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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- 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.

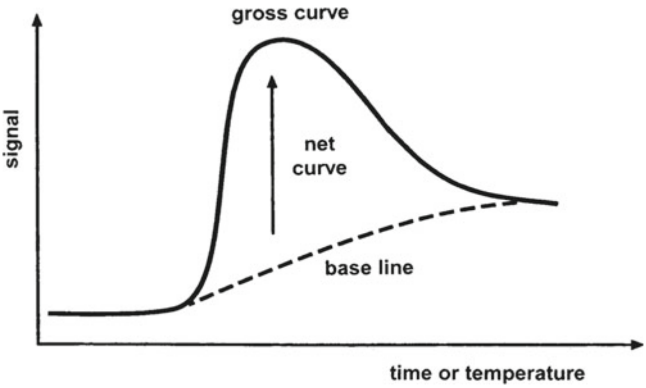

Fig. 1.1 Correlation between gross curve, net curve (curve for analysis), and baseline (reference curve)

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.