# Thermal Process Safety
## Data Assessment Criteria Measures

**Report**

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# ESCIS

**Expert Commission
for Safety in the Swiss Chemical Industry**

Series
## Safety

# Thermal Process Safety

**Data
Assessment Criteria
Measures**

**Booklet 8, 1993**

# PREFACE

*For the assurance of safety in chemical production, systematic risk analysis is an essential tool for checking processes before introduction into the plant. It provides an insight into the complex interaction of the wide range of factors that determine the probability and consequences of possible accidental occurrences involving chemicals, reactions, energies, technical equipment, personnel and organizational factors. With this technique as a basis, purposeful measures can be implemented that reduce the identified risks to an acceptable level. The methodology of risk analysis is described in ESCIS publication No. 4 "Introduction to risk analysis".*

*As a complement to the risk analysis publication, which primarily covers the systematic checking of the safety of developed processes, the present publication emphasizes the optimum design of new processes.*

*It will be shown – particularly for reactions with a high energy potential – that even in the development stage a high degree of safety can already be achieved. This objective can be accomplished to a large extent before operational controls and technical safety measures are considered by taking into account the factors and criteria controlling the thermal process safety.*

*On the basis of the knowledge and experience gained in the chemical industry over the past few years, possible routes to the envisaged goal of safety in chemical production are pointed out but with the full knowledge that the principles and procedures described must be adapted accordingly to each individual case. As a consequence, the order selected and weighting given to the information in the present article should not be taken to imply a mandatory organizational scheme.*

*In comparison with the first edition (1988; in German), this edition has undergone editorial revision, but no basic changes have been made.*

Basle, April 1993

**Expert Commission for Safety in the Swiss Chemical Industry (ESCIS)**

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# THERMAL PROCESS SAFETY

## Introduction/overview

The performance of chemical reactions on an industrial scale is frequently associated with considerable heat change. Even greater amounts of energy can be released when decomposition reactions are initiated unintentionally through unsuitable operations. In order to assure safety in the chemical plant, a *thorough understanding of the thermal hazard potentials* is of central importance. This understanding requires interdisciplinary knowledge of the relationships between the various fields as outlined in the following:

- *Chemistry* is used to gain information regarding the reaction pathways that the materials in question can follow.
- *Physical chemistry* is used to describe the reaction pathways quantitatively: Of particular interest are the *thermal* changes that accompany the reactions and their *kinetics* as a function of temperature and of the concentrations of the raw materials or reactants.
- *Reaction engineering* is used to understand the *control* of the chemical processes on a plant scale. It determines which equipment should be used and how the chemical process should be performed.
- Finally, *risk analysis* is used as a tool to systematically list the hazards inherent in a process and to assess their consequences and probability. The results show whether and with what measures a process can be performed with adequate safety. In other words, how can the process be run with an acceptable level of remaining risk? The decision is based on *data* and *considerations* of the type used by all of the above-mentioned disciplines. Such considerations (and hence the data they are based on) must give equal weight to both normal operation and deviations from the specified conditions. For example the following questions must be addressed: What else could occur in addition to that planned? To what extent must the external conditions deviate to change a controlled condition into an incident having serious consequences?

Risk analyses and safety tests frequently depend heavily on the assessment of existing processes. In the case of risks with far-reaching consequences, measures are often undertaken which keep the probability of occurrence low. The process, in terms of its inherent safety, is not improved by this approach. On the basis of our present knowledge, this procedure leads to an *acceptable* but not necessarily *optimum level of safety.*

The risks inherent in a process are very closely linked to the manner in which it is designed. If the actual *process design* and *development* is understood as an optimization task which includes both safety and environmental protection in addition to economic goals, there is a much better *chance* of arriving at processes whose *intrinsic risks* are as low as possible. The prime aim is to develop processes that are intrinsically safe, in other words processes that proceed automatically to a safe condition even if the control and safety measures fail.

The efforts towards the aim of inherently safer chemical production presuppose that traditional procedures are questioned and new process concepts geared to process safety are developed. This, in turn, is possible only during an *early stage in the process development* and requires good cooperation between the individual specialized disciplines. The consequences of a process risk can be evaluated quite reliably today. It is considerably more difficult, however, to determine *all* causal chains of possible malfunctions and their probability of occurrence. Whereas safety-oriented process modifications can be relied on to limit the consequences, measures undertaken simply to lower the probability of occurrence can fail under certain circumstances or create unforeseen additional complexities and problems. Thus, the aim of process development and the simultaneous safety investigations must primarily be geared to prevent the *consequences of the risks* through safety-oriented process control.

Although no actual systematic procedure is given, the discussion of the thought processes and measurement principles in the present publication should contribute to an increase in process safety.

### Part 1

deals with the *fundamentals* of the thermal phenomena that accompany the reactions as well as their *hazard potential* in the chemical plant. The analysis of potentials first allows a static picture to be drawn identifying the consequences. For control of the potentials, knowledge of the rates at which the quantities of heat are released and dissipated under plant conditions is also needed. A further section thus treats in general form the *heat outputs* of chemical reactions as a function of the temperature and time and introduces the concept of the *heat balance.* This concept also plays an important role in Parts 2 and 3.

After these basic aspects have been reviewed, we turn our attention to industrial practice and investigate *typical case histories.* On the basis of the knowledge gained from these, a practical procedural plan to master thermal process risks is then discussed. It is important here to make a basic distinction between designs required to run the *desired* chemical reaction safely under controlled operating conditions and cases in which

it is necessary to prevent the initiation of *undesired* decomposition reactions.

These different approaches determine the subsequent organization of the present publication.

## Part 2

is devoted entirely to the theme of synthesis reaction control. Firstly, it is demonstrated how the choice of process conditions defines the time dependencies of heat production and the amount of accumulated reaction energy at any given point in the process. How these criteria can be determined and applied to the case of a malfunction is then described. Secondly, heat dissipation in plant operation is discussed. Knowledge of the heat production and heat dissipation then allows a discussion of the heat balance in normal operation. Based on the fundamentals developed, the advantages and disadvantages of various types of processes are then pointed out. A checklist of conceivable process deviations and sensitive influencing factors and a discussion of possible measures conclude the topic of process design in Part 2.

## Part 3

treats the prevention of the initiation of undesired reactions. These usually run slowly under the operating temperatures selected and hence generate only a small amount of heat per unit time. They are critical chiefly in connection with poor heat dissipation conditions.

Use of the concept of the adiabatic "Time to Maximum Rate", which allows characterization of the heat production of a decomposition reaction at a given initial temperature, is introduced. This concept is then applied to various situations including a case where there is a considerable delay in the heat dissipation as a result of insulation. These considerations lead finally to criteria valid for industrial practice and to a discussion of the experimental techniques which can be used to obtain the data necessary for a knowledge of the hazards due to decomposition reactions.

# PART 1

## Fundamentals

### 1.1 Thermal hazard potential

The majority of the chemical reactions employed in industry are exothermic, i.e. they evolve heat (negative reaction enthalpies; for typical values for common reactions, see Figure 1). In addition, the chemicals and reaction masses used are sometimes metastable and hence capable of undergoing further reactions or may "decompose". In some cases, such undesired reactions can release very large amounts of energy.

| Enthalpies of reaction $\Delta H_R$ measured in joules [J] or specific reaction enthalpies $\Delta h_R$ [J kg$^{-1}$] and $\Delta h\grave{}_R$ [J mol$^{-1}$] | | | |
|---|---|---|---|
| | | Energy units: $1\ J = 1\ Nm = 1\ Ws = 1\ m^2kg\ s^{-2}$ $1\ J = 0.239\ cal$ $1\ cal = 4.18\ J$ | |
| **Typical values** | **J mol$^{-1}$** | | **J mol$^{-1}$** |
| Neutralization (HCl) | – 55 000 | Amination | –120 000 |
| Neutralization (H$_2$SO$_4$) | –105 000 | | |
| Diazotization | – 65 000 | Heat of combustion | |
| Sulfonation (SO$_3$) | –150 000 | (hydrocarbons) | –900 000 |
| Nitration | –130 000 | | |
| Epoxidation | – 96 000 | Diazo decomposition | –140 000 |
| Hydrogenation | –560 000 | Nitro decomposition | –400 000 |
| (nitroaromatic compound) | | | |

Figure 1: Enthalpies of chemical reactions

To illustrate the potential destructive power of the energies involved, let us consider two pertinent orders of magnitude. 100 kJ kg$^{-1}$ is a typical value of a heat of reaction, whereas 2000 kJ kg$^{-1}$ represents a highly exothermic decomposition potential (e.g. of an undiluted dinitroaromatic compound). The calculated equivalent energies in Figure 2 show clearly the catastrophic destructive effects the release of such energies can have. This effect is evident even if only part of the energy potential is transformed rapidly into a mechanical form of energy. While it is true that part of the available energy in a reaction runaway is always transformed into latent energy (evaporation and temperature rise), in many cases decomposition gases are produced and subsequently heated. The actual destructive force ultimately originates from the rapid release of pressure contained within process equipment. Examples of reaction vessel explosions in chemical plants (Figure 3) provide a clear illustration of the destructive power expected on the basis of the energy transformations.

### The adiabatic temperature rise

Conditions under which the total available energy potential of the reaction mass is used to heat the mass are called *adiabatic*.

| Typical reaction or decomposition energy used for | Typical reaction energy 100 kJ kg$^{-1}$ | Typical decomposition energy 2000 kJ kg$^{-1}$ |
|---|---|---|
| Adiabatic heating of the reaction mass | $\Delta T_{ad}$ = 50 K | $\Delta T_{ad}$ = 1000 K |
| Evaporation of methanol per kg reaction mass at constant temperature | $\approx$ 0.1 kg MeOH kg$^{-1}$ | $\approx$ 1.8 kg MeOH kg$^{-1}$ |
| Raising the reaction mass to a height h (potential energy) | h = 10 km | h = 200 km |
| Acceleration of the reaction mass to a velocity v (kinetic energy, theoretical value) | v = 0.45 km s$^{-1}$ ($\approx$ 1.5 Mach) | v = 2 km s$^{-1}$ ($\approx$ 6.7 Mach) |

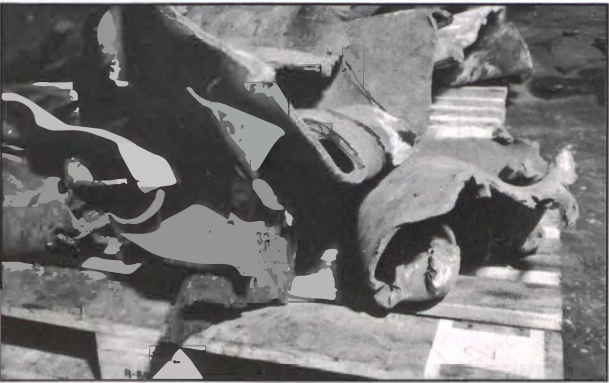Figure 2: Theoretical equivalent energies of typical heats of reaction
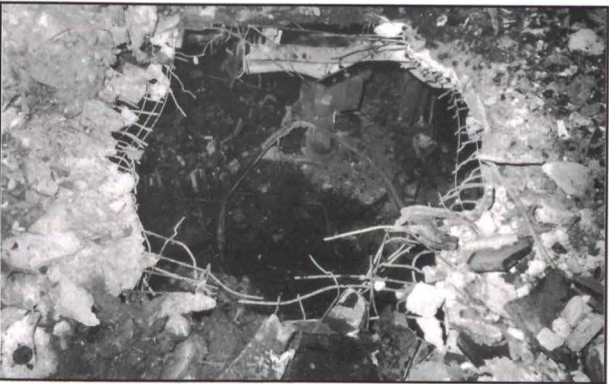




Figure 3: View of the site after a thermal explosion of a reaction vessel; wreckage of the reactor

Risk analysis considerations often involve the assumption of adiabaticity in order to develop a worst case scenario. This type of situation all too often occurs when a malfunction is experienced. One characteristic of the adiabatic temperature profile of a reaction which is usually specified is the "adiabatic temperature rise" $\Delta T_{ad}$. This value is calculated from the specific enthalpy

of reaction $-\Delta h_R$ and the specific heat capacity $c_p$ of the reaction mass:

$$\Delta T_{ad}\,[K] = \frac{-\Delta h_R\,[J\,kg^{-1}]}{c_p\,[J\,kg^{-1}\,K^{-1}]}$$

$\Delta h_R$ can be measured using, for example, microthermal analysis or reaction calorimetry (see section 2.2). The specific heat capacity $c_p$ can also be measured in a similar manner or a good estimation is possible (Figure 4). The temperature dependence of $c_p$ is usually neglected so that high values of $\Delta T_{ad}$ are considered as guiding characteristics rather than quantitative data.

## 1.2 Heat production and heat balance

It is not sufficient to determine the reaction energies, however. Taken alone, they are not a sufficient mea-

| | |
|---|---|
| Water | 4200  J kg$^{-1}$ K$^{-1}$ |
| Organic substances (melt or solution) | 1600–2000  J kg$^{-1}$ K$^{-1}$ |
| Sulfuric acid | 1300  J kg$^{-1}$ K$^{-1}$ |
| Oleum 65 % | 1700  J kg$^{-1}$ K$^{-1}$ |
| Iron | 410  J kg$^{-1}$ K$^{-1}$ |
| Steel | 400–500  J kg$^{-1}$ K$^{-1}$ |

Figure 4: Typical specific heat capacities $c_p$ (room temperature)
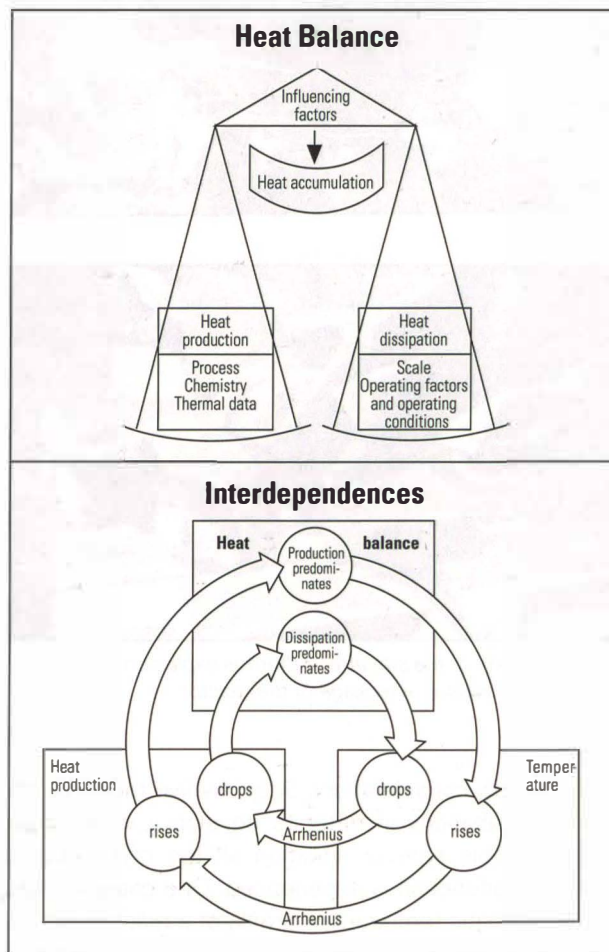


Figure 5: Thermal process safety

sure of the inherent risk of a process or the reaction masses. The energy potential as such represents no hazard if the associated reaction runs slowly enough at the temperatures in question to allow the heat evolved to be dissipated under the prevailing conditions. Any critical analysis of the thermal risks will therefore always be based in one form or other on a *heat balance* between heat production and heat dissipation (Figure 5).

The heat production or *heat output* of a reaction is proportional to the reaction rate and to the reaction enthalpy. The reaction rate for its part is a function of the concentration conditions, which change *with time* through dosing, separation operations or through reaction of the reactants. It is moreover greatly influenced by the temperature (exponential influence of the Arrhenius equation, Figure 6).

The *heat dissipation* depends on the operational temperature gradients that are established within the reaction mass and the apparatus. Their magnitude can change drastically between the operational state (vigorous cooling, stirring) and the unstirred passive situation. The heat dissipation is particularly low in large unstirred masses (see Part 3), and this shifts the heat balance heavily in favor of the heat production on scale-up.

With constant ambient conditions and an on-going reaction, the heat balance represented by the scales in Figure 5 is practically never in equilibrium. This is because of the powerful feedback effect of the temper-

$\dot Q$  $= \dfrac{dQ}{dt}$  Energy per unit time, measured in watts [W]

1 W  $= 1\,J\,s^{-1} = 1\,Nm\,s^{-1} = 1\,m^2 kg\,s^{-3}$
1 W  $= 0.86\,kcal\,h^{-1}$
1 kcal h$^{-1}$  $= 1.16\,W$

The heat output of reaction is equal to the reaction energy released per unit time (dx/dt = rate of reaction):

$$\dot Q\,[W] = \Delta H_R\,[J]\cdot\frac{dx}{dt}\,[s^{-1}]$$

The heat outputs of reaction show an exponential dependence on the temperature in accordance with the Arrhenius equation:

$$\dot Q\,(T) = \dot Q\,(T_{ref})\cdot \exp\left[-\frac{E_a}{R}\cdot\left(\frac{1}{T}-\frac{1}{T_{ref}}\right)\right]$$

$E_a$  is a measure of the temperature dependence (activation energy) [J mol$^{-1}$]
$T$  is the temperature in degrees Kelvin ([K] = [°C] + 273)
$R$  is the gas constant 8.314 J mol$^{-1}$ K$^{-1}$
$T_{ref}$  is the reference temperature to which $\dot Q\,(T_{ref})$ refers [K]

An increase in the temperature by 10 K usually results in a two- to three-fold increase in the rate of reaction and heat output.

Together with the rate of reaction the heat output is a function of time that depends on the process control and the mechanism of the ongoing reaction (change in concentrations through dispensing or reagent consumption). Of particular importance are **autocatalytic reactions** (see section 3.5.3) in which a sometimes dramatic acceleration of the reaction rates and heat outputs can appear with time.

Figure 6: Heat output of reaction

ature on the two influencing factors, heat production and heat dissipation. If the heat production predominates the temperature will rise. Owing to the exponential temperature dependence of the reaction rate, the heat production becomes even more predominant ("supercritical" heat balance) and, eventually, can lead to a *thermal explosion* (see below). If the heat dissipation is predominant ("subcritical" heat balance), the described interdependence acts in the opposite sense; the reaction "falls asleep".

Risk considerations need to take into account heat balance conditions, which differ from one process to another. For instance, in the isothermal operation of a batch process, the scales in Figure 5 are kept in equilibrium artificially by a controlled heating/cooling system. Thus, one of the basic characteristics of the risk inherent in a batch process is the short term response of the temperature of the reacting system to a break-down of this artificial control. By contrast, with a storage problem or, for instance, in the hot discharge of goods, it must be ensured that the heat balance is subcritical over the long term.

## 1.3 Adiabatic temperature profiles and thermal explosion

Should the heat balance ever become supercritical when dealing with a highly exothermic reaction, sooner or later the heat production term increases to such an extent that it is reasonable to neglect the heat dissipation influence on the heat balance completely, i.e. adiabatic conditions prevail. Under these conditions, the reaction progress is determined solely by the relationships governing the heat production.

Any process that proceeds in such a manner is called a *thermal explosion* (thermal runaway reaction). In contrast to detonations and deflagrations, which by definition are initiated by a local ignition source, the driving force in the case of a thermal explosion results solely from the exponential increase in the reaction rate as a consequence of the increasing temperature. In the adiabatic case, the temperature within the thermally exploding mass is homogeneous. To a first approximation (Van't Hoff rule), the rate of a chemical reaction increases by a factor of between 2 and 3 with each 10 K increase in the temperature. The time required to pass a given temperature interval is accordingly halved or reduced by a factor of 3 when the initial temperature is increased by 10 K. This results in the general profile shown in Figure 7. The thermal explosion typically runs very slowly in its initial phase so that if recognized early there is a considerable amount of time available to implement preventive measures.

In the final phase of the thermal explosion, however, a highly exothermic reaction can accelerate in such a manner that practically its entire energy potential can be released within an extremely short instant. Assuming an initial temperature $T_o$ and adiabatic conditions,
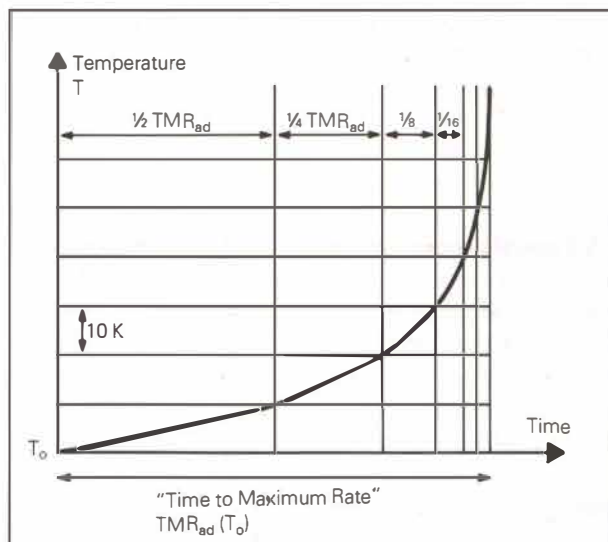


Figure 7: Profile of a thermal explosion

we use the "Time to Maximum Rate" $TMR_{ad}$ ($T_o$) (cf. Figure 31) to characterize the dynamics of the thermal explosion.

## 1.4 Secondary hazard potentials

So far it has been shown that high-energy reactions represent a hazard *per se* when they run under adiabatic conditions. The enthalpy of reaction ($\Delta H_R$) or the adiabatic temperature rise $\Delta T_{ad}$ calculated from it is a measure of the amount of energy released in the worst case. These quantities are also a measure of the energy available, for instance, for the evaporation of a solvent and allow the calculation of the temperature levels that can be attained. These data represent the physicochemical basis for making concrete predictions in a practical case regarding the consequences of a scenario deviating from the plant process.

These consequences depend first of all on *physical* transitions (phase transitions, vapor pressure changes, etc.) which take place at the temperature level reached. Knowledge of these allows an assessment of whether the apparatus can withstand the effects, or whether if the worst comes to the worst the distant surroundings would be affected. Of particular interest is the question of whether additional *chemical* processes could run within the attainable temperature range and in turn lead to temperature increases and thermal explosions. If secondary and decomposition reactions are active at or near the temperatures under consideration, a knowledge of additional thermal data on their reaction energy and kinetics is necessary for assessment of the safety.

The step that leads from the physicochemical reaction properties to the assessment of a concrete operational situation is a critical part of risk control. It can not be easily formalized and requires not only a knowledge of the thermal properties of the raw materials and reactions, but also considerable familiarity with the equip-

ment and the technical and organizational possibilities of the production plant in question.

As an aid for actual practice, typical questions and check points to help answer such questions are outlined in Figure 8.

## 1.5 Special product properties as hazard potential

Certain high energy substances or mixtures of substances can transform their energy into not only thermal explosions but also deflagrations or even detonations. Since such phenomena can increase the risk, for example in conveying or storage, they will be described briefly in what follows.

### Deflagration capability

If a chemical reaction sustains itself in a substance or mixture after a local ignition, forming a propagating reaction zone, the process is called a deflagration. In the present context, it is of prime interest to determine whether given solid or liquid products are capable of deflagration even if oxygen is excluded. Typical ignition sources for such deflagrations are hot surfaces, lumps of smoldering material or local friction stresses caused by tramp material, etc, as well as local incipient decompositions. A prerequisite for deflagration is a sufficiently high release of energy in the reaction zone and the effective transfer of this energy to the adjacent zone. Not only the decomposition energy but also the heat transfer properties, the melting point, the temperature and particularly the liberation of decomposition gases play a part. The rate of propagation can be slow or it can reach or exceed (see paragraph on detonation) the speed of sound depending on the above properties as well as on the mass and its spatial confinement.

The handling of materials capable of deflagration represents an enhanced risk factor. The increased risk is manifest both in the area of probability and severity for the following reasons:

- As a result of the spatial propagation capability, even local overheating can easily affect the entire inventory of decomposable products in a container.
- In contrast to fires, deflagrations of the type mentioned can not be prevented by exclusion of oxygen (inert atmospheres, vacuum, $CO_2$). If at all, they can be stopped by flooding with a great deal of water. Wetting must be ensured, if need be by use of wetting agents.
- In many cases large amounts of gas are evolved and this can lead to pressure buildup or to secondary gas explosions.
- If access to air is possible, a deflagration can turn into a fire, for example by spontaneous ignition of the glowing deflagration residue.

Compounds capable of deflagration when oxygen is excluded include those containing nitro groups (e.g. sodium salt of 4-nitroaniline-2-sulfonic acid, condensed ring systems with at least two nitro groups, metal com-

| Question | Relevant data / information |
|---|---|
| **1st step** | **Physicochemical data** |
| Is the boiling point of the solvent/reaction mixture reached in the adiabatic runaway of the synthesis reaction? Are decomposition gases formed? | – Boiling point<br>– Enthalpy of reaction $\Delta H_R$ (or accumulated part of it, see part 2)<br>– Heat capacity $c_p$<br>– Gas evolution (amount, rate) |
| Can volatile components evaporate after the boiling point has been reached? How quickly will this occur and what pressure can be attained? | – Excess heat of reaction<br>– Reaction rate r' when boiling point exceeded<br>– Heat of evaporation<br>– Vapor pressure curves |
| Are secondary chemical reactions expected at the attainable temperatures and how severe are their consequences? | – Heat of decomposition $\Delta H_d$<br>– Heat output and possible gas release in the secondary reaction at these temperatures<br>– Estimation of the "Time to Maximum Rate" (see Part 3) |
| What reaction products will be formed in the secondary reactions? | – Intuition and knowledge of the chemist<br>– Possibly analytical chemical findings |
| **2nd step** | **Assessment on the basis of operating conditions** |
| – Will the volatile components be condensed in a condenser?<br>– Will its capacity suffice?<br>– Will the reactor/autoclave withstand the expected pressure?<br>– Via what routes can the reaction mass discharge from the reactor?<br>– What shutdown measures are available in the plant and within what time will they become effective? | – Operating conditions<br>– Engineering data |
| **3rd step** | **Hazard potential on discharge of reaction mass** |
| – To what extent will the adjacent or distant surroundings be affected by a blowout? | – Type of volatile components<br>– Expected concentrations<br>– Propagation behavior<br>– Explosion limits<br>– Do ignition sources exist?<br>– Toxic properties of the expected production materials and the possible secondary products |

Figure 8: Assessment of secondary hazard potentials

plexes with minimum one nitro group, etc.) and other high energy structural entities. Additives can have both promoting and desensitizing effects.

Compounds with a low melting point normally undergo deflagration less easily since the melting process consumes part of the energy.

### Detonability

If the rate of propagation exceeds the speed of sound, the phenomenon is known as detonation. With detonations a high speed shock wave (2000 to 8000 m s$^{-1}$)

passes through the material and a coupling between the compression shock and chemical conversion occurs. In a spatially very small detonation zone, a tremendous increase in temperature and pressure takes place within milliseconds. Detonators exhibit different detonabilities (potential for causing damage once ignited) and activation sensitivities – properties which can be determined through special tests. It is generally the case that loose, porous materials and materials of small particle size are easier to detonate than compressed or cast systems. In the case of liquids, detonation sensitivity is considerably increased by the presence of gas bubbles that can be formed, for instance, by vibration or in conveying.

In contrast to thermal explosions and deflagrations, which are always triggered by the prevailing temperature, detonations can be initiated directly by friction or impact. A detonation shock wave always has a highly destructive effect.

Apart from actual explosives (nitroglycerine, trinitrotoluene, picric acid) and initiators (lead azide), certain finished chemical products and intermediates (e.g. ammonium nitrate, dinitrobenzene, highly concentrated nitration masses, etc.) are capable of detonation. Diazonium salts in solution are usually phlegmatized, yet as solid deposits, for example in pipelines and valves, their possible detonability represents a considerable risk.

## 1.6 Analysis of typical incidents

Whereas the previous sections have dealt on a fundamental level with the physicochemical properties of processed materials and the technical factors of the equipment as potential causes for driving the heat balance of chemical processes off course, in what follows a series of incidents that occurred in actual practice will be discussed. In the next section they will be used for a general analysis of the question regarding how such incidents arise and what measures can be implemented to prevent them.

### Case history 1:
### Runaway of aminations

In the amination of chloroaromatic or chloronitroaromatic compounds in aqueous ammonia at temperatures between 160 and 190°C and pressures of 30–40 bar, the reactants are added to the autoclave at room temperature and the reaction started by slow heating of the mixture. During the last 60 years many reactor explosions have occurred leading to extensive damage to apparatus and buildings as well as to injuries to personnel.

### Comment:

Aminations are highly exothermic reactions. In the so-called batch process, the entire energy potential inherent in the starting materials is added at the beginning of the process. Once the mass is heated to the temperature at which the desired reaction runs at a reasonable rate, the *only* possibility to control the reaction is to *assure dissipation* of the heat. If ever the heat production exceeds the heat dissipation either as a result of too rapid heating leading to excessively high reaction rates or owing to a malfunction in the cooling system, the temperature and pressure rise rapidly until the autoclave ruptures. After the appreciable temperature rise owing to runaway of the amination reaction, the high decomposition energy of the nitro group in the chloronitroaromatic compound makes its own contribution to the consequences. In each case, however, the decisive factor is the runaway of the desired amination reaction as a consequence of *inadequate process control.*

### Case history 2:
### Runaway of a sulfonation reaction

To manufacture 2-chloro-5-nitrobenzenesulfonic acid, melted 1-chloro-4-nitrobenzene heated to ca. 100°C is added under pressure over a 20 minute period to 20% oleum at an initial temperature of 50°C. With the reactor closed and the double-walled jacket empty, the temperature increases within an hour to 120–125°C. It is then held at this temperature for several hours by heating to allow the reaction to run to completion at 2 bar pressure. The ill-fated batch was first stabilized at 125°C by brief cooling in accordance with the instructions. Further temperature monitoring was not stipulated. During the next two hours the temperature increased steadily. Shortly after 138°C was registered on the recorder, a violent explosion occurred, the force of which caused the reactor to shift from its platform and the cover was blown through the roof of the building into the surrounding plant area.

### Comment:

In the planned course of the reaction, holding at 125°C over a period of several hours, the desired product is obtained in good yield. This proves that at this temperature the *desired* reaction is the dominant one and the percentage of decomposition reactions is at most relatively small and has virtually no influence on the yield of product. The actual cause of this incident is thus again the runaway of the desired reaction coupled with the lack of temperature monitoring, as well as the fact that in a steam heated jacket practically no heat exchange can take place between the reaction mass and the jacket above the saturated vapor temperature (here 125°C). The main part of the destruction potential arose in this case from the decomposition reaction, which moreover proceeded according to an autocatalytic mechanism, i.e. with a heat output increasing with *time* even at constant temperature.

## Case history 3:
### Runaway of a polymerization reaction

A polymeric product is produced through simultaneous addition of acrylic acid and sodium persulfate solution over a two-hour period to a solution of sodium hyposulfite under reflux at 100–105°C. When the incident occurred, the temperature rose very rapidly to 130°C within one and a half hours after the start of the reaction. At the same time, the reaction mixture was discharged through the gaskets of the vessel into the plant although bursting plates and safety valves had responded.

**Cause:** The investigation showed that at the time of the incident 80% of the acrylic acid mixture but only 10% of the required sodium persulfate solution had been dispensed. Under these conditions a small additional amount of persulfate sufficed to initiate a spontaneous polymerization. Persulfate was not added in accordance with the directions owing to either discontinuous running of the pump or intermittent blockage of the inlet.

### Comment:

In this case the safety of the process obviously depends on the *exact* adherence to the dispensing profile: The reaction rate is a sensitive function of the amount of catalyst present; once this is too high, nothing can be done to halt the rapid progress of the polymerization. Such a process can be performed safely only if the concentration dependence of the reaction rate is known accurately, if invariable reactant quality can be assured and a meticulous check on the process control is performed without fail.

## Case history 4:
### Abnormal progress of a sulfonation process

In the sulfonation of a nitroaromatic compound, a certain amount of reacted sulfonation mass from the previous operation is always added at the start and heated to 85°C at a jacket vapor temperature of 150°C. The melted aromatic compound and oleum are then added simultaneously. Owing to the exothermic reaction the mass heats up further and at the planned reaction temperature of 110°C cooling is switched in automatically.

On the day of the incident, above ca. 100°C a rapid increase in pressure set in. The reactor cover ruptured and the decomposing reaction mass was discharged like a lava stream causing considerable material damage.

The investigation established the following case history and pointed to the reasons underlying the occurrence of the incident.

– At an earlier date the reactor vessel had been fitted with an additional cooling coil inside the tank for a different process. In conjunction with this somewhat unusual arrangement, a space-saving turbine agitator was installed with a high base clearance compared with that of the standard agitator.

– Later, corrosion was found in the auxiliary cooling coil. Since the process that made the auxiliary cooling necessary was no longer being run, this auxiliary cooling coil was temporarily removed.

– The incident occurred six months later after the agitator had been accidentally moved to its topmost position within the available adjustment during a check.

Consequently, the fact that the agitator was not immersed at the start of the reaction can be considered as the primary *cause* of the incident. Owing to the modifications undertaken during the course of the year, no one had been aware of this.

The actual course of the incident is also of interest: Of the two added streams, the light melt of the aromatic compound remained on the surface of the unstirred mass whereas the heavy, cold oleum was present in a lower layer. The temperature sensor in the lower half of the reactor correctly reported the low temperature at this location to the control system, which consequently opened up the steam heating of the jacket fully. This naturally caused the layered reactants to heat up. With increasing volume, immersion of the agitator gradually increased, the accumulated reactants were mixed and their exothermic reaction began. As soon as the temperature reached 170–200°C, the highly exothermic decomposition made its notable contribution to the self-heating process. On the basis of the existing potential it must be concluded that the damage caused could have been appreciably more severe if the thermal explosion had taken place with a reaction mass that was well mixed.

### Comment:

This is another case which points out the risks involved in a system in which an apparently minor deviation in the reaction control, a small change in the agitator position compared with the original level, can have a large influence on its thermal behavior. In addition, although in retrospect the incident followed a logical course, the sequence of events could hardly have been expected to be predicted by risk analysis. The actual cause of the incident can be considered more logically as the degeneration of the operational conditions with time. At the time of introduction of the operation (and the risk analysis), the process safety was undoubtedly acceptable, but not optimum inasmuch as it could be affected drastically by several individual actions. This case clearly demonstrates that long-term control of severe consequences is very demanding. At the very minimum, however, the contribution of the heating to the runaway situation could have been avoided if the maximum possible heating temperature had been physically limited by design. This could have been accomplished, for example, by decompressing and equilibrating the heating vapor at a temperature of

110°C as was required by the process or using a pressurized water heating with a safety valve set to limit the temperature.

### Case history 5:
### Storage at elevated temperatures under heat accumulation conditions

After synthesis in batches of 2600 kg, an intermediate was present in the form of a melt in a reactor heated by non-pressurized water. The melt is normally transferred to relatively small containers where it gradually solidifies. One Friday evening the filling operation could not be completed for technical reasons and the melt had to be left in the reactor over the weekend. It was known that at 90°C an assay loss of the product of 1%/day would occur, but it was decided to accept this loss given the existing exceptional circumstances. The melt was left in the reactor without stirring. On Sunday evening the reactor burst and its cover was blown through the roof of the building. The reactor contents were discharged.

### Comment:

In contrast to the cases discussed previously, the heat output that was the primary cause of this incident arose not from the synthesis reaction but from an undesired decomposition reaction. The material degraded due to the fact that a slow decomposition reaction took place under the storage conditions. The quoted value found in the laboratory indicates a slow reaction rate. But in the laboratory isothermal conditions prevail, whereas under the unstirred plant conditions virtually adiabatic conditions had to be anticipated over the long term. Typical of this *heat accumulation incident* is the relatively long time over which, starting from slow initial rates, a thermal explosion gradually developed. A correct interpretation of the available information could have *predicted* this incident, and it could have been detected at an early stage if a temperature alarm had been installed.

### Case history 6:
### Decomposition of a freshly milled product in a container

A 1400 liter container holding freshly milled product in a tall storage rack attracted attention by severe smoke development. Its cover had been blown off and its contents had flowed out of the container rather like a lava stream. The ongoing reaction could be stopped by flooding the container with water. On the basis of the product data, it must be assumed that the product had heated up slightly during milling and that accelerated self-heating had occurred under the heat accumulation conditions prevailing in the container.

### Comment:

This incident is representative of a series of similar incidents in hot discharging after milling or drying.

Cases are known in which the decomposition products underwent spontaneous ignition and caused widespread fires. A typical feature is that no noticeable problems arose during the actual operation and the thermal decomposition was not manifest until hours after discharging. The heat production rate critical in the bulk contents of the container is appreciably lower than in both the milling and the actual drying operation. The low initial heat release rate correlates with the lengthy period of time during which the system must remain under unfavorable heat accumulation conditions. Considerable acceleration is required before the typical profile development of a thermal explosion becomes apparent.

This case also shows clearly that there is no such thing as a material constant called "thermal stability" and that the term "first exothermicity", which is supposed to occur at a specified temperature, can be misleading. Its direct use should be limited to qualitative reporting of the result of a specified experiment and to soundly based comparative safety assessment procedures, which will be described in the third part of this text.

### Case history 7:
### Self-heating of a product in a heated conveyor line

After a separation operation in a thin-film evaporator, the residue was transported with a screw pump to a control valve. To keep the residue liquid, the entire system had to be heated to above 250°C. On the day of the incident, the product line between the screw pump and the control valve burst. The cause of this was blockage of the control valve. The product flow came to a standstill, the motionless product heated up, initially owing to the power output of the screw pump but soon as a result of heat from an ongoing decomposition. Owing to the temperature rise and the decomposition gases formed, the pressure rose until the line burst. The heating medium (diphyl, 7 bar, 290°C) was released into the work room.

### Comment:

In this example, again the primary cause is not the fact that the reaction mass decomposed but rather the impairment of the material flow and the supply of mechanical energy by the pump.

### 1.7 Conclusions from the incidents; practical procedure to cope with thermal risks

In the analysis of the above and other typical incidents it is important to distinguish whether the *desired* or the *undesired* reaction was the initiating factor.

In incidents directly connected with a *synthesis reaction,* typified by case histories 1–4, the runaway of the desired reaction or the *unsuitable process control* is almost always the primary cause.

This can be explained as follows: The process conditions are designed to perform a specific chemical reac-

tion in accordance with the directions. Accordingly, work is carried out at temperatures at which this reaction is *dominant* and under conditions where the associated heat release can normally be controlled. The cause of the incident is then usually a deterioration of the heat dissipation or an increase in the reaction rate as a result of a deviation from the normal condition. Immediately following the disturbance the initial position for further progress is *unchanged;* i.e. the events immediately following are still determined principally by *how fast* the desired reaction runs at this moment and how much energy reserve it still has as a result of reactant accumulation. It has become usual in these cases to speak of the *excursion potential of the reaction parameters:* what potential "excursions" from their normal values can temperature, pressure, etc. undergo in the case of a malfunction?

A typical incident profile is thus a *primary* temperature excursion due to the *desired* reaction followed by the initiation of an energetic decomposition reaction (Figure 9). Since the striking effects in such incidents are due predominantly to the usually comparatively higher energy potentials of the decompositions, these have often wrongly been made the focal point of risk considerations of synthesis reactions. On the basis of the typical incident profiles of such cases, however, emphasis must clearly be placed on the analysis and the reliable design of the desired process.
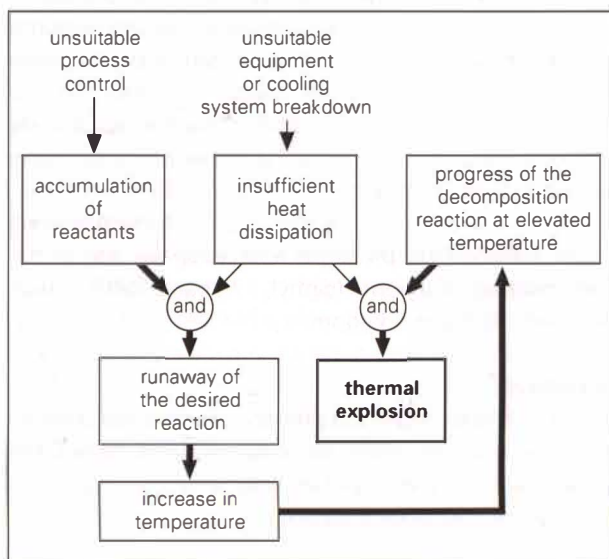


Figure 9: Typical event profile of synthesis reactions

Consequently, for the *analysis* of a given process in normal operation, not only should a well-balanced heat balance be ensured, but also a knowledge of the above-mentioned *excursion potentials* and their consequences is necessary. Whereas control of the heat production in normal operation is generally good, often too little consideration is given to the excursion potentials. Section 2.2 deals with the methodology which can be used to put the necessary considerations on a rational data-oriented basis.

In contrast to the earlier situation, safety in chemical plants has today reached a very high level as the relatively direct routes to incidents have been identified by risk analysis and covered by effective measures. In the remaining incidents, the causal chains are often so complex and devious that they are difficult to anticipate. Case history 4 is an example of this. Especially in cases where severe consequences have been identified, the defensive measures are often complex. Because of their complexity they can fail and hence trigger the incident. The proper course here is to first exhaust the possibilities to minimize the consequences through a safety-conscious design of the processes at the development stage. Pointers to help achieve this objective are discussed further in section 2.5.

The causes in *case histories 5–7* differ completely from those in the runaway of synthesis reactions. The primary heat suppliers are here decomposition reactions and, to begin with, these run rather slowly at the usual temperatures employed in the handling of the materials. That thermal explosions nevertheless occur in the long term in such cases can often be traced to the particularly poor heat dissipation conditions of the type that occur especially in large, unstirred masses. Under such *heat accumulation conditions,* even a storage or holding temperature at which the decomposition reactions would run only very slowly under *isothermal* conditions can be too high. If possible, intermediate storage and holding phases at elevated temperature should also be avoided in these cases. If this is not possible, the heat accumulation situations that often appear in peripheral operations must be identified, properly assessed and accounted for. The requisite knowledge is given in Part 3.

## 1.8 The role of safety tests

Correctly understood safety investigations and the interpretation of the experimental results must be selectively orientated to the operational problem. They must take into account the principal differences, indicated in part in Section 1.7, in the procedure when *physical operations* such as drying, milling, etc., *passive storage* under poor heat dissipation conditions and *synthetic processes* are assessed.

### Assessment of milling, drying, etc.

Although the emphasis of this publication does not concern the safety of unit operations, the traditional procedure employed in the safety tests in regard to physical unit operations will be mentioned briefly here, above all to draw the dividing line between it and risk control in synthesis reactions.

As shown schematically in Figure 10, in the assessment of physical operations it can be assumed from the outset that exothermic processes are undesired. For the determination of safe temperatures, it thus suffices to estimate the temperature ranges of the chemical
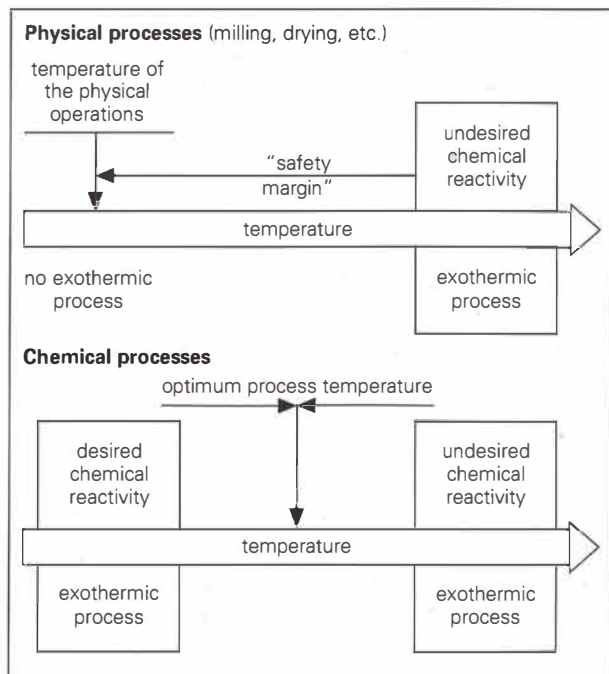
*Figure 10: Different assessment of physical and chemical processes*

reactivity through simple measurements (cf. ESCIS publication No. 1) and to maintain a sufficient "distance" from these. The lower the temperature, the greater the safety. The procedure described reduces the probability of a thermal risk, but does not take into account the consequences. The decision-making sequence can generally be planned, e.g. in directives and then developed as a matter of routine:
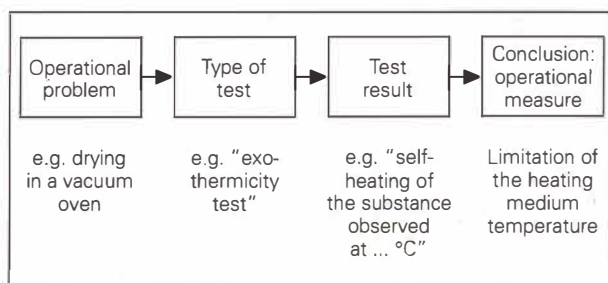


The establishment of the measures is based on knowledge obtained empirically. Experience relates only to the particular measuring instrument used and to the specific situation under assessment so that transfer of the procedure and the "safety margins" to other situations is not admissible.

Inhibition of the heat dissipation through the insulating action of the product itself is as a rule moderate in physical operations. For pronounced heat accumulation situations, as in the case of hot storage of relatively large amounts of product, special considerations are necessary (see section 3.3).

The "safety characteristics" determined in connection with the assessment of physical operations are *material-related* data whose use is meaningful only if the plant operation in question also involves the processing of individual compounds as is the case in physical operations.

## Procedure to ensure the safety of chemical processes

It would be wrong to treat chemical processes in the same manner as physical operations. For chemical reactions the *interplay of reactants* under the *process conditions* selected by the development chemist is important. The prime need is for *reaction data* rather than physical data. It is not a question of changing from conditions under which exothermic reactions run, for this would mean preventing the desired reaction from running at all. This is not only undesirable on economic grounds but it would also be unsafe for the following reason: Any procedure using fixed "safety margins" that functions correctly with physical operations would completely disregard the criterion of the *excursion potentials* in the case of chemical reactions, a criterion which was recognized as so important in the last section. Although these remarks may be thought trivial, they are often neglected in practice.

In this sense, the assurance of safety in synthetic processes requires that due attention be paid to the following general questions in the process design and risk analysis:

1. Does the heat of reaction of the synthesis reaction represent a potential hazard in connection with the apparatus and process conditions selected?
2. Can the heat of reaction be dissipated without risk under the operating conditions in the plant?
3. What scenario is to be anticipated in the event of a malfunction if, for example, the energy supply needed for the cooling breaks down?
4. Do secondary reactions exhibit significant heat evolution rates within the relevant temperature range and what potential hazard do their heats of reaction represent?
5. In what process phases and under what external conditions can ongoing secondary reactions be hazardous?
6. Can a runaway of the primary reaction lead to a rise in temperature which could trigger the secondary reactions or other critical secondary effects?

It will be the task of the second part to show how answers to such questions can be found in concrete cases.

The ability to answer these questions is intimately connected with the activity of process development and differs in principle from the traditional demand for instructions and limits from the safety specialists. Risk management lies rather in the hands of the plant management and those responsible for process development. These are the individuals who are acquainted with the actual boundary conditions and can weigh the

pros and cons of alternative process concepts based on their knowledge of the specific plant and process.

It is not the purpose of this article to employ the proposed approach to define specific test procedures to be used routinely for the assurance of the safety of chemical processes; risk control should be developed rather through a professional understanding of the physics and chemistry of the specific case. The safety specialist is here a partner and an authority in regard to data acquired. He should play the part of an advocate of thermal safety rather than that of an official who as an outsider can only legitimize suboptimum processes or demand elaborate secondary measures.

A particular requirement for an understanding of the safety problems involved is for appropriate forms of organization to allow communication between the various disciplines. Just as important is purposeful project leadership as the intended integration can easily fail in practice if the definition of a task is too particular and the schedule too demanding.

### 1.9 Experimental overview of thermal phenomena of reactions and reaction masses

To access the thermal safety criteria discussed above, the first task is to obtain an overview of the thermal phenomena on the lines of the scheme shown in Figure 10.

For the estimation of thermal potentials, temperature programmed thermal analysis, for example, has proven its worth. By a comparison of the thermograms of samples before, during and after the performance of the desired reaction, conclusions can be drawn regarding the thermal transformations. The temperature dependence of the shape and position of the exothermic signals gives moreover the first qualitative indication of the kinetics of the thermal transformations.

For the definition of the temperature range in which the decomposition reactions are active, isothermal or isoperibolic measurement methods are also useful.

The different methods and their interpretation will be discussed in more detail in Part 3. Here, however, it should be noted once again that in the often used reporting of "onset" temperatures, their dependency on the instrument sensitivity and – in the temperature programmed case – on the heating rate must be borne in mind in the interpretation of the results.

Simply with a knowledge of the planned process and operating conditions and the results of the general measurements discussed above, classification of the cases in regard to probability and consequences of possible abnormal reaction sequences is possible.

If the potentials are low and/or the undesired reactions lie at far higher temperatures in the thermogram than the attainable temperatures in the normal and malfunction case, in many cases a conclusive assessment is possible even at this stage. On the other hand, the screening results can provide an indication of where

the emphases of a more detailed experimental analysis should lie. An efficient development of safety investigations and optimum utilization of the resources requires such an elimination of clearly non-critical cases and the identification of critical cases. Of less importance are the individual test criteria used, which vary from company to company. A noteworthy difference, however, is whether they put their major emphasis on the probability or consequential criteria.

By way of an example let us consider the thermograms of two reactions measured by temperature programmed microthermal analysis shown in Figure 11. In the top case the energy potentials and the adiabatic temperature rise (arrow) are moderate. Further, the position of the decomposition reaction on the temperature axis is clearly above the temperature level attainable in the adiabatic runaway of the desired reaction. In conclusion, this case can be designated non-critical on the basis of the temperature programmed thermal analysis.

In regard to the proximity of the signals and height of the energy potentials, the thermogram of the reactant mixture in the bottom case in Figure 11 represents an example of the other extreme. Here, there exists a clear indication of a thermal risk and hence great importance should be attached to the safety aspects in further treatment of the process.
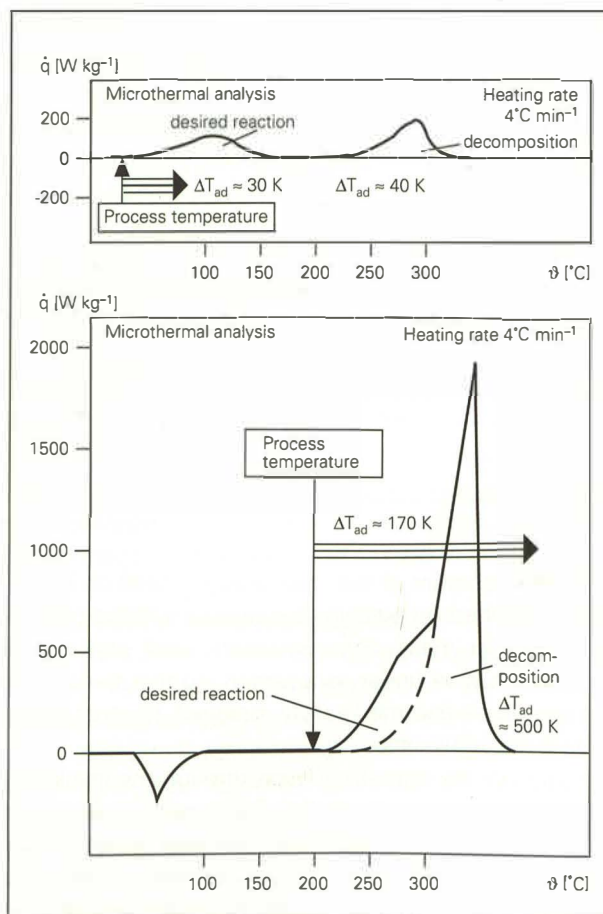


Figure 11: Temperature programmed microthermal analysis; two typical thermograms of different reactant mixtures

# PART 2

## Thermally safe design of the desired process

As shown in the preceding part, for safe process control a knowledge of the thermal behavior of the *desired chemical synthesis* is particularly important for the following reasons:

1. In the temperature range suitable for the synthesis process the desired reaction must proceed at a much faster rate than the side and decomposition reactions. Otherwise the economy of the process would be unacceptable. Consequently, the available heat dissipation capacity must be matched to the thermal properties of the *desired* reaction. Therefore, it is this reaction that determines how rapidly the temperature rises immediately following a breakdown in the cooling system and what temperature level is reached in the first time span after the breakdown. By means of a *temperature excursion* due to a runaway of the desired reaction it is possible that any existing, often high, energy potentials of decomposition reactions are released in a hazardous manner.

2. In the planning of the reaction equipment and the reaction control there exist *freedoms of choice* that allow the process thermal characteristics mentioned in point 1 to be influenced in a controlled manner. If the decisions in process development are made with the *awareness of the consequences for safety,* there exists the *chance* that the safety demands are met to a large extent by the process *per se* without the need for contingency measures, which are sometimes expensive and whose efficacy may be difficult to guarantee.

This second part is thus concerned with the relationships between the design of the synthesis reactions and the thermal safety when implemented in the chemical plant.

### 2.1 Discontinuous processes

If all reactive components are present at the start of the process and the synthesis is then started, e.g. by heating, this is known as "batch" process design. With several consecutive reactions the rate of reaction is determined by the slowest or rate determining step.

If one or more reactive components are added gradually during the reaction ("semibatch"), either the rate of addition or the slowest reaction step can be rate-limiting. In the first case this is known as a *feed or dosing-controlled reaction.* In the second limiting case the addition and the consuming reaction occur at different times so that the actual chemical reaction again runs as a "batch" reaction (see Figure 12).

As far as the thermal safety is concerned, the *feed-controlled reaction* has clear advantages: reaction rate and hence heat production are factors that can be influenced externally. They can be selected in the process development and continually matched in the plant to any change in the heat dissipation conditions. In the case of a complete breakdown of the cooling on power outage, the heat production can be immediately stopped by interrupting the feed. In practice, the ideal case of feed control is possible only with very rapid reactions that proceed like a titration. Since the reaction rate depends on the concentrations of the reaction partners, economically viable reaction rates can often be achieved only if the fed component is also present in appreciable concentration. This is known as *accumulation of the reactants:*

$$\text{Accu (t)} = \frac{\text{molar quantity of the accumulated minority component at process time t}}{\text{equimolar quantity of the components}}$$

Accu(t) indicates the fraction of the total reaction conversion that is still capable of progressing when the feed is interrupted at time t. In the ideal feed-controlled reaction, Accu(t) is always zero; at the start of a batch reaction Accu(t) = 1. For the assessment of the consequences of a cooling breakdown, Accu(t) can be used to calculate the expected temperature rise under adiabatic conditions. Here, it is assumed that the feed is stopped when the cooling malfunction occurs.

$$\Delta T_{ad} (t) = \text{Accu(t)} \cdot \Delta T_{ad, total}$$

The maximum possible temperature excursion in the semibatch type of reaction, $\Delta T_{ad, semibatch}$, is thus reduced to a fraction of the adiabatic temperature rise, $\Delta T_{ad}$, found when the entire reaction is performed batchwise.
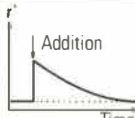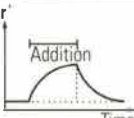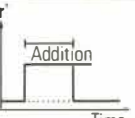
| | "Batch" | "Semibatch" | |
| --- | --- | --- | --- |
| | | partially feed controlled | feed controlled |
| Reaction rate (r˙) Typical profile | Addition | Addition | Addition |
| Dependency | temperature dependent | temperature and feed dependent | feed dependent |
| Accu (t) at maximum | 1 | between 0 and 1 | 0 |

*Figure 12: Types of discontinuous reaction control*

To determine the important characteristic $\Delta T_{ad, semibatch}$, two steps are necessary:

1. Identification of the time of *maximum* reactant accumulation in the course of the process.
2. Determination of Accu(t) at this time and hence the adiabatic temperature rise expected in the worst case.

## 2.2 Knowledge of the heat production and the excursion potentials under process conditions; reaction calorimetry

To follow the characteristic Accu(t) or $\Delta T_{ad, semibatch}$ as a function of the process time, a certain understanding of the process dynamics is required. This includes a knowledge of the chemical and thermal conversion as a function of process design variables such as the temperature and the addition profiles. In several cases, the development of a kinetic model will be worthwhile also for reasons other than those in regard to safety. The procurement of such kinetic information, for instance by following the concentration changes using chemical analysis, is a time-consuming operation and, for this reason, not always feasible for discontinuous processes.

Direct measurement of the *instantaneous heat output* of the reacting system due to chemical or physical processes as a function of the process time has proved its worth in actual practice. This quantity shows directly whether and how quickly chemical conversions occur in the process phase under consideration. The quantities important for a thermally safe process control such as the required heat dissipation capacities and the expected temperature changes in the case of a malfunction can be derived from the measured heat production.

Practically, such measurements are performed in *reaction calorimeters*. A reaction volume of the order of 1 to 2 liters allows the processes to be performed under conditions resembling those in the plant, particularly in regard to agitation, reactant addition and temperature profiles. However, the instrument must also be designed to ensure that the determined quantities depend solely on the properties of the reaction mass and that the factors dependent on the scale and on the specific instrument properties have a minimal influence on or can be eliminated from the experimental result.

These goals are achieved through reaction calorimetry operating, for example, according to the heat flow or heat balance principle.

*The reaction calorimeter based on the heat flow principle* comprises an idealized reactor that – thanks to a rapid, effective control system, a high cooling capacity and a homogeneous jacket temperature – allows virtually ideal isothermal measurement conditions. A thermostat with a high heating/cooling capacity and a rapid circulation of the jacket medium ensure that the heat dissipation is continuously matched to
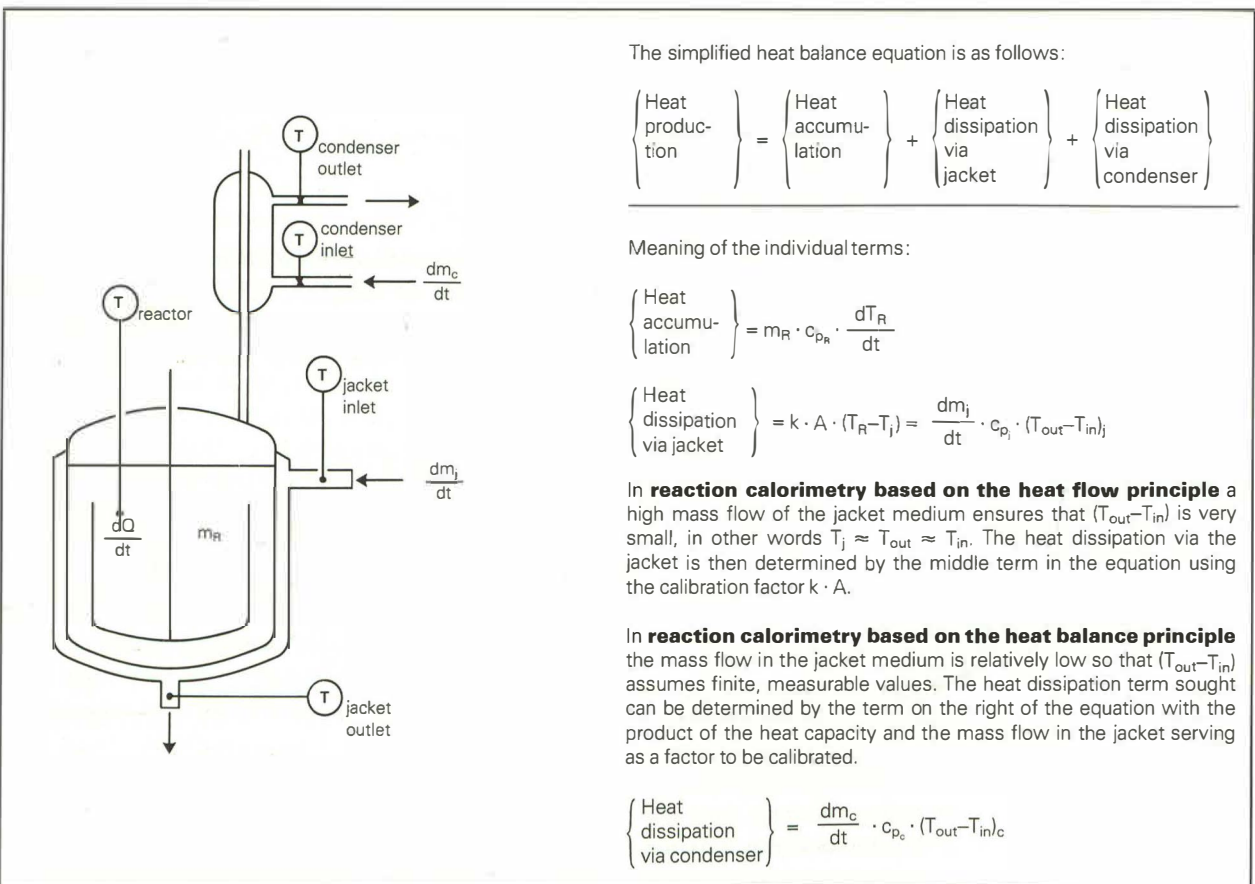


The simplified heat balance equation is as follows:

$$\begin{Bmatrix} \text{Heat} \\ \text{produc-} \\ \text{tion} \end{Bmatrix} = \begin{Bmatrix} \text{Heat} \\ \text{accumu-} \\ \text{lation} \end{Bmatrix} + \begin{Bmatrix} \text{Heat} \\ \text{dissipation} \\ \text{via} \\ \text{jacket} \end{Bmatrix} + \begin{Bmatrix} \text{Heat} \\ \text{dissipation} \\ \text{via} \\ \text{condenser} \end{Bmatrix}$$

Meaning of the individual terms:

$$\begin{Bmatrix} \text{Heat} \\ \text{accumu-} \\ \text{lation} \end{Bmatrix} = m_R \cdot c_{p_R} \cdot \frac{dT_R}{dt}$$

$$\begin{Bmatrix} \text{Heat} \\ \text{dissipation} \\ \text{via jacket} \end{Bmatrix} = k \cdot A \cdot (T_R - T_j) = \frac{dm_j}{dt} \cdot c_{p_j} \cdot (T_{out} - T_{in})_j$$

In **reaction calorimetry based on the heat flow principle** a high mass flow of the jacket medium ensures that $(T_{out} - T_{in})$ is very small, in other words $T_j \approx T_{out} \approx T_{in}$. The heat dissipation via the jacket is then determined by the middle term in the equation using the calibration factor $k \cdot A$.

In **reaction calorimetry based on the heat balance principle** the mass flow in the jacket medium is relatively low so that $(T_{out} - T_{in})$ assumes finite, measurable values. The heat dissipation term sought can be determined by the term on the right of the equation with the product of the heat capacity and the mass flow in the jacket serving as a factor to be calibrated.

$$\begin{Bmatrix} \text{Heat} \\ \text{dissipation} \\ \text{via condenser} \end{Bmatrix} = \frac{dm_c}{dt} \cdot c_{p_c} \cdot (T_{out} - T_{in})_c$$

*Figure 13: Reaction calorimetry*

changes in the heat production in the reactor thanks to variation of the jacket temperature.

The measurement system used for the controller cascade of the thermostat simultaneously measures the temperature difference between reactor and jacket. This difference is directly proportional to the instantaneous heat flow between reaction mass and jacket of the instrument; the proportionality factor (heat transfer coefficient·wetted area = k·A) is calibrated periodically during the experiment using a calibration heating system. Thanks to the rapid control of the jacket temperature, the measured heat flow is identical to the heat production of the reaction mass under investigation.

In a *reaction calorimeter based on the heat balance principle,* the reactor temperature is kept at the target value by changing the inlet temperature of the jacket medium. This inlet temperature and the ensuing outlet temperature are measured at constant flow rate of the jacket medium. As the equation in Figure 13 shows, the heat of reaction is then proportional to the difference between the inlet and outlet temperatures, and the proportionality constant, which is determined by calibration, corresponds to the product of the mass flow and the heat capacity of the jacket medium.

The heat balance principle can also be applied to a reflux condenser.

## Data from reaction calorimetry analysis

Reaction calorimetry allows determination of the instantaneous heat output of a reaction performed in accordance with a process control suitable for the plant. This allows direct deduction of the cooling capacity required in the planned operation.

The integral of the measured heat output over time corresponds to the reaction enthalpy. Controlled heating or cooling ramps also allow direct measurement of the specific heat of the particular reaction mass. The reaction enthalpy and the specific heat are then used to obtain the potential adiabatic temperature rise.

On the basis of the heat production curves measured under the specified process control conditions, conclusions are drawn regarding the dynamics with which energy potential is introduced into the reactor and removed by reaction. This allows identification of the most unfavorable time for a cooling breakdown and estimation of the expected profile of the subsequent runaway reaction. Figure 14 illustrates this using the example of a semibatch reaction.

*Explanations regarding Figures 14a through 14d*

**Figure a:** *Shows the measured heat output as a function of the process time. At time zero linear addition of the reactive component is started. To obtain the desired degree of conversion within a practicable time, work is often carried out with excess reagent in the case of slow reactions. The heat output or rate of the reaction is initially determined by the increase in con-*
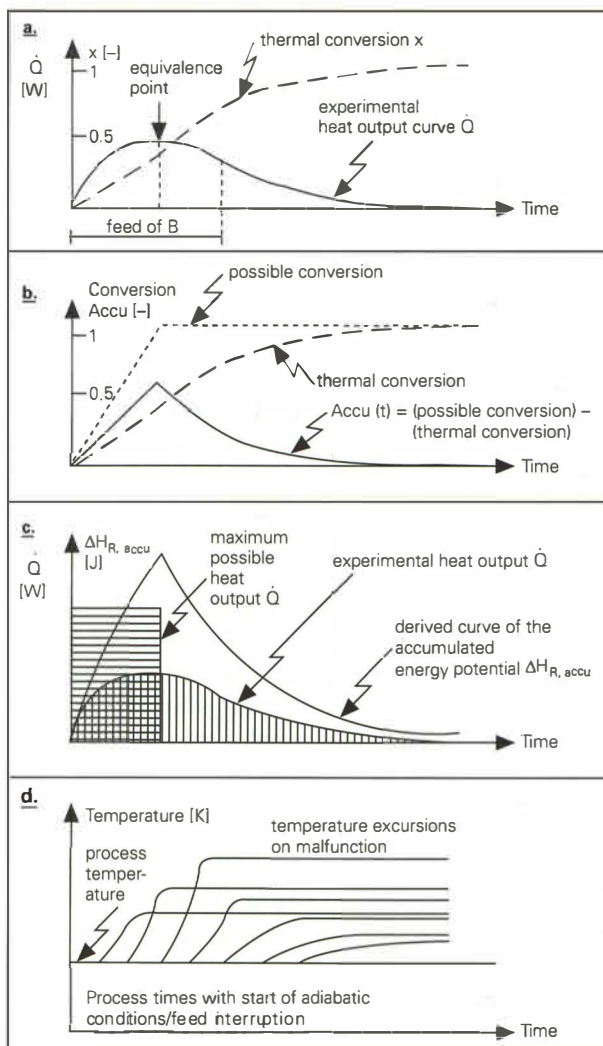


Figure 14: Example of a reaction calorimetry analysis: Reaction A + B → products, semibatch process

*centration of the added component (the contribution of the heat of mixing to the heat signal has been neglected for the analysis). In the later reaction phase the influence of the concentration decrease due to increasing conversion is dominant. The area under the curve corresponds to the total reaction enthalpy $\Delta H_R$.*

*In syntheses, known products are usually produced in high yield from known reactants. The chemical conversion is proportional to the thermal conversion and can be obtained from the experimental curve by dividing the quantity of heat converted since the start of reaction (area under the curve) by the total reaction enthalpy for each point in question on the time axis. The thermal conversion curve is shown dashed in a and b.*

**Figure b:** *To now obtain the reactant accumulation, Accu(t), we compare the conversion curve thus obtained with the theoretically possible conversion according to the actual extent of reactant addition. With addition at a constant rate this increases linearly and equals one at the equivalence point (dotted line in Figure 14b).*

The difference between the theoretically possible conversion and that actually measured is equal to the reactant accumulation (solid line in Figure 14b).

*Figure c:* *An analogous consideration of the same circumstances is shown in Figure 14c. The horizontally hatched rectangle corresponds to the heat release curve of the type which would be expected in a fast reaction (titration) of the same reaction enthalpy. The vertically hatched area is the actual converted energy from Figure 14a. If the difference between the amount of heat introduced since the start of the reactant feed (horizontally hatched) and the amount of heat actually released (vertically hatched) is calculated at various times, the curve of the accumulated potential, also shown in Figure 14c, is obtained directly in units of energy.*

*Up to the equivalence point the potential increases. After the equivalence point it is not increased further even when reactant addition is continued. The addition of an excess of reactants accelerates the reaction (kinetic criterion) but the possible conversion in the case of runaway is now not increased further. (Exception: if a second mole of reagent can react.)*

*Figure d:* *On the basis of the accumulated reactant potential, the temperature profile expected in the malfunction case can now be estimated for any point in time:*

*(1) The attainable temperature level; it can be determined with use of a known or assumed heat capacity of the mass and the quantities from Figures b and c as well as the respective masses:*

$$T_{max} = T_o + \frac{Accu_{max} \cdot \Delta h_R}{c_p}$$

*(2) The initial rate of temperature rise; this is calculated at the time t = o of interest from the heat output $\dot{q}$, which can be read off directly from Figure a, and the heat capacity of the reaction mass:*

$$\left( \frac{\Delta T}{\Delta t} \right)_o = \frac{\dot{q}_o}{c_p} = \frac{\dot{Q}_o}{m_t \cdot c_p}$$

*The rate of temperature rise with time can be estimated from these two quantities or also determined experimentally by switching on the adiabatic control of the reaction calorimeter at the time of interest, i.e. readjustment of the jacket temperature to the value of the reactor temperature (assuming that no critical secondary reaction hazards the experiment).*

## 2.3 Heat dissipation in normal operation

The driving force for a heat flow from one location to another is always a temperature gradient. Such a gradient – for instance between the interior and the cooling jacket of an agitated reactor – can be induced by design or it is established automatically since any system responds to heat locally released by establishing the necessary temperature gradients, thus resulting in a local temperature distribution.

For the description of the heat transfer processes, three principal mechanisms must be distinguished: in **thermal conduction** the heat is transported through the motionless mass, in **thermal convection** heat is displaced locally by transport of material. The mass transport is either **forced** by agitation or it is caused by the temperature and density gradients that are established (natural convection). In contrast to the first two mechanisms, **thermal radiation** is not dependent on material as a carrier.

A list of heat transport mechanisms can be found in Figure 15. In what follows we shall discuss the most important case in **normal operation,** the heat dissipation of the agitated reactor. For the highly hindered heat dissipation in the unstirred case (malfunction, storage problem), see Part 3.

### Heat transfer in agitated tank reactors and tubular reactors

In the agitated tank reactor and the tubular reactor the velocity of flow in the boundary layer decreases to zero at the wall surface, i.e. a film is formed. The total resistance to the heat transfer between contents and cooling medium (1/k) is composed of three parts: the inner film resistance ($1/\alpha_i$), the wall resistance ($d/\lambda_w$) and the outer film resistance ($1/\alpha_o$) (Figure 16).

$$\underbrace{\frac{1}{k}}_{\substack{\text{total} \\ \text{resistance}}} = \underbrace{\frac{1}{\alpha_i}}_{\substack{\text{resistance} \\ \text{of the re-} \\ \text{action mass}}} + \underbrace{\frac{d}{\lambda_w} + \frac{1}{\alpha_o}}_{\substack{\text{resistance} \\ \text{of the apparatus} \\ (1/\gamma)}}$$

where d is the wall thickness and $\lambda_w$ the thermal conductivity of the reactor wall.

With reactor masses with good heat transfer properties (e.g. aqueous solutions) and with good stirring action, the total resistance of the heat transfer is practically identical to the resistance of the apparatus. Poor agitation and materials with low heat transfer coefficients (e.g. sulfuric acid) lead to a considerable increase in the total resistance (Figure 18). The reaction heat transfer coefficient of an agitated reactor $\alpha_i$ can be calculated using the following formula for Newtonian liquids (up to a dynamic viscosity of around 0.4 Pa·s) derived from the Nusselt relation:

$$\alpha_i = \left( \frac{N}{N_s} \right)^{2/3} \cdot Z \cdot \mathbf{Y}$$

| **Thermal conduction** | $\dot{Q} = \dfrac{\lambda \cdot A}{d}(T_1 - T_2)$  [W] | Thermal conductivity |
| | | |



| | $a = \dfrac{\lambda}{\varrho \cdot c_p}$ | Typical values | $\lambda$ [W m$^{-1}$K$^{-1}$] | |
| [K] | | --- | --- | --- |
| $T_1$ layer | $\varrho$ density [kg m$^{-3}$] | Cast iron | 48 | (53°C) |
| | | Stainless steel | 16 | (20°C) |
| $T_2$ | $c_p$ specific heat capacity [J kg$^{-1}$K$^{-1}$] | Glass (Pyrex) | 1.1 | (30°C) |
| | | Asbestos | 0.17 | (50°C) |
| d [m] | The thermal diffusivity represents the ratio of the thermal conductivity and heat storage capacity of a material | Water | 0.62 | (30°C) |
| Area A [m$^2$] | | Sulfuric acid | 0.33 | (20°C) |
| | The mean cooling half life ($\tau$) of a body is proportional to 1/a and the square of the distance d | Toluene | 0.135 | (20°C) |
| | | Air | 0.026 | (25°C) |

Thermal diffusivity

| Typical values | a [m$^2$s$^{-1}$] |
| --- | --- |
| Organic solids and liquids | $0.1 \times 10^{-6}$ |
| Water | $0.14 \times 10^{-6}$ |
| Sulfuric acid | $0.13 \times 10^{-6}$ |
| Air | $18.5 \times 10^{-6}$ |

$$\tau \sim \frac{1}{a} \cdot d^2$$

---

**Forced thermal convection (stirring, flow in tubular reactor)**



Thermal conduction in the film:

$$\dot{Q} = \alpha \cdot A \cdot (T_i - T_w) \quad [W]$$

Most important factors influencing $\alpha$:

Thermal conductivity ⎫
Density ⎪
Heat capacity ⎬ of the medium
Viscosity ⎪
Agitator speed/geometry ⎪
Flow velocity ⎭

Heat transfer coefficient (forced convection)

Relative values with same apparatus:

| Typical values | $\alpha_{rel}$ [W m$^{-2}$K$^{-1}$] |
| --- | --- |
| Water | 1000 |
| Toluene | 300 |
| Sulfuric acid | 230 |
| Glycerol | 50 |

---

**Natural (free) convection**



Driving force for this process is the buoyancy that arises through the differences in density due to the temperature

$$\dot{Q} = \alpha \cdot A \cdot (T_m - T_w) \quad [W]$$

Heat transfer coefficient (free convection)

| Typical values | $\alpha$ [W m$^{-2}$K$^{-1}$] |
| --- | --- |
| Gases | 3– 20 |
| Water | 100– 600 |
| Boiling water | 1000–20 000 |

---

**Thermal radiation**



$$\dot{Q} \sim (T_s^4 - T_a^4)$$

Ratio of the heat losses of a surface at temperature $\vartheta_s$ compared with the losses due to natural convection at an ambient temperature of 20°C through

| $\vartheta_s$ [°C] | natural convection | radiation |
| --- | --- | --- |
| 25 | 1 | 0.6 |
| 100 | 18 | 14.0 |
| 200 | 40 | 50.0 |

Figure 15: Overview of heat transport mechanisms

N is the agitator speed, $N_s$ the standard speed. Z represents the apparatus factor of the reactor interior (dimensions, agitator type) and $\mathbf{V}$ summaries the various material-dependent quantities.

The material constant $\mathbf{V}$ of a reaction mixture can be determined directly in the reaction calorimeter and used for the scale up of heat transfers in the plant reactor.

The relation illustrates the important part played by the agitator in the heat dissipation. When the agitator is idle, the heat dissipation diminishes rapidly and then consists solely of the relatively small contribution of the thermal conduction and the natural convection.

The resistance of the apparatus

$$\frac{1}{\gamma} = \frac{d}{\lambda_w} + \frac{1}{\alpha_o}$$

is determined by the heat transfer properties of the wall and primarily by the flow conditions in the heating/cooling medium circuit. Fouling due to calcification and algae growth can cause the thermal resistance to increase over a period of time.
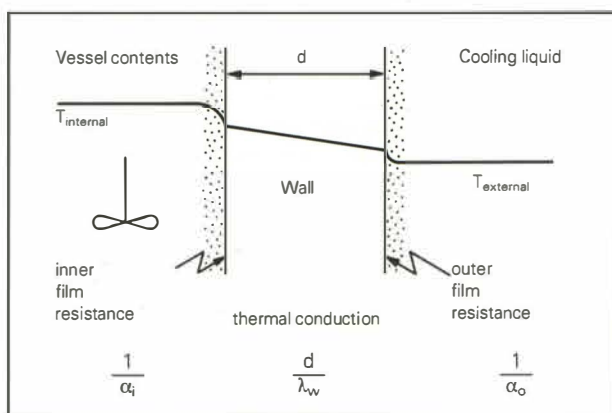


Figure 16: Temperature profile in the region of the wall of an agitated vessel with external cooling

For standard reaction vessels the relationships between the reactor characteristics, the material constant $\mathbf{V}$ and the heat transfer capacity are often recorded in nomograms, which allow the desired quantities to be read off directly.

The instantaneous heat transfer capacities of a reactor can also be estimated during operation from the current internal and cooling medium temperatures (see Figure 19).

| $\mathbf{V}$ [W m$^{-2}$K$^{-1}$] | | | | | |
|---|---|---|---|---|---|
| Water | (20°C) | 24 500 | Toluene | (20°C) | 7 190 |
| | (80°C) | 36 500 | | (80°C) | 7 940 |
| $H_2SO_4$ 96% | (20°C) | 6 010 | Glycerol | (50°C) | 2 800 |
| | (80°C) | 10 700 | | | |

Figure 17: Typical material constants $\mathbf{V}$ for the heat transfer

| Heat transfer coefficient (k value) [W·m$^{-2}$·K$^{-1}$] k | Heat transfer resistance 1/k | = | Thermal resistance due to apparatus [m²·K·W⁻¹·10⁴] 1/γ | + | Material resistance 1/αᵢ | Specific heat dissipation capacity [W kg$^{-1}$] q̇ |
|---|---|---|---|---|---|---|
| | | | 2.5 m³ reactor stainless steel | | sulfuric acid speed: 45 min⁻¹ | |
| 590 | 17 | = | 8.1 | + | 8.9 | 9.8 |
| 420 | 24 | = | 8.1 | + | speed: 22.5 min⁻¹ 15.9 | 6.9 |
| | | | | | water speed: 45 min⁻¹ | |
| 1180 | 8.5 | = | 8.1 | + | 0.4 | 35 |
| 910 | 11 | = | 8.1 | + | speed: 22.5 min⁻¹ 2,9 | 27 |
| | | | 6.5 m³ reactor enamel | | sulfuric acid speed: 36 min⁻¹ | |
| 330 | 30 | = | 21 | + | 9.0 | 4.2 |
| 260 | 38 | = | 21 | + | speed: 18 min⁻¹ 17 | 3.1 |

Figure 18: Examples of the heat transfer in agitated reactors (anchor agitator, double-wall jacket, reaction temperature: 30°C, cooling medium temperature: 20°C)
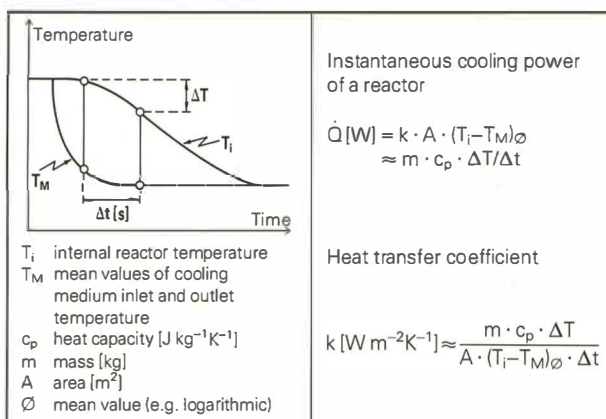


$T_i$ internal reactor temperature
$T_M$ mean values of cooling medium inlet and outlet temperature
$c_p$ heat capacity [J kg⁻¹K⁻¹]
m mass [kg]
A area [m²]
Ø mean value (e.g. logarithmic)

Instantaneous cooling power of a reactor

$$\dot{Q}\,[W] = k \cdot A \cdot (T_i - T_M)_\varnothing \approx m \cdot c_p \cdot \Delta T / \Delta t$$

Heat transfer coefficient

$$k\,[\text{W m}^{-2}\text{K}^{-1}] \approx \frac{m \cdot c_p \cdot \Delta T}{A \cdot (T_i - T_M)_\varnothing \cdot \Delta t}$$

Figure 19: Determination of the heat transfer in the plant

**Heat dissipation in a tank reactor equipped with an external cooling loop**

In certain applications, the heat dissipation can be assured by an external heat exchanger of the appropriate size instead of by cooling via the jacket of an agitated reactor. The movement of the reaction mass is by forced recirculation in a closed circuit. The cooling loop reactor is particularly suitable for highly exothermic, rapid reactions such as catalytic hydrogenations. In this case, the closed circuit also ensures effective, thorough mixing of the hydrogen gas, the catalyst and the reaction mass. The critical point with this reactor as far as safety is concerned also involves stoppage of the recirculatory flow as a consequence of a power outage or due to blockage of the pipelines. Reaction masses that continue to liberate heat when the circulatory sys-

tem fails, whether this be due to reactant accumulation or a decomposition must be identified. A number of incidents in which unstable reaction masses solidified in the pipelines leading to a thermal explosion are known. Typically, the initial temperature increase in the pipe was caused by the energy input of the pump, which continued to operate irrespective of the blockage.

### Heat transfer in a steam-heated reactor

Double-wall jacketed reactors are still today often heated with steam. Depending on the prevailing pressure on the heating medium side, the appropriate saturation temperature of the vapor is established at the surface on the jacket side of the reactor wall at equilibrium. If the wall surface is colder than the steam temperature owing to the fact that the reactor contents have to be heated, the vapor condenses and a liquid film is formed on the surface. The heating power is essentially supplied in such a case by the significant latent heat of condensation of water of 2250 kJ kg$^{-1}$. The heat transfer is very effective with the external heat transfer coefficients in the range 1000–100000 W m$^{-2}$ K$^{-1}$.

If, however, the temperature of the reactor contents exceeds the saturated vapor temperature as a result of even a weakly exothermic process, vapor can no longer condense as no drops can form on the wall surface on the jacket side. The heat transfer resistance due to the apparatus is now characterized by a poorly heat-conducting gas (steam). The steam-heated apparatus consequently represents a one-way street as far as heat exchange is concerned: although the reaction material can easily be heated to the saturation temperature, above this the conditions are practically adiabatic in regard to heat dissipation.

In practice, it is advisable to anticipate that, in principle, the *temperature of the heating medium* can be reached. The safety design should thus be geared to these temperatures even if the process stipulates a lower internal temperature. The equilibrium temperatures for *saturated* vapor are shown in Figure 20. Without equilibration of the freshly generated vapor through the spraying in of water, the existing vapor can be superheated to appreciably higher temperatures.

In cases where overheating of a reaction mass would cause a thermal safety hazard, it is advisable to use indirect heating systems in which steam is used to heat a liquid medium (e.g. pressurized water heating) circulating in the reactor jacket.

| 5 bar | 150 °C |
| 10 bar | 180 °C |
| 16 bar | 200 °C |
| 40 bar | 250 °C |

*Figure 20: Saturated vapor temperatures*

### Heat dissipation through evaporative cooling

The use of a volatile solvent and evaporative cooling often provides an elegant solution in situations with insufficient or inefficient heat dissipation. For example, Figure 21 indicates that the already considerable heat output of 20 W kg$^{-1}$ can be dissipated without any problem by evaporation of the solvent. In connection with safety engineering, the boiling point of a solvent represents a type of barrier that can not be exceeded in controlled operation and, at least for a short period, after a cooling malfunction. Moreover, the use of vacuum systems may allow the boiling point to be matched to the requirements.

The advantages of evaporative cooling described above are counter-balanced by the need to recondense the solvent vapor formed in a controlled and safe manner. Evaporative cooling thus has only limited suitability to dissipate the heat produced as a result of reactant accumulation when a malfunction is experienced. In such a case it must also be anticipated that the cooling of the reflux condenser will no longer be effective. In feed-controlled reactions or with processes having a limited excursion potential, however, the considerable cooling capacity available from the latent heat of vaporization can be used for safe reaction control in conjunction with increased throughput (e.g. shorter addition times, higher reaction temperatures).

If a reaction is run in the neighborhood of the boiling point of the solvent, the selected process temperature should be only just below the boiling point. If not, and, for example, the agitator were to break down, a thermal runaway may develop before the evaporative cooling could take effect. In other words, the heat output could be so high when the boiling point is reached that a critical pressure shock would arise.

### 2.4 Heat balance

In the two previous sections the factors that influence the heat production and the heat dissipation were discussed. If the two quantities are compared with each other, the *heat balance equation* gives the instantaneous change in the heat accumulation of the system at any point in time:

| instantaneous contribution to the heat accumulation at a particular time | = | heat production | − | heat dissipation |
|---|---|---|---|---|
| $m \cdot c_p \cdot \left( \dfrac{dT}{dt} \right)_t$ | = | $r` \cdot V \cdot \Delta h`_R$ | − | $k \cdot A \cdot \Delta T$ |

$\Delta T$ is the difference between the temperature of the reactor and that of the surroundings.

In the *isothermal state* the heat accumulation does not change (the instantaneous contribution to the heat accumulation at a particular time is zero) and the required temperature difference is obtained by setting the heat production equal to the heat dissipation.

*Figure 21: Example of the dimensioning of a system with evaporative cooling*

$$\Delta T_{isothermal} = \frac{r^{\cdot} \cdot V \cdot \Delta h^{\cdot}_R}{k \cdot A} \quad \text{where} \quad \frac{dT}{dt} = 0$$

With *increasing batch size* $\Delta T_{isothermal}$ increases since the contribution of the heat production increases with the volume, i.e. to the third power of the length unit, whereas the heat dissipation increases only with the area A, i.e. with the square of the length unit.

$\Delta T$ is induced by design in the *active,* controlled state or is established *passively* as with a heat producing system the temperature gradient acting as the driving force for the heat dissipation is caused to be built up (autothermic reactor).

If the required $\Delta T$ exceeds the value realizable in practice, the heat accumulation and hence the internal temperature increases steadily. Such a system is *non-stationary.* The increasing temperature causes the reaction rate to increase exponentially (Arrhenius), whereas the heat dissipation term increases only linearly with $\Delta T$: even under initially non-adiabatic conditions this can lead to a thermal runaway.

## Heat balance of an agitated reaction vessel

The relationships between heat production and heat dissipation are shown in Figure 22 for an agitated reactor at a certain point in time. Depending on the slope of the heat dissipation line (overall heat transfer coefficient k), the two curves intersect at one or two points or not at all.

In the *autothermic reactor* (constant jacket temperature), the temperature of intersection point ① is established. If the initial temperature lies somewhat below point ①, the temperature rises as the heat production predominates. Just above this point, the heat dissipation is temporarily greater and the temperature drops until operating point ① is again attained.

At point ① the reaction rates are generally very low, hence the throughputs allowed by the autothermic reaction mode are often insufficient.

If the initial temperature is above point ②, however, or if there is no intersection point of the two curves whatsoever, the heat production is higher at all temperatures. Heating of the reactor contents then occurs and may lead to a thermal runaway if the heat production is not first reduced due to the consumption of reactants.
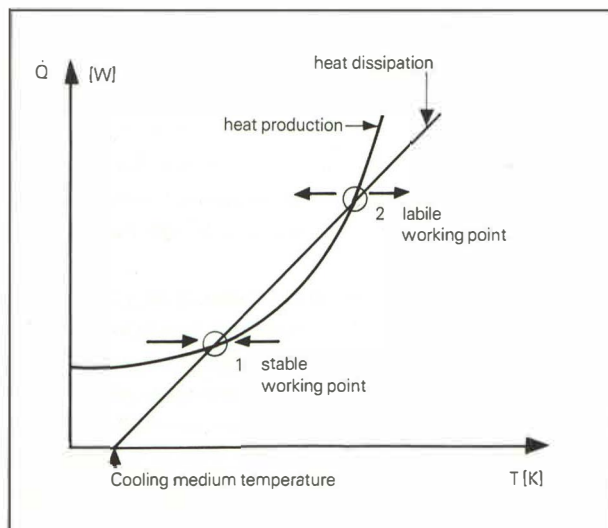


*Figure 22: Heat balance of an agitated vessel*

For economic reasons it is important to use point ② as a working point. This is normally done in the *controlled reactor* and the instability of point ② is compensated through the active change of the jacket temperature or of the heat production curve in the case of variable feed control.

In the light of this discussion it again becomes clear, however, that if the cooling fails or the limit of the cooling capacity is reached, an *unstable situation* prevails. This can be tolerated only if the heat development and the associated temperature rise are not hazardous. This may be the case either with a low excursion poten-

tial as a result of the reactant consumption or because the reaction is not temperature but e.g. feed-controlled (interruption of the feed in the case of a malfunction).

## 2.5 Selection and design of optimum procedures

The *insight* into the correlations outlined in sections 2.1 through 2.4 allows *purposeful* utilization of capacities of production units and at the same time optimization of the safety. A knowledge of the heat balances as well as of the temperature profiles expected if a malfunction occurs forms the basis for the development of new processes and the checking of existing ones.

In order to apply the preceding concepts to their fullest, consideration of *alternative process designs* is important. As an aid here, the most important process options will be discussed with an eye on the thermal process safety.

### Batch processes

Consideration will first be given to batch processes where the reactants are added together and the reaction is initiated by heating or, e.g. through addition of a catalyst. As already discussed in section 2.1, in regard to safety this type of process is in principle less than ideal. This is because if a malfunction occurs at the most unfavorable moment the entire adiabatic temperature rise must be anticipated. Moreover, as the entire reaction mass is exposed to the increased temperature, an adiabatic runaway of the reaction and initiation of a possible decomposition reaction with a large reaction energy would have severe consequences. The choices available in the design of batch processes are limited. If it is desired to keep the temperature level attainable in the case of an adiabatic runaway low, a low initial temperature or high dilution may have to be selected. This can be economically undesirable owing to the long reaction times and the low throughput.

On the other hand, batch processes are technically simple and in certain cases (e.g. rearrangements, self-condensations and polymerizations) unavoidable. If proof is available that even in the malfunction case no critical temperature excursion can occur, a batch process can be performed absolutely safely.

Figure 23 shows a case with favorable and a case with unfavorable kinetics of a batch reaction. Both are controlled with a linear temperature program. The method described in section 2.2 was used to calculate the temperature reached on adiabatic runaway at various times. Case B is thus advantageous as the high potential temperature rises appear in an early phase of the heating program. Thus the high initial adiabatic temperature increase is compensated by a low starting value of the temperature. With little room to maneuver, however, such an argument is critical insofar as small changes in the kinetics (e.g. by a change in quality of the starting material, catalytic effects, problems with
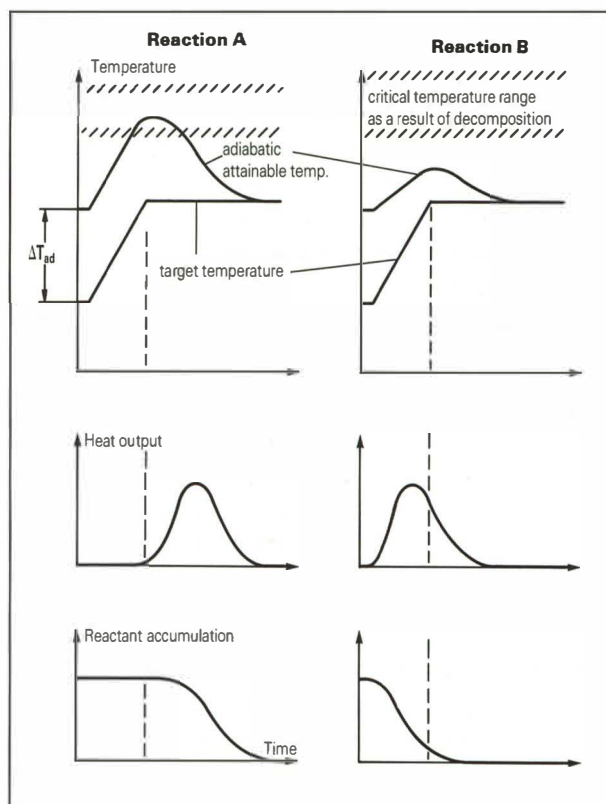


*Figure 23: Batch reaction: initiation of a reaction by heating*

the reaction initiation) could change the result of the analysis considerably.

These considerations also apply particulary to the adiabatic control of batch reactions that are initiated by heating or addition of a catalyst and are intentionally left to react to completion adiabatically. Such types of process are not only economical in regard to energy, but also thermally safe provided the analysis of their thermal data so indicates. The worst thing that can happen to a reaction is considered to happen even without evoking a malfunction.

In summary; it can be stated that although batch processes are in principle rather unsuitable from the safety viewpoint, if conditions are favorable it is with just such processes that reliable clarification of the thermal factors can allow a technically simple and economically beneficial process.

### Semi batch processes with gradual reactant addition

In the safe design of completely or partially feed-controlled reactions, basically the degree of accumulation of the reactants present at any particular time has to be understood and perhaps limited. The limits must be such that the temperature increase expected in the adiabatic runaway of the accumulated reactants itself causes no critical pressure build-up and that any decomposition reactions that run at the attained temperature level are still controllable.

As an example let us look at the sulfonation of a

nitroaromatic compound. Figure 24a shows a micro-thermal analysis curve of the mixed reactants. From the heat of reaction of 185 kJ kg$^{-1}$ together with the heat capacity of the reaction mass, an adiabatic temperature rise of 125°C can be calculated. The decomposition reaction observed at a higher temperature has a high energy potential. The runaway of the desired reaction and an initiation of the decomposition reaction would have very severe consequences.

The central question therefore concerns finding a type of process in which the reaction can be performed within an economically viable time and, if a malfunction occurs, the adiabatic runaway of the desired reaction and the initiation of the decomposition reaction are separated by sufficient time. The concentration, the addition profile and the process temperatures are available as selection parameters for the process optimization. Although low concentrations and long addition times lower the accumulation of reactants, economic considerations set limits to these parameters.

Figure 24b shows the influence of the process temperature on the event after the onset of adiabatic conditions for the above reaction. The curves calculated with a kinetic model are based on the fact that, at the time of *maximum reactant accumulation,* adiabatic conditions set in owing to a failure in the cooling system and at the same time the feed is shut off. The three selected temperatures show in exemplary fashion that a *too low reaction temperature* (here 90°C) exists where the reactant accumulation is so large that on malfunction the adiabatic runaway reaction immediately leads to temperatures at which the decomposition reaction also runs away rapidly. The two-stage progress of the runaway curve is easily recognizable. On the other hand, the process temperature of 190°C is clearly *too high.* Although the desired reaction proceeds with very little reactant accumulation, at this processing temperature the decomposition reaction is already so rapid that it would run away in the adiabatic case. This would occur within a short period and even during the isothermal process a marked loss in yield would have to be anticipated. The intermediate process temperature (140°C) was selected in our example so that after failure of the cooling the time to runaway of the decomposition reaction is as long as possible and defensive measures could still be taken. (Since completely adiabatic conditions were assumed in the calculation, a thermal runaway nevertheless occurs later; in reality in the time available the adiabatic progress could be interrupted by initiated measures or existing small cooling effects.)

The above considerations should show how important it is to support the critical analysis relating to the malfunction case. Experience teaches us that "intuitively", motivated solely by safety concerns, too low temperatures are often preferably selected because – often wrongly – in safety considerations a great deal of weight is attached to the decomposition reaction and
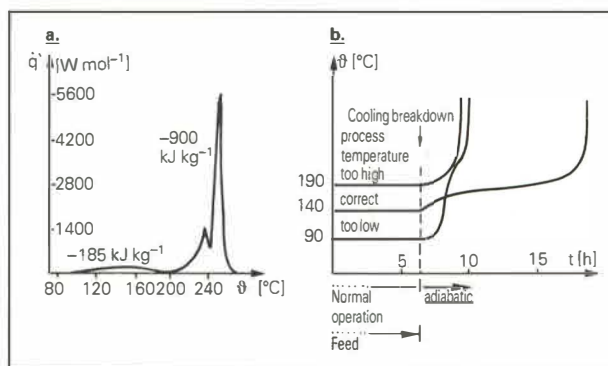


Figure 24: Sulfonation of a nitroaromatic compound

not enough to the desired reaction. In certain cases, however, as shown above, if the temperature selected is too low, a real safety problem arises. Regarding the selection of a temperature that is high enough to meet the safety requirements, at the same time appropriate consideration must be given to achieving an effective as possible utilization of volume and time.

In the example treated, one can go one step further and even use the reactant accumulation as the guiding variable for process control:

In the analysis of the reaction calorimetric curves plotted in Figure 25a, the potential temperature rise as a consequence of reactant accumulation has been assessed as unacceptable and a procedure with a lower concentration selected (Figure 25b). This results in a slowing down of the reaction, a smaller throughput and a greater solvent consumption.

If the accumulation curve in Figure 25a is considered as a function of time, it can be seen that the condition assessed as critical holds only over a short period of time. Before and after this phase the process is not considered critical from a heat accumulation viewpoint.

In the process alternative of Figure 25c, the observed reactant accumulation is fed back to the feed controlling program, which reduces the *feed* after attainment of the acceptable degree of accumulation so that, from this point on, the added quantity of reagent corresponds exactly to the actual amount consumed by the reaction, i.e. the degree of accumulation remains constant. Once the degree of accumulation again becomes less than the acceptable value at a later instant, the feed rate can be increased.

To realize this in practice, an approximated addition profile can be derived from the kinetic description of the reaction. Thanks to advances in rapid online analysis or through the real time simulation of the reaction in a process control system (using "observers" or Kalman filters), it will perhaps be possible in future to use the degree of accumulation determined in the ongoing plant process directly for feed control.

## Synchronous additions

An example of a somewhat more specialized version of the feed-controlled reaction mode is the case which
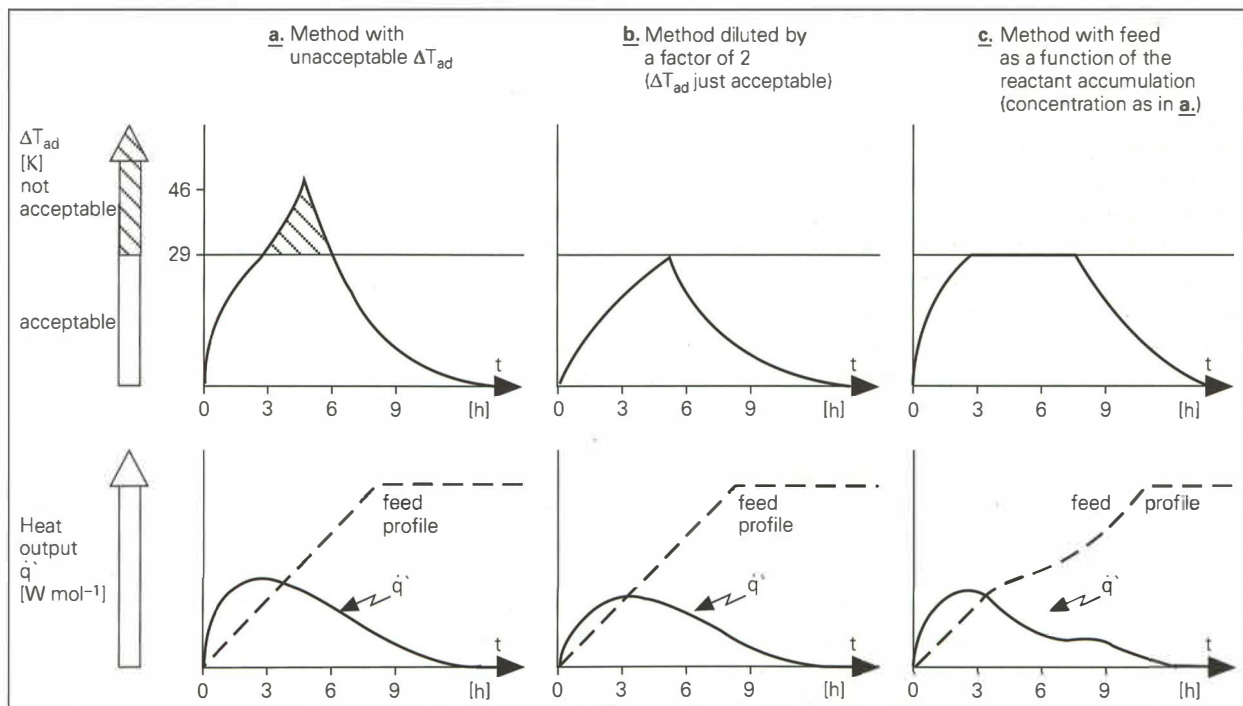
Figure 25: Feed as a function of $\Delta T_{ad}$

involves adding two reactive components simultaneously. On the one hand, this has the disadvantage that in comparison with the batch or semibatch reaction the concentrations of the two reactants are rather low and thus the reaction rate is comparatively slow. This can normally lead to a poorer throughput and an increased reactant accumulation. On the other hand, the low reactant concentration can be desirable if either of the two reaction partners can enter into potentially undesirable reactions (polymerizations) with itself or with the solvent. As a result, the probability of these reactions significantly competing with the desired reaction should be decreased.

Additional examples involve catalytic hydrogenations, e.g. of nitroaromatic compounds in which unstable intermediates (I) such as hydroxylamines could accumulate:

$$\text{Nitroaromatic} \xrightarrow{H_2} \text{Intermediate} \xrightarrow{H_2} \text{Product}$$

The nitroaromatic and the intermediate are in competition for the added hydrogen. Through simultaneous addition of the aromatic compound with the amount of hydrogen required for the total reaction, the reaction can be so controlled that the unstable intermediate undergoes continuous reaction to the final product.

**Continuous reaction modes**

For the design of a continuous reactor, a priori use of reaction engineering skills is relatively common. This provides a means by which the safety criteria are more easily incorporated in the process design when compared with the case of the discontinuous reaction control, where it is tempting to regard the plant apparatus simply as a larger version of the familiar laboratory vessel used by the synthetic chemist.

Further, in the continuous reactor where the reactants are added continuously and reaction mass is continuously removed, a reduction in the amount of reaction mass potentially exposed to a significant process deviation is possible when compared with a batchwise process. This reduction in the inventory of potentially more hazardous – for instance more toxic – chemicals is advantageous in regard to the thermal safety of the operation.

The following conditions must be fulfilled for this:

1. To ensure that a small volume suffices, the reaction must be fast.
2. It must be ensured that unreacted reactants do not reach a downstream storage tank otherwise any thermal problem would simply be shifted to the tank.

To fulfill condition 1 it may be necessary to select a relatively high reaction temperature. If the products are thermally unstable, they must subsequently be effectively cooled or continuously used up in a downstream process.

Although no chemical processes are performed in the thin-film evaporator, it can serve as an example of a continuous process; thanks to the short residence time the separation of solvents by distillation is possible under conditions where the decomposition of the distillate or residue occur at a rapid rate and can release a considerable quantity of heat.

A frequently employed continuous reactor is the *ideal mixed, continuous stirred tank reactor* (CSTR) (Figure 26): Here the outflow of the product mixture is equal to the inflow of the reactants so that the volume remains constant and stationary concentration conditions are

27

established. Owing to the thorough mixing in the reactor, the concentrations of the reactants and products in the outflow are equal to those in the bulk reaction medium.

The formula derived in Figure 26 shows that at a specified conversion a smaller reaction rate constant (k`) must be balanced by a larger volume. A knowledge of the reaction kinetics is thus necessary in the dimensioning of the continuous-stirred tank reactor. Through the selection of the reactor volume and the flow rate, the production quantity per unit time and the conversion $(1 - C_A/C_{A_o})$ at which the reactor is operated can be chosen. As with batch reactors, in safety considerations it must be ensured that the heat balance of the normal operation is favorable and that on malfunction the potential of unreacted reactants (Accu = $C_A/C_{A_o}$) allows no critical excursion of the temperatures in the adiabatic case. If the reactor is designed for a high conversion $(C_A/C_{A_o} \ll 1)$, the excursion potential is small, but if the reaction rate is to be sufficiently high a larger volume may be needed. Malfunctions can occur in the continuous-stirred tank reactor, particularly if the flowthrough is stopped thus cutting off the cooling effect due to the cold inflow.
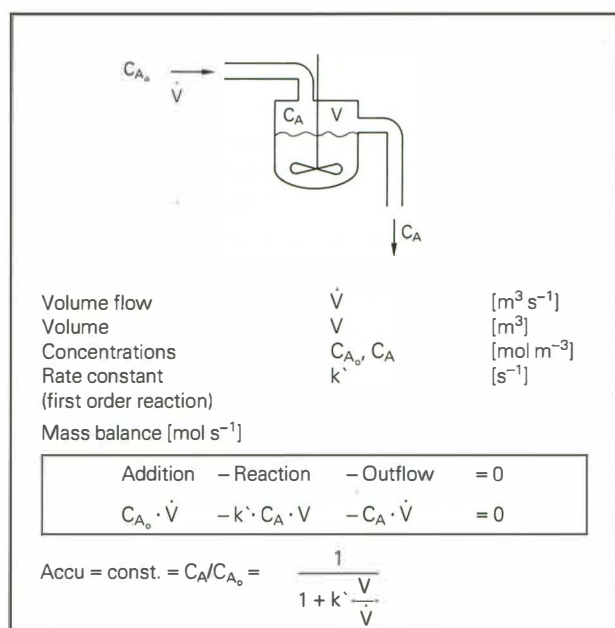


| Volume flow | $\dot{V}$ | $[m^3\ s^{-1}]$ |
| Volume | $V$ | $[m^3]$ |
| Concentrations | $C_{A_o}, C_A$ | $[mol\ m^{-3}]$ |
| Rate constant | k` | $[s^{-1}]$ |
| (first order reaction) | | |

Mass balance $[mol\ s^{-1}]$

| Addition | – Reaction | – Outflow | = 0 |
|---|---|---|---|
| $C_{A_o} \cdot \dot{V}$ | $- k` \cdot C_A \cdot V$ | $- C_A \cdot \dot{V}$ | = 0 |

$$\text{Accu} = \text{const.} = C_A/C_{A_o} = \frac{1}{1 + k` \cdot \dfrac{V}{\dot{V}}}$$

*Figure 26: The ideal perfectly mixed continuous-stir tank reactor*

To increase the total conversion under otherwise identical conditions, often a cascade of several continuous-stirred reaction vessels connected in series is used. This allows a smaller total volume.

In regard to the safety criteria, the first reactor is the most critical since here the driving force and hence the reaction rate and the rate of heat production as well as the reactant accumulation $C_A/C_{A_o}$ are greatest. Through interconnection of reactors of different sizes (sequence important with relatively complicated kinetics) and, for instance, through partial reactant recycling, additional design possibilities are opened up. The boundary conditions in regard to the available choice are mostly determined by the planned selectivity.

As a further ideal case of a continuous reactor, the *tubular reactor* can be mentioned here:

The reactants are mixed at the start and the reaction proceeds while the reaction mass continues to flow in the tube. The tube length needed for a desired conversion is determined by the reaction rate. Favorable for the heat balance is the very high surface/volume ratio with long, thin tubes as well as the generally increased heat transfer coefficient when compared with the agitated tank reactor as a result of the high turbulence of the flow.

The tubular reactor is similar to the batch reactor inasmuch as the reactant accumulation at the start equals one. Here "start" refers to the location in the tube compared with the start of the process time in the discontinuous batch reactor.

The first part of the tube is thus the critical part of the isothermal tubular reactor as there not only the reaction potential but also the release of heat is high. Here there exists a danger of an unstable heat balance and hence of a local overheating ("hot spot"). This can be avoided by changing the longitudinal temperature profiles (temperature of the added reactants, heating-cooling zones along the tube).

The description of this special type of reactor intended for dedicated plants closes our brief insight into the diversity of the possible alternatives to the classical agitated reactor.

## 2.6 Measures

The risk analysis of a process utilizes the knowledge of the process and the possible excursion potentials to predict the probability and consequences of possible malfunctions. As a result of this assessment, measures are designed to reduce the risk to an acceptable level. We distinguish three categories of measures:

• eliminating measures
• preventive measures
• contingency measures

Before the planning of complicated measures, it is practical to ask the question whether it would not be better to eliminate the identified hazards by a conceptional change in the process rather than merely attempt to counter them by secondary measures. If, for example, it is possible to replace a batch process by a continuous process or to eliminate buffer storage and hence to drastically reduce the quantity of reactive or toxic intermediates temporarily present, a significant increase in the inherent safety of the operation may be accomplished. The effort involved in the development work must be compared with the cost savings of the secondary measures and the principal advantage that there is

no longer any remaining risk of an eliminated hazard being activated through an unforeseen mechanism.

In contrast to conceptual improvements of processes to reduce the consequences, the aim of preventive and contingency measures is to keep the probability of an identified malfunction as low as possible. The justifiable work involved is determined primarily by the consequences of the abnormal progress. On the one hand, it is sensible to apply the principle that in the case of potential incidents with severe consequences, a single fault can never be allowed to be the triggering factor. On the other hand, with technically protected, redundant monitoring and corrective measures even highly sensitive processes can be performed with an acceptable level of remaining risk. In contrast to technical measures, it is not justifiable to attempt to prevent an event with far-reaching consequences simply by personnel and organizational measures. As far as this axiom is concerned, however, it should be noted that each technical measure also involves an organizational measure as the safety equipment requires monitoring and maintenance.

For the assurance of the thermal process safety, the planning and monitoring of *limits,* particularly of temperature limits, is of special importance. Such limits only make sense if, when they are exceeded, clearly defined actions can be initiated. It is also important to know within what time period contingency measures must be effective. Whereas fully automated emergency measures usually become active very rapidly, the time needed for manual or even improvised measures is generally long and must be tested practically.
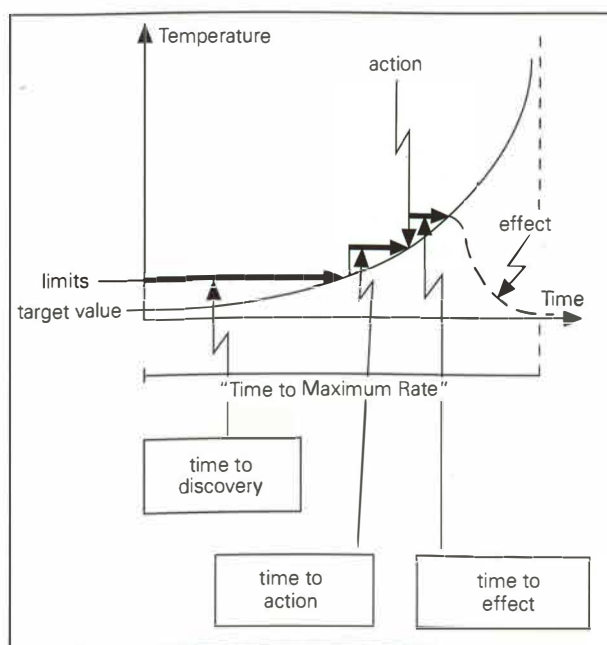
Figure 27 illustrates the considerations required in the assessment of the time dependence of such emergency measures.

- The time intervals considered are related to the quantity "Time to Maximum Rate" of the runaway reaction. This quantity is usually known only as an estimate and is moreover extremely sensitive to measurement errors and fluctuations in the identity of the samples investigated. It is thus advisable to err on the safe side and use a conservative value for the TMR in any risk analysis.
- To avoid false alarms and to take the noise of the experimental signal into account, the temperature limit must be set above the target temperature by a certain amount. Owing to the exponential form of the temperature-time curve, under certain circumstances a relatively long time is required before this limit is reached.
- After discovery of the deviation, once again a certain time that depends greatly on the operating conditions will elapse until the correcting action is triggered.
- Finally, the initiated measures need a time interval that depends on the physics of the system before they start to become effective.

**Possible contingency measures are for instance:**
- **Full cooling**

If the reactor is operated with a controlled cooling system with reserve capacity, switching to full cooling is a first measure. Critical in this connection is that the temperature does not fall below the solidification point of the mass otherwise a crust would form resulting in an adverse effect on the heat transfer.

- **Emergency cooling**

If the cooling system fails, depending on the situation the supply of water from a hydrant to the cooling jacket or the provision of an independent emergency cooling system is conceivable. It should be noted here that thorough mixing of the product to be cooled is essential for efficient cooling. Over the short term, imperfectly mixed, relatively large masses behave to a large extent adiabatically, even if cooled on the outside. Cooling attempts sometimes employed in the event of breakdowns involve spraying the outside of reactors with a hose. Such attempts are effective only if there is sufficient agitation or the temperature drop is significant enough to ensure that natural convection sets in.

- **Emergency intermixing**

Here the injection of nitrogen through the bottom outlet has proved a feasible makeshift measure for thorough mixing. It is advisable to check in a practical experiment whether the system suffices for mixing of the entire reaction mass in the plant equipment.



Figure 27: Chronological development of contingency measures

• **Aborting the reaction by "quenching"**

The potentially hazardous reaction is terminated by addition of a suitable component. Here the material added can stop the reaction through the effect of dilution, lowering of the temperature through the heat of mixing and possibly heat of fusion (addition of ice) or even through chemical inhibition. Critical factors are the rate of addition, the mass ratios, the required empty volume and agitation. A further possibility involves the discharge of the reaction mass, for example to a lower-lying tank containing water. This measure is particulary suitable when the design of the discharge step can be similar to that normally used for the workup step after the reaction. Discharging generally requires more time and is less reliable than dilution.

• **Venting**

Assessment of the venting requirements of thermally sensitive reaction masses with runaway potential and the subsequent dimensioning of the vents and lines are complex. There exist examples of incidents in which an unforeseen pressure release through reactor ports or rupturing glass parts has prevented a vessel explosion. On the other hand, runaway reactions have caused reactors to explode even though the manhole was open. Incorporation of venting in the design as a contingency measure is thus effective only for selected reaction systems whose reaction and flow behavior is known exactly. In addition, for environmental reasons it is generally necessary to lead the vented reaction mass into a receiver and remove the gases by means of scrubbers. This makes the measure very expensive and in some cases, particularly in multi-purpose and old plants, practically impossible. In what follows, the limitations associated with the design of emergency pressure relief systems are listed.

– With known systems (e.g. ammoniacal amination masses, polymerization masses from monomers with high vapor pressure) that have a high vapor pressure in the vicinity of the reaction temperatures, a small temperature excursion can lead to the attainment of the actuation pressure, e.g. of a bursting disk. Thus the main effect of the measure consists in the powerful cooling through evaporation of volatile components of the vented reaction mass. It is known, however, that non-ventable systems exist in which considerable vapor pressures are not attained until the reaction rate and hence the gas generation rate (evaporating components and gaseous decomposition products) due to the temperature rise is far too rapid for effective venting. (For example, sulfuric acid reaction masses.)

– Above a certain gas generation rate, irrespective of the chemical composition of the mass, foaming occurs during the venting process, i.e. instead of just gases a mixture of liquids and gases enters the vent opening and the downstream venting system. Whereas the maximum flow velocity of gases is

| Product: | Ident. No.: |
| Risk analysis for process: | Building: |
| Author: | Date: |

| Characteristics of desired reaction | (if need be use a new form for each reaction stage) |
| --- | --- |
| Batch size: | . . . . . . . . . . . . . . . kmol |
| at start | . . . . $m^3$ = . . . . kg |
| at end | . . . . $m^3$ = . . . . kg |
| Gross heat effect: | . . . . . . . . . . . . . . . kJ kg$^{-1}$ |
| this corresponds in the adiabatic case to a temperature rise of: | $\Delta T$ = . . . . . . . . K |
| Process temperature | . . . . . . . . . . . . . . . °C |
| Heat capacity of reaction mass known/assumed: | . . . . . . . . . . . . . . . kJ kg$^{-1}$ K$^{-1}$ |
| Reaction rate: | |
| controlled by: | . . . . . . . . . . . . . |
| limited by: | . . . . . . . . . . . . . |
| Gas development: | |
| Amount: | . . . . . . . . . . . . . l kg$^{-1}$ |
| Course: | . . . . . . . . . . . . . |
| Reactant accumulation: | |
| (If no or only partial feed control) | |
| Maximum value | . . . . . at . . . . . (time) |
| calculated adiabatic temperature rise in malfunction case: | $\Delta T$ = . . . . . . . . K |
| Attainable final temperature: | . . . . . . . . . . . . . °C |
| on malfunction at time: | . . . . . . . . . . . . . |
| Consequences when this temperature reached: . . . . . . . . . . . . . . |
| (e.g. if boiling point exceeded, pressure buildup, decomposition reactions, evaporation of solvents, etc.) |

Figure 28: Risk analysis form for the desired reaction

around 300 m s$^{-1}$, the discharge of two-phase flows is reduced to a few meters per second, and this diminishes the venting capability of any given pipe system dramatically.

– Venting devices, particularly bursting disks, can also be weak points in that they respond involuntarily and release chemicals into the surroundings.

– For protection against overpressures due to physical events, venting devices are officially stipulated. It is generally advisable to use safety valves instead of bursting disks. Valves close again when the pressure becomes less than the lower limit of the set response pressure and thus prevent discharge of excessive quantities of material.

## 2.7 Chemical and technical fault analysis

To close Part 2, which has concentrated on the *desired* process, Figure 28 shows a printout of a form used in

| Control questions | Pointers |
|---|---|
| **Chemistry other than expected** | |
| What reactions can the substances present undergo in principle? | – Chemical knowledge, literature<br>– Thermochemistry<br>– Possible by-products/intermediates<br>– Chemical analysis<br>– Matrix of substances present<br>– Analogous cases<br>– ... |
| What chemical and physical properties can change the course of reaction? | – Reactant quality<br>– Catalytic influences<br>– Inhibitors<br>– Physical specifications (surface, inhomogeneity, solubility)<br>– Active concentration of individual reaction partners<br>– Selectivity criteria<br>– Thermal ageing, auto-catalysis<br>– ... |
| **Wrong design of the process control** | |
| Is the process design suitable for the performance of the reaction in the envisaged apparatus? Are the preconditions that have been taken into account ensured? | – Wrong kinetic assumptions<br>– Feed rate too high<br>– Temperature too low<br>– Poor initialization<br>– Imperfect mixing<br>– Unsuitable reaction apparatus<br>– ... |
| **Process deviations and technical malfunctions** | |
| What is the influence of deviations from the intended process control variables? With what variables does a small deviation suffice for a powerful effect (sensitivity analysis)? How do the deviations arise? | – Process duration<br>  – unintentional holding phases<br>  – phase separation on standstill<br>  – restart after standstill<br>  – ageing<br>– Process temperature<br>  – heat of reaction<br>  – heating medium |

| Control questions | Pointers |
|---|---|
| **Process deviations and technical malfunctions (continued)** | |
| | – mechanical energy (heat of stirring)<br>– wrong feed rate<br>– wrong batching<br>– wrong reactants<br>– imperfect mixing, agitator action<br>– sequence of the work steps<br>– change in vessel material<br>– immersion depth of agitators and probes<br>– pressure<br>– extraneous gases<br>– ... |
| What technical malfunctions lead to the process deviations and what are the consequences? | – Breakdown of cooling<br>– Breakdown of perfect mixing<br>– Possible wrong control<br>– Leaks<br>– Leaking valves<br>– Heating/cooling medium influx<br>– What is the position of the control elements in the passive state?<br>– What critical paths can they open?<br>– ... |
| How are malfunctions detected and reported? | – What measured variables are critical?<br>– Are the probes located where critical process deviations can be detected at an early stage?<br>– Redundancy of the measured variables and signal circuits<br>– Power outage<br>– ... |
| What changes in the plant appear over the course of time? | – Documentation of the modifications<br>– Checking the risk analysis<br>– Ageing of the plant<br>– Corrosion<br>– ... |

Figure 29: Systematic check points for the thermal safety of the desired reaction

practice to record the most important findings of risk considerations in the checking of a process concept or a finished process. A checklist, which can be used for systematic discussion of the possible factors that influence the thermal process safety in a concrete example, is shown in Figure 29.

## Avoidance of decomposition reactions

In Part 2 the discussion centered around the control of the desired chemical reactivity. In this part we now turn to the undesired reactions, which we summarize under the general heading, decomposition reactions. Simply to avoid yield losses the process temperatures are generally so selected that the decomposition reactions at most run slowly and consequently also release only comparatively small amounts of heat. They can, however, represent a potential hazard if:

- the temperature is increased relative to the planned operating temperature. This can be the result of a runaway of the desired reaction in the case of a malfunction (see Part 2) or through undesired heating to a *too high temperature,*
- the *heat dissipation* is severely *inhibited,* i.e. if the heat production despite its small magnitude predominates in the heat balance and a thermal explosion develops (cf. case histories 5-7 in section 1.6),
- in special cases a decomposition reaction is accelerated autocatalytically by long holding,
- considerable amounts of gas are released.

In Part 3 we first consider in detail the parameters suitable for the characterization of decomposition reactions. Next the relationships governing heat dissipation under various characteristic heat accumulation conditions are reviewed. These two influencing factors in turn form the basis for consideration of the heat balance, which is necessary for establishing safe limiting conditions for practical situations.

A further section is devoted to the understanding of experimental investigation techniques and their interpretation.

### 3.1 Characterization of the decomposition behavior; the adiabatic temperature profile

First, the decomposition behavior of a sample will be characterized irrespective of the operational heat balance. It is practical in this connection to refer again to the adiabatic limiting case in which no heat is dissipated and the dynamics of the temperature profile are determined completely by the thermokinetic behavior of the material under investigation.

As already mentioned by way of introduction in Part 1, the adiabatic profile of a reaction can be characterized by the two parameters *adiabatic temperature rise* $\Delta T_{ad}$ *and "Time to Maximum Rate"* $TMR_{ad}$.

$\Delta T_{ad}$ determines what temperature is attained on reaction runaway. From Figure 30 it is also apparent, however, that if $\Delta T_{ad}$ is large the rate of temperature rise – and with it the rate of pressure rise – can assume
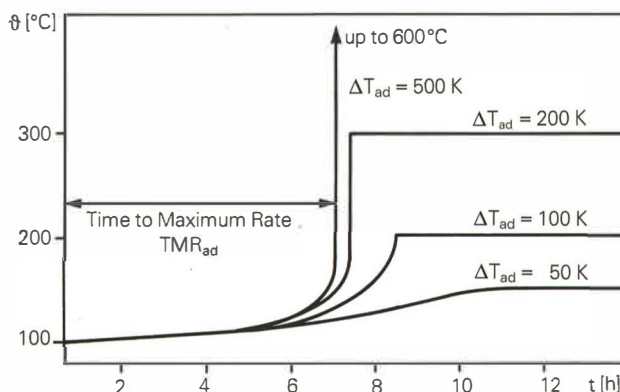


Figure 30: Adiabatic reaction profile as a function of the energy potential (adiabatic temperature rise, $\Delta T_{ad}$)

Assumptions:  First order reaction
Initial power: $1 \, W \, kg^{-1}$ at $100\,°C$
Activation energy: $100 \, kJ \, mol^{-1}$

hazardous values whereas at smaller $\Delta T_{ad}$, e.g. $50\,°C$ a flat dependence of temperature on time is observed.

This can be explained as follows: The conversion x of the reaction at time t is:

$$x = \frac{1}{\Delta T_{ad}} \int_0^t \frac{dT}{dt} \, dt$$

where the rate of temperature rise dT/dt is a function of the absolute temperature T and the conversion x:

$$\frac{dT}{dt} = \underbrace{\frac{\dot{q}_\infty}{c_p}}_{\substack{\text{constant} \\ (\dot{q}_\infty = \text{reference} \\ \text{heat output} \\ \text{at } T = \infty)}} \cdot \underbrace{e^{-E_a/RT}}_{\substack{\text{Arrhenius} \\ \underline{\text{term}} \\ \\ \text{accelerating} \\ \text{influence}}} \cdot \underbrace{(1-x)^n}_{\substack{\text{Reactant} \\ \underline{\text{consumption}} \\ \underline{\text{term}} \\ \text{decelerating} \\ \text{influence}}}$$

with increasing temperature and increasing conversion

At low $\Delta T_{ad}$ the conversion x increases rapidly and the reactant consumption term dominates the rate of temperature rise before the temperature and hence the Arrhenius term has increased to a high value.

On the other hand, at high $\Delta T_{ad}$ the rise in temperature achieved is already so large at relatively small conversion x that the experimental influence of the Arrhenius term dictates the progress. Here, rates of temperature and pressure rise can accelerate so rapidly that the destructive power of the thermal explosions can easily

exceed that of gas and dust explosions and in some cases can reach that of solid detonations.

The above-mentioned dominance of the Arrhenius term at high $\Delta T_{ad}$ also has a simplifying consequence for the estimation of the parameter $TMR_{ad}$. For high $\Delta T_{ad}$ the reactant consumption term can be neglected without incurring any large error (synonymous with the assumption of zero-order reaction kinetics). With this assumption $TMR_{ad}$ can thus be estimated with the simple formula shown in Figure 31 without the need to know the reaction mechanism.

$$TMR_{ad} = \frac{c_p \cdot R \cdot T_o^2}{\dot{q}_o \cdot E_a} \; [s]$$

$c_p \; [J \, kg^{-1} \, K^{-1}]$    Heat capacity (estimation, measurement)
$R = 8.314 \; [J \, mol^{-1} \, K^{-1}]$   Gas constant
$T_o \; [K]$    Absolute initial temperature (°C + 273)
$\dot{q}_o \; [W \, kg^{-1}]$    Specific heat output at $T_o$
$E_a \; [J \, mol^{-1}]$    "Activation energy" (= measure of the temperature dependence of $\dot{q}_o$, must be estimated, e.g. from measurements)

Figure 31: Estimation of the "Time to Maximum Rate" under adiabatic conditions, $TMR_{ad}$
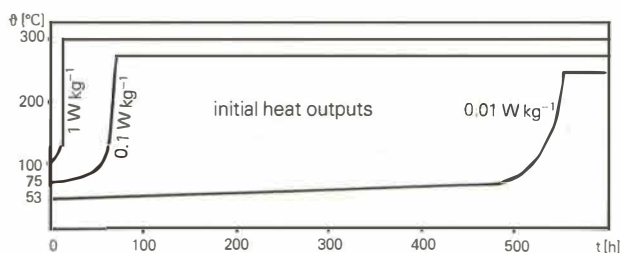


Estimated $TMR_{ad}$:
at 100°C:   6.4 h
at   75°C:   56   h
at   53°C: 490   h

Figure 32: Adiabatic temperature profiles as a function of the initial heat outputs (assumptions as in Figure 30, $\Delta T_{ad} = 200 °C$)

*The formula in Figure 31 shows a relationship between the heat production rate $(\dot{q}_o)$ of reaction at the starting temperature and the "Time to Maximum Rate" under adiabatic conditions.*

Since the heat production rates $\dot{q}_o$ increase exponentially with temperature, the decrease in the characteristic runaway times $TMR_{ad}$ with increasing temperature is also exponential. In accordance with the Van't Hoff rule of thumb mentioned in Part 1, $TMR_{ad}$ becomes less by a factor of about two to three when the initial temperature $T_o$ is around ten degrees higher.

Figure 32 shows a calculated example of adiabatic temperature profiles for various temperatures together with the times $TMR_{ad}$ estimated from the formula in Figure 31.

From laboratory measurements of $\dot{q}$, computed run-

away times can serve as decision aids. It must be noted, however, that small deviations such as measurement errors, possible fluctuations in quality and above all catalytic effects can have an influence that is of similar magnitude to that due to temperature changes of several tens of °C. In autocatalytic reactions, non-thermal effects can also have an accelerating action and specific consideration must be given to these.

## 3.2 Heat balance under heat accumulation conditions

In the last section we considered the adiabatic limiting case in which only the heat production of the reaction played a part.

Under real operating conditions, sooner or later a certain cooling effect will appear as the increasing internal temperature gradually causes a temperature gradient to be built up. The extent of the resulting cooling action depends on the thermal resistance that separates the mass under consideration in the center of a container or reactor from the ambient temperature. The thermal resistance can here lie principally in the mass itself, in the wall or in the jacket medium.

Figure 33 summarizes various practical cases. The different location of the main thermal resistances must be taken into consideration in the assessment of the heat balance. Since the agitated tank reactor was treated in detail in Part 2, here we now turn to the case of a container filled with a solid in which the heat transport is to a large extent determined by the heat conduction in the substance itself.

### Heat accumulation in a solid

For an understanding of the heat balance in such a system, we employ the following model considerations:

Figure 34 shows a section from the center to the surface of a cylindrical mass, e.g. a product to be stored in a drum. We shall consider the spatial temperature profile that develops along the axis marked by r.

Let us further assume that a heat producing reaction is running and follow the developing temperature profile at various times. At time zero the temperature in the interior of the cylinder is homogeneous and equal to the temperature of the surroundings. We shall now consider one of the internal volume segments. Up to time 1 its temperature increases owing to the heat production. The same happens with the immediately adjacent volume elements since they naturally comprise the same reacting material. In the absence of a temperature gradient, no heat is exchanged between the segments; adiabatic conditions prevail. The only volume element that loses some heat to the surroundings in the initial phase is the outermost; thus, its temperature lags somewhat behind the temperature of its nearest neighbor on the inner side so that gradually some heat also flows from this to the outside.
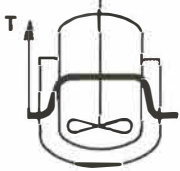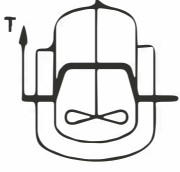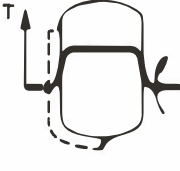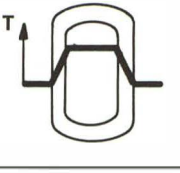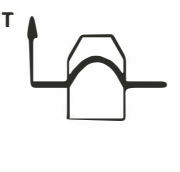
| | Cases | Heat transport | | | |
|---|---|---|---|---|---|
| | | In the mass | In the wall | In the jacket medium/ outer surface | Temperature profile |
| good heat transport | agitated vessel, low viscosity mass | good heat transport through agitation | negligible wall thickness hence low wall resistance | thermal resistance is determining |  |
| | agitated vessel, highly viscous mass | material constant V determines heat transport | negligible wall thickness hence low wall resistance | comparatively low thermal resistance |  |
| | storage tank or unstirred reactor, thermostated with liquid medium, low viscosity mass | heat transport limited by natural convection (typically: 5 times greater thermal resistance than agitated vessel) | negligible wall thickness hence low wall resistance | comparatively low thermal resistance |  |
| | storage tank without insulation, low viscosity mass | relatively good heat transport through natural convection | negligible wall thickness hence low wall resistance | natural convection of outside air and radiation limit the heat transport | |
| | insulated storage tank or unstirred reactor with empty double jacket, low viscosity mass | no natural convection since no effective temperature gradient within the mass | high heat transfer resistance (low k value) of insulated wall determines heat transport | |  |
| poor heat transport | container with solid or highly viscous mass | heat transport through conduction in the mass is determining | comparatively minor influence | |  |

Figure 33: Where is the main thermal resistance in practical cases? (marked fields = dominant thermal resistance)

This process continues progressively inward. Clearly, the further a volume element from the surface, the longer the time needed to detect the increasing temperature difference compared with the surroundings. The time that elapses until the cooling effect reaches the innermost volume element increases with the square of its distance from the surface, *i.e. the innermost volume element remains adiabatic during a time characteristic of the dimensions and heat dissipation properties of the mass.*

*The characteristic time of the heat dissipation must now be compared with the time $TMR_{ad}$ representing the heat production.* The question whether a thermal explosion occurs in a given system can now be easily answered:
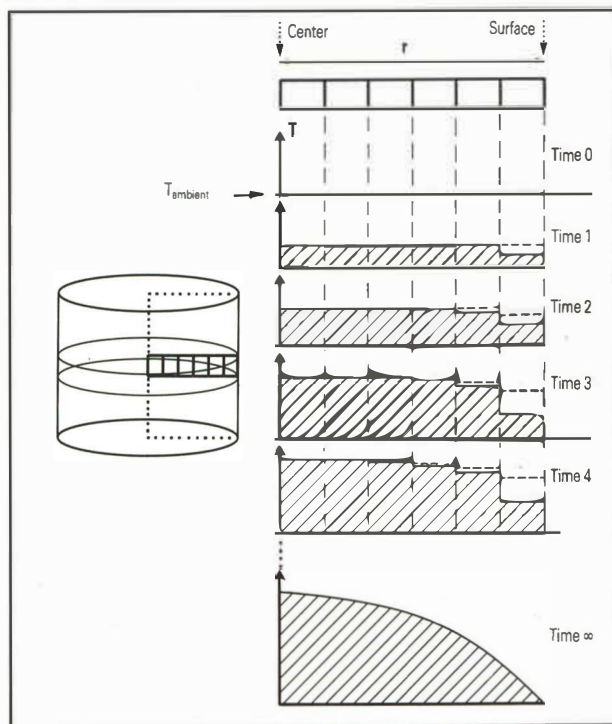
Figure 34: Model consideration for thermal conduction in a solid (see text)

If $TMR_{ad}$ is appreciably shorter than the characteristic time of heat dissipation, the innermost volume element can behave adiabatically during the whole period and a thermal explosion can develop virtually unhindered.

If, on the other hand, the heat dissipation asserts its influence considerably earlier, the development of the thermal explosion will be interrupted and a quasi-stationary state is established that is only disturbed when, e.g. the reactant consumption begins to reduce the heat production rates.

The explicit heat balance described above can be calculated by means of a computer simulation method using the concept of finite elements. A finite number of volume elements is taken into account and a heat balance equation is set up for each one using experimental kinetic data and the laws of heat conduction.

The temperature profiles shown in Figure 35 were obtained by such a calculation assuming the same decomposition reaction for each case as follows:

In case A, an initial temperature of 100 °C was selected that, as in the above model consideration, is equal to the temperature of the surroundings at the start. With the kinetic data used (zero-order reaction), it can be
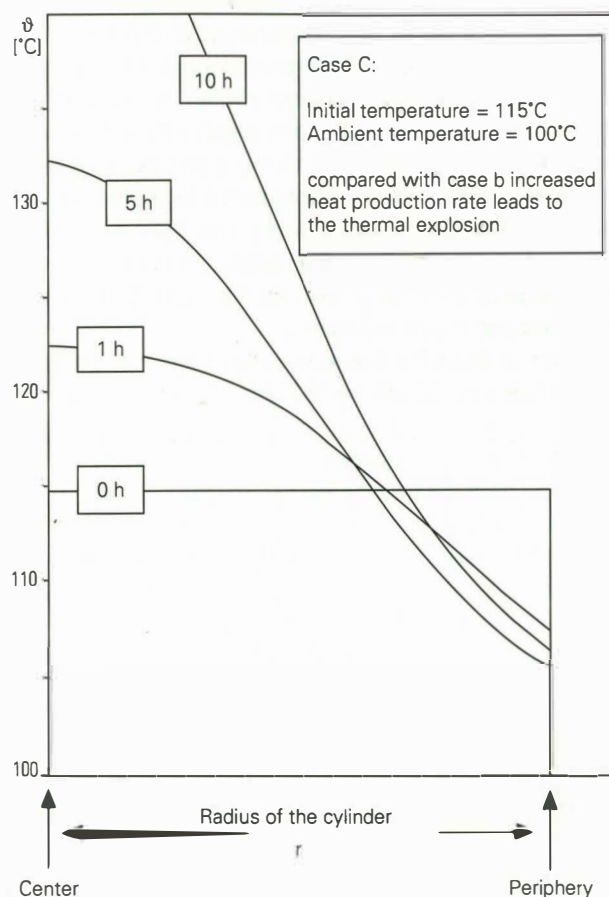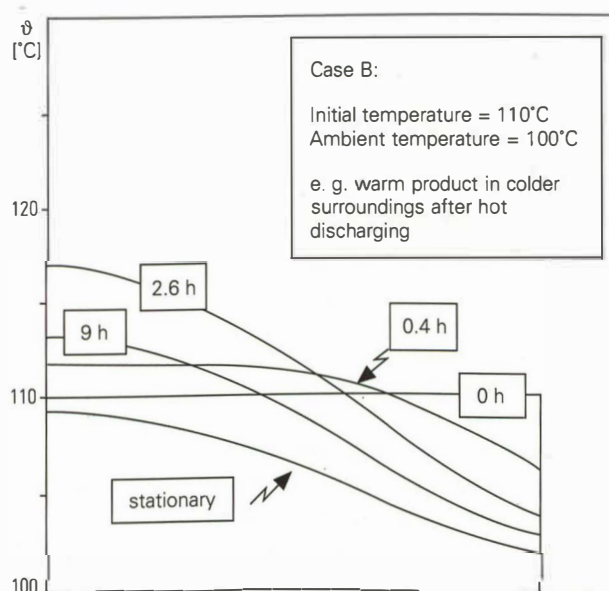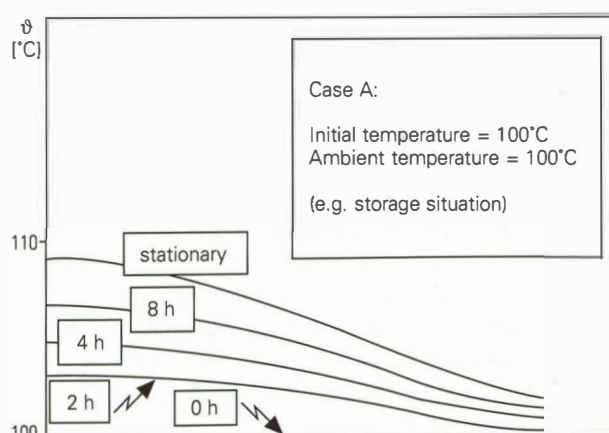


Figure 35: Spatial temperature profiles in a cylindrically shaped mass at various times (specified in hours) before the attainment of equilibrium

seen that a stationary state is established after a lengthy period of time.

In contrast, in cases B and C an internal and initial temperature greater than the temperature of the surroundings was assumed. This is a situation typical of **hot discharging,** e.g. after drying. Despite the temperature gradients already existing at the periphery, a thermal explosion occurs in case C at the center. The opposing effects, exponential temperature rise in the center and cooling at the periphery, are clearly recognizable.

Case B with an initial internal temperature of 110°C is just below the critical limit.

If the temperature profiles are considered at various times, it can clearly be seen that the center is subject to adiabatic conditions at the start. As a result, the temperature at the center rises exponentially. It is only after a certain time that the temperature gradient penetrating inward in the direction of the center becomes effective. This causes the heat dissipation to predominate over the heat production even at the center. After a lengthy period of time the stationary state known from case A is established.

In the consideration of the above cases, it is clear that a change, e.g. in the initial temperature causes a relatively sharp change between harmless and accelerated temperature profiles. This becomes even more obvious from Figure 36 in which the time dependence of temperature profiles of a different model reaction taking place in a storage drum have been calculated as a function of the temperature of the surroundings. It can be seen that the transition between a temperature rise, scarcely noticed in practice, and a very critical temperature profile occurs within the narrow ambient temperature range of 90 to 95°C. For reactions of higher energy the transition is even sharper.

In order to illustrate the influence of the mass, Figure 37 shows the results for different volumes and tem-

| | Maximum temperature rises and associated runaway times observed in the center of the sphere | | | |
|---|---|---|---|---|
| inital spec. heat output $\dot{q}_o$ at ambient temperature $\vartheta$ | under heat accumulation conditions | | | |
| | minor | moderate | severe | adiabatic |
| $\dot{q}_o$ | $\vartheta$ | mass = 0.5 kg | mass = 50 kg | mass = 5000 kg | |
| 10 W kg$^{-1}$ | 129°C | 191°C after 0.9 h | 200°C after 0.9 h | 200°C after 0.9 h | 200°C after 0.9 h |
| 1 W kg$^{-1}$ | 100°C | 5.8°C after 8 h | 200°C after 7.4 h | 200°C after 7.4 h | 200°C after 7.4 h |
| 0.1 W kg$^{-1}$ | 75°C | 0.5°C after 12 h | 13.2°C after 120 h | 200°C after 64 h | 200°C after 64 h |
| 0.01 W kg$^{-1}$ | 53°C | | 0.7°C after 154 h | 165°C after 632 h | 200°C after 548 h |

Figure 37: Influence of the "extent of heat accumulation" on the reaction progress

peratures. Spherically shaped masses were considered as representative of various characteristic heat accumulation situations (spheres are easier to calculate than other shapes). The ambient temperatures (equal to the initial temperatures) were so selected that the initial heat outputs differed by an order of magnitude each time.

It is first apparent that under severe heat accumulation conditions or at high initial reaction rates, there is no difference between the calculated runaway times and the adiabatic times. In these cases the heat dissipation is too slow in comparison with the adiabatic runaway times and can not influence the reaction profile.

It is not until small amounts of substance or small initial heat outputs are considered that the heat dissipation begins to become active in the center and lowers the adiabatic temperature rise.

To assure the safety of a given situation it is thus important that the temperature is matched to the prevailing heat accumulation conditions or the duration of exposure is sufficiently short (conditions at the left and bottom of the table).

### 3.3 Critical heat outputs and characteristic response times of the heat dissipation in unstirred materials

#### Solids

For a non-isolated 200 l drum containing a solid that undergoes an energetic reaction, the following two simplifications are reliably applicable:

a. The influence of the heat transfer at the periphery (natural air convection) is neglected in comparison with the heat conduction in the interior (valid in general for large volumes and non-isolated walls).
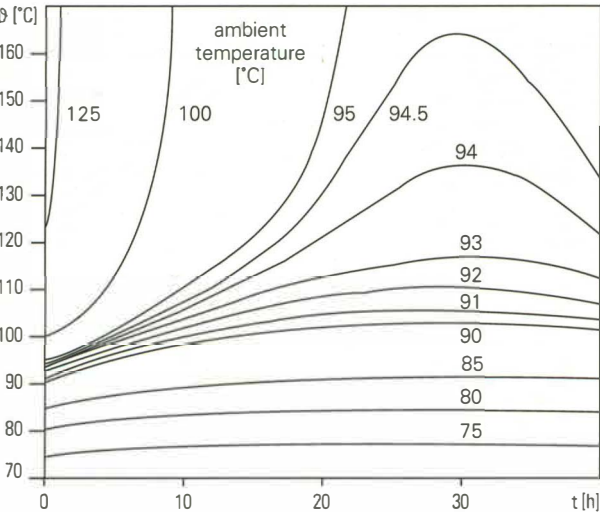


Figure 36: Temperature profiles under heat accumulation conditions (center of a cylinder) as a function of the ambient temperature (= initial temperature), (first order reaction with $\Delta T_{ad} = 200\ °C$, amount = 5 kg)

b. Neglect of the reactant consumption (reliably applicable to the initial phase of highly energetic reactions which determines the course of events; the special case of autocatalytic reactions, where this does not hold, will be discussed separately).

With these assumptions, the critical heat output can be specified by a formula due to Frank-Kamenetskii (Figure 38).

$$\dot{q}_{crit} = \delta_c \cdot \frac{\lambda \cdot R \cdot T_o^2}{\varrho \cdot r^2 \cdot E_a} \qquad [W\,kg^{-1}]$$

| | | typical values: |
|---|---|---|
| $\lambda$ | thermal conductivity | $0.1\ W\,m^{-1}\,K^{-1}$ |
| R | $8.314\ J\,mol^{-1}\,K^{-1}$ | |
| $\varrho$ | density | $1\,000\ kg\,m^{-3}$ |
| r | radius [m] | |
| $E_a$ | activation energy | $100\,000\ J\,mol^{-1}$ |

$\delta_c$ is a dimensionless criticality parameter that assumes the following values as a function of the geometric shape:

$\delta_c = 3.32$   sphere of radius r (greatest possible value)
$\delta_c = 0.88$   layer insulated on one side with a thickness r much less than the other two dimensions (smallest possible value)
$\delta_c = 2.5$   cube (r = half of side length)
$\delta_c = 2.37$   cylinder of height = 3 × radius r

Figure 38: Critical heat outputs in a solid following Franck-Kamenetskii

**Liquids**

Recent work has provided evidence that for unstirred liquids in actual reactors the natural convection can make a considerable contribution to the heat transport in the reactor interior. The effectiveness of the convection is greatly dependent on the temperature difference between the peripheral and the center zones. It is practically independent of the volume and directly proportional to the material characteristic $\mathbf{V}$ as in the case with agitation (see section 2.3 and Figure 17).

With a temperature difference of 10 K (a value which by way of comparison would also appear in a solid with an ongoing highly exothermic reaction under conditions of a heat balance just below the critical borderline), the heat transfer of the liquid due to natural convection in the interior of the reactor ($\alpha_i$ cf. page 20) is of the order of 10 to 20 % of the corresponding value in an agitated vessel under standard conditions.

However, this requires that no controlling thermal resistance appears *in the container wall* (cf. Figure 33). The resistance in the wall must be so small that it does not contribute to any temperature rise of the reactor contents and the wall thus *remains at the initial temperature*. This is the case if it behaves like a vessel thermostated with a liquid heat transfer medium. Even with an uninsulated tank, air convection at the outer surface causes a comparatively rapid heat removal. On the other hand, in the case of a reactor with an insulated wall or an empty double-wall jacket, the wall temperature would closely follow an increase

in the internal temperature. In such cases the influence of convection would be absent.

A summary of the critical heat outputs for various cases is shown in Figure 39. In this figure the critical time ($TMR_{ad}$), temperature and heat production for a particular kinetic model are given for a corresponding vessel size and design. The same kinetic model as before has been used to compile the data. For example, conditions under which the reaction takes place in a $1\,m^3$ isolated storage tank and with an initial temperature of $141\,°C$, where the heat production rate is about $50\ mW\,kg^{-1}$, would cause the system to selfheat to a maximum heat production rate in 7 days.

### 3.4 Consideration of the heat accumulation risks in practice

An initial step to overcome heat accumulation situations in actual practice involves the *identification* of the critical material mixtures, process steps and apparatus design. This is particularly important since heat accumulation hazards often appear in rather peripheral units or process steps that are not an obvious focal point of the process risk analysis. For example, the operation of melting of a reactant or the filling of a relatively large quantity of warm product often presents heat accumulation problems. In these cases, the heat balance can be unfavorably influenced by both an increase in the heat production and a reduction in the heat dissipation. Operational causes that can lead to this are shown in Figure 40. With the identification of potential heat accumulation hazards a crucial step is taken to handle the decomposition risks. A possible thought scheme is shown in Figure 41.

The *assessment* of identified heat accumulation risks is based on the type of heat balance considerations described in the preceding sections. In doing this type of assessment, it is first necessary to estimate which heat outputs or runaway times are considered as critical (cf. section 3.3). The second step is then to do the experimental determination or estimation of the expected heat outputs of the particular material mixture (see section 3.5). Next when the assessment of the overall hazard (risk) to an operating unit is made it is necessary to make a clear distinction between plants with monitoring capabilities and those without. The following statements will provide guidance when assessing risks associated with heat accumulation.

- In situations such as storage or transport in which the chemicals are not the direct responsibility of the plant and neither monitoring nor correction measures are possible, the heat balance must clearly and over the long term lie on the favorable side.
- Operations where severe heat accumulation conditions exist and the heat balance is supercritical must be given consideration when the runaway takes a long time to occur. In such cases, the time can be enlisted as a second assessment criterion if an oper-
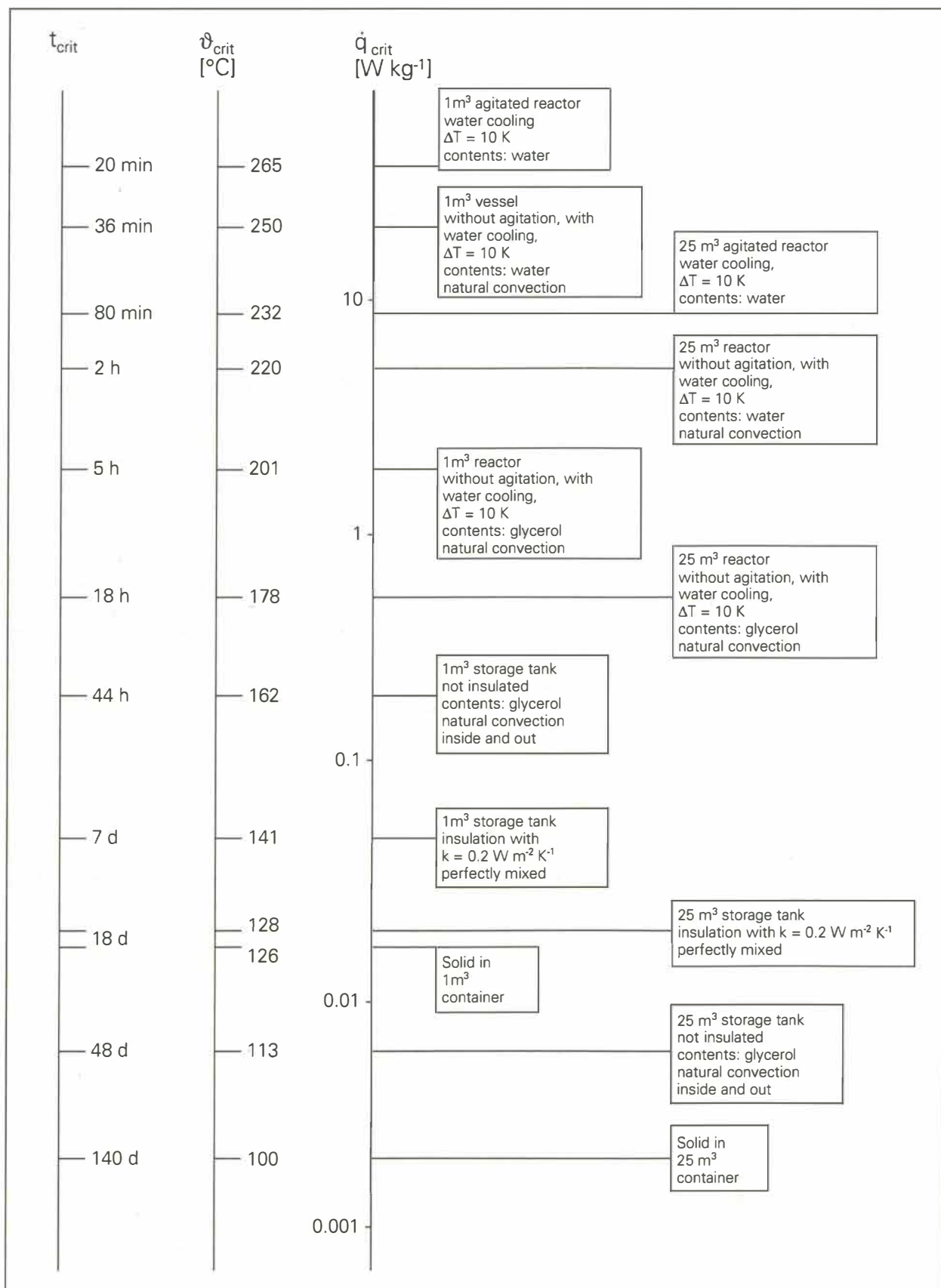
Figure 39: The orders of magnitude of critical heat outputs have been estimated for several illustrative situations. The numerical values are based on many assumptions and cannot be used indiscriminately for precise assessments. As an illustration, the temperatures $\vartheta_{crit}$ of a selected model reaction $(E_a = 100000 \; J \; mol^{-1})$ are given at which it attains $\dot{q}_{crit}$ under different situations. $t_{crit}$ is the calculated time that just corresponds to $TMR_{ad}$ of the reaction at this temperature; it is a measure of the maximum allowable response time of the cooling for subcritical behavior

ational control is possible. Here – with consideration of an appropriate safety factor – the expected runaway times ($TMR_{ad}$) can be compared with the operational exposure time. With these values known, the control intervals as well as the time needed for the discovery and correction can be determined (cf. section 2.6). For the usual plant conditions, expected runaway times of more than one day could be considered acceptable. If these $TMR_{ad}$ values lie between several hours and one day, intensive monitoring, for example, is necessary. This type of analysis requires a knowledge of possible deviations in the product quality or an unforeseen caking of relatively large amounts, etc. as trouble areas. Even shorter times can be perfectly acceptable in special cases such as those involving continuous systems with automated correction measures.

The specification of runaway times used here to characterize the thermal behavior of substances has the advantage over the more abstract terms of heat balance in that it gives the plant supervisor a direct indication, at least within an order of magnitude, of how much time he has available to take the requisite actions.

He should be aware, however, that estimated runaway times can be very sensitive to influencing factors. Not only a small change in temperature but also a slight shift in the kinetics, e.g. as a result of fluctuations in the product quality can greatly influence these times. In connection with the safety considerations, however, nobody would rely on a "best case" calculation. Thus,

consideration of the order of magnitude of the time represents a valuable orientation and decision aid.

## 3.5 Experimental methods to characterize decomposition reactions

The characterization of the thermal behavior of materials and reaction mixtures is often carried out in a specialized test laboratory. The following overview of experimental methods is primarily intended for the nonspecialized reader for whom the operational application of the experimental results is of prime importance. He should primarily be aware of the informative value of data determined according to various measurement principles and know their possibilities and limits. In keeping with the aim of this publication, the prime goal is to convey insights into physicochemical relationships that can be used in different ways by individual companies and, depending on the situation to be assessed, can be incorporated to a relatively large extent in test procedures or made use of periodically.

This section is thus organized as follows. Firstly, several *fundamental considerations* applicable to all types of experiments will be described. Next, an insight into the various *measurement principles* is given. As a first step towards an understanding of the informative value of experimental results such an insight is important. The laws governing the heat balance discussed earlier naturally also apply to the measuring instruments and it is important to be aware of the extent to which the experimental results are independent of the
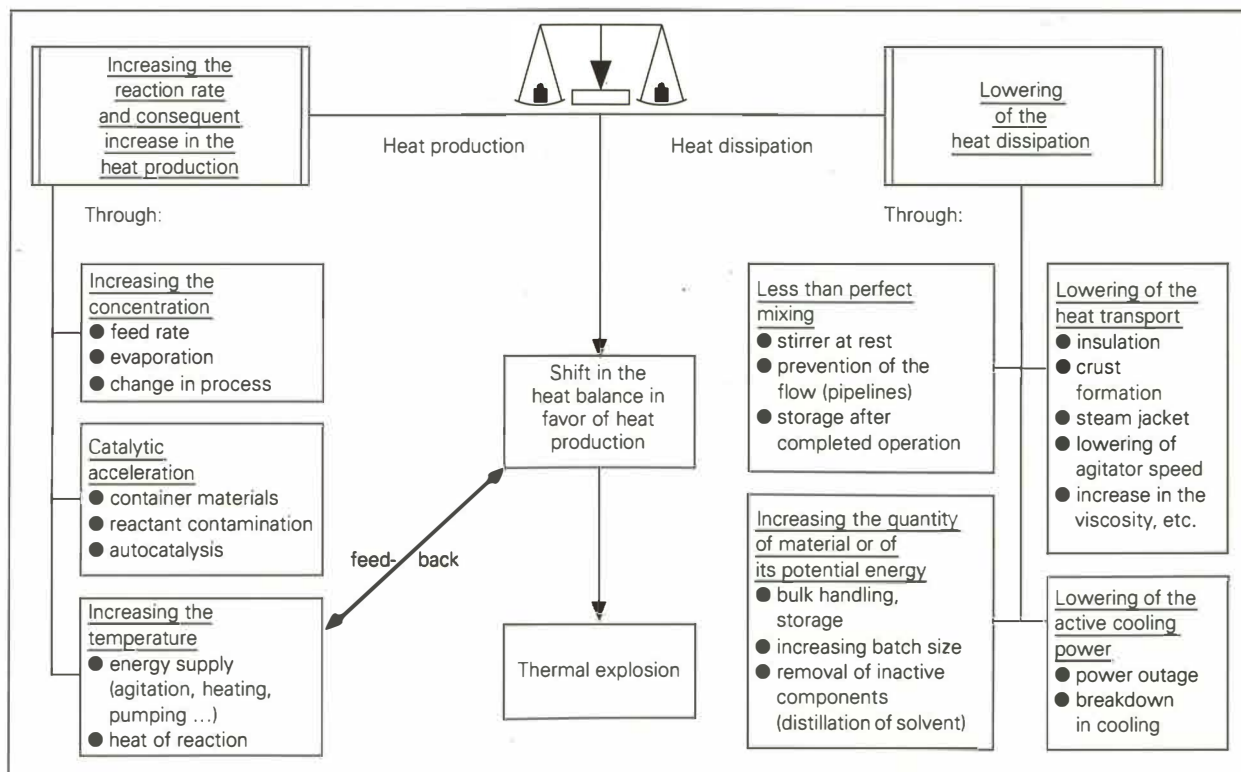


Figure 40: Identification of the phases critical in regard to heat accumulation

size of the samples, or what *scale-up consideration* is necessary in order to bridge the sometimes dramatic differences between the heat balance in the laboratory and that in the plant. Finally, in a third section the various measurement techniques classified according to their temperature regime (isothermal, adiabatic or isoperibolic), their results and the interpretation of these results are discussed from a more practical standpoint.

### 3.5.1 Fundamental points regarding experimental techniques

First let us remind ourselves of the demand already mentioned several times that for a prediction of the thermal process safety it is not sufficient to investigate the process conditions that normally appear. Rather, a measure must be found of how much of a deviation, e.g. of a process parameter is needed to trigger a hazardous runaway reaction. In addition, the time dependency of the runaway is also needed. In order to gain information on an undesired reaction, every effort must be made to design the experiments such that the undesired process in question actually runs. Thus it should be possible, if necessary by means of an inter-/ extrapolation, to state the following: "Under the *conditions of measurement* x', y', an undesired reaction proceeds at rate z, hence for the *plant conditions* x, y the following can be deduced...". This is to be preferred to a less informative experimental result of the type "While exposing the reaction mass for x hours to temperatures of y degrees, as envisaged in the plant procedure, no exothermicity could be found". In the context of risk analysis the positive experimental results in regard to the decomposition reaction allow a direct statement of the consequences. From the relative proximity of the measurement conditions to the plant conditions it is possible to make a pronouncement regarding the probability.

In the thermal characterization of reaction masses it must be noted that these often contain volatile fractions. With all types of measurement in which a quantitative result is required, this makes the use of *pressure resistant* measuring vessels imperative. The evaporation of individual volatile components would disturb the experimental result in two ways: the heat changes to be measured due to the chemical reactions would be masked by the endothermic heats of evaporation and the identity of the samples would be lost. Open measurement vessels are suitable only if the thermal behavior of nonvolatile samples has to be investigated.

This is particularly the case in assessments of drying operations or, e.g. in the curing of resins. In addition, the retention of gaseous products can also influence the thermal kinetics.

The information provided by an experimental result is only as good as the extent to which the sample repre-

| | QUESTIONS | KEY THEMES |
|---|---|---|
| **Hazard identification** | **A.** With what mixtures of substances can any hazard at all appear on the basis of the **energy potential?** | • Chemical properties expected from the structural formulae (high energy groups, reactive partners, high concentrations, e.g. melting) <br> • General thermogram (temperature programmed thermal analysis) |
| | **B.** In what process phases (positional and chronological) must the appearance of pronounced **heat accumulation conditions** be anticipated? | • Figure 40 |
| | **C.** What **malfunctions** can cause a breakdown in the cooling, the perfect mixing or the material flow leading to heat accumulation conditions? | • Figure 40 |
| | **D.** Listing of those process phases with potential heat accumulation hazard | • Combination of points A (energy content) and B/C (operating factors) |
| **Hazard assessment** | **E.** Starting from normal conditions, how easily can critical states be reached? (Through deviations in the temperature, the quality of the participating reactants, the holding time, the heat transfers, etc.) | • Thermokinetic data (heat output as a function of temperature, reaction mechanism, time expected to thermal runaway) <br> • Operating conditions <br> – maximum attainable temperature <br> – exogenic heat sources <br> – extent of possible heat accumulation (amount, insulation, etc.) |
| | **F.** What **process parameters** are critical in the individual process phases? | • Selection from the above criteria, system parameters that can be influenced, malfunction |
| **Measures** | **G.** Constructional and design measures to **avoid** heat accumulation hazards | • Small hold-up, large heat capacity, hot water instead of steam, feed control of reaction |
| | **H.** **Measurement** and **alarm systems** for the critical process characteristics; setting of limit values | • Criteria to recognize the deviation, required advanced warning time, required action time |
| | **I.** Preparation of possible **contingency measures** | • Emergency actions, emergency power supply, reliability, responsibilities <br> • Consequences of emergency measures such as flooding <br> • At what position can a process be aborted not according to plan and what directions must be heeded here? |

*Figure 41: Consideration of the heat accumulation hazard in risk analysis*

sents the plant samples to be assessed. The analysis of isolated reactants and products is often poorly suited to the assessment of reaction masses. Cases are known in which solvents etc. have a powerful influence on the reactivity of compounds. For example, nitroaromatic compounds decompose in sulfuric acid appreciably faster than in the pure state. It is also common practice to investigate the influence of possible contaminants (vessel material, rust, water, impurities, etc.) on the course of the reaction by comparison of samples with and without contaminants. Since the principal task involves the identification of a possible influence, it is generally advisable to add more contaminants than is necessary.

Like the sample identity, the actual measurement is also subject to experimental fluctuations and systematic errors. It is therefore necessary to be aware of these limitations in the interpretation of the results. However, the limits of the experiments must also be compared with the normally large safety factors. It makes absolutely no sense, for instance, to know a heat of decomposition more accurately than $\pm 10\%$ if a value twice or half as large would make no difference to the safety assessment. What is important is to identify those cases in which the sensitivity analysis shows that the safety of the process is borderline. In such cases, a critical safety report, for example, must be supported by two or more types of measurements and the scale-up based on a number of different methods.

### 3.5.2 Measurement principles: scope and limitations

In the preceding sections it was shown how the heat output due to a chemical reaction or the time to runaway of a reaction, $TMR_{ad}$, can be used to assess the risk of a decomposition reaction in the plant environment. It was also shown that a relation exists between the two quantities in accordance with the formula in Figure 31.

The aim is thus to measure if possible one or both of these quantities. In the language of heat balance they both describe the heat production side. In order to determine this factor separately, care must be taken to rule out any influence of the second factor, the heat dissipation. In other words, the experiments would have to be so designed that as far as the heat dissipation is concerned the volume of the samples has no influence on the experimental result, i.e. no temperature gradients should appear in the sample. This is possible under two limiting conditions of the heat balance:

| | Heat balance |
|---|---|
| **isothermal limit case** corresponds to the operational case of an agitated and controlled reactor | heat production = heat dissipation; heat accumulation ($\Delta T$) = 0 |
| **adiabatic limit case** corresponds to the extreme malfunction case | heat accumulation = heat production; heat dissipation = 0 |

As we have seen, the conditions for the isothermal case in a controlled agitated reactor in the laboratory or the plant are virtually fulfilled. For the adiabatic case, however, they are only satisfied to a large extent and over a lengthy period of time in the center of a very large unstirred mass.

As solids, for example, can not be easily stirred and as the sample size is subject to limits in the experiment, the required limiting conditions can not be easily realized in the laboratory. In order to approximate in the experiment a condition that allows a measurement result that is subject to a minimal influence of the dimension-dependent heat dissipation, the following experimental techniques are employed.

### Microthermal analysis

Microthermal analysis as well as certain highly sensitive calorimeters employ the principle accredited to Boersma (Figure 42). It is distinguished by the fact that the temperature probe is installed outside the measuring vessel. The measured variable is the temperature gradient that is established *between the measuring vessel and the surroundings*[1] (or between a sample and reference vessel to compensate the energy needed for heating the heat capacities in the temperature-programmed experiment).
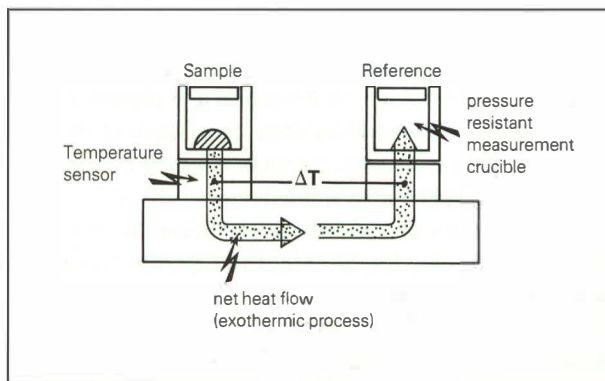


*Figure 42: Microthermal analysis*

The heat released in the sample dissipates via the thermal resistance *in the instrument.* This is calibrated with an electrical heating source or a process with a known thermal change (e.g. heat of fusion). Any heat change due to an unknown sample can then be measured quantitatively. While the heat accumulation which develops in the unstirred solid sample causes a time delay between the heat output and its measurement, detection of the total amount of released energy is unaffected.

If the sample is sufficiently small or if the rate of heat production to be measured is low, the time distortion of

---

[1] The heat flow is either established passively via a thermal resistance due to the apparatus (DTA, Differential Thermal Analysis) or in an active system the difference in the heating power needed to maintain the sample and reference cell at the same temperature in the temperature-programmed mode is determined (DSC, Differential Scanning Calorimetry).

the experimental signal is of no consequence. The delay time can also be measured and this allows correction of the delayed experimental signal. The relatively small sample quantities used in microthermal analysis guarantee sufficient temperature homogeneity within the sample and thus even high heat outputs can be measured quantitatively. (In a 10 mg sample the excess temperature in the center is around 0.5 K at a power of 100 W kg$^{-1}$.) For this reason, microthermal analysis is particularly well suited to the determination of the energy potential of a sample in a temperature-programmed measurement of the type shown in Figure 11. It has also proved its worth in practice as an isothermal measurement method.

The need for a sample representative of the operational conditions of interest places high demands on the sample preparation technique. This need, however, can easily be met even for mixtures of substances by use of microanalytical techniques. Depending on the consistency and composition of the reaction masses, the components are either weighed into the measurement bomb directly or preparation is effected on a larger scale with representative sampling.

## Adiabatic measurement principles

The second possibility to obtain experimental results under homogeneous temperature conditions and dependent only on the properties of the sample involves the adiabatic limiting condition under which no heat dissipation occurs. In the plant, it is primarily large masses that behave adiabatically over the long term. In the laboratory, adiabatic conditions must be approximated by special control techniques.

The temperature of the sample is measured and used as a setpoint value for control of the ambient temperature, i.e. the temperature gradient between the substance and the surroundings is virtually zero (Figure 43). Since in this type of measurement the controlling temperature reference is constantly changing – the controlling initial temperature of a time interval is in each case the final temperature of the preceding interval – measurement errors can cumulate over the course of time. In regard to temperature measurement and temperature control accuracy, adiabatic controls are thus very



*Figure 43: Adiabatic measurement mode*

demanding and it is important to limit the total time of the experiment. This can be accomplished by the selection of a sufficiently high initial temperature so that at any point during measurement the phenomena to be measured are significantly greater than the drift rate occasioned by the control accuracy.

Simply to lower a drift rate to below 0.01 K min$^{-1}$ places very high demands on an adiabatically controlled laboratory instrument. For a significant experiment the rate of temperature rise at the temperature set at the start must be considerably higher than the drift rate, say at least 0.02 K min$^{-1}$. For a high energy reaction this is equivalent to demanding that the experimental time be restricted to a maximum of approximately 10 hours. With weakly exothermic reactions the boundary condition mentioned is tantamount to limitation of the experiment to even shorter periods.

Since the temperature increases during the experiment, the question regarding the heating of the sample vessel is of great importance. The heat capacity of the sample vessel is of necessity coupled thermally with that of the sample mass and can not be neglected, particulary in cases where pressure vessels are used. Without special measures the sample vessel acts as a heat sink which draws energy from the sample, i.e. the temperature homogeneity requirement and the adiabatic requirement are not completely fulfilled.

A possible solution to this problem lies in the fact that the heat capacities and thermal resistances can be determined, e.g. by calibration and that a special control with specific excess jacket medium temperatures ensures that the heat needed to heat the wall ($m \cdot c_p \cdot dT/dt$) is added by the jacket medium. Another possibility involves heating the vessel wall with an appropriately controlled auxiliary heating to distribute the necessary heat as quickly and as homogeneously as possible over the vessel heat capacity. The required heating power is proportional to the time derivative of the temperature and requires special control.

Another arrangement involves design of the experiment so that the heat capacity of the vessel is wittingly taken into account and in a thermal sense added to the process mass. The measured temperature curve then no longer corresponds to the adiabatic temperature profile; however, it still contains kinetic information that can be evaluated taking the heat capacity and the weight of the vessel into account. As a measure of the extent of the influence of the vessel heat capacity, a factor, $\Phi$, is defined as follows:

$$\Phi = 1 + \frac{c_{p_h} \cdot m_h}{c_{p_s} \cdot m_s}$$

| | |
|---|---|
| $c_p$ | = specific heat capacity |
| m | = mass |
| Index h | = sample holder |
| Index s | = sample |

For an ideal adiabatic experiment $\Phi$ is equal to 1. A factor $\Phi = 2$ means, for example, that only 50 % of the heat released is used to heat the sample mass. The influence of $\Phi$ on the experimental result is discussed
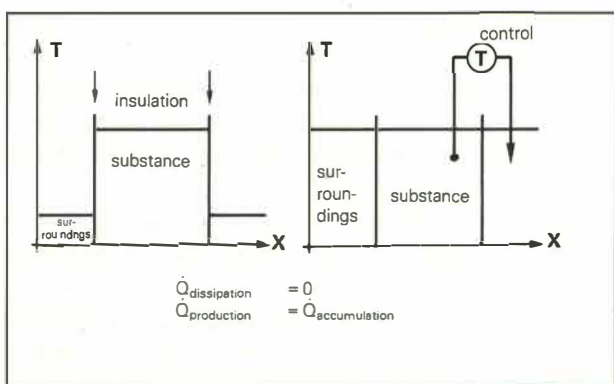
in the following subsection on the use of the experimental methods.

## Isoperibolic measurement mode

In order to achieve better handling of the samples as well as to attain a greater measurement sensitivity, the tendency is to use larger sample quantities. The price that has to be paid is a relatively severe deviation from the "pure" isothermal limiting case. As a result, the heat dissipation specific to the laboratory scale begins to exert its influence on the measurement result. Its influence must be kept within limits through careful selection of the experimental conditions or taken into account in the interpretation. Such measurements in which the temperature of the surroundings is controlled by the instrument and which involve observation of the temperature that is established in the center of the sample are called isoperibolic.

In an isoperibolic experiment the thermal resistances across which the temperature difference is determined as the measured variable are located in part in the wall of the measuring vessel and in the instrument and in part in the sample itself (Figure 44).
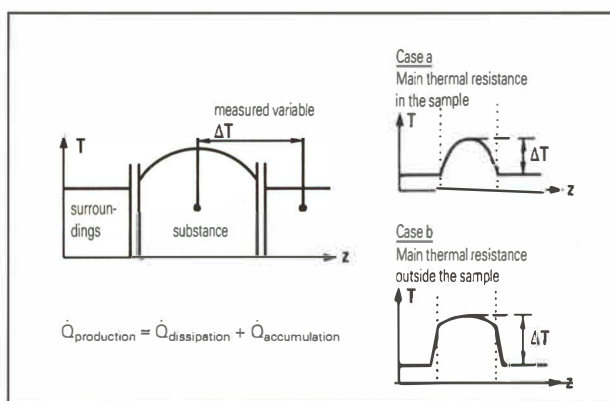


Figure 44: Isoperibolic measurement mode

The temperature gradient in the sample depends not only on the heat output of the reaction under investigation (which itself is influenced by the sample temperature profile that is established), but also on the heat dissipation properties of the sample (heat transport through heat conduction and/or convection).

Under certain conditions, isoperibolic experiments can be used so that the sample nevertheless has sufficient temperature homogeneity and a quantitative calibration is possible.

To achieve this, the main heat dissipation resistance must be outside the sample (case b in Figure 44) and it should be ensured that the heat balance of the entire system lies well below the critical condition for a thermal explosion in the measuring cell. This can be approximated with relatively small samples and by limitation of the measuring range to sufficiently low heat outputs. (A measurement arrangement with a high energy sample of 20 grams would thermally explode if a power of

ca. 15 W kg$^{-1}$ were to be released at the set measurement temperature.)

Isoperibolic experiments are thus predominantly used to identify temperature ranges where a tested sample exceeds a certain relatively low heat output. A heat output that can be realistically detected in such a way on a 10–100 g scale is of the order 500 mW kg$^{-1}$.

## 3.5.3 Application and interpretation of different test methods

In section 3.5.2 it was made clear that the performance of meaningful experiments is demanding and depends on the adherence to certain boundary conditions. In what follows we discuss the application of the methods to characterize decomposition reactions. We assume here that the demands discussed above regarding the experimental technique are met. Figure 45 summarizes features, suitability and limits of the various measurement principles and temperature regime.

## Measurements with linearly increasing temperature

In the temperature-programmed measurements, the container with the substance and possibly a reference vessel (empty or filled with a thermally inert substance) are heated in a furnace with a linear heating rate. Owing to the thermal inertia of the sample container its temperature lags somewhat behind the furnace temperature. The measured variable is $\Delta T$, the temperature difference between sample and reference or between sample and furnace temperature. If an empty reference vessel is used and in the absence of a thermal change in the sample, $\Delta T$ is determined during the heating cycle by the heat capacity of the sample. If a thermal process occurs, e.g. melting of the substance or a chemical reaction, the measured variable $\Delta T$ changes. In the quantitative measurement setups (see previous section), the energy needed to heat the sample or the heat output emanating from it can be calculated from $\Delta T$ with a calibration factor.

As can be seen from Figure 46, the signal thus obtained is the sum of heat capacity effects and the required heat outputs of the sample. Temperature-programmed thermal analysis thus requires an interpretation in which the baseline of the thermochemical effects is defined within the region of the signals. It is usually undertaken by the experimenter and embodies, particularly as far as the "start" of the interpreted signal is concerned, a certain license. The areas under the curves can be evaluated as the energy potential of the observed reactions.

Temperature-programmed thermal analysis is particularly suitable to obtain an overview of the temperature ranges in which a sample exhibits thermal activity and the magnitude of its energy (cf. section 1.9). Typically, mixtures of reactants prepared in the laboratory are

| | Factors influencing the experimental results | | Principal suitability of the results |
|---|---|---|---|
| | determined by the measurement mode (ignoring the measurement accuracy) | determined by the substance property | |
| temperature programmed measurement | heating rate | time and temperature dependence of the heat output | determination of energy potentials; temperature ranges of thermal activity |
| isothermal measurement (at given temperature) | | heat output as a function of time | thermal kinetics, heat output at constant temperature |
| isoperibolic measurement (at given ambient temperature) | sample size, insulation of the vessel, arrangement of the temperature sensor | time and in part temperature dependence of the heat output. Physical properties such as thermal conductivity, density, $c_p$, convection | boundaries of the critical conditions of the laboratory experiment, empirical scale-up rules |
| adiabatic measurement (at given initial temperature) | heat capacity of the vessel | time and temperature dependence of the heat output | temperature-time profiles in the (limited) adiabatic state of the laboratory experiment |

Figure 45: Comparison of measurements with different temperature controls

investigated. It is often of particular interest to take samples of a chemical process at different times (e.g. during investigation by reaction calorimetry) and to compare their thermograms.
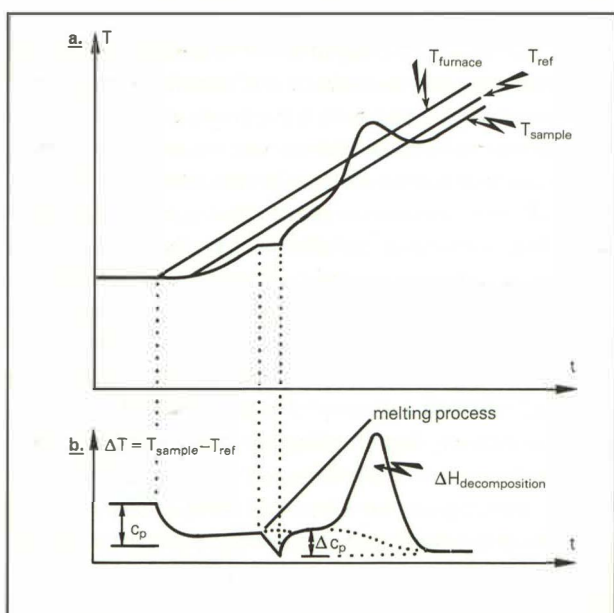


Figure 46: Temperature programmed measurement (a) with quantitative evaluation (b)

### Measurements with isothermal temperature control

The heat outputs $\dot{Q}$ of a (decomposition) reaction depend on the *temperature* and the *reaction conversion* with time. A knowledge of these two influencing factors is necessary for a complete description of the decomposition kinetics. The isothermal measurement mode has in the first place the advantage that it separates the two factors by allowing the temperature to be kept constant in the experiment and the heat output to be followed as a function of time. The temperature influence can then be obtained by comparison of

several *isothermal* curves measured at different temperatures.

Figure 47 shows various types of results of isothermal measurements. Two cases are represented. In the first case, the heat production is greatest at the start and then steadily declines (reaction of "nth order", Figure 47a). In the second case, an acceleration of the initial heat output with time and the appearance of a maximum is observed (Figure 47b). In typical industrial reaction masses, the second case occurs quite often.

Although the mechanistic chemistry of such reactions has been determined in only a few cases, this behavior can be explained with an *autocatalytic* kinetic model, and the concept "formal autocatalysis" is often invoked to characterize such behavior. In addition to the case shown in Figure 47b, an acceleration of the heat output with time by a factor between 3 and 10 is typical. There also exist cases where, during an obvious induction time, practically no heat is released and then a very sharp acceleration (chain reaction) is observed (Figure 47c). The induction times of such reactions show an exceptionally large temperature dependence.

Such clearly defined "autocatalytic" behavior is naturally also important for the safety of a chemical plant
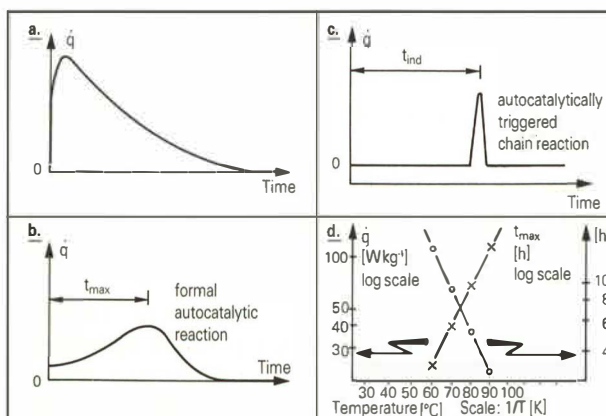


Figure 47: Results of isothermal thermal analysis

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simply because a stable plant situation can be changed into an unstable state by ageing alone. Once a chain reaction is initiated in the plant, the time between the first indication and the thermal explosion is often much too short to allow the use of effective counter-measures. Hence, particular attention must be given to the identification of these rather seldom cases (examples, see Figure 48) in order to obtain a picture of the effects and induction times expected. Especially important in this case is the question of possible catalytic influences from materials of construction. These often have a large effect on possible autocatalytic induction times.

| | Possible catalyst |
|---|---|
| Benzyl chloride and trace iron | HCl/FeCl$_3$ (Friedel-Crafts reaction) |
| Polymerization of methyl acrylate | chain reaction |
| Hydrolysis of cyanuric chloride | HCl |
| Decomposition of ammonium bisulfite | ? |
| Decomposition of ethylene dicyanide | HCN |

Figure 48: Examples of systems with pronounced autocatalytic behavior

Let us now return to the cases shown in Figure 47a and 47b and investigate the temperature dependence of the experimental results obtained under isothermal conditions for a single reaction step.

Even with formal autocatalytic reactions, it is readily apparent that the dependency of the curve shape on the temperature usually follows the Arrhenius equation. In other words, with increasing experimental temperature the time until the attainment of a selected reference point (for example the maximum) is shortened by a factor equal to that reflecting the increase in heat output of the observed curve point (see Figure 47d). As a result, the area under the entire curve corresponding to the heat of reaction (heat output multiplied by time = $\Delta h_R$) remains constant within experimental error. If the logarithm of the above-mentioned factor is plotted as a function of the reciprocal of the temperature of the isothermal measurement as in Figure 47d, a temperature dependence corresponding to the Arrhenius equation is obtained which can be used to estimate heat outputs at temperatures lower than those accessible by experiment. The uncertainty of such an extrapolation becomes greater the wider the temperature range to be covered. In particular, the possibility that another reaction is rate limiting in the lower temperature range must be taken into consideration. In many cases this would be known from temperature-programmed measurements. The amount of effort needed to safeguard against the estimated heat outputs is again greatly dependent on the operational problem. If the estimated heat outputs lie well below that identified as critical for the plant, further clarification is unnecessary. If not, either a measurement using highly sensitive calorimetry or an indirect determination of the

isothermal heat change rates is advisable for purposes of confirmation.

The appearance of several thermally separated, consecutive reaction steps detected in the temperature-programmed measurements is usually better investigated by observation of a series of isothermal measurements.

## Indirect determination of the isothermal heat outputs

Each thermal change under isothermal conditions corresponds to a chemical conversion. The decomposition reactions to be assessed generally originate from a substance of known chemical identity. With the aid of, for instance, the energy of the entire conversion known from temperature-programmed thermal analysis, a simple calculation (see example in Figure 49) based on the analyzed *content loss* after a selected thermal ageing time can be used to draw conclusions regarding the heat change. Since the isothermal ageing in regions of low chemical activity of the sample can be extended by any length of time, this indirect method allows very high "sensitivities" to be achieved. In order to obtain significant information and to eliminate the complicating influence of the chemical conversion on the reaction kinetics, it is advisable to select ageing temperatures and times at which the content loss is noticeable but has not progressed too far.

Example 1:
Total energy potential 720 kJ kg$^{-1}$

Content loss at
100°C (analysis)          1 % h$^{-1}$

$$\rightarrow 7.2 \text{ kJ kg}^{-1} \text{ h}^{-1} \rightarrow \dot{q} = 7200 \; \frac{Ws}{kg} \cdot \frac{1}{3600 \text{ s}} = 2 \text{ W kg}^{-1}$$

Example 2:
Total energy potential:  720 kJ kg$^{-1}$
Residual energy potential after
the thermal loading
(e.g. 15 h at 100°C):      600 kJ kg$^{-1}$

$$\rightarrow \dot{q} = \frac{120\,000 \text{ Ws kg}^{-1}}{15 \cdot 3600 \text{ s}} = 2.2 \text{ W kg}^{-1}$$

Figure 49: Transformation of chemical to thermal conversions

A particularly simple form of the indirect estimation of the heat output involves comparison of the temperature-programmed thermograms before and after the isothermal heat ageing (determination of the so-called "residual heat"). Again conclusions can be drawn regarding the average heat changes during thermal ageing on the basis of a decrease in the thermal potential during the conditioning period. This decrease is normally overestimated slightly in order to err on the side of caution.

## Interpretation of isothermal measurement results

The heat outputs needed for the safety analysis and their temperature dependence (cf. Figure 47d) follow directly from the isothermal measurement results. The question now has to be asked regarding which of those measured heat outputs during the isothermal experiments should be selected for considerations of the heat balance or for the estimation of the adiabatic runaway times. It should be remembered here that in an adiabatic temperature profile the greatest influence on the runaway time is during the *initial phase* of the thermal conversion.

For thermal kinetics of nth order (Figure 47a), use is thus made of the *maximum heat output* at the start. This approach, depending on the total energy of the reaction, gives a realistic to somewhat conservative (neglect of the reactant consumption) estimation of the adiabatic runaway time[2].

If the initial value of the heat output were to be used for formal autocatalytic reactions, the calculated runaway time would be too long. This is because in addition to the increase in the heat production due to rising temperature an accelerated effect through the change in ageing with time is effective. In a precautionary interpretation for self-accelerating systems, the safety analysis should be based on the *maximum* heat output determined under isothermal conditions. This assumption is conservative at the start where the true heat production rate is lower than that at the maximum occuring some time after the thermal exposure. However, the assumption made can also be justified on the basis that the thermal prehistory under plant conditions is less clearly defined than in the experiment.

In principle, a series of isothermal measurement curves provides complete information on the thermokinetic behavior of a substance. With this type of measurement the temperature profiles for any conditions can be calculated with explicit use of the temperature and time dependencies. As a rule, such additional work is not normally justified and the calculated curve profiles simulate rather an accuracy that is not only generally unnecessary but also unrealistic for safety analyses owing to the spread in the plant samples and error sources in the experimental techniques.

## Adiabatic measurement methods

In contrast to the isothermal experiment, in adiabatic measurements the two parameters that determine the heat output, the temperature and the reaction conversion, vary at the same time. The progress of the reaction causes the temperature to rise and this increase in temperature in turn increases the reaction rate. As long as the experimental conditions are really adiabatic ($\Phi = 1$), this has the advantage that the temperature-time curve obtained is, in principle, obtained with a single measurement. Implicitly, these measurements also contain information concerning the reaction mechanism and its temperature dependence. Curves such as those shown in Figure 32 are obtained and the runaway times $TMR_{ad}$ can be read off directly.



1) zero order kinetics

2) first order kinetics
   with high $\Delta T_{ad}$

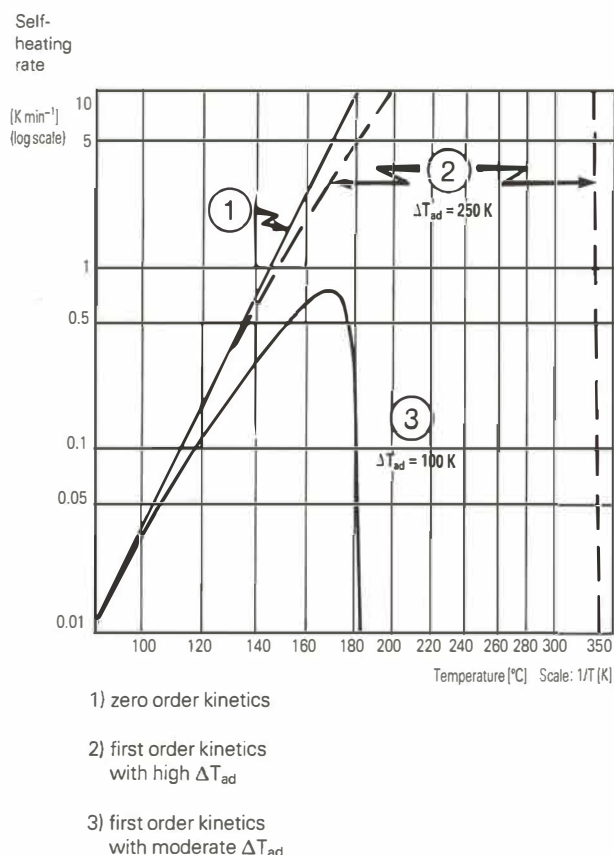3) first order kinetics
   with moderate $\Delta T_{ad}$

*Figure 50: Self-heating rates in an adiabatic experiment*

For interpretation of the data, again a linear representation of the Arrhenius equation can be considered, but this time the rates of temperature rise are plotted on the ordinate. In Figure 50 the self-heating rates of an *ideal adiabatic* experiment are shown linearized. The measurements begin at the temperature (85°C) at which the self-heating rate of 0.01°C min⁻¹ is exceeded. During the time of measurement, the temperature rises. The rise in the rate of reaction and the corresponding rate of temperature rise also increase, initially according to the Arrhenius equation. The smaller the total temperature rise potential, the earlier the decelerating influence of the reactant consumption becomes noticeable. The activation energy $E_a$ can be read off from the initial slope of the curve and this allows extrapolation to other temperatures and the conversion of the initial rates of temperature rise into heat outputs and runaway times $TMR_{ad}$.

In practice, this type of analysis is often complicated by the fact that several reaction steps influence the experimental result. Moreover, for autocatalytic mechanisms, the initial slope of the Arrhenius diagrams shown in

---

[2] Depending on the time response of the instrument, the initial value is not known exactly since equilibration must first occur.

$$\dot{q}_{T_o}[W\,kg^{-1}] = \left[\frac{dT}{dt}\right]_{T_o} [K\,s^{-1}]\cdot c_p\,[Ws\,kg^{-1}\,K^{-1}]$$

$$\dot{q}_{T_o} = \dot{q}_{T_{ref}}\cdot exp\left[-\frac{E_a}{R}\cdot\left(\frac{1}{T_o}-\frac{1}{T_{ref}}\right)\right]$$

$$TMR_{ad} = \frac{R\,T_o^2}{\left[\dfrac{dT}{dt}\right]_{T_o}\cdot E_a}$$

cf. Figure 6

Figure 47d is steeper than expected from the activation energy and this can lead to expectations of heat outputs that are too low, particularly in extrapolations to lower temperatures. Data of autocatalytic reactions can thus not be extrapolated in a simple manner.

With highly energetic reactions and high initial temperatures, rates of temperature rise are sometimes attained in the later stage of the adiabatic profile that can no longer be followed by the control system. In addition, the measurement vessels can rupture. In such cases either the investigation is restricted to the initial phase of the reaction or a high $\Phi$ factor is selected intentionally (cf. p. 42). Figure 51 shows, for example, the influence of the $\Phi$ factor on the experimental result. The measured heat outputs are reduced by the factor $\Phi$ and this causes a parallel shift in the lines for the values without reactant consumption. The total temperature rise is also smaller by $\Phi$. As a result of the effectively smaller temperature rise, the kinetics of the event are also distorted in the measured curves. The influence of the reactant consumption becomes noticeable quicker than with a smaller $\Phi$. This influence due to $\Phi$ can be back calculated only by setting up formal kinetic models, but complicated signal structures and complex reaction mechanisms impose limits to this.

## Isoperibolic measurement mode

In this measurement mode the temperature difference $\Delta T$ between the sample and the surroundings that results from the difference between heat production and heat dissipation in the given isoperibolic system is followed for a relatively long time. Here, sooner or later, either a decay in $\Delta T$ as a result of the reactant consumption appears (subcritical heat balance) or a thermal explosion occurs in the measuring vessel (cf. Figure 52). By repetition of the experiments at different temperatures, e.g. in steps of 10 K, the highest furnace temperature is determined at which the self-heating is not more than, e.g. 2 K. By way of convention the determined temperature is called the *limit temperature* of the experiment.

In the reporting of such limit temperatures the selected experiment and the sensitivity of the experimental result must be specified so that the scale-up factors between experiment and the situations to be assessed can be taken into account in the interpretation.

The isoperibolic measurement mode has been in use for over 30 years. To assess concrete situations,
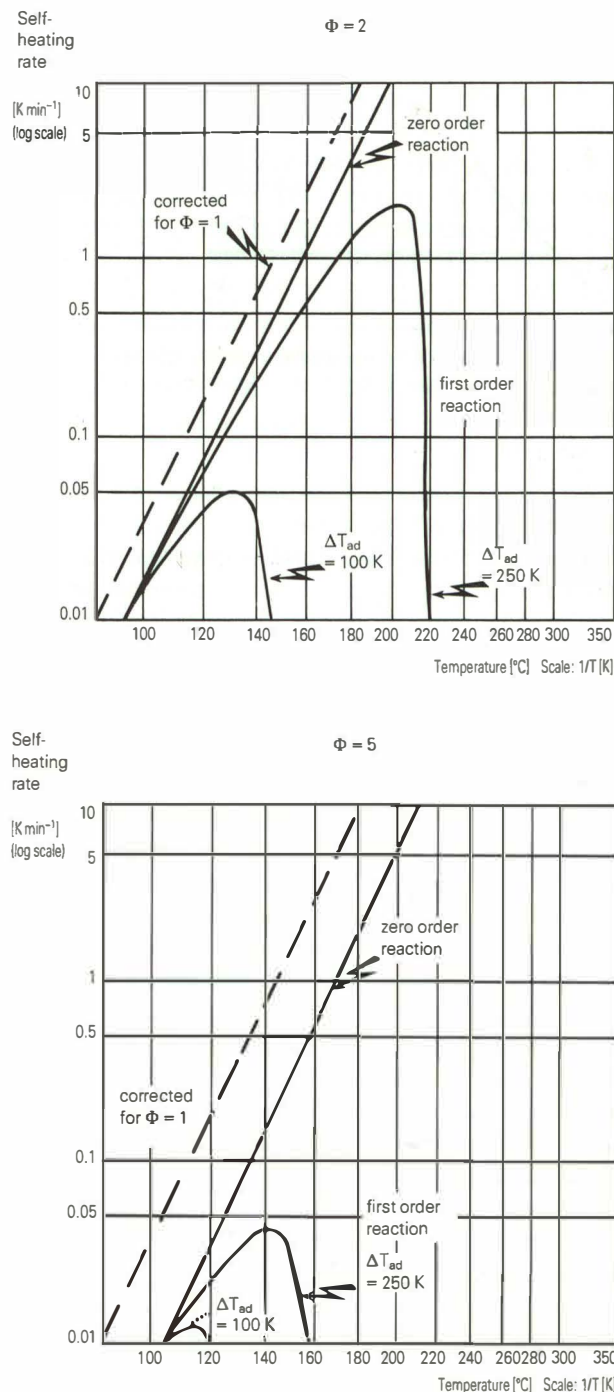




*Figure 51: Influence of the heat capacity of the vessel (factor $\Phi$) on results of adiabatic measurements (cf. Figure 50)*

"safety margins" are often defined. Thus, for example, for the assessment of drying a "maximum allowable heating medium temperature" is specified which is below the experimental limit temperature by a given amount specified in degrees.

Above all in the description of the test results, those temperatures at which a certain experiment starts to exhibit exothermic effects are often called "onset temperatures" or temperatures of the "first exothermicity". This can be misleading if it is also implied that such temperature values are material constants and
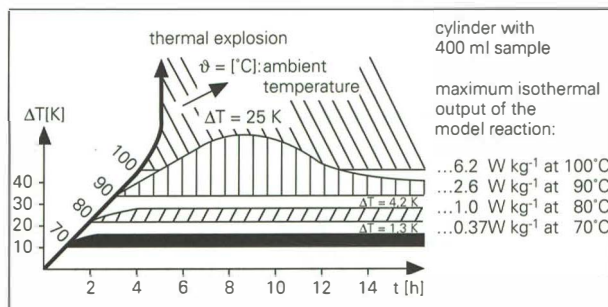
*Figure 52: Isoperibolic measurement series (three-dimensional) representation, first order reaction with $\Delta T_{ad} = 200$ K)*

that a reaction does not occur below these temperature limits and "begins" above them.

The reader of this article naturally knows that this is not the case. On the contrary, some chemical activity occurs at all temperatures. It is just that the rate of these reactions depends on the temperature. In order to define which rates and therefore which temperatures are critical, information regarding the heat dissipation is also needed before a decision in a given operational situation can be made.

As long as the experimental "onset temperatures" are understood as limit temperatures (e.g. of an isoperibolic experiment) or as those temperatures at which the heat outputs to be measured exceed the *sensitivity limit of an experiment,* they can be used for a partial description of the experimental findings.

The establishment of "safety margins" is often more or less empirical, e.g. on the basis of the occurrence of an incident. But it is important to note that the "safety margin" should include not only a margin in the sense of conservative oversizing but also the scale-up factor between laboratory and plant.

The following example will serve to illustrate these relationships and to facilitate the interpretation of isoperibolic measurement results.

Let us consider a decomposition whose power exceeds the sensitivity of an experiment of, for example,

500 mW kg$^{-1}$ (corresponds, for instance, to a 200 ml Dewar experiment) at 150°C. With somewhat conservative assumptions (formula, Figure 38) this value corresponds approximately to the critical heat output of a non-isolated volume of ca. 5 l (Figure 53).

This means that the sensitivity limits of our experiment or the limit temperature defined by convention now correspond directly to the critical safety limit of the given reacting mass in a cylinder of volume 5 l. If, for instance, the stability of the same substance has now to be assessed in a 200 l drum, the critical heat output is lower. According to the formula for the critical heat output, this depends on the reciprocal of the square of the cylinder radius, i.e.

$$\text{Scale-up factor} \;=\; \frac{\dot{q}_{crit,\,1}}{\dot{q}_{crit,\,2}} \;=\; \frac{r_2{}^2}{r_1{}^2}$$

In our example the (thermal) scale-up factor is thus around 12. In order to now determine that temperature above which a thermal explosion must be anticipated during storage of our substances in a 200 l drum, we take into account the scale-up factor of 12 in the Arrhenius plot of Figure 54. In general, the slope of the Arrhenius lines (activation energy, obtained only after additional, say isothermal, measurement) is unknown. It is thus preferable to select a relatively low value of the activation energy for the estimation. In our example a critical temperature of 100°C results for a moderate activation energy (e.g. 70000 J mol$^{-1}$), for a rather conservative value of 40000 J mol$^{-1}$ a critical temperature of 60°C is found.

From this discussion it becomes apparent that *the difference in scale* between experiment and operation is paralleled by a *lowering of the critical temperature.* As long as the difference in scale is not too large it is perfectly legitimate to generalize the above consideration and to assign a "safety margin" in degrees to the scale-up difference.

| | Experiment 500 mW kg$^{-1}$ | 5 l scale-up | 200 l |
|---|---|---|---|
| Radius | | 0.08 m | 0.28 m |
| Rel. scale-up factor | 1 | 1 | 12 |
| Sensitivity or critical heat output | 500 mW kg$^{-1}$ | 500 mW kg$^{-1}$ | 40 mW kg$^{-1}$ |

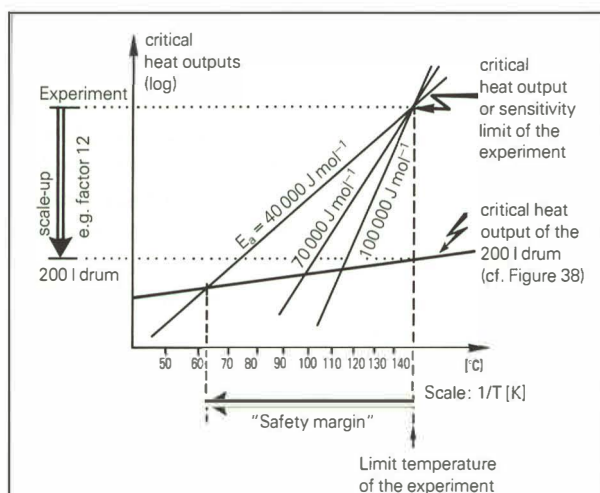*Figure 53: Scale-up of the critical heat output*



*Figure 54: Comparison of the critical heat outputs of different scales*

It becomes equally clear, however, that limits are set to a scale-up that can be bridged in such a manner: For fairly large scale-up factors the conservatively estimated critical temperatures would be unrealistically low. From the representation in Figure 54 it also becomes clear why a knowledge of the activation energy can improve the reliability of the prediction of critical conditions.

### 3.5.4 Concluding remarks

The critical discussion of the different measurement techniques to characterize decomposition reactions has pointed out the demanding nature of informative experiments. It has also shown, however, that routes nevertheless exist to reach the goal in different ways. With a proper understanding of the problem it is possible on the basis of what has been said to set up test procedures that *take into account the operational problems* and classify the large number of clear-cut cases as well as identify the few cases in which additional measurement effort is necessary. Here, the wide range of measurement principles with their individual advantages and disadvantages can undoubtedly be a great help in support of a safety-related conclusion obtained by different routes.

# Appendix 1

## List of variables

| | | |
|---|---|---|
| A | m² | Active heat exchange area |
| Accu | – | Relative accumulation of the minority component |
| a | m² s⁻¹ | Thermal diffusivity |
| $C_{A0}$, $C_A$ | mol m⁻³ | Concentrations |
| $c_p$ | J kg⁻¹ K⁻¹ | Specific heat capacity |
| d | m | Wall thickness, distance |
| $E_a$ | J mol⁻¹ | Activation energy |
| h | km | Height |
| $\Delta H_R$ | J | Enthalpy of reaction |
| $\Delta H_d$ | J | Enthalpy of decomposition |
| $\Delta h_R$ | J kg⁻¹ | Specific heat of reaction |
| $\Delta h`_R$ | J mol⁻¹ | Specific heat of reaction |
| k | W m⁻² K⁻¹ | Heat transfer coefficient |
| k` | s⁻¹ | Reaction rate constant |
| M | kg mol⁻¹ | Molar mass |
| m | kg | Mass |
| ṁ | kg s⁻¹ | Mass flow |
| N | rpm | Stirrer speed |
| p | N m⁻² | Pressure |
| Q̇ | W | Heat output |
| q̇ | W kg⁻¹ | Specific heat output |
| q̇` | W mol⁻¹ | Specific heat output |
| r` | mol m⁻³ s⁻¹ | Reaction rate |
| r | m | Radius |
| T | K | Temperature |
| $\Delta T_{ad}$ | K | "adiabatic temperature rise" |
| $TMR_{ad}$ | s | Time to Maximum Rate |
| t | s | Time |
| v | m s⁻¹ | Velocity |
| **ϒ** | W m⁻² K⁻¹ | Material constant for heat transfer in an agitated vessel, see p. 20 |
| V | m³ | Volume |
| V̇ | m³ s⁻¹ | Volume flow |
| x | – | Conversion |
| Z | – | Apparatus factor, see p. 20 |
| z | m | Spacial coordinate |
| α | W m⁻² K⁻¹ | Heat transfer coefficient |
| 1/γ | m² K W⁻¹ | Apparatus resistance |
| λ | W m⁻¹ K⁻¹ | Thermal conductivity |
| ϑ | °C | Temperature |
| Φ | – | Influence factor of vessel heat capacity, see p. 42 |
| ϱ | kg m⁻³ | Density |
| τ | s | Cooling half life |

## Indices

| | |
|---|---|
| a | ambient |
| accu | accumulated part |
| ad | adiabatic |
| c | condenser |
| crit | critical |
| d | decomposition |
| h | sample holder |
| i | inner, internal |
| in | inflowing |
| j | jacket |
| m | medium |
| n | corrected jacket (temperature) |
| o | initial, outer |
| out | outflowing |
| R | reactor |
| ref | reference |
| rel | relative |
| s | standard, sample, surface |
| $T_o$ | at temperature $T_o$ |
| t | at time t |
| ∅ | mean value |
| w | wall |

## Symbols

| | |
|---|---|
| Δ | difference, rise |
| ≡ | identically equal to |
| ≙ | corresponds to |
| = | equal to |
| ≈ | approximately equal to |
| ~ | proportional to |
| $\dfrac{dA}{dt}$ | rate of change of A |

## Constants

| | | |
|---|---|---|
| R = | 8.314 | J mol⁻¹ K⁻¹ |
| $\delta_c$ | – | criticality parameter, see Fig. 38, p. 37 |

## Appendix 2

### Index

# Appendix 3

## Supplementary reading

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No. 1 **Tests de sécurité pour produits chimiques,** 1985, 2ᵉ édition revue et élargie

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Regeln für die betriebliche Sicherheit, 1989, 3., erweiterte Auflage

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Rules for Plant Safety, 1988

No. 3 **Inertisierung**
Methoden und Mittel zum Vermeiden zündfähiger Stoff-Luft-Gemische
in chemischen Produktionsapparaturen und -anlagen, 1992, 2., überarbeitete Auflage

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Methods and means to avoid ignitable substance-air mixtures in chemical production
equipment and plants (in preparation)

No. 4 **Einführung in die Risikoanalyse**
Systematik und Methoden, 1986, 2., unveränderte Auflage

No. 4 **Introduction à l'analyse des risques**
Systématique et méthodes, 1981

No. 5 **Mahlen brennbarer Feststoffe**
Sicherheitsbeurteilung des Mahlgutes, Schutzmassnahmen an Mahlanlagen,
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No. 5 **Broyage des substances combustibles**
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Tests de contrôle des substances à broyer, 1987

No. 6 **Trocknen von Feststoffen**
in Luft- und Vakuumtrockenschränken, in Schaufeltrocknern, 1985

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No. 8 **Thermische Prozess-Sicherheit**
Daten, Beurteilungskriterien, Massnahmen, 1989, 2. Auflage

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Data, Assessment Criteria, Measures, 1993

No. 9 **Behelf für die Durchführung von Sicherheitsüberprüfungen (Safety Audits)**
Grundsätze, Systematik, Methodik, Stichworte, 1991

No. 10 **Risikoanalyse im Zusammenhang mit der Störfallverordnung (StFV)**
Behelf zur Erstellung von Kurzberichten und Risikoermittlungen für Betriebe mit Stoffen,
Erzeugnissen und Sonderabfällen, 1991

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