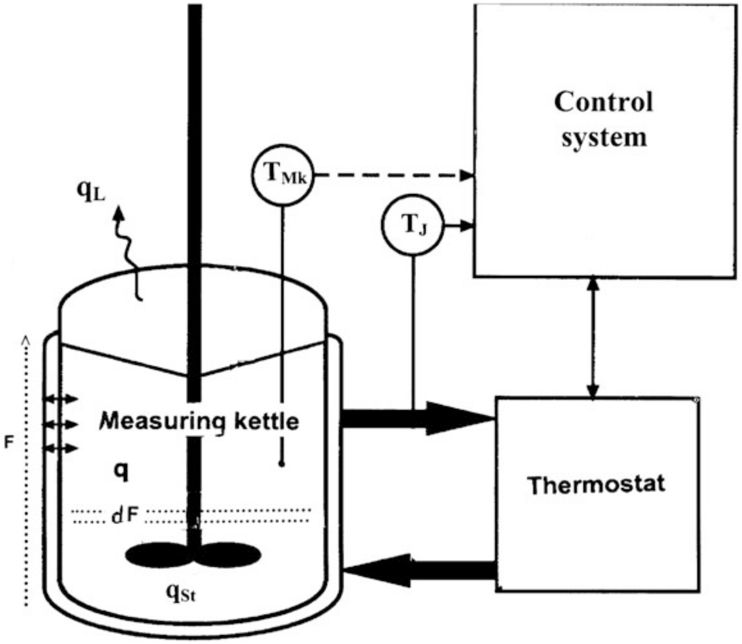

Fig. 7.1 Flowchart of so-called heat-flow calorimeter by Regenass

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
$T_{\mathrm{J}}[F]$: Temperature in the turbulently flowing fluid in jacket at the value of F behind the outlet
T_{J}: Temperature of the outflow of jacket
$\overline{T}_{\mathrm{J}}$: Balanced average temperature of turbulent flow through the jacket
ΔT: Temperature difference $T_{\mathrm{Mk}} - T_{\mathrm{J}}$

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:

$$
\begin{aligned}
q &= (k \cdot F) \cdot \left(T_{\mathrm{Mk}} - \overline{T}_{\mathrm{J}}\right) - (k \cdot F)_0 \cdot \left(T_{\mathrm{Mk}} - \overline{T}_{\mathrm{J0}}\right) - (p_{\mathrm{L}} - p_{\mathrm{L0}}) - (p_{\mathrm{St}} - p_{\mathrm{St0}}) \\
&\qquad \text{or using} \\
&\qquad \Delta T_0 = T_{\mathrm{Mk}} - \overline{T}_{\mathrm{J0}} \\
&\qquad \Delta T = T_{\mathrm{Mk}} - \overline{T}_{\mathrm{J}} \\
&\qquad \Delta p_{\mathrm{L}} = p_{\mathrm{L}} - p_{\mathrm{L0}} \\
&\qquad \Delta p_{\mathrm{St}} = p_{\mathrm{St}} - p_{\mathrm{St0}} \\
&= (k \cdot F) \cdot \Delta T - (k \cdot F)_0 \cdot \Delta T_0 - \Delta p_{\mathrm{L}} - \Delta p_{\mathrm{St}}. \\
&= (k \cdot F) \cdot \left[\Delta T - \Delta T_0 \cdot (k \cdot F)_0 / (k \cdot F) - \Delta p_{\mathrm{L}} / (k \cdot F) - \Delta p_{\mathrm{St}} / (k \cdot F)\right] \\
&= [k \cdot F](t) \cdot [\Delta T(t) - \Delta T_{\mathrm{kF}}(t) - \Delta T_{\mathrm{L}}(t) - \Delta T_{\mathrm{St}}(t)] \\
&= [k \cdot F](t) \cdot [\Delta T(t) - \Delta T_{\mathrm{Base}}(t)] \\
&= [k \cdot F](t) \cdot \Delta T_{\mathrm{q}}(t).
\end{aligned}
\tag{7.3}
$$

- 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.

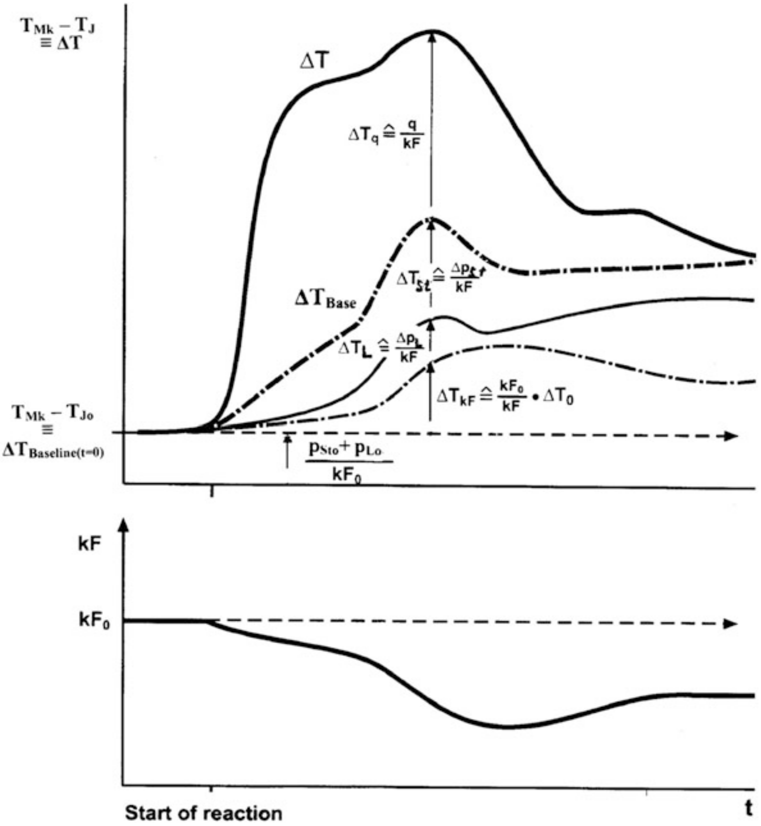

Fig. 7.2 Determining the thermal reaction power q from change in temperature ΔT and baseline ΔT_{Base} as well as course of (K · F) versus reaction time

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 $\Delta T_{Base}(t)$ 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.

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