Jörg Steinbach

Safety Assessment for Chemical Processes

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Preface

Loss prevention represents an interdisciplinary area of teaching and research activities. The integral term itself emphasizes this characteristic as it combines substance related process and equipment related plant safety. The comprehensive approach of loss prevention led to its development into an independent discipline. Taking courses to learn about the fundamentals should be mandatory to all students in chemical engineering. Today process safety is regarded to be equally important as ensuring quality, environmental sustainability and economic feasibility for all manufacturing processes in the chemical industry.

This book in its condensed presentation of these fundamentals is written for chemical engineers and chemists either working in research, development, production or engineering departments as well as to those working for supervising authorities. At the same time it can be used as a textbook in graduate courses at university.

The above-mentioned comprehensive approach of loss prevention necessitates the description of all of the following topics in a balanced way:

- determination and interpretation of substance related safety data, as they characterize the hazard potential
- organizational and engineering safety concepts, as they influence the probability of the occurrence of an event
- methods of hazard analysis as they ensure the procedure to obtain the safety assessment to be systematic
- methods of reliability analysis and risk quantification including simulation techniques
- a discourse of the *man/machine* interface
- relevance of legal requirements and voluntary programs such as Responsible Care

This book is intended to cover the first three topics with emphasis on engineering safety concepts.

The introduction to loss prevention terminology is followed by an outline of the systematic approach to obtaining hazard assessments for chemical processes and physical unit operations. Subsequently, experimental methods for safety investigations of substances and mixtures are described and the interpretation of the results is discussed. The main part of the book deals with the investigation and assessment of chemical reactions under normal as well as under upset operating conditions.

A separate chapter addresses the problems related to handling dust explosible substances. This is followed by a short description of the main hazard identification methods.

Two selected examples demonstrate the plant related safety concepts and the variety of accompanying aspects. One of them, the design of emergency relief systems including catch tanks, was chosen because of ongoing discussions and research activities.

Finally some personal remarks should be granted. I learned most of the theoretical background to in this book from my teacher and mentor Professor Peter Hugo. For the industrial experience reflected here I have to give special credit to my friend and former colleague Dr. Theodor Grewer, who helped me with my first steps more than twelve years ago. I must not forget to mention Dr. Barbara Böck, Linda Mundt and Cornelia Clauß, who always assisted me from the publisher's side.

Finally, none of this would have been possible without the support and tolerance which my wife Barbara and my sons Andreas, Matthias and Michael have now given me for the second time in three years. To all mentioned here I would like to express my gratitude at this point.

Berlin 1998
Jörg Steinbach

Contents

Symbols and frequently used abbreviations

A	mass transfer area, heat transfer area
B	thermal reaction number
BR	batch reactor
c	concentration
c_P	specific heat capacity
CSTR	continuously stirred tank reactor
d	diameter of the agitator
d_P	particle diameter
D	diameter
D^*	dimensionless reactor diameter
D_{eff}	effective diffusion coefficient
Da	Damkoehler number
E	activation energy
f	radical yield factor, friction factor
g	gravitational constant
G	mass flow per unit area
h	Thiele modulus
$h(t)$	equivalent isothermal reaction time
H	height
He	Henry coefficient
HR	heating rate
$\bar{j}$	material flow per unit area
$j_{1,2}$	Antoine constant
k	rate constant
$k^*(T)$	zero-order rate constant
k_∞	pre-exponential factor
L	length
m	mass
MG	molecular weight
n	number of moles, reaction order, agitator revolutions
Ne	Newton number
Nu	Nusselt number
$\bar{o}$	vector of a surface element

p	pressure
P	stability parameter
PFTR	plug flow tube reactor
Pr	Prandtl number
$\dot{q}$	specific heat output rate
$\dot{Q}$	heat output rate
r	radius
r, r(T)	rate of reaction
R	universal gas constant
Re	Reynolds number
S	sensitivity
SBR	semibatch reactor
St	Stanton number
t	time
T	temperature
TMR	time to maximum rate
u	velocity
u^*	dimensionless velocity
U	overall heat transfer coefficient
v	specific volume
V	volume
$\dot{V}$	volume flow
x	vapour mass fraction
X	conversion
Y	relative amount of accumulated substance
z	axial coordinate
Z	real gas factor

α	heat transfer coefficient, stability parameter, relative degree of filling, outflow coefficient
β	mass transfer coefficient, stability parameter
γ	mass fraction
Δh	specific enthalpy
ΔH	enthalpy
ΔT_{ad}	adiabatic temperature rise
ε	volume increase factor, volumetric vapour fraction
η	degree of utilization of porous particles, viscosity
ϑ	dimensionless temperature difference

Θ	dimensionless feed time
κ	dilution factor, isentropic coefficient
λ	stoichiometric input ratio, heat conductivity
ν	stoichiometric coefficient
ξ	friction factor
ρ	density
σ	surface tension
τ	residence time
τ_C	time constant of cooling
τ_D	feed time
φ	volume factor
Φ	thermal inertia
$\Phi(X)$	dimensionless reaction rate
ψ	ratio of reaction to mass transfer rate, dimensionless temperature overheating
ω	entropy parameter

A	limiting component
App	apparatus
C	cooling
D	dosage
eff	effective
end	end of time
g	gaseous
l	liquid
lg	liquid/gas two-phase
max, Max	maximal, maximum value
R	reaction
S	steady state
B.P.	boiling point
W	wall
Z	decomposition
∞	referenced to the pre-exponential factor
0	initial or reference state

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1 Basic Terminology in Loss Prevention

It is essential to the assessment of safety measures, from a legal as well as from a societal point of view, to have a common understanding of the basic terminology used. Examples are words like hazard or safety. In this context it must be emphasized that the majority of terms expresses probabilities, which are not generally quantifiable. Day to day practice, however, requires certain safety definitions to come up with concrete measures in order to fulfil the promise of safe manufacturing processes.

1.1 General Safety Terms

One source among others for the definition of safety terms is the German Industrial Standard *DIN 31000 Part 1* [1]. Mentioned are

- damage
- risk
- limit risk
- hazard
- safety
- safety standards
- protection

The definitions given are quite abstract and in part even use legal language. Besides the necessity to be correct, which has to be met by an official standard, the wording must be applicable not only to the chemical process industry but to all industrial activities, which also causes it to be very general. Consequently, these definitions have to be translated into a specific terminology which renders the phrasing relevant and comprehensible to the chemical industry. Assistance for this task can be obtained from several sources, such as the *German Federal Law on Immission Protection*, the *OSHA-PSM* guideline, the HSE-guide on *Chemical Reaction Hazards* or the CCPS guidelines, *Guidelines For Chemical Reactivity Evaluation And Application To Process Design* and *Chemical Process Quantitative Risk Assessment*, [2, 3, 4, 5, 6].

Of the afore-mentioned safety terms, damage and protection are probably the two most generally understood. Their interrelation supports this. Protection is the effect of a selected measure to preserve a value against damage. According to today's understanding, human beings, the environment and goods in general are values to be protected with equal efforts. However, it is more reasonable to begin the logical chain with a different term.

1.1.1 Hazard Potential and Expectable Damage

The initial point of all considerations with the aim of a safety assessment is the so-called *hazard potential.* It results from the combination of the handled amount of substance and its dominant hazardous property (Figure 1-1).

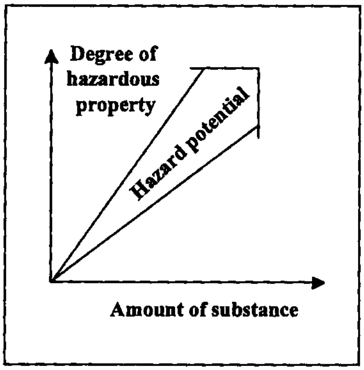

Fig. 1-1. Hazard Potential

An example for a hazardous property is the flammability of a solvent, which can be scaled from low to high using the flash point.

In order to deduce the *expectable damage* from the hazard potential, the mode of operation has taken into account, as presented in Figure 1-2. In this context the expectable damage is often referred to as the *weighted hazard potential,* because the event is only anticipated.

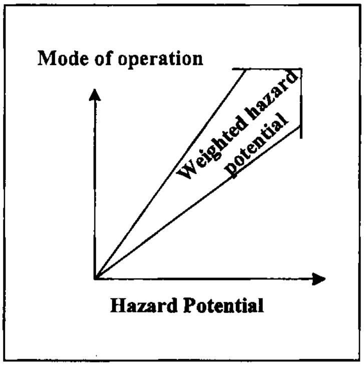

Fig. 1-2. Weighted hazard potential

Making use of a pseudo mathematical formulation these descriptions may be expressed as:

hazardous property * amount of substance = hazard potential
hazard potential * mode of operation = weighted hazard potential
= expectable damage

The storage of a highly flammable substance, which under normal conditions is gaseous, shall be discussed to exemplify the above. The hazard potential, as mentioned, results from the combination of the amount of inventory stored and the hazardous property of high flammability. Quite obviously the storage poses a risk if the substance is released accidentally and ignited. The resulting damage depends strongly on the type of release. In the case of pressurized storage the high internal pressure will cause a large mass flow of the liquefied material through the leak and the pressure difference to ambient will result in a flash evaporation. In the case of low temperature storage the liquefied material will be released with a smaller rate and subsequent pool formation. Evaporation will proceed at a significantly lower rate because the latent heat required has to be withdrawn from the ground. This process will even slow down with decreasing temperature of the surface. Consequently, with respect to risk assessment the consideration of different modes of operation results in a higher rating for the weighted hazard potential of the storage under pressure than for that of the low temperature design.

1.1.2 Risk

The assessment value which is obtained by the combination of the damage to be expected from an event and its probability or frequency of occurrence is the so-called *risk*.

The incident probability itself is mainly determined by the implemented protective and preventive acting measures. These represent the basis of safety of the process. Therefore, using an analogous formulation, risk is determined by the combination of the basis of safety and the weighted hazard potential as shown in Figure 1-3.

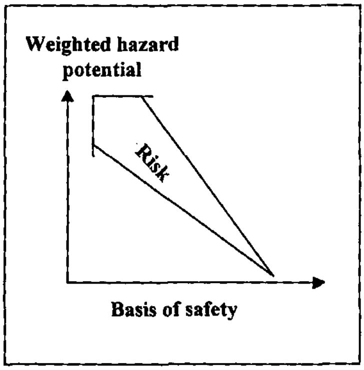

Fig. 1-3. Risk

The basis of safety, as outlined above, results from partly organizational, partly technical measures dedicated to preventing identified hazard potentials from taking effect. The systematic hazard identification procedures are discussed in Chapter 6 in more detail. Each element of this basis of safety is of a certain quality which is given by its type of action, the degree of efficiency and its availability. A first simplistic classification for some elements is given in Table 1-1:

Table 1-1: Simplistic classification for some basis of safety elements

Element Properties	Type
Degree of Efficiency (DoE) = 1	Incident Preventing Element
Availability = 1	Highly Available or Self-safe-Element
DoE * Availability = 1	Incident Preventing Protection Element
DoE < 1 + Availability = 1	Incident Mitigating Protection Element

The quality of purely organizational measures to prevent the occurrence of an incident will have to be rated differently to that of simple technical installations, and this is different again to that of highly available systems installed in multiple redundancy.

In this context the term "safety technical regulation" can be circumscribed in a form relevant to practice. This regulation is aimed at preventing the incident occurrence due to a specific hazard potential. Adherence to it ensures this by reducing the event probability to a level which is negligible with respect to common sense standards. This is put into practice by demanding the installation and implementation of a specified high integrity protection system. In the pseudo mathematical formulation already used above this can be expressed:

Quality of the Protection System $\rightarrow +\infty$
consequently: Event Probability = 1/Quality of the Protective System $\rightarrow 0$
consequently: Risk = Weighted Hazard Potential $*$ Event Probability $\rightarrow 0$

These considerations lead to the most problematic part of definitions and interpretation of terms: the acceptable risk, sometimes also called limit risk. A totally risk free activity, also referred to as zero risk, is feasible only if the activity is not exercised! If it has been decided to go for a quantitative risk statement, this is unavoidably accompanied by the request for a scale to enable the assessment of the result. The definition of such a scale presents a subjective decision on the acceptability of risk, which splits the scale into the regions "dangerous" or "hazardous" and "safe". The value for the limit risk has to be fixed in such a way that it takes into account the acceptability for the damage facing party and at the same time the tolerability from a third parties' point of view. With this background it becomes obvious that the definition of a limit risk comes close to a philosophical task on the political field with societal impact.

This is reflected also by discriminating between *individual* and *societal risk*. In the case of individual risk, the risk to a single person, who is either directly involved in the process performance or affected by damages caused by maloperation of the process, is assessed. In contrast, societal risk indicates the possible number of fatalities in their dependence on event probability. The difference of the two risk values shall be demonstrated in a short example.

A large tank is to be installed above ground in less than 200 m distance from a school. The tank shall serve the heating system of the school with fuel. The individual risk of a pupil to die from the explosion effects of unintentionally released material shall be as low as 10^{-7} / year or once in 10 million years. This is achieved by installing a state-of-the-art tank using high integrity equipment only. Such a risk value is generally regarded as trivial or negligibly small. The societal risk, however, would tell us, that the total number of fatalities to be expected for an event with this low probability would amount to the majority of pupils and teachers present at the incident time. This may demonstrate the discrepancy between the individual risk, which for a certain process may be trivial small, and the societal risk, which at the same time for the same process, may be unacceptably high.

Only in a limited number of countries have individual risk limit values courageously been defined. One famous definition is the British *Fatal Accident Rate* (FAR). Operations with a FAR of less than 0.4 are regarded as safe. The FAR is defined as the number of fatalities per 1000 employees in their average working life time of 25 years. The answer to the question whether those relatives who have just lost a loved one find consolation in the statement that the probability for one worker in a company with 1000 employees to die from the consequences of a process is once in 30000 years can easily be found by the reader.

The second problem not to be underestimated is the actual determination of a quantitative risk or of an equivalent probability value. In principle, the necessary mathematics as well as tools such as fault trees with their logical *and* and *or* gates are well-known and established [6]. The difficult part is the acquisition of the necessary basic data, such as failure rates of components or the quantification of human errors. This acquisition may be accomplished within reasonable limits for monoproduction plants and processes. Such installations dedicated to the manufacture of one and the same product time after time are characterized by a very limited number of tasks and load changes per unit, which helps with data generation. It quickly comes close to an impossible task to generate the necessary data for multi-purpose batch plants like those widely used in the fine chemicals industry. They are characterized by frequently changing different chemical processes accompanied by numerous tasks and load changes per unit. In this case it becomes necessary to rely on estimates, which finally yield somewhat arbitrary looking results.

Considerable scepticism with respect to the benefit of the final result arises, if the following drawbacks are all taken into account:

- the absolute value for the individual risk related to a certain process does not provide any indication of the actual date of the event occurrence
- the differing values for individual and societal risk are difficult to assess reasonably
- noticeable uncertainties exist with respect to the input or basic data

This has led to a situation in which the chemical industry in certain countries, such as Germany, more or less refuses to apply absolute risk techniques. Exceptions are made with respect to comparative studies, which make use of an identical data base.

In Germany the deterministic approach is favoured. Quantitative techniques are applied to characterize possible incident outcomes and expected damages. An incident probability of 1 is formally attributed to all incidents considered. The final risk rating is performed qualitatively. Global harmonization, however, will make it necessary to perform a common discourse on benefits and disadvantages of quantitative risk techniques in the future.

1.2 Basic Terminology for Plant/Process Operation

The term *severe incident* is quickly used today by the media as well as by the general public for numerous situations, and companies are often just as quick in rejecting this term. Thus, a certain prejudice has developed that denying the severity of an incident is common practice in industry; and this has in turn led to an emotionalized discussion, which is neither tolerable nor justifiable nor actually necessary. In order to improve the current situation, some terms are supplemented here to the previous paragraphs to provide a basis of facts for future discussion.

In plant and process operation the following modes are commonly distinguished:

- normal operation
- operation within predefined design limits
- upset operating conditions
- incident

These are complemented by the following safety concepts:

- inherently safer designed process
- incident preventing measures
- outcome mitigating measures

Their interaction is best explained graphically, as shown in Figure 1-4.

As long as the process is performed within the parameter ranges defined in the manufacturing procedure, it is regarded as being run under *normal operating conditions*. Quite often the parameter limits defining the normal operating conditions are identical with those required by quality standards to meet the specification. All measuring and control devices installed to ensure normal operating conditions are rated as *operational installations.*

If a process deviation occurs, which causes a variable

- to exceed the range of normal operating conditions
- but this is detected by a measuring and control device and
- corrective action
  - either automatically
  - or manually

  brings the process back into the normal operation range and
- if the process may proceed without any further endangerment

the situation is regarded an *upset process condition.* All measuring and control devices used here are *supervising systems* with corrective action. In case that

- the correction does not succeed
- and/or a release of substance must be expected, which generates a hazardous situation to either human beings, the environment or other goods,

installations should be provided which prevent an incident occurrence with the *highest safety-technical reliability.* They are rated as incident preventing *protection systems.*

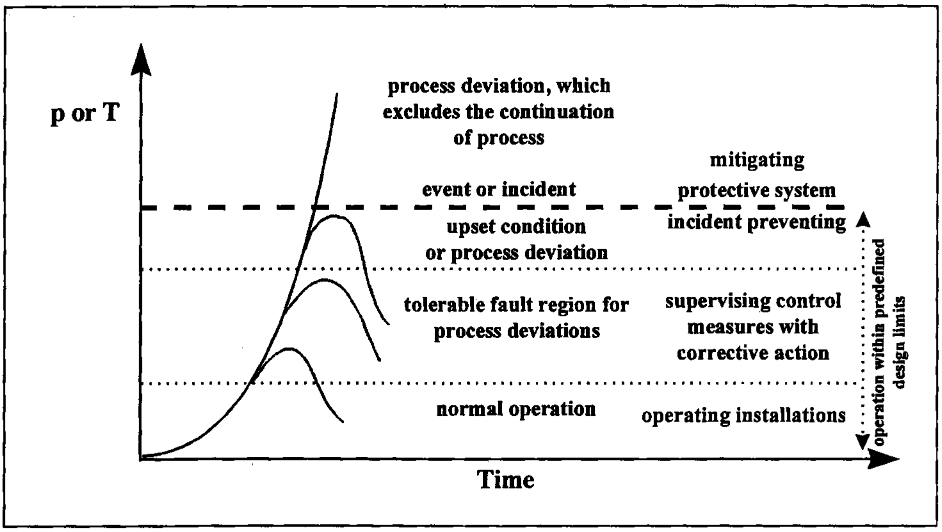

Fig. 1-4. Interaction of process status and basis of safety concepts

The region in which supervising as well as incident preventing installations operate is called the *tolerable fault region.* If these installations operate successfully the plant design limit will not be exceeded, at least not for a significantly long period. This prevents any loss of containment. For this reason the sum of the normal operating region and the tolerable fault region is defined as the *operating region within design limits*.

Provided that an upset condition does not force the process to leave the design region even if no corrective action takes place, the process is regarded as *inherently safe*.

In case a loss of containment is unavoidable, substance is released and the extend of damage done determines the discrimination between event and incident.

At this point it is helpful to introduce the term *endangerment*. The endangerment is obtained by combining the weighted hazard potential and the number of human beings possibly affected by any event (Figure 1-5).

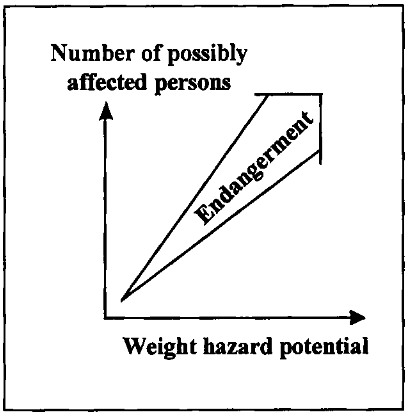

Fig. 1-5. Endangerment

The degree of endangerment is smaller if damage causing effects are limited to a closed area out of bounds for all employees than in the case of an open plant environment with a certain presence of several employees and possible effects on the neighbouring area.

Using this definition helps to realize, that

- a significant amount of substance must have been released and
- a direct endangerment of human beings, the environment and goods must accompany the situation

for an event to escalate to a severe incident. In any case, if a person dies or suffers irreversible health damage the situation, must be regarded as a severe incident. All installations operating after the release of substance has occurred are known as *incident mitigating protection systems*.

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2 Procedure for Process Safety Investigations

Chapter 1 has demonstrated that those responsible for the operation of a plant must have a thorough understanding of the process which is carried out there. Only this knowledge enables to carry out a safety assessment, which is mandatory due to his personal responsibility as well as a prerequisite in order to prove the implementation of adequate safety measures to the public. Consequently the following tasks can directly be deduced for any one responsible for plant operation:

1. the process must be characterized experimentally,
2. the normal operating conditions have to be assessed with the help of criteria which must be applied when translating the experimental results to actual plant conditions,
3. possible process deviations must systematically be identified, characterized and assessed with respect to process safety relevance,
4. requirements and recommendations for safety installations and/or process modifications have to be deduced from the total of all these considerations and must be implemented.

This procedure for safety investigations is often referred to as *PHASE* [7]. The acronym stands for Process Hazard Assessment and Safety Evaluation, and the procedure is shown graphically in Figure 2-1. It has to be performed for every process and each sub-step involved. It is even more important to repeat this procedure after each relevant process or plant modification.

The necessary effort resulting from this requirement, namely to assess each process with the same thoroughness independent of scale or development stage, is hardly feasible for research dedicated companies. It therefore becomes necessary to define different degrees of detail and the extent of investigations without knowingly accepting safety risks. Such a responsible stepwise procedure is developed by the following approach. The first step is to discuss the life cycle of a process. The possible damages caused by a process maloperation will change for different life cycle phases.

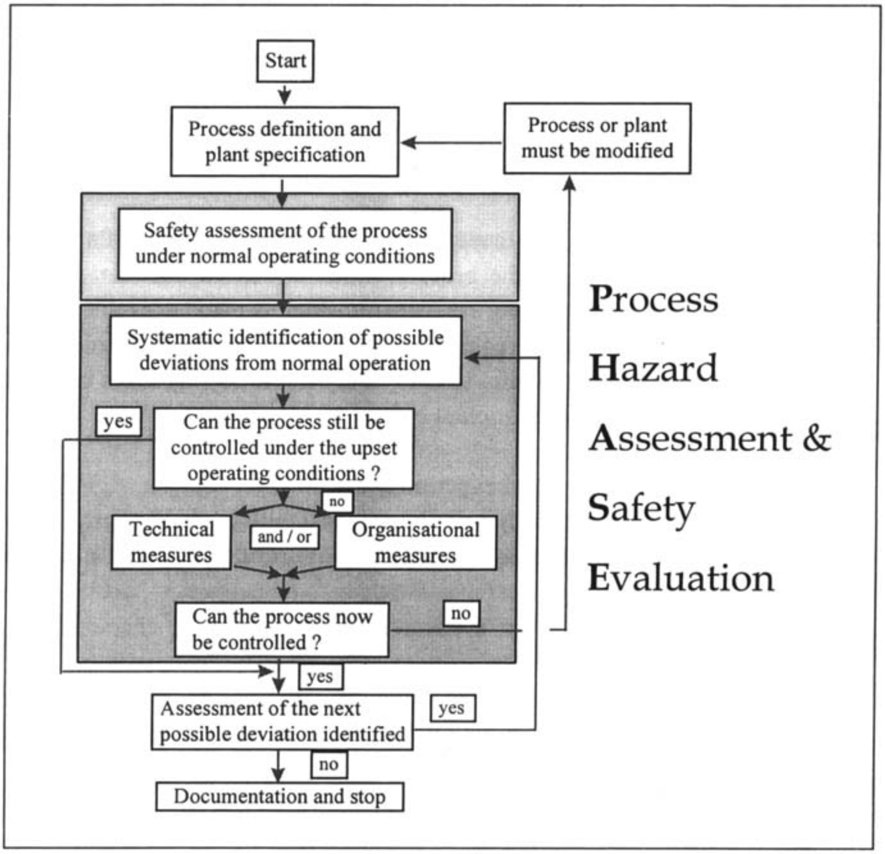


Fig. 2-1. Procedure for process safety investigations

2.1 Scope of Investigation in its Dependence on the Process Development Stage

According to common industrial practice, a process will undergo the steps shown in Figure 2-2. The amount of substance necessary to perform a research process, which consists of several synthesis steps and physical unit operations, is very small. Often the amount of finally gained product is only a few hundred milligrams. If unexpected effects are encountered during such laboratory experiments, possible consequences will be limited to the fume cupboard area. This statement, however, only holds true if all occupational health standards are strictly adhered to. A systematic safety assessment as described above is then not necessary at this stage.

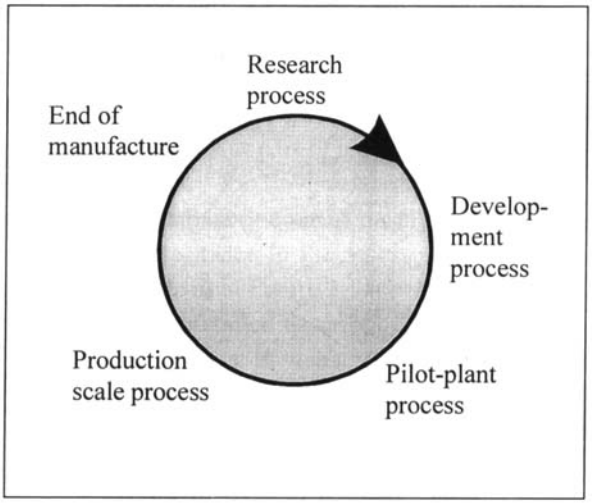


Fig. 2-2. Life cycle of a chemical process

Instead of such a thorough assessment, the substances should be screened for explosive properties with the help of estimation methods, supported by a thorough literature survey. Handling of explosives should be avoided wherever possible. Published health and safety data should additionally back up the safe handling on the laboratory scale.

In addition, management procedures should be in place to safeguard a recording of safety relevant observations for further use on the development scale. A couple of examples shall be outlined here.

A typical procedure on laboratory scale is the determination of the melting point for solid materials. If the substance was obtained in colourless crystals and turns to a black mass while being heated up this is a strong and reliable indication for limited thermal stability. Foaming during distillation, formation of side and consecutive products in the case of longer stirring periods or after drying are further examples. All these observations must be available for use in the life cycle progress.

It is the task of development to optimize the route of synthesis with respect to environmental sustainability, economy, and quality. When a certain maturity of the process has been achieved the first larger scale-up step is undertaken. The damage which can possibly be caused by a maloperation of this significantly larger process has to be assessed quite differently. Nonetheless, it still remains controllable as, in the case of the chemical process, the ratio of heat transfer area to reaction volume is still very favour-able for batches of 0.5 to 2 kg. At this stage it is recommendable to perform a *basic assessment*, which allows for a preliminary evaluation of the normal operating conditions and reliably indicates the presence of secondary processes, such as decomposition reactions. The type of tests used for such a basic assessment are discussed in detail in Chapter 2.3.

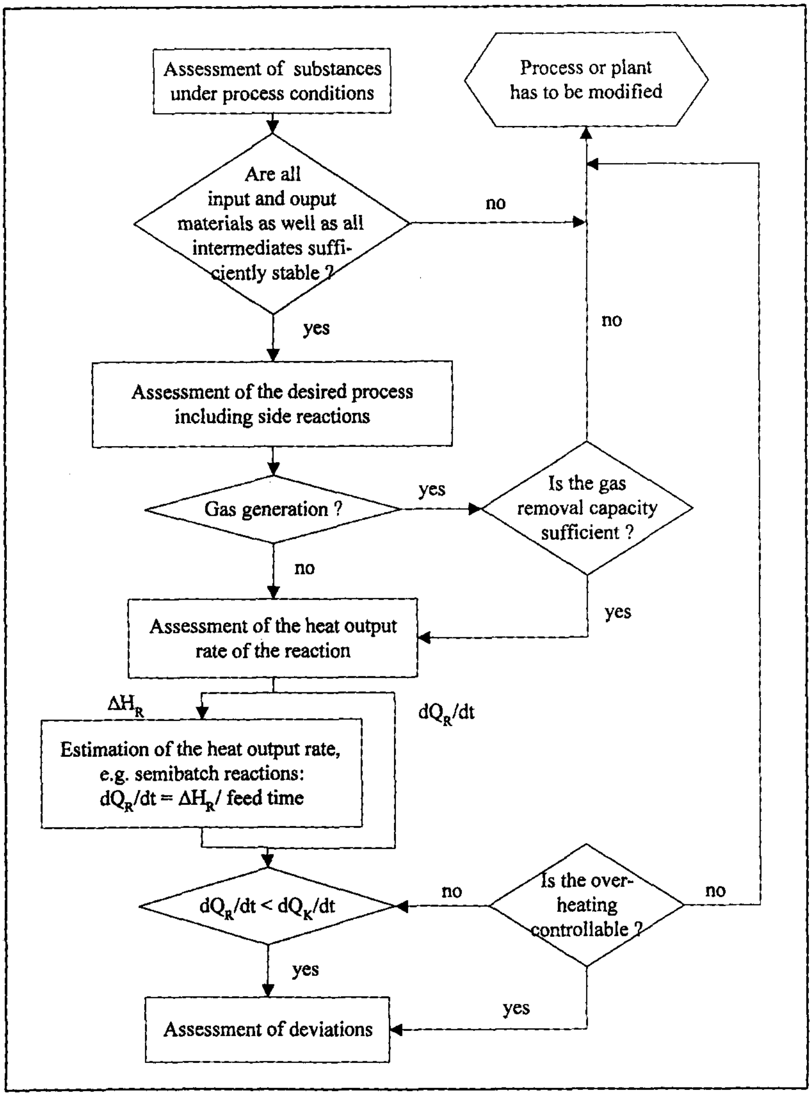


Fig. 2-3. Iterative assessment procedure for normal operating conditions

Before the first run of a process in pilot plant is undertaken, the first comprehensive evaluation of the normal operating conditions must be completed.

At the same stage of the life cycle, it is necessary to have accomplished a systematic identification of possible process deviations. This identification of possible deviations represents a major contribution to the overall safety of the process. It should be performed at this stage as its results essentially determine the safety technical requirements either to be implemented in the design of the production plant or to be compared with installations in an existing plant as part of a compatibility check.

In 1994 the German Secretary for Environmental Protection and Reactor Safety requested a guideline from his advisory council on plant safety (TAA), which was to provide a flow-sheet type of assistance to the assessment of a process under normal operating conditions [8]. It is shown in Figure 2-3.

The procedure described is a detailed description of one sub-step in PHASE. Like PHASE itself, this step also is iterative in character. The methods needed to determine all necessary data and their evaluation criteria are given in Chapter 4.

When the pilot plant process is transferred to production the evaluation of the normal operating conditions has to be repeated to account for the changing parameters due to the scale up. Furthermore, the quantitative assessment of process consequences under deviating operating conditions must have been completed.

Further on, as already mentioned above, the hazard evaluation for normal as well as upset operating conditions has to be repeated whenever significant plant or process modifications are undertaken.

2.2 Definition of Significant Plant or Process Modifications

In consequence of the above-mentioned demand for repeated assessments, when significant plant or process changes are made, a rating for minor and major modifications is required. A very careful approach for plant modifications was published by the Center of Chemical Process Safety (CCPS) in their series of guidelines for process safety management [9]. In their recommendations, minor changes remain restricted to *100 % replacement in kind* or *like for like replacements*. Any other modifications exceeding those are subject to a safety assessment

It turns out to be even more difficult to find a responsible definition for minor or major process modifications. One option is to take into account the amount of substance handled. This actually goes in line with the approach taken to develop the stepwise increasing scope of experimental investigations outlined in section 2.1. The majority of experiments on research and development scale only consume 0.5 to 1 g and are performed in closed fume cupboards. Most changes introduced by a laboratory technician due to personal observations may be significant with respect to the chemical mechanism but rather negligible regarding process safety. Negative effects should still be limited to the inner part of the fume cupboard. The same changes, such as doubling the amount of solvent, increasing the process temperature by 5 K or accelerating a feed rate, may have severe consequences when introduced on plant scale. Even skilled operators may not be able to assess these changes correctly in advance. From the above it may be concluded that minor process modifications should be restricted to those introduced on laboratory scale. On plant scale, independent of pilot or production type, a management procedure must be in place which ensures the safety investigation for each modification of the manufacturing procedure considered.

2.3 Types of Investigations Corresponding to the Life Cycle Progress

The tests to be performed and their evaluation must be very efficient to have a good cost-benefit balance. This is achieved by focusing the activities on the main areas of hazard related to chemical production:

- explosion
- fire
- emission

An explosion is the result of a sequence. Prerequisite to an explosion is the unintended release of a flammable substance in the presence of an oxidizing agent and an ignition source. This event, in turn, can be the consequence of a single process deviation or a whole event chain.

An example shall illustrate this. While performing a chemical reaction in a flammable solvent, a loss of cooling is encountered. The temperature of the reaction mass rises and reaches a level at which parallel or consecutive reactions begin to dominate the heat production rate. The increased heat release leads to a continuing temperature rise up to the boiling point of the solvent. Accidentally the connection to the reflux condenser is shut, so that a closed system exists. The still ongoing heat release leads to a further increase in temperature, which is now accompanied by a pressure increase.

If additional gas generation occurs due to one of the chemical reactions the pressure increase may be accelerated. If the emergency relief system is not adequately designed the vessel will rupture and release the flammable solvent, which this way will come into contact with oxygen-containing air. The scenario just lacks the ignition source for the explosion to happen. The ignition sources may vary in character, from hot surfaces, electrostatic discharges to sparks from welding activities.

Fire is also the consequence of an event very similar to that discussed for an explosion. Both events, fire and explosion, may result in further events causing additional damage. One example is the heat radiation emitted from the fire which will cause a thermal stress on neighbouring installations or material stored close by.

An emission may already be the hazardous event itself due to the toxicity of the material released, but it may also be just the prerequisite to fire or explosion, if the material emitted is flammable.

These small examples and their elaboration with respect to the main areas of hazard - fire, explosion and emission - show which properties of substances and processes have to be investigated:

- The thermal stability of substances and mixtures under process conditions,
- the process related heat production and pressure rates in their dependence on time,
- the ignitability and flammability of substances and mixtures under those temperature, concentration and pressure conditions present in the process
- the toxic properties.

The determination and assessment of toxic substance properties has developed its own science, which cannot be covered here.

The main factors influencing the problem considered here are:

- the number of processes to be assessed at the different stages of their life-cycle process, such as research, development and production,
- the changing availability of sample material for safety investigations at those life cycle steps
- the differing extent of damage to be anticipated in its dependence on scale of manufacture.

It becomes obvious that the test methods suitable to characterize the different hazard areas must reflect the different demands resulting from the enumeration given.

The assessment of laboratory processes, as mentioned in section 2.1, mainly relies not on experimental investigations but on theoretical tools and data available in the literature or dedicated data bases.

For scaled-up development processes a *screening* must be performed within the framework of the mentioned basic assessment, checking:

- the thermal stability of all substances involved in the process
- the total heat release for each process step
- ignitability and flammability

using only small amounts of material as test samples.

It cannot be emphasized strongly enough that a process assessment based on screening can seldom be more than a preliminary evaluation. One reason is the small amount of samples used, which directly provokes the question regarding representativeness and reproducibility of the test results. At the same time, unfortunately, these small samples yield an increase of a factor which strongly influences the sensitivity of thermal tests, the so-called thermal inertia Φ. The degree of thermal inertia is defined as the heat capacity ratio of the total system to the sample.

$$\Phi = 1 + \frac{m_{app} \cdot c_{P,app}}{m_{sample} \cdot c_{P,sample}} \tag{2-1}$$

A high value of the Φ factor is equivalent to a low or strongly reduced sensitivity of the test method. This has to be accounted for when transferring the experimentally obtained results to the actual plant conditions.

The second important reason lies in the limited information yield of such screening tests. This statement shall be explained with the help of Figure 2-4, which describes a scenario for an exothermic discontinuous batch process [10]. It shows the performance of a desired process, which suffers from a loss of cooling at the time 1. Depending on the accumulated amount of unreacted material at the time of malfunction a certain temperature increase will be observed up to the level called *maximum accessible temperature of the synthesis reaction MTSR.*

If the cooling failure happens immediately after the reactants have been added together, the temperature increase (MTSR-T_0) is equal to the adiabatic temperature increase of the synthesis reaction, which itself is directly proportional to the total amount of heat release of this process step. In case the MTSR is high enough to increase the reaction rates of consecutive or decomposition reactions to a significant value, then this first temperature increase will be followed by a second one up to the level T_{end}.

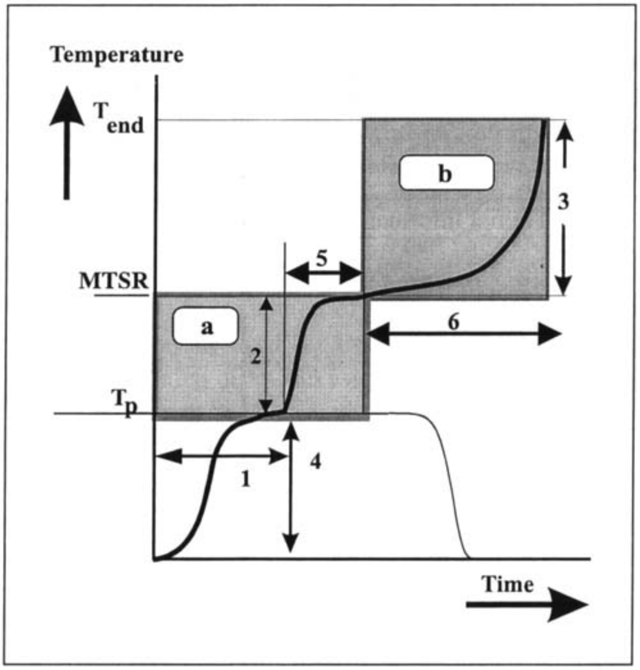


Fig. 2-4. Schematic presentation of a cooling failure scenario according Gygax [10]

Consequences: a = desired reaction b = secondary effects

1: time to cooling failure 2: temperature increase due to loss of cooling

3: temperature increase due to secondary reactions

4: temperature increase under normal operating conditions

5: time to reach MSTR 6: adiabatic induction time of the secondary process

Screening tests can only provide approximations regarding the levels of the maximum process temperature under isoperibolic operating conditions and of the MSTR. In addition, the possibility of exothermic secondary effects may be indicated. A prognosis of the time dependence, labeled 5 and 6 in figure 2-4, can be obtained only if a simultaneous determination of kinetic parameters is possible. With a few exceptions, these tests are not rated screening methods any more. A survey on the different information obtainable from thermodynamic or kinetic test methods is presented in Table 2-1.

Following the rationale given, more sophisticated test methods must be used to obtain a comprehensive assessment of normal operating conditions and a closer estimate of possible damages resulting from upset conditions, which is required for the optimized development process. In order to be rated sophisticated such tests must meet certain requirements:

- test conditions should be as close as possible to the actual plant conditions
- test results should be transferable to plant conditions without or at least with as little as possible model corrections to the data measured.

Table 2-1: Overview on the information obtainable from thermodynamic and kinetic test methods

	Thermal Information	Kinetic Information
Desired Reaction	Heat of Reaction Heat Capacity MTSR p_{max}	Degree of Accumulation temperature = f (time) pressure = f (time)
Undesired Reaction	Heat of Reaction T_{end} p_{max}	Conditions necessary to trigger secondary process: temperature, time and concentration temperature = f (time) pressure = f (time)

The first requirement is mainly important for the assessment of chemical reactions. In the overwhelming majority of chemical processes, not only the chemical conversion into the single desired product takes place. Instead, the desired reaction is accompanied by numerous parallel and consecutive reactions. Under the defined operating conditions resulting from the optimization work, the effect of these simultaneous reactions on yield and selectivity has been minimized by the choice of mode of operation (continuous, batch or semibatch) and of process parameters, such as pressure, temperature, concentration, pH-value, mass flow rates etc. A performance of the safety tests under conditions deviating from those chosen for the plant process would inadvertently favour those secondary reactions in a different manner. Values for the gross value of heat output and reaction rate obtained this way would not be suitable for any process safety evaluation. Modern reaction calorimeters, like those commercially available today, enable the conduction of experiments with sufficient similarity to actual plant conditions.

The second requirement is of equal importance to all process steps, whether they are chemical or physical in character. Chemical reaction processes become critical especially if the heat generated cannot be removed from the system. Those so-called adiabatic operating conditions can best be characterized by methods which either work adiabatically themselves or isothermally. These are regarded as sophisticated because heat losses from the test system are either exactly known or clearly defined.

Isothermal calorimeters, which operate according to the heat compensation principle, allow the measurement of heat flows as low as microwatts per gram, a magnitude which is necessary to determine critical storage or drying volumes directly. Adiabatic calorimeters were optimized with respect to low Φ factors, achieving values close to one. Plant scale processes have Φ factors in the range of 1, as the heat capacity of the reaction mass exceeds that of the apparatus significantly. Such adiabatic test methods are especially suitable for the investigation of upset operating conditions. The results from such measurements may be used for the design of protection systems such as emergency relief valves, bursting disks and catch pots. Screening tests, however, have Φ factors of 2 and higher, with the consequence that results from such tests are not automatically applicable for such design purposes.

Table 2-2 summarizes the recommendations made.

Table 2-2: Overview on the recommended procedure for safety assessments

Life-cycle progression state	Scope of testing	Test methods
Laboratory process	Literature search Theoretical considerations	Chemical structure Oxygen balance
kg-scale	Safety characterization of substances and mixtures	Screening tests
Pilot-plant	1. Complete assessment of normal operating conditions 2. Identification of possible process deviation	Reactions: Reaction calorimetry Physical unit operations: adiabatic or other sophisticated methods
Production scale and process Modifications	Complete assessment of all steps and deviations	Adiabatic calorimetry and other sophisticated methods

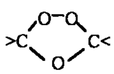
Safety Assessment for Chemical Processes
by. Jörg Steinbach

3 Test Methods For The Thermal Stability Assessment Of Substances And Mixtures

3.1 Theoretical Considerations For Laboratory Processes

As mentioned several times in the previous chapters, the assessment of the hazard potential, which is related to substances and their handling in a certain laboratory synthesis, is performed with the help of theoretical considerations, which are based on experience. One of the first steps is the search for reactive functional groups in the chemicals' structure

Table 3-1: Typical functional groups of unstable chemical compounds

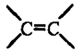
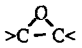
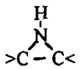
$-NO_x$	Nitro or Nitroso compounds
$-ONO_2$	Esters of Nitric Acid
$>N-X$	Halogen-Nitrogen compounds
$-N^+\equiv N|$	Diazonium salts
$-N=N-$	Azo compounds
$-O-O-$	Peroxides and Peracids
	Ozonides
$-C\equiv C-$	Acetylene, Acetylides
$-N_3$	Hydrazoic Acid, Azides
$-NH-NH-$	Hydrazides
$-ClO_4$	Perchloric Acid, Organic Perchlorates
$-C\equiv N^+-O^-$	Fulminates, Oximates

Over several decades, negative experiences were collected or extracted from the literature. The evaluation resulted in the recognition that certain events were directly related to such reactive functional groups, so that the latter can be used to put the events in a certain order. This resulted in reference books of which at least one should expressly be highlighted: Bretherick's Handbook on Reactive Chemicals [11].

For a preliminary assessment the reactive functional groups included in Tables 3-1 and 3-2 may be used.

Especially the substance class of organic peroxides shall be commented on. Numerous unsaturated hydrocarbons, alcohols, ethers and some cyclic hydrocarbons, such as naphthane, tend to form peroxides in the presence of air.

Table 3-2: Typical functional groups with the ability to polymerize

	Olefins
	Epoxides
	Aziridines

None of these enumerations may claim to be fully comprehensive. Strong oxidizers as well as strong reducing agents have not been mentioned so far. Examples are:

oxidizing agents	reducing agents
HNO_3	Metals (e.g. Zn)
CrO_3	Organometallic compounds
$KMnO_4$	Hydrides
Nitrating acid	Silanes
H_2O_2	Hydrogen
SO_3/Oleum	
Cl_2	

Nonetheless the enumerations provide a good aid to research chemists for a first assessment of a new synthesis. The finding that the substances to be handled contain one or more of the functional groups or belong to one of the substance classes mentioned provides strong indication that substances with a high thermal potential are involved in the process. Increased occupational health and safety measures should be the consequence. Additionally it should be mandatory for those indications to be fully documented in order to be of use when the process is transferred from research to development. It would be ideal if a preliminary experimental screening was initiated already at this early stage of the life cycle to obtain temperature limits for a safe handling of the critical substances.

These considerations should be backed up by a thorough literature search. Bretherick's book provides the possibility to search for substances as well as reaction classes. The safety recommendations compiled in this book are now available as PC database system also.

In a next step the involuntary handling of possible explosives must be excluded. For this purpose the following procedure has become widely accepted: the calculation of the so-called oxygen balance (c.f. equations 3-1, 3-2):

$$C_XH_YO_Z + \left(x + \frac{y}{4} - \frac{z}{2}\right) \cdot O_2 \rightarrow x \cdot CO_2 + \frac{y}{2} \cdot H_2O \tag{3-1}$$

$$\text{oxygen balance} = -\frac{1600 \cdot \left(2 \cdot x + \frac{y}{2} - z\right)}{MW} \tag{3-2}$$

In principle the inherent molecular oxygen content of the substance considered is evaluated, neglecting the potential of other hetero atoms to react with oxygen. In the case of a high self-oxidizing potential of the investigated substance the probability is to be rated high that it will also exhibit explosive properties. The results of typical sample calculations are listed in Table 3-3:

Table 3-3: Oxygen balance of selected compounds

Substance	O_2 balance
Nitrobenzene	-163
Trinitroglycerol	+3.5
Dinitrotoluene	-114

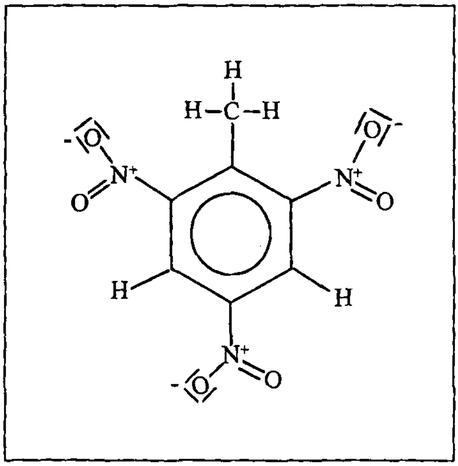
The result is assessed by checking whether or not the calculated result lies above -200. If this turns out to be the case, explosibility tests have to be performed even before laboratory scale work is undertaken. The tests recommended for this purpose are described in section 3.3.

Another recommended method for the estimation of the hazard potential related to a synthesis is the calculation of the enthalpy of reaction with the help of increments. The methods using increments rely on a thermodynamic basis. One of the most common method makes use of the tables of atomic bond energies available in the literature. Educts and products are split into units of known bond energies, the increments. These are subsequently balanced in the well known thermodynamic way:

$$\Delta H = \sum_{i=1}^{\substack{i=\text{number}\\ \text{of products}}} \sum_{j=1}^{\substack{j=\text{increments}\\ \text{in i}}} \left(m_j \cdot E_j\right)_i - \sum_{k=1}^{\substack{k=\text{number}\\ \text{of educts}}} \sum_{j=1}^{\substack{j=\text{increments}\\ \text{in k}}} \left(m_j \cdot E_j\right)_k \qquad (3\text{-}3)$$

m_j is the frequency with which an increment j occurs within component i or k, and E_j is the bond energy value of the increment j. The procedure shall be illustrated with the help of the following example.

Problem: Estimate the decomposition energy of trinitrotoluene (TNT). All data cited originate from [12].



		kJ/mole
Benzene ring bonds	6x	513.3
phenyl-alkyl bond	1x	355.5

cont.		kJ/mole
phenyl-hydrogen bonds	2x	407.4
alkyl-hydrogen bonds	3x	413.2
C-N nitro bonds	3x	360.3
O-N bonds within nitro group	3x	269.6
N=O bonds within nitro group	3x	601.2
TNT-atomization energy		9183.0

Postulating the following stoichiometry for the decomposition products:

$$5.25\,C + 1.5\,N_2 + 2.5\,H_2O + 1.75\,CO_2$$

their atomization energy amounts to

$$(5.25 \cdot 717.2) + (1.5 \cdot 946.2) + (2.5 \cdot 927.8) + (1.75 \cdot 1608.6) = 10319.1 \text{ kJ/ unit mass}$$

The difference is equal to a decomposition energy of -1136.1 kJ/mole TNT. This value is slightly higher than the -1046 kJ/mole TNT cited in reference [13]. This deviation is easily explained by a problem immanent to the method: the correct prediction of the decomposition products. Changing the postulated stoichiometry to

$$3.5\,C + 1.5\,N_2 + 2.5\,H_2O + 3.5\,CO$$

would lead to a calculated result of -836.5 kJ/mole TNT. Knowing these restrictions, it may nonetheless be stated that the magnitude is estimated reasonably correctly.

The American Society for Testing Materials ASTM provides a computer program named CHETAH for the purpose of similar calculations. This program is recommended too if a first estimate of the energy release accompanied by a process is desired. However, in this case considerable effort is necessary to get acquainted with the concept as well as with the computer program.

In practice, the limits of such methods are easily reached if organometallic compounds are involved in the process, for example in Grignard reactions, as there are hardly any increment data available in the literature for such chemical entities.

To assess the thermal controllability of the process, the value obtained for the heat of reaction by using one of the methods cited above has first to be multiplied by the mass fraction of the limiting component A of the process and divided by its molecular weight in order to obtain the specific heat of reaction. Dividing this result by the specific heat capacity of the reaction system yields the so-called adiabatic temperature rise ΔT_{ad} :

$$\Delta T_{ad} = \frac{\Delta_R H \cdot \gamma_A}{\nu_A \cdot MW_A \cdot c_P} \qquad (3\text{-}4)$$

This adiabatic temperature rise may be regarded as one of the most relevant technical safety data and will be of great importance in all that follows. It represents the temperature rise which will theoretically be observed as a heating up due to a total accumulation of all heat released and no heat exchange with the surroundings. $\Delta T_{ad} = 50$ K is regarded as a first value of reference. Reactions with smaller values are commonly regarded as well controllable while such with larger values should not be performed without extended safety precautions or in a diluted form.

3.2 Screening -Methods For kg-Scale Processes

It was outlined in chapter 2 in detail that screening tests primarily have the purpose, to provide a first characterization of the safety relevant substance properties as part of the basic assessment. It was further explained that the determination of the thermal stability of a substance is of the greatest importance. The most frequently used methods for this purpose are those that investigate thermal stability using very small amounts of sample material only. The most widely used test equipments to perform such investigations are the DTA (difference thermal analysis) and DSC (differential scanning calorimetry).

3.2.1 Difference Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC)

Fundamentals

In daily routine both terms, DTA and DSC, are used synonymously. This actually is quite a simplification as both differ significantly in their measuring and control set-up as well as their sensitivity. Nonetheless, practice shall prevail and therefore they shall be discussed together in respect to their advantages and disadvantages when applied as safety testing tools to determine the thermal stability of substance and mixtures.

In principle, the experimental set-up consists of an oven with temperature control, two sample containers - one for the material to be tested and one for a thermally inert reference material - and thermocouples in order to measure the thermal effects. Target values of a measurement are the time-dependent heat release rate and its integral value, which is equal to the total energy conversion. The experiments are usually performed in one of the two following designs:

• temperature scan:	the temperature is increased with a constant rate. This kind of test is regarded as the standard screening test
• isothermal:	as the name states, the temperature is kept constant for the duration of the experiment.

If the test equipment follows the DTA set-up, the temperature difference between sample and reference container is registered. A feed back control loop to the oven temperature does not exist. In a DSC set-up, however, this control loop is implemented, adjusting the oven temperature in such a way that the temperature difference between the containers is zero and the temperature set value follows the following relationship at all times

$$T|_t = T_{Start} + HR \cdot t \qquad HR = \text{heating rate} \qquad (3\text{-}5)$$

This is accomplished by controlling the heating power of both containers separately. This is also be called a compensation principle. If an exothermic effect occurs in the sample container, the heating power for this container has to be reduced, whereas in the opposite case of an endothermic effect the heating power must be increased for the sample container.

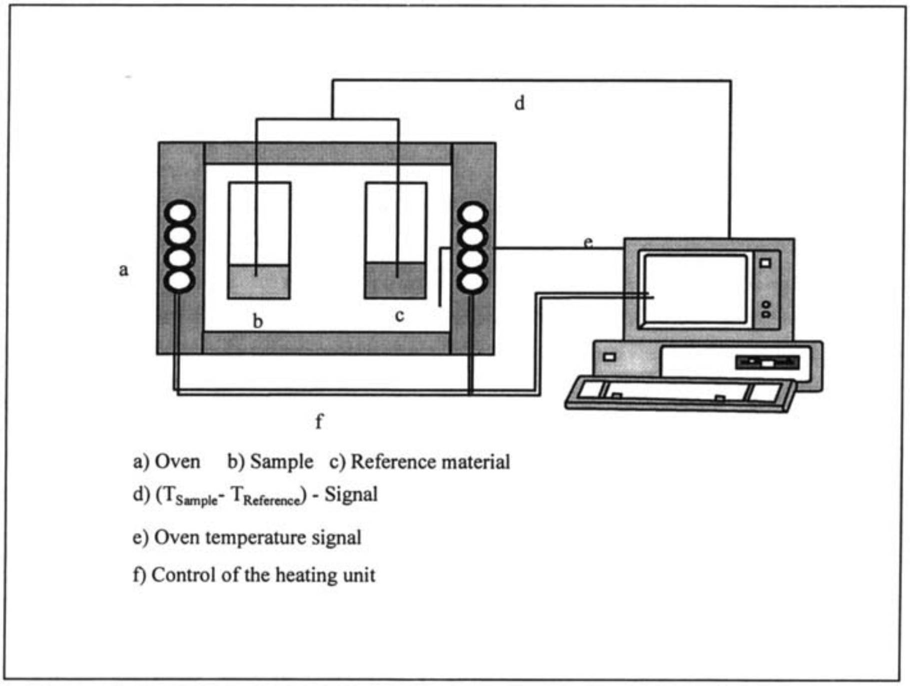


Fig. 3-1. Basic set-up of a DTA

It follows from the description of the different set-ups, that in the case of the DTA a transformation of the temperature difference signal into a power signal is necessary, which can only be accomplished with the help of a calibration function. This is not necessary with the DSC set-up, as the target value (the heating rate) may directly be obtained by multiplying the power amount necessary to compensate for the difference between sample and reference container with (–1). This is actually one of the reasons why the results obtained from a DSC measurement have a higher accuracy compared to those from DTA-tests [14].

The importance of the container material

The manufacturers of thermoanalytical equipment offer sample and reference containers made of a variety of materials. A suitable choice of the container material is very important as one aim of the test is to simulate the substance or substance mixture behaviour under normal as well as upset process conditions.

If the DTA or DSC are used as true screening tools in experimental safety testing, which in other words, means that there is not much more information available on the substance to be tested than the explosibility assessment according to the oxygen balance calculation, it may generally be recommended to use stainless-steel sample containers, which can withstand pressure up to 200 bar for the first tests.

When interpreting the results, however, it is important to bear in mind the possibility that the thermal effects observed are influenced by the interaction of the container material and the sample. If the chemical structure indicates this possibility, these first runs should be followed by further tests using chemically inert sample containers. The variety ranges today from pure glass containers, those with gold or Teflon coating to pure carbon containers. The use of such containers, however, is usually accompanied either by pressure or temperature measuring constraints.

The sample

The best measuring technology is not worth anything if the sample does not represent the material to be handled on the plant. DTA or DSC sample amounts are very small. They usually vary from 5 to 20 mg. Great care is demanded if the sample is truly to be representative. Three examples shall be discussed here in more depth, also to provide guidance on how best to overcome the problems:

- investigation of an isolated substance,
- of a homogeneous reaction mixture
- of a heterogeneous reaction mixture.

If an isolated substance is to be characterized, at least two aspects must be observed: firstly the purity of the material to be tested, secondly its manufacturing procedure.

The probability that a substance shows a strongly exothermal decomposition is severely influenced by its purity. ppm-amounts of impurities may already influence the temperature range of observable decomposition as well as the total heat output significantly [15]. If a substance is isolated according to a specified degree of purity the sample for safety testing has to be a sample from the plant manufacturing process. A pro analysis material of the same chemical substance obtained from another source would not be representative.

These considerations, however, lead to a general question. Is it at all possible to obtain a representative result for the safety assessment of the investigated process from a single measurement using a screening tool? Only accidentally, of course! It can hardly be expected that a 10 mg sample taken from a 200 kg batch isolated by spray drying will contain all impurities in representative amounts. It would require an ideal mixing process prior to sampling if the representativeness of the sample is not to be purely accidental. It is therefore highly recommended, whenever possible, not to rely on just one measurement. A reliable safety assessment becomes possible only if several measurements obtained under identical conditions are available and if their reproducibility is taken into account.

The second case, the preliminary assessment of a homogeneous liquid phase reaction performed batch-wise, is somewhat more complex. First a batch process has to be defined. This term is used for the discontinuous production process in which all reactants involved are filled into the reaction vessel completely at the beginning. This charging is commonly followed by a heating phase up to a desired temperature. The continuously stirred mixture is usually kept at this temperature level until the desired extent of reaction has been reached. This is followed by different work-up procedures and product isolation steps. The reaction engineering characteristics, which form the basis for the safety assessment, are given in detail in Chapter 4.

Due to the fact that all reactant material is completely charged initially, the highest reactant concentration is observed at the very beginning of the process. This is equivalent to the presence of the highest thermal potential in respect to the educts. Consequently it is recommendable for a first series of samples to characterize this initial phase.

Towards the end of the reaction time of a well developed process the highest product concentrations may be expected. Unfortunately this may not be true only for the desired components. The products of undesired parallel or consecutive decomposition reactions will also reach their highest concentrations at the end of the process. A second sample series should therefore characterize this final reaction phase.

Reactive intermediates, which due to their reactivity may have a higher thermal potential than educts or products, are not identified by either series. Therefore, it is advisable to take additional samples during the course of the reaction to allow a continuous assessment of the changing hazard potential as a function of the altered composition of the reaction mixture.

It becomes even more difficult if the representativeness of a sample has to be assured for heterogeneous processes. The degree of mixing for a liquid/liquid or a liquid/solid system achieved in a three necked laboratory flask usually differs significantly from the mixing degree on plant scale and is even harder to compare with the situation in a DTA or DSC sample container, in which no mixing occurs. In this case it is helpful to prepare artificial testing mixtures, which represent the desired mass ratio of the phases involved as well as differing ratios. This way a relatively quick overview can be obtained as to whether or not insufficient mixing, represented by the samples with deviating mass ratios, exhibits a safety problem due to an intensified hazard potential. Kinetic information however, can hardly be obtained for such heterogeneous systems.

The evaluation of temperature scanning experiments

Measurements in which the temperature is increased following a predefined ramp belong to the majority of experiments performed, because they are not very time-consuming and provide a great information gain. The three major results are:

- the total energy conversion of the physical or chemical transition process,
- the temperature range in which the transition is measurable/observed
- the temperature at which the maximum heat output is observed.

In principle, the total heat output can be obtained by integrating the measured power or signal attributed to the transition as a function of the temperature. A prerequisite to this integration is the definition of the base line. The temperature values for which the power signal deviates from the baseline for the first and last times, respectively, define the range in which the transition can be observed. The absolute threshold value depends on the individual measuring sensitivity of each device.

All three results do not represent physicochemical data. Each one of them depends on the applied heating rate in a different manner. Figure 3-2 shows three typical thermograms for an exothermic decomposing substance using three different heating rates.

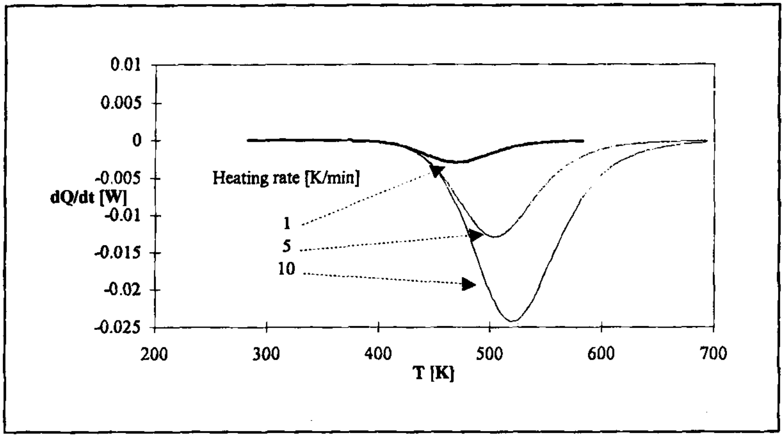


Fig. 3-2. DTA-thermograms of an exothermic decomposing substance recorded with three different heating rates

The measurement performed with a heating rate of 10 K/min shows the most distinct signal compared to the other traces. The initial and final peak temperature required to define the base line and to subsequently integrate the peak are easily identified and fixed. The trace obtained with a heating rate of only 1 K/min, however, is significantly less pronounced and the heat effect due to the exothermic decomposition reaction is far more spread in terms of time. In this case it is more difficult to decide on the upper and lower boundary temperature for the base line and the determination of the total heat output. This flattening of the peaks is accompanied by a reduction of the maximum observable power values. In part this can also be attributed to a decreasing sensitivity of the testing devices with slower heating rates.

Simultaneously the peak maxima are shifted to lower temperatures as the heating rate is reduced.. To a less significant amount this is also true for the detectable beginning of the peak, also called onset temperature.

The shift in onset temperature is caused by a variety of reasons. If DSC or, even more importantly, if DTA tests are performed applying high heating rates, the measuring system is not able to sustain a thermal equilibrium at all times. This is due to the high Φ factor, which, as outlined in section 2.3, is a measure for the thermal inertia of a system. The measured signal is initially dominated by the heating process and therefore does not reflect the heat output effect of the transition process correctly. The same phenomenon is also responsible for the fact that the maximum power values do not represent time but device specific values, which must not be used for further-reaching interpretations. The measurements performed with slower heating rates are, at least in this context, the more accurate ones. This becomes even more obvious when more than one reaction is involved in the investigated process. While the simultaneous reactions may not be identifiable or distinguishable when applying high heating rates, they become observable as shoulders when using low heating rates. If a DSC device of good quality is used for the measurements, the thermal equilibrium of the testing system is more easily achieved and sustained, because it is not the oven temperature which is controlled but the difference between sample and oven temperature. This concept results in a higher degree of measuring accuracy.

The shift in temperature, at which the maximum power signal is recorded, however, is primarily due to kinetic effects and is observed in both devices. This effect actually is evaluated for the thermal stability assessment of substances or mixtures.

In conclusion, it may be stated that the application of low heating rates results in temperature shifts of the onset and the peak maxima to lower values. They provide the chance to identify the presence of side-reactions. On the other hand the traces tend to be flat, which makes the base-line determination more difficult and leads to inaccuracies in the determination of the total heat output of the investigated process.

If, on the other hand, the heating rate is too high, the value of the maximum heat output rate may be erroneous, an error which subsequently also leads to false, in this case too high, values for the total heat output. The only way to avoid the risk of unnecessary errors in the total heat output determination is the application of several heating rates. Measurements with heating rates ranging from 1 to 10 K/min are recommended. The value for the total heat output of the investigated transition process should be determined as the result of averaging at least three values obtained from runs with three different heating rates. As a by-product at least three data sets of maximum power output and corresponding peak maximum temperature are recorded. These now have to be interpreted.

The next step in the evaluation of scanning experiments is to check on how strongly the shift in temperature of the maximum heat output rate depends on the heating rate. The kinetic background to this shift is best recognized when these data are plotted in an Arrhenius-type diagram. An example is shown in Fig. 3-3 using the data from Fig. 3-2. The slope of the observed linear relationship may be interpreted as a pseudo activation energy.

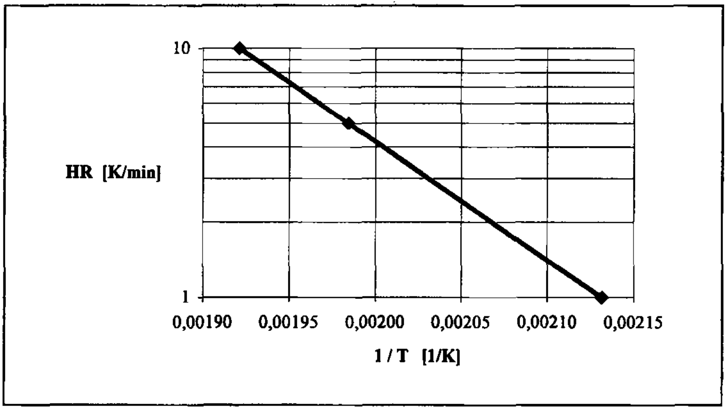


Fig. 3-3. Relationship of heating rate and temperature at which the maximum heat output rate is observed for the thermograms shown in Figure 3-2

It is known from the investigation of exothermic reactions that the activation energy usually ranges from 40 to 100 kJ/mol. This corresponds to slope values between 4500 to 12000 K in the Arrhenius-type diagram. Investigations carried out by Berthold and Loeffler in 1983 [16] and by Grewer in 1988 [15] showed that a normal temperature shift of the maximum power signal and an abnormal shift can be distinguished. The shift is regarded as normal if the temperatures at which the maximum heat output rate is observed differ by 40 K when the heating rate is varied by a factor of 10. Shifts of significantly more than 40 K are regarded as abnormal. This fact is exemplified in Figure 3-4.

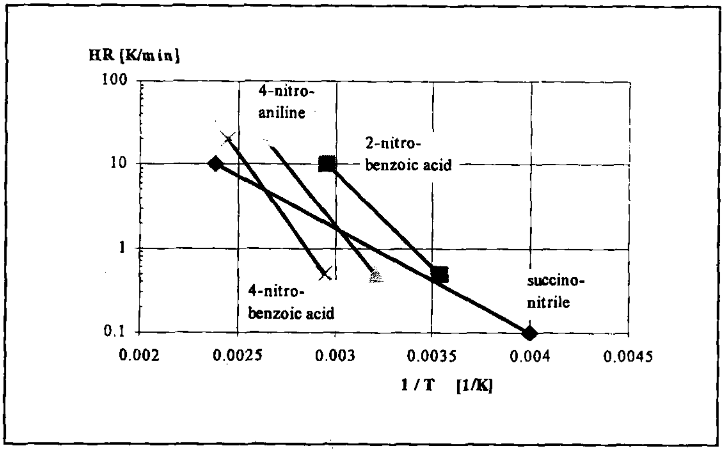


Fig. 3-4. Normal and abnormal temperature shifts of the maximum power signal in its dependence on the heating rate for different substances according to Grewer [15]

For the three compounds 4-nitroaniline, 2-nitrobenzoic acid and 4-nitrobenzoic acid, the relation between heating rate and the temperature at which the maximum power signal was observed is nearly identical, which results in very similar values for the slope in Figure 3-4. The value of the slope corresponds to the degree of shift, which is regarded as normal, and amounts approximately to

$$\frac{d\ln(\mathrm{HR})}{dT} \cong 0{,}057\ \mathrm{K}^{-1} \tag{3-6}$$

In the case of the nitrile, however, the slope has a value of 0,027 K^{-1}. This roughly corresponds to a temperature shift of 85 K for a variation of the heating rate by a factor of 10.

This result is important, because one evaluation method for DTA or DSC scanning experiments is the so-called *100 K - rule of thumb* [17]. It says:

> *An exothermic transition process that shows an observable onset in a DTA or DSC scanning experiment, performed with a heating rate of 10 K/min, at least 100 K higher than the recommended manufacturing process temperature will not pose a thermal hazard under plant operating conditions.*

Like most rules of thumb, this one, too, may lead to dangerous misjudgments with respect to the thermal process safety, if not applied correctly. The following shall demonstrate this. One of the fundamental theories used for the safety assessment of exothermic chemical reactions is explained in detail in Chapter 4.2: ***the thermal or heat explosion theory by Semenov*** [18]. The central statement of this theory is that an explosion-like runaway of an exothermic chemical reaction will always occur

- if the equilibrium between heat production and heat removal is left in favour of heat production and
- if at every temperature higher than the initial equilibration temperature the temperature gradient of the heat production rate due to the chemical reaction exceeds the gradient of the heat removal rate.

The mathematical equation which describes the critical balance between heat removal and heat production of a zero-order chemical reaction has the following form:

$$\frac{1}{e}=\frac{k^{*}(T)\cdot E\cdot \Delta T_{ad}\cdot V\cdot \rho\cdot c_{P}}{U\cdot A\cdot R\cdot T^{2}} \tag{3-7}$$

The dependence of the reaction rate on temperature can be approximated by the simple Arrhenius law. The further analysis is based on the assumption that the measurable onset in a DTA represents exactly the moment when the equilibrium state described above is left. Such a situation must also be observable under plant conditions. If the equation of critical balance for the measuring system is divided by the corresponding equation for the plant system, the following equation is obtained:

$$\frac{T_2^2}{\exp\left(-\frac{E}{R\cdot T_2}\right)}=\frac{T_1^2\cdot V_2\cdot U_1\cdot A_1}{\exp\left(-\frac{E}{R\cdot T_1}\right)\cdot V_1\cdot U_2\cdot A_2} \tag{3-8}$$

If, in a first approximation, the overall heat transfer coefficient is assumed to be identical for both systems and if the geometric ratio is taken to be constant

$$\frac{\text{Height}}{\text{Diameter}}:\quad \frac{H}{D}=\frac{H}{2\cdot r}=2 \tag{3-9}$$

it can be shown after some transformations that the temperature at which the critical equilibrium prevails depends on the activation energy and on the scale of the process.

The scaling factor itself is expressed in this case as a mass ration of DSC sample amount and material per plant batch.

$$1 = \exp\left(\frac{E}{R}\cdot\left(\frac{1}{T_1}-\frac{1}{T_2}\right)\right)\cdot\left(\frac{T_1}{T_2}\right)^2\cdot\sqrt[3]{\frac{m_2}{m_1}} \qquad (3\text{-}10)$$

Figure 3-5 shows the critical heat production rates calculated with the help of Equ. 3-3 for a 1 m^3 batch, which correspond to the measured onset in a DTA, assuming three different activation energies. It is of special interest to observe that the temperature at which the critical heat output rate is produced is shifted to much lower values with increasing scale.

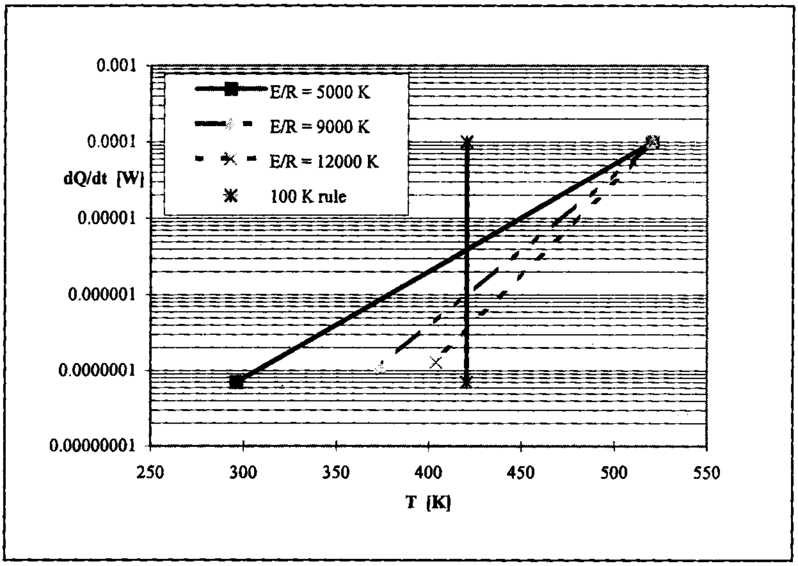


Fig. 3-5. Dependence of the critical heat production rate after Semenov on temperature assuming different activation energies in comparison to the 100 K-rule.

Figure 3-5 also demonstrates that the 100 K-rule provides a reasonable safety margin between the measured DTA-onset, applying a 10 K/min heating rate, and the process temperature only if the reaction rate of the transition observed in the DTA experiment depends strongly on temperature. If the activation energy is comparably small a much greater safety margin becomes necessary as the temperature at which the critical power is released, is shifted by far more than 100 K. The same activation energies correspond to the large temperature shifts of the peak maximum observed in DTA tests if the heating rate is varied.

At this point practical experience and theoretical scientific background have to be combined reasonably:

1. A safety concept which is entirely based on empirical safety margins should only be used in its reversed form, if absolute correctness is assumed.
2. Consequently, the 100 K-rule should have the following wording:

   An exothermic transition process,

   - *which is characterized by a normal shift of the peak maximum temperature measured in DTA scanning experiments with varying heating rates, i.e. the corresponding slope amounts to approximately 0,057* K^{-1}*, and*
   - *has a DTA onset in the 10 K/min experiment, which is* ***closer*** *to the manufacturing process temperature than 100 K,*

   has to be investigated more thoroughly applying other test methods, as this transition may pose a thermal hazard potential under plant operating conditions.

3. If there is only a very limited amount of substance available for hazard testing, an exception may be allowed in the sense that a first trial run to manufacture the desired product on small scale may be granted on the basis of the 100 K rule. This demands the full recognition of all boundary conditions mentioned above. The reasoning for this exception accounts for the very negative assumptions used in the theoretical treatment, such as the zero-order kinetics.
4. If one of the boundary conditions or one of the amendments to the newly formulated 100 K-rule is violated, the safety concept must not be based on this rule.

With these constraints in mind, the temperature shift of the peak maximum observed in DTA scanning experiments using different heating rate contains significant safety information. Even more important, however, is the fact, which has now repeatedly been shown that reliable information for the safety assessment of chemical processes cannot be obtained from a single measurement but from a series of measurements only.

Evaluation of Isothermal Measurement

Isothermal measurements are far more time-consuming, but the information content and the quality of the results are at least as good as, if not even better than those from temperature programmed tests. The main results are

- the total heat output due to a physical or chemical transition process,
- the peak shape, which provides a unique indication on the kinetics
- an estimation on the time to maximum reaction rate.

As has been outlined for scanning experiments, the determination of the total heat output for the transition process requires the fixing of the lower and upper integration limits of the power signal. In the case of isothermal experiments the identification of the end point is the more problematic one as the power signal usually approaches the baseline asymptotically. If the upper integration limit is chosen to be an early time value, the value for the total heat output will be an underestimation compared to the true value.

Again, one way to avoid this problem is the conduction of several isothermal runs with increasing initial temperature. In parallel to the increasing initial temperature a rise in the maximum power signal will be observed, resulting in more pronounced peaks. From a certain temperature level onwards this will also yield a good reproducibility in the determination of the total heat output.

The actual importance of isothermal DTA- measurements, however, has to be attributed to the first kinetic information to be obtained without the high degree of empiricism described for the scanning experiments. Fundamental to this is the basic process which underlies the DTA-/DSC experiment. It is a classical batch process. As described in the context of the importance of the samples used for micro thermoanalytical measurements, a batch process is characterized by the complete charging of all reacting materials at the beginning. If the chemical process follows an n-th order formal kinetic rate law, then the heat production rate must have its highest value at the very beginning of the isothermal experiment and must subsequently decay exponentially. If this is not the case, then this is an indicator for a much more complex kinetic situation. Figure 3-6 shows examples of isothermal measurements are representative for a reaction rate which following n-th order formal kinetics.

There may be an observable influence on the measured signal by the initial heating process necessary to reach up to the desired isothermal measuring temperature. The degree of influence observed will be dependant on the individual equipment. Due to this start-up effect the time at which the maximum heat output rate will be observed may be delayed slightly.

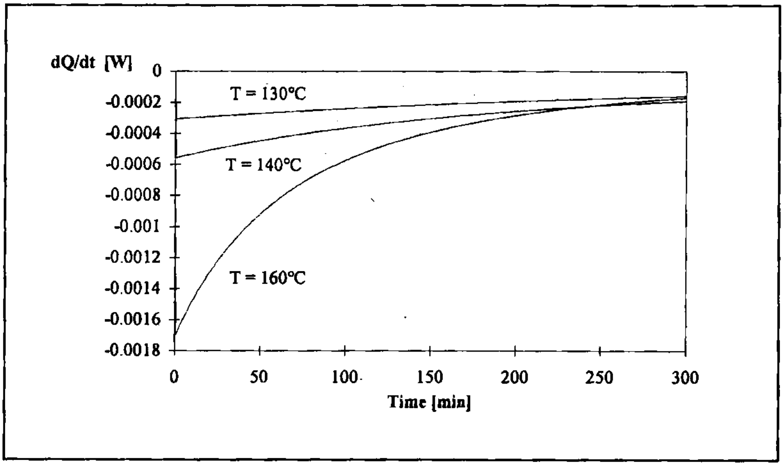


Fig. 3-6. Typical traces of isothermal DSC - measurements for an n-th order kinetic reaction mechanism; n>1

However, this delay will be short and approximately independent of the measuring temperature. In case of a significant delay and a strong dependence on the isothermal measuring temperature, the process investigated either shows an autocatalytic behaviour or can only be described by several reactions proceeding simultaneously. Typical thermograms for this case are presented in Figure 3-7.

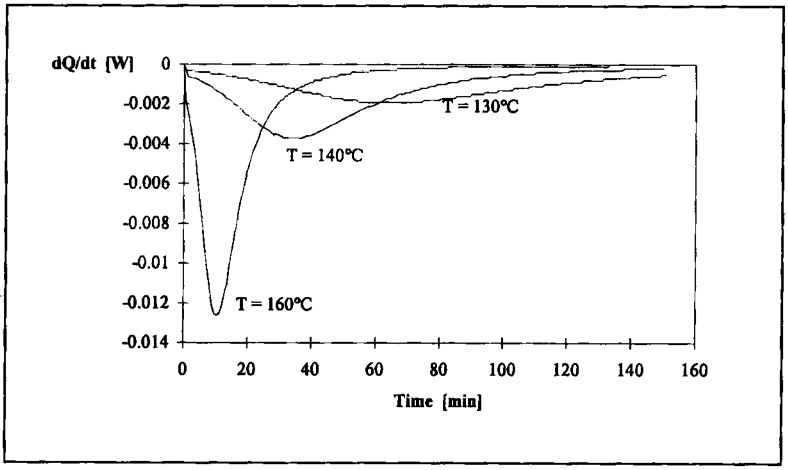


Fig. 3-7. Typical isothermal thermograms for an autocatalytic reaction

Alternatively to the 100 K rule, the safety assessment of a process can be based on the time to maximum rate under adiabatic conditions calculated from the results of isothermal DTA / DSC measurements. It has to be emphasized that the time to maximum rate must not be mistaken for the adiabatic induction time τ_{ad}, which is discussed in detail in Chapter 4.4. The time to maximum rate is better known in its abbreviated form TMR, which shall be used in the following paragraphs. The TMR can be deduced from Semenov's thermal explosion theory [18], which can be found in Chapter 4.2. Assuming a zero order chemical reaction performed in a batch reactor under adiabatic conditions, which means that there is no heat exchange with the surroundings, and a temperature dependence of the reaction rate, which can be described by the Arrhenius relationship, Frank-Kamenetskii was able to find an approximate solution to the exponential integral, which must be solved to calculate the time necessary to reach the point of highest reaction rate [19]

$$\mathrm{TMR} = \frac{R \cdot T_0^2}{E \cdot \Delta T_{ad} \cdot k_\infty \cdot \exp\left(-E/_{R \cdot T_0}\right)} \tag{3-11}$$

or by substituting Equ. (3-4) for the adiabatic temperature increase into Equ. (3-11):

$$\mathrm{TMR} = \frac{c_P \cdot R \cdot T_0^2}{E \cdot \Delta_R h \cdot k_\infty \cdot \exp\left(-E/_{R \cdot T_0}\right)} = \frac{c_P \cdot R \cdot T_0^2}{E \cdot \dot{q}_0} \tag{3-12}$$

If the heat exchange of the DTA sample container with the surrounding is regarded as negligible under isothermal measuring conditions, then the values obtained for the maximum specific heat output rate $\dot{q}_0$ and the corresponding measuring temperature T_0 may be used in Equ. (3-12), which is valid only for adiabatic conditions. In order to estimate the TMR for any other operating temperature, the activation energy must be determined first.

In a generalized form the heat balance for a chemical process may be formulated as:

$$\dot{Q}_{\text{accumulation}} = \dot{Q}_{\text{reaction}} - \dot{Q}_{\text{cooling}} \tag{3-13}$$

Under isothermal conditions there is no accumulation. Additionally, negligible heat exchange was assumed, which eliminates the cooling term. Consequently, the measured heat output rate may directly be attributed to the chemical heat release rate, which itself according to Arrhenius depends exponentially on the temperature. A plot of the measured maximum of the heat release rate in a semi logarithmic scale over the reciprocal value of the measuring temperature in absolute degrees Kelvin should therefore yield a straight line. According to the linearized model given in Equ. (3-14), the slope of this straight line is equal to the activation temperature E/R. In order to be able to obtain an estimate of the maximum heat output rate at other temperatures it is recommended to use specific power values, which means that the measured values should be divided by the sample mass for these kind of plots.

$$\ln\left(\dot{q}\big|_{\max}\right) = \ln\left(\nu_A \cdot V \cdot \Delta_R h \cdot r_{\max,\infty}\right) - \frac{E}{R} \cdot \frac{1}{T_{\text{isoth.}}} \tag{3-14}$$

This procedure is exemplified for the two processes which were characterized by isothermal DTA and whose thermograms were given in Figure 3-6 and 3-7. The plot for the determination of the corresponding activation temperatures is shown in Figure 3-8.

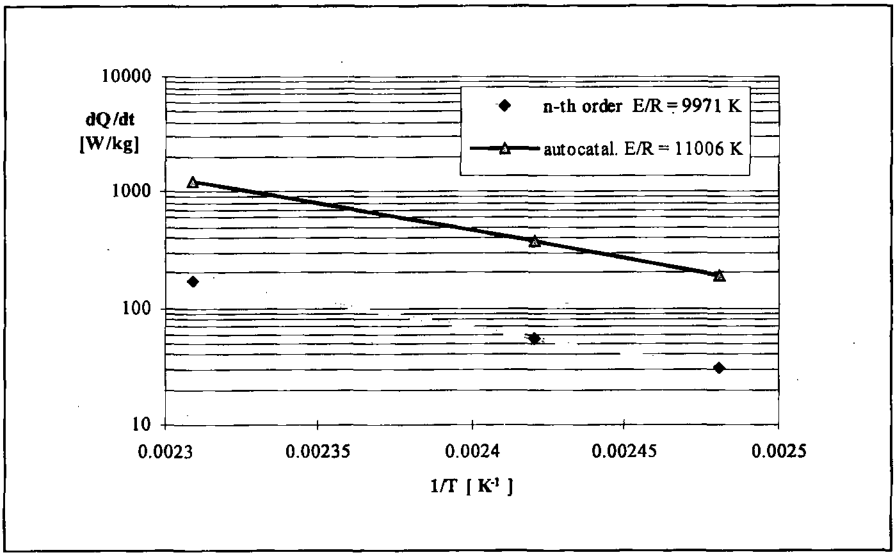


Fig. 3-8. Approximate determination of the activation temperatures E/R from isothermal DTA/DSC measurements, demonstrated for the examples shown in Figures 3-6 and 3-7

Having determined the activation temperature, Equ. 3-12 can now be used to calculate the TMR for all measured values of the maximum heat release rate and the corresponding measuring temperature. The value for the specific heat capacity must either be obtained separately or estimated reasonably. With the help of a plot of

$$\frac{\text{TMR}}{T_0^2} \quad \text{vs.} \quad \frac{1}{T_0}$$

estimates for the TMR at other process temperatures may be obtained. An example is given in Figure 3-9.

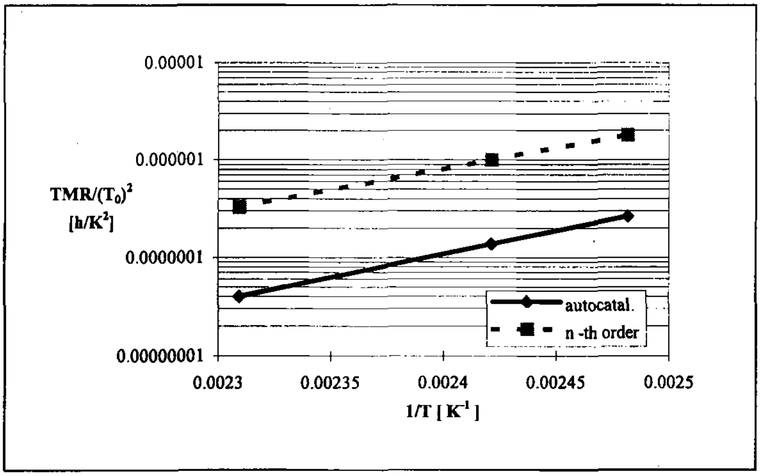


Fig. 3-9. Exact plot for the determination of TMR - values at different process temperatures for the two chosen examples

The interpretation of the y-axis, however, is rather difficult. Fortunately, experience has shown that this strict mathematical separation of variables is not necessary for daily routine. Absolutely sufficient results may already be obtained from a simplified plot of the TMR using a semilogarithmic scale over the reciprocal value of the absolute temperature. This is demonstrated in Figure 3-10, which additionally includes a mark for 50°C as a sample value for the process temperature to be assessed. The linearity allows the extrapolation to this process temperature by all means.

The following Table 3-4 shows estimated values of the TMR for both examples derived from the procedure outlined in comparison to values obtained from simulation using the exact kinetics and modelling true adiabatic conditions.

Table 3-4: Comparison of TMR values from isothermal DTA measurements and induction times obtained by exact simulation

	TMR [h]	simulated τ_{ad} [h]
n-th order reaction	83,5	97,9
autocatalytic reaction	23,0	73,0

The result of this comparison may be regarded as representative. The adiabatic behaviour of an n-th order chemical reaction is predicted with reasonable accuracy while the result of the estimation for the autocatalytic process is much too critical. However, the result gives a prediction which is definitely on the safe side, this way supporting the safety of the process.

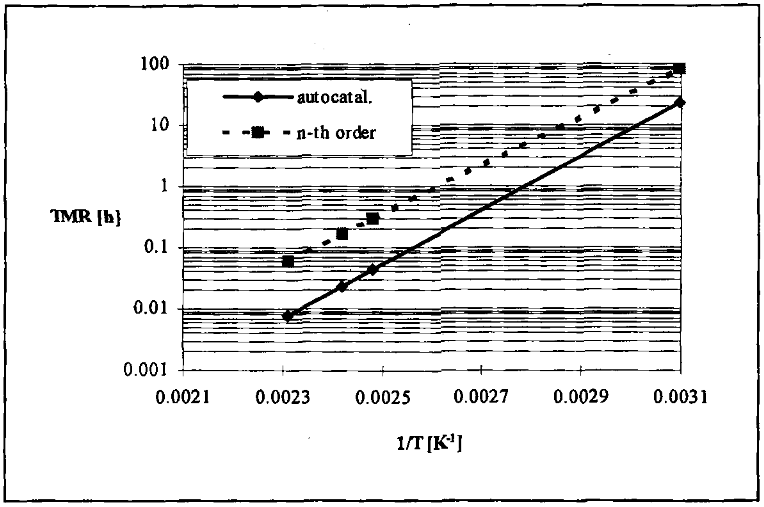


Fig. 3-10. Simplified TMR - plot for the chosen examples

But the deviation for the autocatalytic process is rather strong. In any case, criteria are required which allow an assessment of the TMR value to discriminate times representing an uncontrollable hazard potential and tolerable times.

Unfortunately there is no limit value which may be regarded as scientifically sound and correctly fixed. In principle it remains necessary to make a case by case assessment accounting for individual boundary conditions which are plant, process, and company specific. The only thing which may be provided here is general guidance on how to fix the value individually.

The model on which the TMR is based is the adiabatic self-heating process ignoring any consumption of reacting material. This is usually referred to as a worst case scenario. Under normal operating conditions quite a significant amount of energy is lost to the surroundings, therefore not contributing to the self-heating process anymore. Additionally there will be a consumption of reacting material in reality, which will limit heat release and duration. The TMR now indicates the time the process requires to reach the point of highest heat release rate starting from a certain initial temperature under adiabatic conditions. In other words, the interpretation of a TMR predicts the time available for corrective action.

In reality the operator does not have the complete TMR available for such action, as the temperature gradient will already have exceeded values which would allow an effective correction long before the maximum gradient is reached. Consequently the assessment of a TMR must account for its possibility and sensitivity to detect a maloperation. The latter is determined by the number and quality of technical measures implemented and the organizational precautions and preparations taken for such corrective action. If a process is mainly manually controlled, the identification of an upset operating condition will strongly depend on the frequency and the duration of the operator's presence while the sensitivity is a question of the quality of observation. This will be influenced by the quality of the operator training program as well as personal experience. For such a situation experts from industry recommend a limit value of 24 hours [8,20]. This may be stated as a rule:

> *If the TMR of a process, determined by isothermal micro calorimetric methods, amounts to less than 24 hours for the desired operating temperature, further testing is recommended before the first plant run, in order to identify necessary safety recommendations.*
>
> *An exothermic process with a TMR longer than 24 hours for the desired operating conditions will not pose an uncontrollable hazard potential under plant conditions.*

Depending on the actual plant design and company specific boundary conditions a case by case assessment may lead to a reduced limit value for the TMR.

3.2.2 The Carius Tube Test

Besides the commercially available DTA / DSC equipment there are quite a variety of micro calorimetric measuring techniques, which are suitable to characterize the thermal stress capacity of substances and mixtures using only small amounts of sample material. Some of these are also commercially available, others are self-made.

The main feature of the Carius tube test, which was developed by ICI as the so-called 10 g tube test, is the simplicity of its set-up (cf. Figure 3-11) [21]. As the name already says, a 10 g sample is filled into a special Carius tube, which has a dip in the bottom to accommodate a thermocouple. The top may be closed using a metal/glass fitting, which contains a pressure sensor. The tube is placed into an oven, which may be heated up in a controlled linear way. In analogy to the DTA-set-up the temperature difference between sample and oven temperature as well as the pressure are recorded.

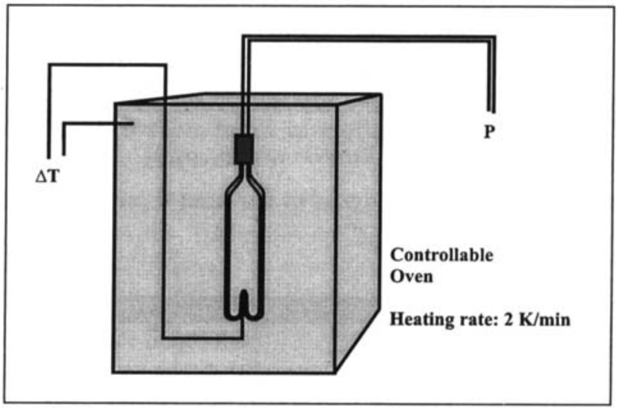


Fig. 3-11. Basic set-up of the Carius tube test

The run is evaluated in completely the same way as described for the temperature-programmed DTA runs. Additional information may be obtained from the residual pressure observed after the equipment has been cooled down to ambient temperature. This residual pressure will indicate the amount of gas formed during the test run. A semilogarithmic plot of the pressure over the reciprocal absolute temperature will provide a pattern which allows the discrimination between pure vapour phase and gas generating systems. In the first case a linear increase should be observed while in the latter case a curved pattern should be identifiable.

Two commercial versions are obtainable of this test. One is close to the original described here, while a slightly modified version is called RADEX [22]. The RADEX uses only 5 g sample material but allows for the simultaneous measurement of four samples per run due to a modified oven. This enables a time effective way to check on reproducibility or on material compatibility by adding traces of construction and other plant material, which might get into contact with the actual sample to be tested, into some of the four test tubes.

3.2.3 The Miniautoclave Test

The pressure resistance of the sample containers used in all previously described testing methods is rather limited. Depending on the material the sample containers are made of and even more on the sealing mechanism used to close them, the pressure resistance varies from a few bars for aluminum pans and glass crucibles or tubes, like those used for DTA or 10 g tube tests, up to 200 bars for stainless steel containers. If the occurrence of a higher pressure is expected, it is recommended to use miniautoclaves for such investigations, which are also commercially available (c.f. Figure 3-12).

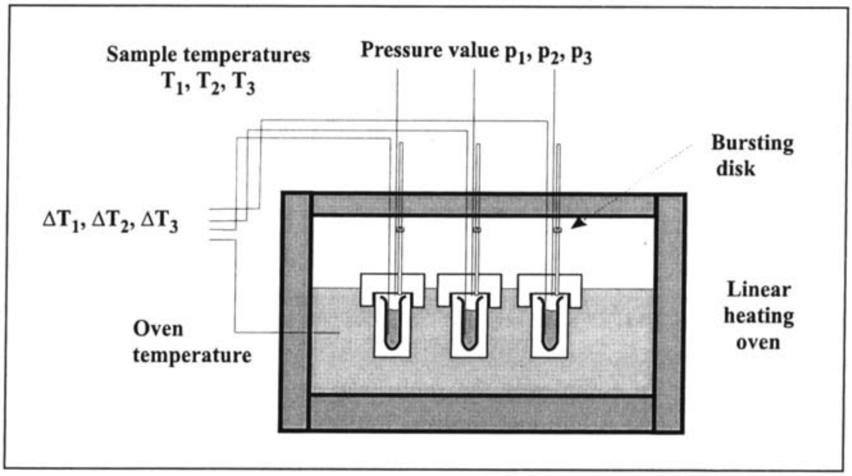


Fig. 3-12. Basic set-up of the miniautoclave test

These stainless steel autoclaves usually withstand pressures up to 1000 bar and use approximately 2 g samples. While the pressure measurement can be performed with very good accuracy, the recording of thermal effects is problematic. This is due to the extremely high Φ factor of this measuring system.

This draw-back is not extremely important, because the safety technical problems which accompany substances forming large amounts of gas due to a thermally initiated decomposition are absolutely dominated by the resulting pressure rise. The hazard associated to the thermal effect may be rated comparatively low. Besides the pressure measurement the remaining set-up and the data evaluation is in complete analogy to the DTA principle.

3.2.4 Open Cup Measuring Techniques

One of the fundamental principles to be observed in the field of safety technology is that a hazard assessment has to be based on worst case assumptions. This applies in all cases, whether a physical unit operation or the safe handling of substances, mixtures or a chemical reaction is evaluated. This principle has already influenced the design of hazard testing methods in part. For example, the majority of methods to screen the thermal behaviour of substances use closed cells. This is preferred as any pressure build-up will have an accelerating effect on the kinetics. In addition, the maximum pressure observed experimentally will give a good indication on the suitability of the plant equipment intended for use. In the case of incompatibility, a different equipment has to be looked for.

In a few cases, however, it turns out to be advantageous if complementary tests are performed with open test cells. Examples are one very simple and one relatively sophisticated test:

- the open Carius tube test DTA
- thermogravimetry in combination with DTA.

The test-tube DTA mainly consists of a heatable aluminum block, which has drilled holes to accommodate 5 to 6 Carius tubes. Thermocouples are directly inserted in the sample, and one is used to measure the aluminum block temperature [23]. As in all other cases of thermal stress tests, the aluminum block may be heated up linearly or its temperature is kept constant at a predefined set value. It is therefore very similarly designed to a conventional DTA set-up. The advantage of this test is the easy detectability of flammable gases formed due to the decomposition process. Actually it is not important whether the flammable gases originate from a decomposition or an evaporation. To detect such gases usually a glowing red platinum wire is held above the opening and a possible ignition is observed.

The draw-back inherent to all open testing systems lies in the significant heat loss which accompanies all evaporation or gas generating processes. This diminishes the thermal sensitivity significantly.

In the case of the combined DTA/TGA (thermogravimetric analysis), open DTA test crucibles are hooked on a high precision balance and then vertically inserted into the heating chamber of the DTA. This way thermal effects and loss of mass may be recorded simultaneously and quantitatively. Due to this arrangement, such effects are extremely well identifiable which show strong exothermic transitions only if a critical amount of volatile components have been evaporated thus heightening the concentration of the unstable compound. This is extremely helpful if the thermal stability of distillation or rectification residues has to be assessed.

3.3 Further Basic Assessment Test Methods For kg-Scale Processes

In Section 2.3 it was explained that the burning and ignitability behaviour of substances has to be characterized in addition to the thermal stability as part of the basic assessment. The methods commonly used for this purpose and their evaluation shall be outlined here briefly.

3.3.1 The Burning Test For Solids

The aim of this test is to characterize the burning behaviour of a solid in a settled-down state. It is one of the oldest techniques used in chemical hazard assessment and is a well-established part of all standard test procedures to be found in companies belonging to the chemical industry.

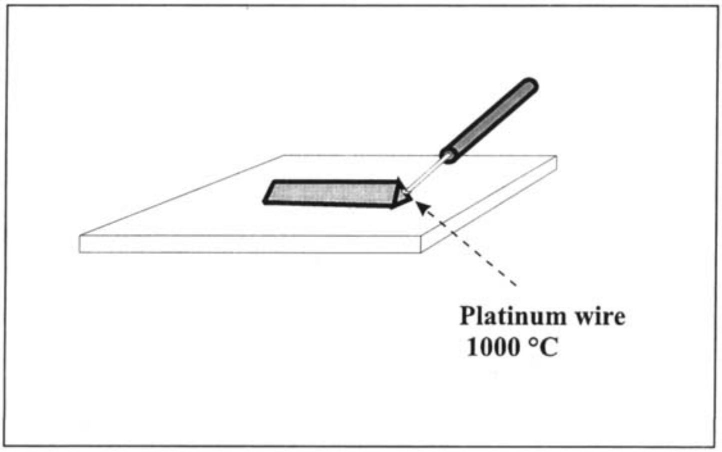


Fig. 3-13. Schematic presentation of the burning test

The information obtained from this test is of great relevance to the characterization of dust explosible substances. Consequently it is documented in many technical standards on dust explosions, such as in Append. 2 of the German VDI 2263 *Burning dust and dust explosion, hazards, assessments and protective measures* [24].

Approximately 15 ml of a dried sample are piled up conically on a ceramic plate covering roughly 4 cm in length and 2 cm in width. An electrically heated, glowing red platinum wire is brought into contact with the sample and the burning behaviour is observed (c.f. Figure 3-13).

When drying processes are to be assessed, it is recommendable to perform the burning test at elevated temperatures instead of room temperature. For this purpose the pile is placed in a quartz glass tube and heated in an oven. During the actual test the sample is removed from the tube to enable better observation conditions. It is recommended to ensure that the heating process does not last longer than one hour. The assessment is documented using the so-called burning number B.N. The criteria are presented in Table 3-5.

Table 3-5: Assessment criteria for the burning test

			Reference substances	
	Type of reaction	B. N.	room temperature	100°C
no fire propagation	no ignition	1	Sodium chloride	Sodium chloride
	short ignition followed quickly by extinction	2	Tartaric acid	Zn-stearate
	local burning or smouldering with very limited propagation	3	D (+) Lactose	
	propagating glowing decomposition without spark emission or flameless decomposition	4	4-Amino-3-hydroxynaphthalene-2,7-disulfonic acid	
propagating fire	firework-like combustion or slow, controlled burning with flames	5	Sulfur Ammonium-dichromate	D (+) Lactose
	fast combustion with or without flames	6	black powder	

3.3.2 Test On The Ignitability Of Solids

This test is aimed at the identification of possible ignition sources by bringing the solid sample into contact with a variety of such, each representing a different ignition energy. Additionally it is observed whether the combustion prevails after the ignition source has been removed again. For this purpose a 10 mm^3 to 3 cm^3 sample is piled up conically on a ceramic plate and exposed to the following ignition sources:

1) 5 trials with a Ce/Fe spark obtained from a household gas igniter held as close as 5 mm to the sample
2) flame of a conventional match
3) tip of a burning cigarette
4) 5 trials by warming up the sample with the reduced flame of a Bunsen burner for 10 seconds each time
5) 5 trials with a glowing red silver wire of 5 mm diameter which is pushed into the pile for 10 seconds each time
6) throwing the sample into a glowing red iron dish

The assessment is performed with the help of symbols and abbreviations defined in Table 3-6.

Table 3-6: Evaluation of the ignitability test for solids

Observation	Symbol or abbreviation
the sample is not ignited	–
the sample ignites but extinguishes immediately after	(+)
the sample ignites and burns completely or smoulders or forms smoke	+
the sample ignites, pops and burns	+Pop
the sample ignites and explodes	+Expl.
forms smoke without flame	Comb.

In addition, the following tests and observations, respectively, are conducted and documented:

- in the case of smoke or fog formation the gas phase is tested for flammability with the help of a Bunsen burner flame, in order to obtain indications on the possible risk of a confined explosion due to the formation of smouldering vapour-air mixtures
- provided that a substance can be ignited either with the help of the reduced flame of a burner or the Ce/Fe spark in less than one second, the substance must be rated *highly flammable*.
- substances which can be ignited with the reduced flame of a burner or the silver wire only if they are exposed to this ignition source for more than one second, are rated *flammable*
- substances which are ignited only in the glowing red iron dish are regarded as being of *low flammability*.

3.3.3 Flash-point of Liquids

The flash-point is used to characterize the fire and explosion hazard potential of a liquid. According to the German Industrial Standards DIN 51755, 51758, and 51376, the flash point is defined as the lowest temperature referenced to ambient pressure of 1013 hPa at which , under exactly specified measuring conditions, sufficient vapour of the liquid tested is generated that a flammable vapour-air mixture is formed, which can be ignited by an external ignition source [25,26,27].

The testing methods are well defined in numerous standards. Tests with open and closed sample cups are discriminated. The following Table 3-7 provides an overview on the most relevant standards.

The great variety of methods described explains why no example is presented here of the basic measuring set-up. It is recommended to consult the primary sources for this purpose, which are referenced in Table 3-7. It is rather more important is to discuss parameters which influence the absolute flash-point values and to make some remarks regarding their interpretation. It is important to understand that the flash-point is no physicochemical property of a substance but a technical safety data, the value of which strongly depends on the measuring technique.

Table 3-7: Overview on relevant standards for flash-point determination methods

Open Cup		Closed Cup	
with stirrer	without stirrer	with stirrer	without stirrer
	ASTM D 92 ASTM D 1310 BS 4688 BS 4689 DIN 51376 IP 35 IP 36	AFNOR M 07 ASTM D 93 BS 2839 BS 3442 DIN 51758 GOST 6356 IP 33 IP 34 IP 170	AFNOR M 07 AFNOR T 66 ASTM D 56 ASTM D 3278 BS 3442 DIN 51755 DIN 53169 DIN 53213 IP 33 IP 170 NF T 60-103

For the evaluation of the fire and explosion hazard potential, which is part of handling flammable liquids, flash-points are categorized in hazard classes. The number of classes depends on the kind of handling regulated. For the chemical industry, use and storage are of the greatest importance, regulated for instance in the German VbF [28], followed by transport with tank cars, on rail, with ships or aircrafts, which are all treated in individual regulations.

The German VbF first discriminates between liquids completely miscible with water in any ratio and such which are not miscible with water in every ratio. The latter are split into three classes, all starting with the letter A:

liquids with a flash point of less than 21 °C	A I
liquids with a flash point between 21 and 55 °C	A II
liquids with a flash point between 55 and 100 °C	A III

All liquids miscible with water in any ratio which have a flash point of less than 21 °C are classified as B. Special attention is necessary if a process requires the use of liquids classified either as A I or B.

The flash point is strongly influenced by the presence of impurities. Already a small amount of a lower boiling impurity will result in a significant decrease of the flash-point measured. This is the reason why flash points found in the literature should not be used arbitrarily. In most cases, are measurements of one's own characterizing the actual plant material is more recommendable. The problem shall be elucidated further by citing a study conducted back in 1989 [29]. 23 frequently used organic solvents were listed with flash-point data originating from four different data bases and two literature sources. It was taken care that only those solvents were included in this table which according to the different sources had their flash-point data measured in identical testing systems. Table 3-8 contains this list.

The table was evaluated using criteria mentioned in the German DIN 51755, which define the allowed variability in repeated measurements. According to this standard, experimental deviations

- of 1.5 K for substances with flash points between 5 and 65 °C,
- of 3 to 4 K, depending on viscosity, for substances with flash points lower than 5 °C,
- of 3 K for substances with flash points above 65 °C.

are allowed. Only in 12 out of those 23 substances was the variability in the data reported sufficiently small to comply with the stated requirements.

One of the few commercially available data bases with truly validated flash point data is CHEMSAFE™, by the German DECHEMA e.V. [32]. The validation was undertaken by the Physical Technical Federal Institute in Braunschweig, Germany.

Flash points of mixtures cannot simply be deduced from the data of the pure components. This is due to the quite complex relationship which describes the vapour pressure behaviour of mixtures. Only for the comparatively simple case of binary mixtures, algorithms are known which allow the calculation of the flash-point with satisfying accuracy [e.g. 33].

Flash points of aqueous solutions pose another special problem. In general, the water mass fraction must be quite large to yield a higher flash point than that belonging to the pure organic compound. A well-known example is ethanol, which as a pure substance is rated B in accordance with the German VbF. More than 30 wt-% of water are necessary to observe a flash point higher than 21 °C, which is not subject to classification any more. All this is valid only for solutions. In the case of surface layer formation, the organic phase will dominate the flammability behaviour.

Table 3-8: Flash points of a variety of organic solvents - comparison of tabulated data originating from different sources [29]

	Flash-point °C					
Substance	US Environmental Pollution Agency Database	LSI Safety Data Bank of Schering AG	Design Institute for Physical Property Data DIPPR	US Occupational Health Service Database Hazardline	Nabert-Schön [30]	Process Engineering Calculation Methods [31]
Acetone	-24	-19	-18	-20	-19	-19
Acetonitrile	13	2	6	6	2	2
n-Butanol	29	35	29	29	29	29
Cyclohexane	-20	-18	-20	-20	-18	-18
1,4-Dioxane	12	11	12	12	11	12
Acetic acid ethyl ester	-7	-4	-4	-4	-4	-4
Ethanol	13	12	13	13	12	11
Ethylene glycol	111	110	111	111	111	111
Diethyl ether	-45	-40	-45	-45	< -20	-41
n-Heptane	-4	-4	-4	-4	-4	-4
n-Hexane	-22	-26	-22	-22	< -20	-26
Isobutanol	28	27	28	28	27	-
Isopropanol	12	12	12	12	12	12
Isopropyl ether	-28	-22	-28	-28	-	< -20
Methanol	11	11	11	11	11	11
n-Pentane	-	-49	-40	-49	< -20	< -40
n-Propanol	25	15	15	23	15	15
Toluene	-	6	4	4	6	6
Tetrahydrofuran	-	-17	-14	-14	-17	-17
Dimethylformamide	-	58	58	58	58	58
tert.-Butanol	-	4	11	11	11	11
n-Amyl alcohol	-	49	33	33	49	33
2-Butanol	-	-	24	24	24	24

3.3.4 Ignition Temperature of Liquids

The ignition temperature is used to characterize the susceptibility of a liquid to self-ignite at a hot surface. This conforms to its definition as the lowest temperature under standardized conditions at which ignition is observed if a liquid gets into contact with a hot surface in the presence of air. Standards which describe the test method in detail are the German DIN 51794 and the European Directive L383-A98, annex 9 [34,35].

From a safety technical point of view the ignition temperature is of special importance as a variety of installations in a chemical plant may have hot surfaces. Examples are steam supply pipelines with missing insulation or electric motor coverages. Saturated steam of 6 bar has a temperature of 180 °C. After some time of operation the pipe surface will have reached the same temperature. Assuming the use of diethyl ether in an indoor plant room through which the pipeline runs and an accidental release of the ether resulting in its contact with the hot surface, such an ignition might happen. The assessment of the ignition temperatures measured follows these and equivalent considerations. Their documentation may be found in e.g. the German DIN/VDE 0165. This standard defines six temperature classes, T1 to T6, assigned to different temperature ranges [36]. They are presented in the following Table 3-9.

Table 3-9: Temperature classes according to DIN/VDE 0165 [36]

temperature class	range for the ignition temperature	maximum allowable surface temperature for plant installations
T1	> 450 °C	450 °C
T2	> 300 ≤ 450 °C	300 °C
T3	> 200 ≤ 300 °C	200 °C
T4	> 135 ≤ 200 °C	135 °C
T5	> 100 ≤ 135 °C	100 °C
T6	> 85 ≤ 100 °C	85 °C

The basis of safety expressed in these temperature classes follows a simple rationale: In a plant

1. only such compounds may be handled which have a higher ignition temperature than the maximum allowable surface temperature of an installation permitted in the temperature class considered, and

2. only those components may be installed that have a guaranteed maximum surface temperature lower than the maximum permitted in this temperature class.

Table 3-10: Ignition temperatures of a variety of organic solvents - comparison of tabulated data originating from different sources [29]

	Ignition temperature °C					
Substance	US Environmental Pollution Agency Database	LSI Safety Data Bank of Schering AG	Design Institute for Physical Property Data DIPPR	US Occupational Health Service Database Hazardline	Nabert-Schön [30]	Process Engineering Calculation Methods [31]
Acetone	603	540	538	465	540	465
Acetonitrile	524	526	524	524	-	-
n-Butanol	365	340	343	365	340	340
Cyclohexane	260	260	260	245	260	245
1,4-Dioxane	180	375	180	180	375	375
Acetic acid ethyl ester	800	460	427	427	460	430
Ethanol	423	425	423	363	425	360
Ethylene glycol	413	410	-	400	410	400
Diethyl ether	180	170	180	160	170	160
n-Heptane	223	215	223	215	215	213
n-Hexane	261	240	234	225	240	225
Isobutanol	427	407	427	416	430	-
Isopropanol	399	425	399	399	425	399
Isopropyl ether	443	405	443	443	-	435
Methanol	464	455	464	385	455	385
n-Pentane	309	285	260	260	285	258
n-Propanol	371	405	371	413	405	385
Toluene	536	535	536	480	535	482
Methylene chloride	662	605	662	556	605	605
Tetrahydrofuran	-	230	-	321	260	260
Dimethylformamide	-	440	-	445	440	420
tert.-Butanol	-	482	478	480	470	470
n-Amyl alcohol	-	300	300	300	300	300
2-Butanol	-	-	406	405	390	390

The ignition temperature also is not a physicochemical substance property but an experimental result dependent on the measuring equipment. Therefore the same care is required for the use of published data as was described for the flash point. Besides all common causes for erroneous data like the presence of impurities, the ignition temperature is subject to another influence parameter, the time delay until ignition is observed. This time delay may easily amount up to three minutes and more. If the observer does not wait long enough, the ignition temperature will be reported too high.

Table 3-10 gives proof of the above-made remarks. It originates from the same comparative study cited in section 3.3.3. Only in the case of 6 out of 24 substances the ignition temperatures published vary within the range, which is experimentally permitted according to standard DIN 51794.

The data base CHEMSAFE™, which was already mentioned in the context of published flash point data, again, contains PTB validated data only.

3.4 Partial Testing for Explosion Risk

Besides the theoretical analysis of the oxygen balance, some results from tests performed as part of the basic assessment also give good indication on an explosion risk related to handling a certain substance. Primarily these are energy values determined with the help of DTA or DSC measurements, the burning number, and first results obtained from the ignitability test of solid substances.

In the sense of a testing flow sheet, it is helpful to fix criteria which directly lead to further testing on explosive properties if certain results are obtained from the above mentioned tests. This reduces the effort to perform all relevant tests at all times. Fortunately, these criteria do not have to be hard and scientifically proven. It is fully sufficient if they are derived empirically and if it is ensured that they are adjusted provided new results demand this.

Approximately 25 years ago a working group was established, initially with participants from Switzerland and Germany only, today with further European partners, which has dedicated its work to the development of test methods and their evaluation. A significant part of its work was published by Grewer et al. [15,20]. According to the expert opinion of this working group, further testing on explosive properties is always recommended

- if the exothermic energy release measured in a DTA or DSC exceeds -700 J/g or
- if the burning test resulted in a burning number greater equal to 4, or
- if the ignitability test result is: Ce/Fe: +, glowing red iron dish: +Pop or +Expl.

At this point it has to be emphasized again that, due to their empirical character, these criteria are *neither concluding nor absolute,* and provide a first guidance only.

If the basic assessment or other results indicate an explosion risk, a variety of test methods is available to verify and characterize this substance property. If a positive verification is obtained, this result has to be notified immediately to a special national agency, which is uniquely authorized to carry out certified testing. Some agencies are listed below:

USA Associate Director for Hazardous Material Safety
RSPA/DOT
Washington D.C. 20590

U.K. Health and Safety Laboratory, HSE
Harpur Hill, BUXTON
Derbyshire SK 17 9 NJ

Japan Technology and Safety Division
Transport Policy Bureau
Ministry of Transport
2-1-3 Kasumigaseki Chiyoda-ku
Tokyo 100

Germany Federal Institute for Material Testing and Research, BAM
Unter den Eichen 87
D-12 205 Berlin

They are not only responsible for certified testing but in addition for classification in terms of UN recommended transport of dangerous goods or nationally specific legislation on explosives.

The three most relevant testing methods are:

- the drop hammer test
- the friction test
- the Koenen test

The Drop Hammer Test for Liquids and Solids

A sample of either 100 mg of a solid or 40 mm^3 of a liquid is enclosed in an impact device consisting of two co-axial steel cylinders, one above the other in a hollow cylindrical steel guide ring. The sample is subjected to a mechanical stimulus exerted by a drop weight falling on the upper steel cylinder. A number of slightly different set-ups exist, of which two shall be mentioned here: the BAM apparatus and the Fa. Kühner apparatus according to Lütolf. In the case of the Kühner equipment, the drop weight has a mass of 5 kg and the fall height equals to 0,8 m, resulting in an impact energy of 39 Nm. With the BAM apparatus, drop weight and height of fall can be varied as given in Table 3-11. The basic set-up is sketched in Figure 3-14.

Applying the drop weight with the highest mass available for the BAM apparatus from a height of fall of 0,4 m gives the same impact energy as exerted by the Fa. Kühner apparatus.

Table 3-11: Test Variables for the BAM Drop Hammer Test

drop weight [kg]	height of fall [m]	impact energy [Nm]
1	0,10 - 0,50	0,98 - 4,9
5	0,15 - 0,60	7,30 - 29,4
10	0,35 - 0,50	34,30 - 49,0

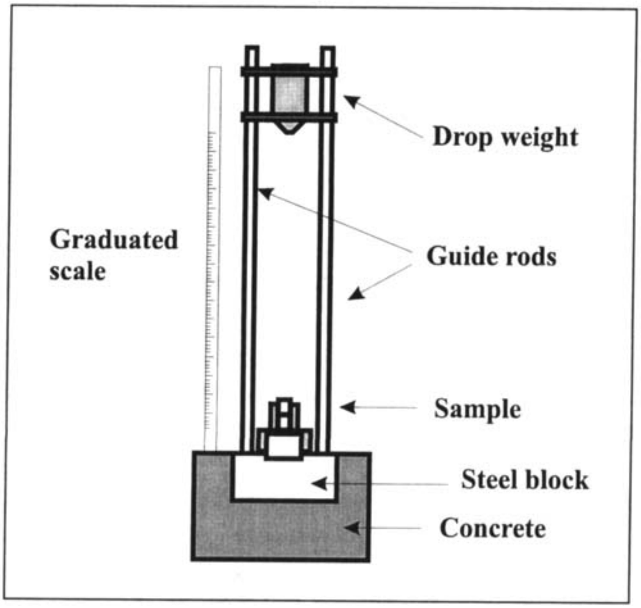


Fig. 3-14. Schematic presentation of a drop hammer apparatus

The substance is tested in at least 6 trials; some internal company procedures set the maximum number of trials to 10. A trial is regarded as positive if either detonation, fire, sparks or strong smoke development is observed. Often, a first test series is performed with the sample wrapped in aluminum foil, which increases the impact sensitivity, and a second test series without the wrapping only in those cases where a positive trial was recorded in the first series. A substance is rated *impact sensitive* if a positive result was obtained only with the aluminum foil, and rated posing an *explosion risk* with at least one positive result without the foil.

The less hazardous rating, sensitive to impact, must not be underestimated, especially not in those cases where this property was determined for a liquid to be conveyed. If the liquid is to be pumped with the help of a piston pump, compression gas bubbles may be formed, which may exert a shock impact comparable effect on the liquid and initiate an explosion-like decomposition.

Consequently, if a substance sensitive to mechanical impact is to be handled, all steps in the working procedure have to be investigated carefully with respect to effects with comparable consequences. Provided an explosion risk was detected, further testing, which includes the Koenen test and tests on the sensitivity to a detonation shock wave and ability to propagate the detonation, is highly recommended before a concluding safety assessment is performed.

Friction Test for Solids, Pastes and Gel-Type Substances

One of the recommended test methods for the determination of friction sensitivity was also developed by the German BAM [38]. If the substance to be tested is a solid, drying and sieving is recommended. This increases the sample's sensitivity to an extent, which most probably exceeds the same under process condition. For the test the sieve fraction is used which has passed the 0,0005 m mesh. Approximately 10 mm^3 are spread over 0,1 m on a specific part of a porcelain plate. A specially shaped porcelain peg, which is fixed to a loading arm, is once moved forward and back over the sample, thus exerting a mechanical stimulus.

The friction force is varied by changing the masses on the load arm. The mass on the load arm may vary from 0,5 to 36 kg, which is equivalent to forces from 5 to 360 N. With each mass a maximum of 6 trials are performed until a positive result has been obtained.

The evaluation distinguishes between

- no reaction,
- decomposition, amongst other things detectable by change of colour or odour,

- ignition,
- crackling and
- explosion

The susceptibility is characterized by the lowest force value in Newton which in at least one out of six trials gives ignition, crackling or explosion.

The substance is rated posing an *explosion risk*, if at least one test with the maximum friction force of 360 N gave a positive result.

The steel cartridge test according to Koenen [38]

In this third test a possible explosion is triggered by heating the substance under confinement. The basic test set-up is shown in Figure 3-15.

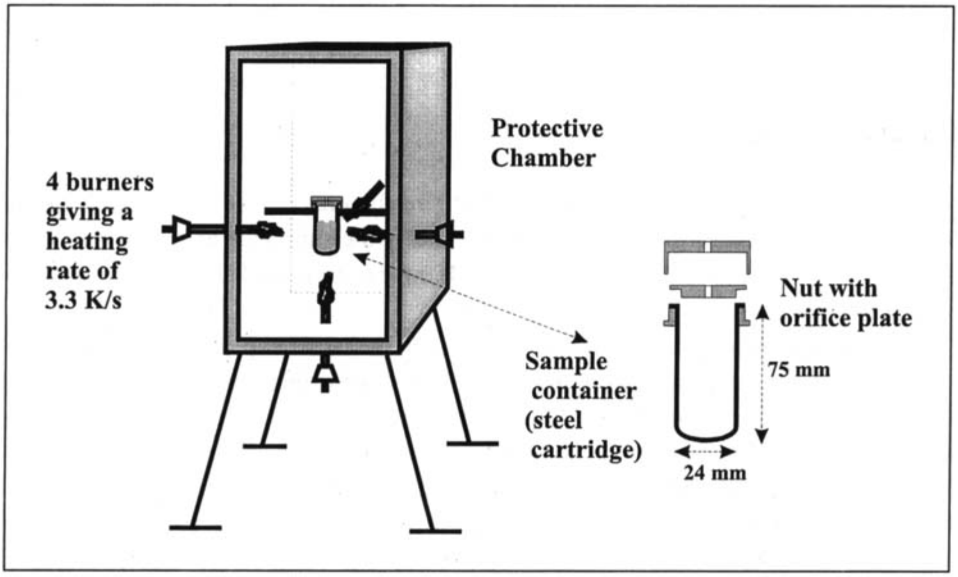


Fig. 3-15. Basic set-up of the steel cartridge test according to Koenen

Four burners supplied with propane or another fuel gas in such a way that they provide a heating rate of 3,3 K/s ± 0,3 K/s, are fixed in three of the four side walls and the bottom wall so that the flames are directly orientated towards the centrally fixed steel cartridge. The steel cartridge itself has to be made of deep drawn sheet steel of 5 mm thickness, being 75 mm in length and 24 mm in inner diameter. The open end of the tube is flanged using a threaded collar, a nut and an orifice plate, which is available with diameter holes from 1 to 20 mm. A 28 cm^3 sample is used.

A stopwatch is started at the moment when the four burners are lit, and the following observations are recorded:

1. the time t_1 from the moment the burners were lit to a first optical or acoustic sensing of the beginning decomposition. In the majority of cases the decomposition is accompanied by the formation of gas or smoke. Due to the high velocity in the orifice plate this gaseous release can be heard as a whistling sound.
2. the time t_2, which is equivalent to the time difference between t_1 and the occurrence of an explosion. In order to discriminate between a material fatigue effect and the destruction of the steel cartridge due to the explosion at least three large fragments or many smaller ones should be found.

A substance is rated posing an *explosion risk* if an explosion occurs in at least one out of three trials with a hole diameter of 2 mm or greater.

Important Remark on Explosion Risk

It is of great importance to emphasize that already **one** positive result in **one of the three** test methods described is sufficient to classify the substance as posing an explosion risk. In other words, the three test methods have to be regarded as being independent of each other.

It is mandatory to clearly discriminate between the terms explosion risk and explosible. All substances posing an explosion risk are explosible. But not all explosible substances pose an explosion risk. Explosible substances include the above and those which can be made to explode by detonation or otherwise. To characterize susceptibility to detonation and ability to propagate it, other tests are performed, such as the Trauzl lead block test, the 1'' or 2'' steel tube test, or the USA GAP test. An extensive discussion of detonating substances and numerous measuring results can be found in [39].

In this context only a small overview on explosible substances and their technical safety data shall be given in Table 3-12. Its main purpose is to provide a better feeling for magnitudes and the semantics introduced.

2,4-Dinitrotoluene is a typical example for an explosible substance not posing an explosion risk. Negative results for the drop hammer and friction test and a too small limit diameter of only 1 mm in the steel cartridge test result in its not being classified as posing an explosion risk. A booster triggered detonation, however, results in an explosion strength of 222 ml/10 g which comes close to TNT.

Table 3-12: Overview on safety data of explosible substances

Substance	ΔH_{dc}	Drop Hammer	Friction Test	Steel Cartridge Test			Lead Block	Propagation of a detonation in the steel tube test
	[J/g]	[Nm]	[N]	t_1 [s]	t_2 [s]	Ø [mm]	[ml/10 g]	
5-Amino-1,2,3-thiadiazole	-1365	7,5		9	4	3,5	77	2 "
Ammonium-perchlorate	-1463	25		21	0	8	194	1-2 "
TNT	-4305	12		52	29	5	288	1 "
Nitro-glycerine	-6312	0,2		13	0	24	515	1 "
2,4-Dinitro-toluene	-4440	no reaction up to 39 Nm	no reaction up to 360 N	49	21	1	222	1 "

3.5 Deflagration Testing

Another substance property is of special safety relevance: the ability to decompose in form of a chemical reaction which propagates in the material at subsonic velocity by thermal energy transfer. The most important aspect is that this so-called deflagration may even occur in the absence of oxygen. The related problem becomes more obvious if a protective measure is to be selected with the purpose of preventing the occurrence of a deflagration. In order to prevent a decomposition reaction that proceeds as a fire or an explosion, the oxygen content in the ambient atmosphere is reduced by the addition of an inert gas. This most frequently selected protective measure is pursued until the oxygen concentration is lower than a critical minimum limit value, which is necessary for the combustion process. This safety procedure is called *inertization*. In the case of a deflagration, which may occur in complete absence of oxygen, it is a fully unsuitable measure.

This property is known for solids as well as liquids. Known examples for deflagrating solids are free radical initiators such as Azo-isobutyronitrile (AIBN), colour pigments like pigment orange CI 12075, or inorganic compounds such as hydroxylammonium sulfate [40]. Some organic peroxides are known examples for liquids having this property [41].

Scanning DTA/DSC experiments may provide a very good indication whether or not such a property has to be anticipated. If decomposition energies of more than -500 J/g were released in an extremely short time period, further testing for deflagration properties is recommended. Short time periods in DTA scanning experiments mean that the observed peaks are sharp and have a steep slope. A further very simple method to screen for deflagration properties is the spatula test. A small sample amount is piled on the tip of the spatula, which is then held into the flame of a Bunsen burner. If a spontaneous decomposition or an instant combustion is observed the suspicion is supported.

The deflagration is characterized by its propagation velocity. This is the velocity with which the reaction zone spreads through the material.

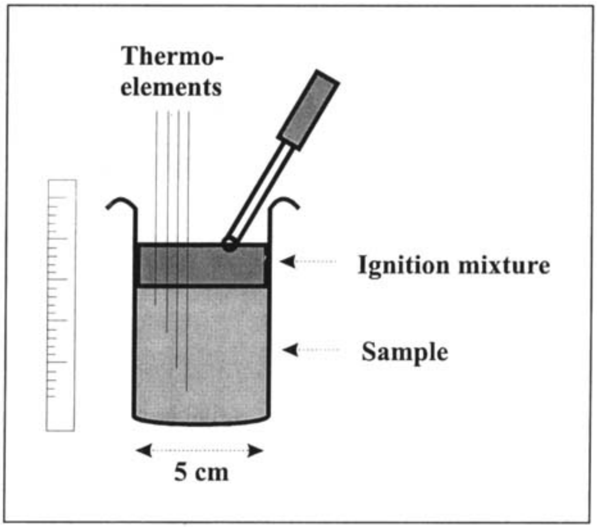


Fig. 3-16. Simple test set-up for the estimation of the deflagration velocity

The necessary measurement can be performed in a simple glass beaker (c.f. Figure 3-16). In order to achieve an initiation of decomposition as uniformly as possible, the use of an ignition mixture is recommended by Gibson consisting of silicon and lead oxide in a ratio of two to one [42]. The deflagration velocities may vary quite significantly from less than 1 cm/min up to several 100 cm/min.

Liquids are most easily tested in a 200 ml Carius tube. The decomposition takes place in the gas phase close to the liquid surface. This is the reason why the decomposition can be initiated by warming up the liquid surface. The heat production rate of the decomposition provides enough energy to support a continuous evaporation of the substance into the reactive zone. In many cases the gaseous decomposition products are flammable themselves. To avoid the dispersion of flammable gases while the experiment is performed, it is recommended to fix a small flame close to the tube's upper end to assure a controlled combustion.

It is important to discriminate the deflagration process from a normal combustion which, at first sight, seems to be problematic if the deflagration of a liquid is initiated with an open flame. But quite on the contrary, the tube test allows this very unequivocally, as the liquid level with the reactive zone close to its surface drops in the course of the experiments and an easily visible spatial separation develops between the reaction and the combustion zone.

For a detailed treatment of this very special substance property and further testing and characterization methods, [15] should be consulted.

The transfer of the experimental result to a safety technical concept depends on the individual substance and the desired handling. In most cases the possible alternatives are limited to mitigating measures such as the installation of pressure relief systems.

3.6 Assignment of Testing Methods to Process Unit Operations for the kg-Scale

From the great variety of testing methods available only those should be selected which provide a purpose orientated safety information for each step of the manufacturing procedure. A first discrimination should be made between chemical reactions and physical unit operations.

The unit operations can be divided further. Table 3-13 provides a recommendation which test methods should be applied to obtain a safety assessment for the different types of process operations.

> *This recommendation is neither concluding nor a guarantee that all possible hazard potentials related to handling a certain substance on the kg-scale will be detected or can be assessed completely, if the above mentioned test methods have been applied!*

The safety technical consequences deduced from the experimental results obtained for a kg-scale manufacturing process are usually very complex in character. It is more important that *the handling of explosion risk posing substances is reliably excluded and that strongly exothermic secondary processes*, which may demand an intensified temperature control or even a process modification, are identified. Burning and ignition test results may already require inertization at this step in the life cycle development.

On this scale it is furthermore important to identify characteristics of the system which must be looked upon quite thoroughly to ensure a safe scale up and which influence the basis of safety to be implemented on plant scale.

Table 3-13: Assignment of safety technical test methods and modes of process operation for the kg-scale

Test method	**Type of operation**				
	Chem. reaction	drying, granulation, etc.	distillation	milling, micronizing	filtration, centrifugation, etc
DTA / DSC, etc closed	scan and isothermal in combination with pressure measurement	scan and isothermal	scan of the mixture and of distillation residues with increasing concentration	scan	scan
Carious tube test DTA,DTA/TGA		yes	scan of distillation residue	yes	
miniautoclave	only if DTA/DSC not possible				
burning test		yes		yes	yes
ignition test		yes		yes	yes
flash point			yes		
ignition temperature			yes		
drop hammer					
friction test	depending	on DTA/	DSC, burning and	ignition	test
steel cartridge test			dto.		
deflagration test			dto.		

3.7 References to Other Problems and Test Methods

Approximately 50 different test methods for the determination of safety data are currently known at the moment, the majority of which is comparable in set-up and objective. In Chapters 3.2 to 3.5 only the most important methods were mentioned. Some more are described in Chapter 5 *Dust Explosible Substances*, as they are specifically related to this problem.

A more detailed discussion on methods for the characterization of explosions and detonations can be found in the monographs of Grewer and Yoshida [15,39].

Measuring devices for the determination of pure substance property data, such as the lower and upper explosion limits of liquids or gases, are quite complex and are usually not part of the repertoire found in safety laboratories. One explanation for this. is the existence of numerous data bases and printed publications containing such data for the majority of basic chemicals used. For the not so frequently occurring case that such data are required but can neither be retrieved nor approximated with the help of theoretical methods with sufficient accuracy, national institutes like those mentioned in section 3.4 and special laboratories can be consulted.

In the context of with classification for the transport of hazardous goods a number of other and partially very specific test methods have been developed and described. Their documentation can be found in the test manual of the so-called *UN - Orange Book* [43].

Safety Assessment for Chemical Processes
by. Jörg Steinbach

4 Methods for the Investigation and Assessment of Chemical Reactions

4.1 Reaction Engineering Fundamentals

The assessment whether or not a chemical reaction can be performed in a safe and controlled way under normal as well as upset operating conditions is based on models originating from chemical reaction engineering. This explains why some fundamentals of these models have to be introduced first.

This cannot and shall not be a substitute for a text book on chemical engineering. On the contrary, it is advisable to turn to specialist literature on chemical and especially on reaction engineering for the derivation of certain facts. Highly recommended examples are the standard text books by Westerterp and by Baerns, Hofmann, Renken [44,45]. The aim of this introduction is to fill the gap between experimentally obtained results and plant technical requirements from a safety engineering point of view. This transfer of experimental data to true plant conditions and the compatibility assessment of plant and process remain the main tasks of chemical safety engineering.

A chemical transition process is always characterized by its stoichiometry and its extent of reaction independent of the mode of process operation. The rate of change in extent, however, depends on the mode of process operation, on the reaction rate and, in the case of heterogeneous reactions, on the mass transfer. In order to account for the mode of operation appropriately, models are required for the different reactor types. This is all comprehensively described in the overall mass balance of the system.

The thermal behaviour of a chemical reactor depends on the thermodynamics of the process, on the reaction rate, which has already been mentioned above, but also on the mode of exchange with the environment. This is completely described in the overall heat balance of the system. The following sections will present the main balance equations, which are required for the subsequent safety assessment, as well as definitions and interpretation of characteristic numbers used in their presentation.

4.1.1 Stoichiometry and Extent of Reaction

In Chapter 2 it was explained why it is absolutely necessary to have a clear definition of plant and process at the beginning of a safety technical assessment. Consequently, one of the first steps has to be the formulation of the stoichiometric equation of the reaction. All descriptions used in this book assume the validity of the common physicochemical convention that the stoichiometric coefficients ν_i of all educts are negative and those of products are positive.

$$|\nu_A| \cdot A + |\nu_B| \cdot B \rightarrow |\nu_C| \cdot C \qquad (4\text{-}1)$$

If the chemical reaction is described correctly, then the stoichiometric balance must also be fulfilled. The *stoichiometric balance* says:

> *The amount produced or consumed of one substance due to the chemical reaction has to be consumed or produced in a stoichiometrically equivalent amount by all other substances participating in the reaction.*

If the stoichiometric balance is to be expressed in the form of a mathematical equation, it is necessary to discriminate between continuous and discontinuous processes. The following equation is valid for a discontinuous process:

$$\frac{n_K - n_{K0}}{\nu_K} = \frac{n_J - n_{J0}}{\nu_J} \qquad (4\text{-}2)$$

For a continuous process the molar amounts have to be substituted by the mole flow rates. These stoichiometric balances are almost generally valid. The limits of this validity are met if the start-up behaviour of continuous reactors is discussed or if one component is selectively removed from the balance system. If this stoichiometric balance is transformed and if only the initial condition of a chemical process with two educts is considered, the *stoichiometric input ratio* λ is obtained:

$$\lambda = \frac{\nu_J \cdot n_{K0}}{\nu_K \cdot n_{J0}} \qquad K, J = \text{educts} \qquad (4\text{-}3)$$

If the educts are charged in exactly stoichiometrically equivalent amounts, then λ equals 1. In case of non stoichiometric input amounts the indices are generally assigned in such a way that the maximum value for λ is 1. With this convention the component in the denominator is the *excess component*, the one in the numerator the *limiting component*, which in the further text is generally indexed A. If the term

$$n_{i0} - n_i \tag{4-4}$$

is divided by the initial number of moles of component i, the defining equation for the extent of reaction in i is obtained.

$$X_i = \frac{n_{i0} - n_i}{n_{i0}} \tag{4-5}$$

If the ratio is formed between the extent reaction in i and its maximum extent, the ***relative extent*** or ***conversion*** is obtained. In order to distinguish the conversion from the extend of the reaction i, the former is not indexed.

$$X = \frac{X_i}{X_{i,max}} \tag{4-6}$$

In the special case of the limiting component, the extent in A and the conversion are identical as the maximum extent in A amounts to 100%. This property is used to simplify the formulation of all the following balance equations and other relationships. They will all be referenced to the extent in A. A retransformation to calculate any other variables always remains possible.

If the stoichiometric balance is considered again, this time in its differential form, between an arbitrarily chosen component participating in the reaction and the limiting component

$$\frac{dn_i}{\nu_i} = \frac{dn_A}{\nu_A} \tag{4-7}$$

integration and subsequent transformation yield the generally valid relationship between the actual number of moles of a component and the conversion.

$$n_i = n_{i,0} - \frac{\nu_i}{\nu_A} \cdot n_{A,0} \cdot X \tag{4-8}$$

4.1.2 Reaction Rate

The flow chart showing the iterative safety assessment procedure for a chemical process under normal operating conditions (c.f. Section 2.1) has its central step in the evaluation of an adequate thermal design of the process. This is shown in a simplified form as the comparison of the chemically produced heat and the heat removal capacity of the system. A necessary prerequisite to this assessment of the suitability of the design is the knowledge of the time course of the heat production rate, which itself is directly proportional to the chemical reaction rate. This explains the pivotal significance of the identification of a reaction rate law that describes the investigated process with sufficient accuracy, and its parameters.

The Principle of Kinetic Model Reduction

In the introduction to this section a wording was used which is of some importance to chemical process safety: *knowledge of a reaction rate law which describes the investigated process with sufficient accuracy*. Nature is complex, so that the desired process is very rarely the only one to proceed under the conditions chosen for the manufacture of a desired plant product. Normally, numerous reactions take place simultaneously. Based on experience and know-how the development chemist was able only to optimize the process with respect to operational conditions up to an extent that the desired process is favoured. But it remains part of reality that the heat production rate measured and the reaction enthalpy obtained by its integration represent gross values which are formed as the sum of all simultaneously contributing reactions.

Trying to set up a physicochemically exact kinetic model for all simultaneously proceeding reactions with identification of all parameters would be a task so extremely time-consuming that it could not be justified economically. Even modern computer programs, which use non-linear optimization techniques for the parameter adjustment in complex models, require an amount of analytical information on all substances participating in the process which is not to be underestimated [46].

For chemical process safety, however, it remains satisfactory if the entire process can be described, as initially stated, with sufficient accuracy. A reaction rate law which allows a good description of the experimentally obtained results, is called *formal kinetics*. The immanent parameters, such as reaction order, pre-exponential factor, and activation energy, must not be interpreted as physicochemical values any more but are reduced in their meaning to statistical adjustment parameters.

The procedure described here is called ***model reduction***. The further-reaching background to this approach, which actually provides its justification, is the principle of compensating errors. Such errors are always made if single independent procedures are combined to one comprehensive overall process. The decisive prerequisite for error compensation to take effect is the determination of the model parameters under conditions as close as possible to the true process conditions.

If this requirement is transferred to the determination of formal kinetic parameters, the boundary condition to be observed is that the safety technical laboratory experiment tries to imitate the actual plant conditions as exactly as possible. For example, this excludes the application of formal kinetic parameters obtained in a batch reactor for the prediction of the behaviour of a continuously stirred tank reactor.

Kinetics of Homogeneous Liquid-phase Reactions

Simple homogeneous liquid-phase reactions can be described with the help of formal kinetic rate laws in which the reaction rate r depends on the concentrations of the reactants, on the temperature and possibly on the homogeneous catalyst only. Examples of such formal kinetic rate laws are presented in Table 4-1.

Table 4-1: Examples of simple formal kinetic rate laws

n-th order reactions:	$r = k \cdot c_i^n$
$n = 1$	$r = k \cdot c_A$
$n = 2$	$r = k \cdot c_A^2$ or $r = k \cdot c_A \cdot c_B$
fractional rational rate law for homogeneously-catalyzed reactions	$r = \frac{k \cdot c_A \cdot c_B}{1 + b \cdot c_A}$
reactions with autocatalytic behaviour	$r = (k_0 + k_1 \cdot c_C) \cdot c_A \cdot c_B$

The contents of the complete Chapter 4 will demonstrate the advantage of transferring the dependence of the formal kinetics on concentrations to a dependence on conversion. For this purpose Equ. (4-8), which was derived in Section 4.1.1, is used to express the relationship between concentration and conversion for all different reactants. The index 0 indicates initial conditions for discontinuous and input values for continuous processes, respectively.

For the limiting component Equ.(4-9) is obtained

$$c_A = c_{A0} \cdot (1 - X) \tag{4-9}$$

for all other educts

$$c_i = c_{i0} \cdot (1 - \lambda \cdot X) \tag{4-10}$$

and for products respectively

$$c_C = \left(\frac{\nu_C}{-\nu_A}\right) \cdot c_{A0} \cdot X \tag{4-11}$$

All equations presented are bound to the additional condition of complete absence of products at the very beginning.

If these equations are used to substitute the individual concentrations in the different formal kinetic rate laws, it becomes possible in principle to split the resulting rate laws into one term representing the initial rate r_0 and a second, which stands for a dimensionless reaction rate

$$\Phi(X) = \frac{r}{r_0}, \tag{4-12}$$

describing the conversion dependent part. Table 4-2 shows the resulting new equations for all rate laws in Table 4-1.

In addition, Figures 4-1a-c show the courses of the dimensionless reaction rates in their dependence on conversion for the examples of an n-th order, a homogeneously catalyzed, and an autocatalytic reaction. The similarity of different dependencies of the dimensionless reaction rate on conversion for the first two examples presented indicates that a description of actual measured reaction rates should be possible with a very simple power rate law in many cases. The power n has to be interpreted as an approximated effective order of reaction.

Autocatalytic effects, however, are not described sufficiently exactly with such a simple approach.

Table 4-2: Examples of simple formal kinetic rate laws after the substitution of concentrations by conversion

	Initial Rate r_0	$\Phi(X)$
n-th order reactions:	$k \cdot c_{i0}^n$	$(1-X)^n$
n-th order reactions:		
$n=1$	$k \cdot c_{A0}$	$(1-X)$
$n=2$	$k \cdot c_{A0}^2$ or $k \cdot c_{A0} \cdot c_{B0}$	$(1-X)^2$ or $(1-X)\cdot(1-\lambda \cdot X)$
fractional rational rate law for homogeneously-catalyzed reactions	$\frac{k \cdot c_{A0} \cdot c_{B0}}{1+b \cdot c_{A0}}$	$\frac{(1-X)\cdot(1-\lambda \cdot X)}{1-P_1 \cdot X}$ with $P_1 = \frac{b \cdot c_{A0}}{1+b \cdot c_{A0}}$
Reactions with autocatalytic behaviour	$k_0 \cdot c_{A0} \cdot c_{B0}$	$(1+P \cdot X)\cdot(1-X)\cdot(1-\lambda \cdot X)$ with $P = \frac{k_1 \cdot c_{A0}}{k_0}$

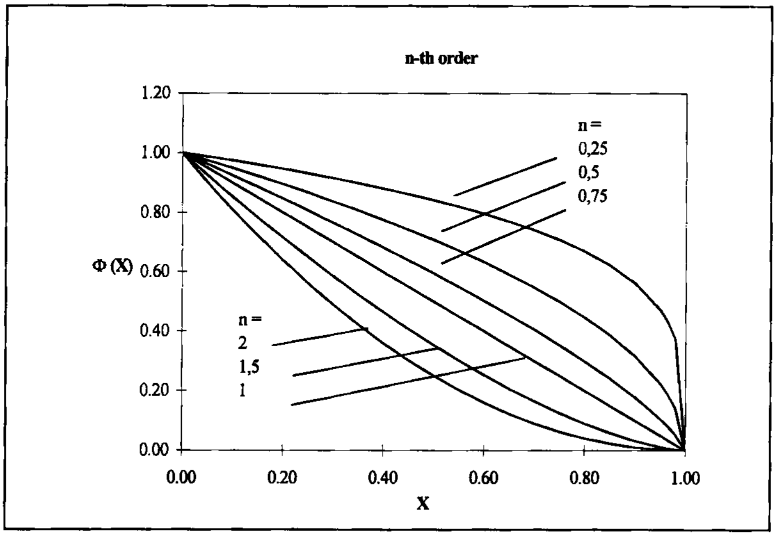


Fig. 4-1a. Course of the dimensionless reaction rate Φ(X) for an n-th order formal kinetic rate law

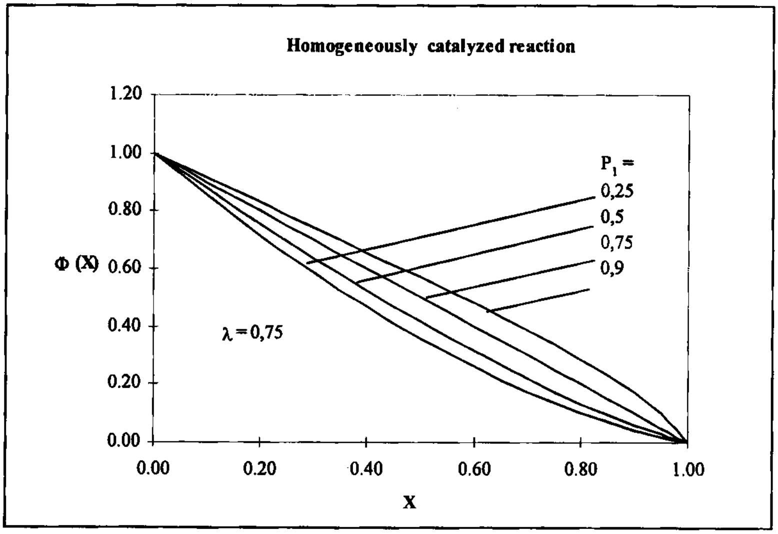


Fig. 4-1b. Course of the dimensionless reaction rate Φ(X) for homogeneously catalyzed reaction rate laws

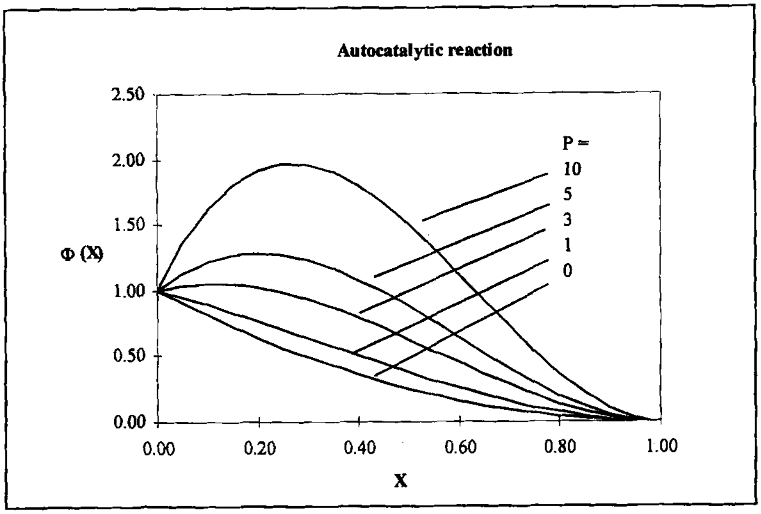


Fig. 4-1b-c. Course of the dimensionless reaction rate Φ(X) for autocatalytic reaction rate laws

In most cases the dependence of the reaction rate on the temperature follows the Arrhenius relationship.

$$r(X,T) = r_0(T) \cdot \Phi(X) = r_{0,\infty} \cdot \Phi(X) \cdot \exp\left(-\frac{E}{R \cdot T}\right) \tag{4-13}$$

This kind of reaction rate formulation bears the advantage that the initial rate, being referenced to the pre-exponential factor only, as well as the dimensionless reaction rate Φ(X), are independent of the temperature.

Kinetics of heterogeneous systems

A great number of chemical reactions are performed in two phase systems. It is well-known that these are very different in character, namely:

- gas/liquid
- liquid/liquid
- liquid/solid
- gas/solid

The calculation principle on which the assessment of design for such reactors is based is a substitution of the multi-phase reaction system by a quasi-single-phase model. In two-phase systems both reactants have to get into contact at a certain place. Consequently a reaction and a transport phase are distinguished. If the mass transfer rate from the transport to the reaction phase is very fast compared to the actual reaction rate, the process in total is dominated by the reaction kinetics. In order to discriminate this situation from one taking the mass transfer into account, it is referred to as *micro-kinetically dominated*. In this case all formal kinetic laws presented for homogeneous systems may be applied directly.

However, if the mass transfer rate is equal to or even slower than the reaction rate, such systems are regarded as mass transfer dominated. A so-called *macrokinetics* is introduced for their description which makes use of an effective reaction rate.

$$r_{eff} = r_{0,eff} \cdot \Phi_{eff}(X) \tag{4-14}$$

This effective reaction rate is referenced to the total reaction volume when inserted into the mass balances of the individual reactor types. Factually the reaction proceeds in the reaction phase only. This has the effect that the relationship between micro- and macrokinetics has to account for the volume ratio of the two phases, which is best done by introducing a volume factor φ. Furthermore, the effective reaction rate has to include the critical ratio of reaction to mass transfer rate, expressed with the variable ψ. In combination, this yields the following equations 4-15 and 4-16.

$$r_{eff} = \frac{\varphi \cdot r_0}{1+\psi} \cdot \Phi_{eff}(X) \tag{4-15}$$

$$\frac{1+\psi}{\Phi_{eff}(X)} = \frac{1}{\Phi(X)} + \frac{\psi}{(1-X)} \tag{4-16}$$

For different heterogeneous systems, specific correlations of φ and ψ have to be inserted. They are compiled in Table 3-4. The first-mentioned phase shall always be the transport phase primarily containing reactant A, the second refers to the reaction phase with reactant B.

Table 4-3: Parameters for the effective reaction rate of heterogeneous systems

Heterogeneous system	φ	ψ	Concentrations	Other important relations
liquid/solid	$\frac{V_l}{V_{reactor}}$	$\frac{(-\nu_A) \cdot r_0 \cdot V_l}{\beta \cdot A \cdot c_{A0}}$	$c_{A0} = \frac{n_{A0}}{V_l}$	
liquid/liquid	$\frac{He \cdot V_{rct.-ph.}}{V_{reactor}}$	$\frac{(-\nu_A) \cdot r_0 \cdot V_{rct.-ph.}}{\beta_A^* \cdot A \cdot c_{A0}}$	$c_{A0} = \frac{n_{A0}}{V_{Tr.-ph.}}$ $c_{B0} = \frac{n_{B0}}{V_{rct.-ph.}}$	$\frac{1}{\beta_A^*} = \frac{He}{\beta_{Tr.-ph.}} + \frac{1}{\beta_{rcts.-ph.}}$
gas/liquid	$\frac{He \cdot V_l}{V_{reactor}}$	$\frac{(-\nu_A) \cdot r_0 \cdot V_l}{\beta_A^* \cdot A \cdot c_{A0}}$	$c_{A0} = \frac{p_{A0}}{R \cdot T}$ $c_{B0} = \frac{n_{B0}}{V_{lq.}}$	$\frac{1}{\beta_A^*} = \frac{He}{\beta_{gas}} + \frac{1}{\beta_l}$
gas/solid	$1 - \frac{V_s}{V_{reactor}}$	$\frac{1-\eta}{\eta}$ with $\eta = \frac{1}{h} \cdot \left(\frac{1}{\tanh(3 \cdot h)} - \frac{1}{3 \cdot h} \right)$		$h = \frac{d_p}{6} \cdot \sqrt{\frac{k \cdot c_{A0}^{n-1}}{D_{eff}}}$

The parameters η and h, which are mentioned for gas/solid reactions, are the degree of utilization of porous particles and the Thiele modulus, respectively. For the exact deduction of these values, the calculation of partition equilibria as well as surface layer and overall mass transfer coefficients it is referred to [44].

Two other findings are of greater relevance to safety technical considerations:

1. If microkinetics follows a first order rate law, then it is identical with macrokinetics. This is the case because all mass transfer steps which come first in sequence are also first-order transition processes, so that the process in total also remains first order.
2. With the quasi-single phase approach and the corresponding introduction of an effective reaction rate it is sufficient from a safety assessment point of view to determine the macrokinetics experimentally. The effective reaction rate deter-

mined for a heterogeneous system may be inserted in the criteria to be presented for the safety assessment of homogeneous systems.

4.1.3 Ideal Reactor Models

The diversity of chemistry applied in the manufacture of today's chemical products finds its mirror image in the number of different reactor types. Nonetheless, it is possible to model the majority of industrially relevant reactor types with the help of four ideal reactors or their combination by suitable abstraction. In doing so, continuous, semi-continuous and purely discontinuous reactor types and manufacturing procedures are discriminated.

Reactors for the Continuous Manufacture of Products

In models for continuous ideal reactors, the continuously stirred tank reactor, **CSTR**, and the plug flow tube reactor, **PFTR**, are distinguished. Both are shown schematically in Figure 4-2. Both are characterized by a simultaneous input feed of educts and solvents on one side and a removal of the reaction mixture on the other side with a constant reaction rate. As a consequence, the reaction volume remains constant in both reactors throughout the reaction period.

CSTR and PFTR, however, represent limiting cases in respect to the degree of mixing within the reaction volume. In the case of the CSTR, complete mixing is assumed, which yields locally uniform reaction conditions regarding concentration and temperature. The balance equations for the PFTR, in contrast, assume ideal plug flow. Therefore the axial mixing may be neglected and the reaction conditions change along the flow direction.

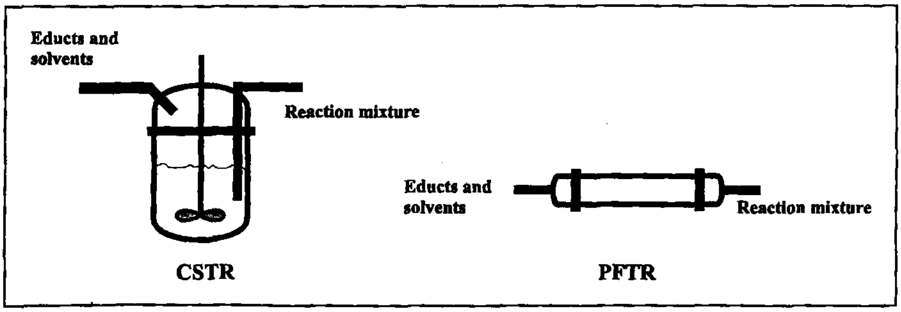


Fig. 4-2. Models of ideal reactor types for continuous operation

From a safety technical point of view continuous reactors have the advantages that

- they are well controllable, as they are operated in a steady state and
- large heat transfer areas can be installed.

Their disadvantage lies in

- a difficult, partially even critical start-up and shut down operation.

For the purely discontinuous reactor operation the ideally mixed batch-reactor, **BR**, is used. All educts and solvents are charged initially. Under agitation the mixture is warmed up until the desired process temperature is reached. The reactor is operated at this temperature for a certain reaction time t_R, which corresponds to the desired conversion. This is followed by an operational phase to isolate the product. From a safety technical point of view the BR is the reactor causing a maximum of problems, for

- the maximum reaction hazard potential is present right at the beginning,
- an extension of heat transfer area is difficult and
- the reactor operates in a non-steady state throughout the whole process time.

The fourth model of an ideal reactor can be described as a sort of combination of CSTR and BR. It is the semi-continuously operated, ideally mixed, stirred batch reactor, **SBR**. This is operated by charging one or more components and auxiliary materials initially and feeding at least a second reactant, with or without further auxiliary materials, at a constant rate over a certain period.

This mode of operation is accompanied by advantages in comparison to pure batch operation, which from a safety point of view cannot be estimated high enough:

- provided a correct design the heat production rate can be fully controlled by the feed rate.

The only disadvantage, which becomes obvious by comparing SBR and CSTR

- is the completely unsteady operation throughout feed and past-reaction phase.

The basic modes of operation of BR and SBR are schematically summarized in Fig. 4-3.

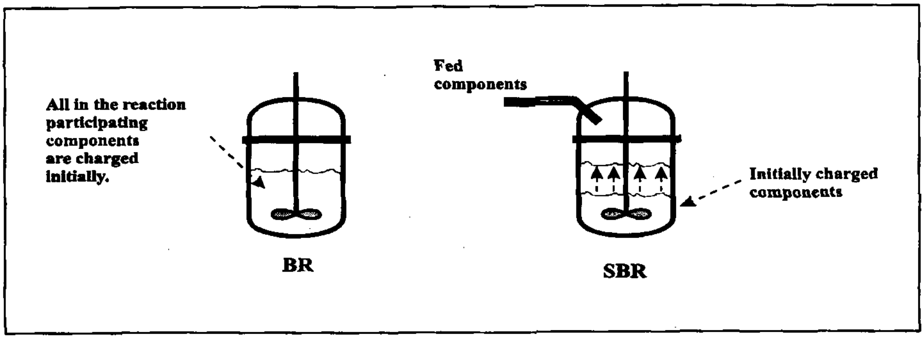


Fig. 4-3. Models of ideal reactors for discontinuous and semi-continuous operation

4.1.4 Introduction of Characteristic Numbers

A chemical process is a combination of a chemical substance transition and a technical apparatus. The main factors which are influenced by thermodynamics, kinetics and design properties of the apparatus can be combined in three characteristic numbers. These are:

the adiabatic temperature increase $$\Delta T_{ad} = \frac{(-\Delta_R H)\cdot c_{A0}}{(-\nu_A)\cdot \rho \cdot c_P} \tag{4-17}$$

the Damkoehler number $$Da = \frac{(-\nu_A)\cdot r_0 \cdot t_{charact.}}{c_{A0}} \tag{4-18}$$

the modified Stanton number $$St = \frac{U\cdot A\cdot t_{charact.}}{V\cdot \rho \cdot c_P} \tag{4-19}$$

ΔT_{ad} provides direct information on the exothermic effect of the chemical reaction. Therefore it is of special importance for the safety assessment of chemical processes. Typical values range from 10 K for either highly diluted syntheses or for reactions with a very small exothermicity, up to 400 K for highly concentrated or strongly exothermic reactions. Decompositions may even have significantly higher values.

The Damkoehler number Da represents the ratio of a characteristic reaction time to the kinetic time constant of the reaction and is therefore a measure for the reaction time. The attribute "characteristic" refers to the individual definition necessary for each reactor type. As will be shown in Section 4.1.5, the characteristic times for ideal reactors are the reaction time for the batch reactor, the feed time or time of dosage for the semi-batch reactor and the mean residence time, sometimes also called space time, for both continuous types. The orders of magnitude for the Damkoehler number vary from 0,01 for slow batch processes to 100 and more for feed-controlled semi-batch operations or continuous manufacturing with high mean residence times.

The third characteristic number, which was first introduced by Westerterp as a modified Stanton number, combines all relevant parameters which determine the cooling capacity of a chemical reactor. This characteristic number is equivalent to the time constant of cooling in the dimension bearing domain

$$\tau_c = \frac{V \cdot \rho \cdot c_P}{U \cdot A} \tag{4-20}$$

referenced to the characteristic reaction time. Its deduction includes the common assumption that the product of density and specific heat capacity of the reaction mixtures as well as the product of overall heat transfer coefficient and heat transfer area remain approximately constant over the reaction period. Stanton numbers usually range from 3 for plant scale reactors to 20 for laboratory equipment.

This group of characteristic numbers is supplemented by the so-called thermal reaction number

$$B = \frac{E \cdot \Delta T_{ad}}{R \cdot T^2} \tag{4-21}$$

It provides a direct measure of the hazard potential related to the process. It combines thermodynamics and reaction kinetics by being directly proportional to the temperature dependence of the reaction rate represented by the activation temperature E/R and the adiabatic temperature increase. Reactions with a small to moderate hazard potential are characterized by thermal reaction number values around 2, and processes with an extremely high potential have values up to 50 and more. To illustrate the meaning especially of this number, which, if applied correctly, has a similar significance to the adiabatic temperature increase for chemical hazard assessment, the relationship between activation temperature, adiabatic temperature increase and the thermal reaction number B is presented in Fig. 4-4. As a typical process temperature 25°C is assumed.

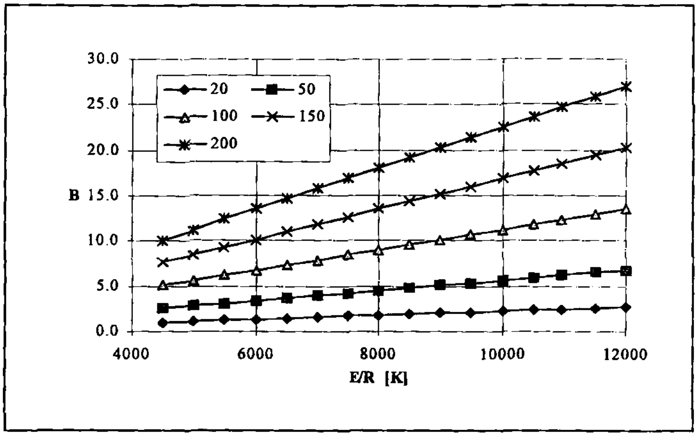


Fig. 4-4. Dependence of the thermal reaction number B on the activation temperature; $T_R = 298{,}15$ K; parameter: ΔT_{ad}

With the help of these characteristic numbers, mass and heat balances can now be derived in dimensionless form for the ideal reactors considered.

4.1.5 Mass Balances of the Ideal Reactors

The mass balance for one component participating in the reaction can, as a first step, be formulated generally in words:

Time dependent change of the amount of substance i within the reaction volume = **Input mass rate of substance i through feed stream** − **Output mass rate of substance i through removal feed stream** + **Converted amount of substance i by chemical reaction**

and in a second step in mathematical terms

$$\int_V \frac{dc_i}{dt}\cdot dV = -\oint\left(\vec{j}_i \cdot d\vec{o}\right) + \int_V \nu_i \cdot r \cdot dV \qquad (4\text{-}22)$$

where $\vec{j}$ and $\vec{o}$ stand for the vectors of the mass flux density and the surface element, respectively. Applying the Gaussian theorem, the following general solution is obtained:

$$\frac{\partial c_i}{\partial t} = -\mathrm{div}\,\vec{j}_i + \nu_i \cdot r \tag{4-23}$$

Following the reasoning given in section 4.1.1, all further considerations will focus on the limiting component A. In analogy to the reaction rate the mass balance can be derived in a dimensionless form when discussing the change in conversion. In order to transform the time axes into a dimensionless form the same characteristic time, specific for each ideal reactor, is used, which was introduced with the group of characteristic numbers. After substitution and some rearrangement the following equation is obtained:

$$t_{\text{charact.}} \frac{\partial X}{\partial t} = \frac{t_{\text{charact.}}}{c_{A0}} \cdot \mathrm{div}\,\vec{j}_A - \frac{\nu_A \cdot r_0 \cdot t_{\text{charact.}}}{c_{A0}} \cdot \Phi(X) \tag{4-24}$$

A closer examination results in the recognition of the Damkoehler number as the term with which the dimensionless reaction rate is multiplied. This leads to a simplification for the *general dimensionless mass balance:*

$$t_{\text{charact.}} \frac{\partial X}{\partial t} = \frac{t_{\text{charact.}}}{c_{A0}} \cdot \mathrm{div}\,\vec{j}_A + \mathrm{Da} \cdot \Phi(X) \tag{4-25}$$

The mass balance of the CSTR

If the divergence of the mass flux density of the limiting component A is investigated for the CSTR, it can be shown that in a first approximation it may be equated to the difference in input and output mole streams:

$$\mathrm{div}\,\vec{j}_A \cong \frac{\dot{n}_A - \dot{n}_{A0}}{V_R} \tag{4-26}$$

The property of a constant reactor volume in the CSTR presumes the equality of input and output volume flow rates. With this prerequisite fulfilled the molar flow rates may be substituted by the product of concentration and volume flow rate, directly yielding the quotient

$$\tau = \frac{V_R}{\dot{V}} \tag{4-27}$$

It describes the mean residence time of the reactor and shall be used as the characteristic time for the CSTR. Insertion and substitution of the relevant terms in the general mass balance results in the *unsteady mass balance of the CSTR*:

$$\tau \frac{dX}{dt} = -X + Da \cdot \Phi(X) \tag{4-28}$$

After a start-up period the CSTR is usually operated in a steady state. Under this normal operating condition no change in conversion can be observed any more such as that prevailing during start-up and shut down. Consequently, for normal operating conditions the *stationary mass balance* is valid *for the CSTR*:

$$Da = \frac{X}{\Phi(X)} \tag{4-29}$$

The mass balance of the PFTR

For the sake of simplification, the treatment of the PFTR shall be limited to steady state operations. For a more detailed reaction engineering discussion of the PFTR operated under unsteady conditions it is referred to the literature earlier recommended [44]. Furthermore it shall be assumed that the input and output volume flow rates are constant and that radial gradients in concentration shall be negligible. The first assumption allows the use of the mean residence time as the characteristic time. The assumption that no axial concentration gradients are present allows the restriction to a one-dimensional analysis of the divergence in the axial direction z of the reactor. With these boundary conditions one obtains:

$$\operatorname{div} \vec{j}_A = \frac{d\,j_A}{dz} = -\frac{c_{A0} \cdot L}{\tau} \cdot \frac{dX}{dz} \tag{4-30}$$

After substitution the following mass balance is derived:

$$L \cdot \frac{dX}{dz} = Da \cdot \Phi(X) \tag{4-31}$$

which after integration over the reactor length leads to the *stationary mass balance of the PFTR*:

$$Da = \int_{0}^{X_{z=L}} \frac{dX}{\Phi(X)} \tag{4-32}$$

The mass balance of the BR

As outlined in the introduction, the BR operates unsteadily at all times. For this type of reactor the characteristic reaction time is defined arbitrarily as the period between the initial charging of all reactants and the moment at which a predefined degree of conversion is obtained. As there are no input and output streams during this period the divergence term in the mass balance is cancelled. With the given boundary conditions,

$$t_R \cdot \frac{dX}{dt} = Da \cdot \Phi(X) \tag{4-33}$$

is obtained and integration over the characteristic time period yields the *unsteady mass balance of the BR*

$$Da = \int_{0}^{X_{t=t_R}} \frac{dX}{\Phi(X)} \tag{4-34}$$

The resulting equation is completely identical with the steady-state mass balance of the PFTR. This is an important finding for process safety. It allows the experimental characterization of a tube reactor process to be performed batch-wise on laboratory scale without violating the boundary conditions to be observed when applying model reduction. The demand of a parameter determination under closest proximity to plant conditions remains fulfilled. The sequence along the length of the tube reactor is completely equivalent to the time sequence of a batch process.

The mass balance of the SBR

From a mathematical point of view the SBR is the most complex of the four ideal reactors because of its unsteady operation over the whole reaction period and its changing reactor volume due to the dosage. Therefore it is more convenient to use mole numbers for the description instead of concentrations. In addition it has to be observed that the actual number of moles of the fed component present in the reactor cannot be calculated directly by the stoichiometric coupling introduced but by an extended version only which accounts for conversion and time. The added reactant and the initially charged reactant will be indexed A and B, respectively, in the following text. If the conversion is known the number of moles of B present at any time can be calculated according to:

$$n_B = n_{B0} \cdot (1 - X) \tag{4-35}$$

and the number of moles of A according to:

$$n_A = n_{B0} \cdot (\lambda \cdot \Theta - X) \tag{4-36}$$

Θ is a dimensionless time defined as the real time referenced to the feed time τ_D, which is necessary to add the total amount of A with a constant rate of dosage. τ_D is the characteristic time of the SBR:

$$\Theta = \frac{t}{\tau_D} \tag{4-37}$$

Following its definition, Θ equals 1 when all of A has been added. λ is the stoichiometric input ratio, this time with the convention that the added component is in the numerator.

$$\lambda = \frac{\nu_B \cdot n_{AD}}{\nu_A \cdot n_{B0}} \tag{4-38}$$

The volume increase is best accounted for by the introduction of a parameter ε, which describes the ratio of the total volume added to the initial volume.

$$\varepsilon = \frac{V_D}{V_0} \tag{4-39}$$

This way the time dependent reaction volume can be formulated:

$$V = V_0 \cdot (1 + \varepsilon \cdot \Theta) \tag{4-40}$$

Having introduced these relationships it now becomes possible to calculate the corresponding concentrations of A and B.

All ideal reactors discussed up this point had the characteristic of a constant reaction volume. This allowed the calculation of the dimensionless reaction rate by forming the ratio of the actual to the initial reaction rate. In the special case of the SBR the change in volume has to be accounted for, which leads to the following equation:

$$\Phi(X,\Theta) = \frac{V \cdot r}{(V_D + V_0) \cdot r_0} \tag{4-41}$$

If all terms derived are now substituted into the general mass balance set-up for the initially charged component, the *general mass balance for the SBR* is obtained:

$$\frac{dX}{d\Theta} = Da \cdot \frac{1+\varepsilon}{1+\varepsilon \cdot \Theta} \cdot \Phi(X,\Theta) \tag{4-42}$$

The initial concentrations, which are required for the calculation of the initial reaction rate and the Damkoehler number, are preferably referenced to the final volume. This, on the one hand, allows for a straightforward calculation of the post-feed reaction phase as the final SBR concentrations directly correspond to the input concentrations of the concluding batch phase. On the other hand, this allows for a simple comparison to other ideal reactors without additional recalculations.

4.1.6 Sample Solutions for Isothermal Operating Conditions

In Table 4-4 sample solutions for the steady-state mass balances of CSTR and PFTR and the obtainable conversion in a SBR at the time of stoichiometric input amount are compiled. Isothermal operation is assumed. The calculations refer to the following simple formal kinetic rate laws:

- first-order reaction,
- n-th-order reaction
- second-order reaction with non-stoichiometric input ratio

Table 4-4: Solutions of the different mass balances for simple formal kinetics

		CSTR	PFTR resp. BR	SBR
1st-ord.	Da	$-\nu_A \cdot k \cdot \tau$	$-\nu_A \cdot k \cdot \tau$ $-\nu_A \cdot k \cdot t_R$	$-\nu_A \cdot k \cdot \tau_D$
	X↔Da	$X = \frac{Da}{1 + Da}$	$X = 1 - e^{-Da}$	$X = 1 - \frac{1}{Da} \cdot \left[1 - e^{-Da}\right]$
nth-ord.	Da	$-\nu_A \cdot k \cdot c_{A0}^{n-1} \cdot \tau$	$-\nu_A \cdot k \cdot c_{A0}^{n-1} \cdot \tau$ $-\nu_A \cdot k \cdot c_{A0}^{n-1} \cdot t_R$	$-\nu_A \cdot k \cdot c_{A0}^{n-1} \cdot \tau_D$
	X↔Da	$Da = \frac{X}{(1-X)^n}$	$X = 1 - \left[1 + (n-1) \cdot Da\right]^{\frac{1}{1-n}}$	can be solved numerically only
2nd-ord. $\lambda \neq 1$	Da	$-\nu_A \cdot k \cdot c_{B0} \cdot \tau$	$-\nu_A \cdot k \cdot c_{B0} \cdot \tau$ $-\nu_A \cdot k \cdot c_{B0} \cdot t_R$	$-\nu_A \cdot k \cdot c_{B0} \cdot \tau_D$
	X↔Da	$X = \frac{Da \cdot (1 + \lambda) + 1}{2 \cdot Da \cdot \lambda} \cdot (1 - Fl)$ $Fl = \sqrt{1 - \frac{4 \cdot \lambda \cdot Da^2}{\left[1 + (1 + \lambda) \cdot Da\right]^2}}$	$X = \frac{1 - e^{Da \cdot (1-\lambda)}}{\lambda - e^{Da \cdot (1-\lambda)}}$	$X = 1 - \sqrt{\frac{2}{\pi \cdot Da}}$

The equation given for the calculation of the conversion at the stoichiometric input point in a SBR for a second order reaction is an approximation derived by Hugo [47]. The solutions for the BR and the steady-state operated PFTR are identical for the reasons given when deducing the different mass balances.

A closer examination of the different solutions shows that the conversion-time dependence for a second order stoichiometric reaction performed in a PFTR is identical with a first order reaction conducted in a CSTR. This can be explained by the different mixing patterns of the PFTR and the CSTR.

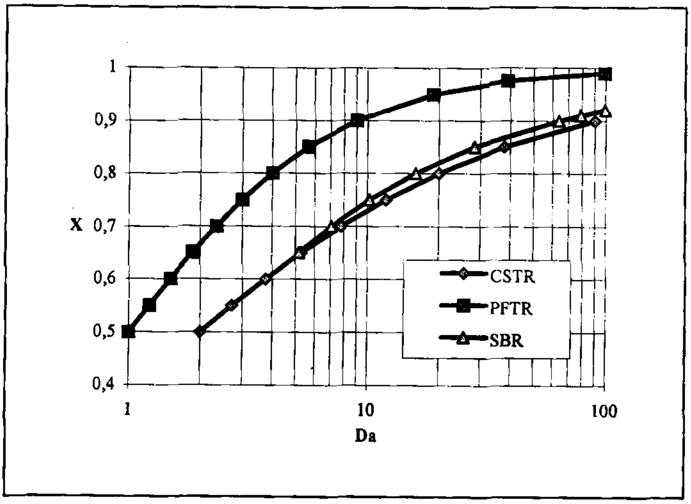


Fig. 4-5. Conversion-time relationship for isothermally operated ideal reactors

To illustrate this further, the concentration-time relationship of ideal reactors is graphically shown in Figure 4-5. This is supplemented by the concentration-time profiles for a second order reaction performed in a SBR in Figure 4-6.

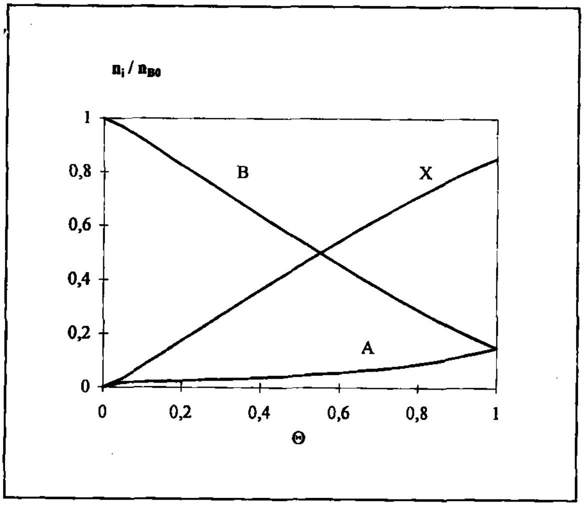


Fig. 4-6. Concentration-time profiles in an isothermal SBR second order reaction; $Da_0 = 27$ $\varepsilon = 1$; $\lambda = 1$

A item of special information of relevance to all further elaborations can be obtained from the SBR concentration profiles. The largest non-reacted amount of added component A is accumulated at the time of stoichiometric input. In the example given, this is at the end of feed-time as λ was chosen to equal 1. If A is added in excess the remaining reaction potential is limited by the accumulation of the initially charged reactant once the point of stoichiometric input has been passed.

4.1.7 The General Heat Balance of Cooled Ideal Reactors

General heat balance

The general heat balance of a chemical reactor can be put into words in analogy to the mass balance:

Time dependent change in amount of heat within reaction volume	=	**Input heat flow through feed stream**	-	**Output heat flow through removal stream**	+	**Consumed or produced amount of heat per unit time by chemical reaction**	+	**Heat flow exchanged through the heat transfer area per unit time**	+	**Other heat sources and sinks within the system**

and mathematically expressed after the application of the Gaussian theorem:

$$\frac{\partial}{\partial t}\left(\rho \cdot c_P \cdot T\right) = -\operatorname{div}\vec{q} - \Delta_R H \cdot r \qquad (4\text{-}43)$$

This formulation assumes that the process is performed under a constant ambient pressure. Strictly considered Equ. 4-43 should therefore be called an enthalpy balance. But in daily routine the established terminology is heat balance. The vector $\vec{q}$ stands for the heat flux density. In setting up a heat balance many more sources and sinks have to be accounted for than in the case of the mass balance. This is indicated by the box for additional sources and sinks enclosed by the dotted line which is enumerated in addition to the main heat fluxes, such as the heat flow exchanged through the heat transfer area. An example for such other heat sources may be the power input of the agitator in a highly viscous system.

As a first approximation it is assumed that the change in value for the product of density and heat capacity during the course of reaction can be neglected and that all calculations may use a mean value. Furthermore it is recommendable to transfer the time variable into a dimensionless form. Substitution and transformation yields:

$$t_{\text{charact.}} \frac{\partial T}{\partial t} = \frac{-t_{\text{charact.}}}{\bar{\rho} \cdot \bar{c}_P} \cdot \operatorname{div} \vec{\dot{q}} - \frac{\Delta_R H \cdot c_{A0}}{\nu_A \cdot \bar{\rho} \cdot \bar{c}_P} \cdot \frac{\nu_A \cdot r_{0,\infty} \cdot t_{\text{charact.}}}{c_{A0}} \cdot \Phi(X) \cdot \exp\left(-\frac{E}{R \cdot T}\right)$$

(4-44)

The extension of the term describing the chemical heat production rate by the stoichiometric coefficient and the concentration of the limiting component, both in numerator and denominator, leads to the characteristic numbers of ΔT_{ad} and Da_∞ and subsequently to a simplified formulation of the *general heat balance*:

$$t_{\text{charact.}} \frac{\partial T}{\partial t} = -\frac{t_{\text{charact.}}}{\bar{\rho} \cdot \bar{c}_P} \cdot \operatorname{div} \vec{\dot{q}} + \Delta T_{ad} \cdot Da_\infty \cdot \Phi(X) \cdot \exp\left(-\frac{E}{R \cdot T}\right) \tag{4-45}$$

For such chemical reactors which are characterized by an ideally well mixed reaction volume, therefore allowing the assumption of a uniform temperature distribution, a transfer of this differential heat balance to an integral balance is possible by multiplying it with the volume of the system balanced. This way the *general integral heat balance* for well mixed reactors is obtained:

$$t_{\text{charact.}} \cdot \frac{dT}{dt} = \frac{t_{\text{charact.}}}{V_R \cdot \bar{\rho} \cdot \bar{c}_P} \cdot \dot{Q}_{\text{chem.}} + \frac{t_{\text{charact.}}}{V_R \cdot \bar{\rho} \cdot \bar{c}_P} \sum_{\substack{\text{sources a.} \\ \text{sinks}}} \dot{Q} \tag{4-46}$$

with

$$\frac{t_{\text{charact.}}}{V_R \cdot \bar{\rho} \cdot \bar{c}_P} \cdot \dot{Q}_{\text{chem}} = \Delta T_{ad} \cdot Da_\infty \cdot \Phi(X) \cdot \exp\left(-\frac{E}{R \cdot T}\right) \tag{4-47}$$

The last term, which is equal to the sum of all additional heat flux sources and sinks, has to be defined for each reactor type individually. In the remaining text the mathematical symbol for averaging used for the mean values of density and specific heat capacity is omitted for simplicity.

The heat balance for the cooled CSTR

The safety assessment of a process performed in a CSTR must not be restricted to the steady state operating conditions but has to include the dynamic reactor behaviour.

The following deduction of the heat balance assumes that the characteristic of a constant reactor volume is valid for the steady state as well as for the dynamic operating conditions. Such a boundary condition remains valid in practice also if the reactor is filled with an amount of either pure solvent or the product mixture of a foregoing batch, equal to the reactor volume under stationary operating conditions before the start-up of the CSTR is initialized.

The CSTR is characterized by a continuous input and output mass flow. Consequently, the heat balance has at least to account for the convective heat transport as well as for the heat transfer through the reactor wall.

$$\dot{Q}_{conv} = -\dot{V} \cdot \rho \cdot c_P \cdot (T - T_{in}) \qquad (4\text{-}48)$$

$$\dot{Q}_C = -U \cdot A \cdot (T - T_C) \qquad (4\text{-}49)$$

For the time being, low viscous systems shall be considered only. With this restriction the power input by the agitator may be neglected as a first approximation. In addition, the absence of any further heat sources or sinks, such as evaporation cooling, is assumed. In a next step the special theoretical case that all components fed into the reactor do not react with each other shall be discussed. If the two terms defined in Equ. (4-48) and (4-49) are inserted into the general integral heat balance and if the steady state is evaluated, a mixing temperature T_0 will be observed:

$$T_0 = \frac{T_{in} + St \cdot T_C}{1 + St} \qquad (4\text{-}50)$$

with Equ.(4-19)

$$St = \frac{U \cdot A}{\dot{V} \cdot \rho \cdot c_P}$$

This temperature T_0 is called *reference temperature of the CSTR*. Its introduction serves to simplify the final heat balance equation as well as the discussion of different operating conditions. To illustrate the latter statement: the reactor behaviour for a certain process performed in a reactor with well-known properties will always be identical if initial and reference temperature as well as mean residence time are kept constant, independent of the combination of feed and coolant temperature which results in this reference temperature. The terms for convective heat transport and for the heat exchange of the reactor wall can now be combined into one heat removal term using this reference temperature.

$$\frac{t_{\text{charact.}}}{V_R \cdot \rho \cdot c_P} \sum_{\substack{\text{sources}\\ \text{\& sinks}}} \dot{Q} = -(1+St)\cdot(T-T_0) \tag{4-51}$$

In defining the accumulation term, two different heat capacities have to be discriminated, the heat capacity of the reactor and of the reaction mixture. The most convenient form to account for this fact is the application of the thermal inertia Φ, which was introduced in Chapter 2:

$$\Phi = 1 + \frac{m_{App} \cdot c_{P_{App}}}{V_R \cdot \rho \cdot c_P} \tag{2-1}$$

With its use the ***unsteady heat balance of the cooled CSTR*** using dimensionless numbers is obtained:

$$\Phi \cdot t_{\text{charact.}} \cdot \frac{dT}{dt} = \frac{t_{\text{charact.}}}{V_R \cdot \bar{\rho} \cdot \bar{c}_P} \cdot \dot{Q}_{\text{chem.}} - (1+St)\cdot(T-T_0) \tag{4-52}$$

The heat balance of the cooled PFTR

The deduction of the heat balance shall remain restricted to the stationary operated tube reactor at this point, allowing the neglection of any radial profiles. This goes conform with the earlier approach for the deduction of the corresponding mass balance.

The prevailing task in designing a cooled tube reactor safely on a technical scale is the limitation of local temperature differences, which develop along the length of the reactor, to small values. This is achieved by an intensive cooling. In the special case of the PFTR the main resistance for the heat removal lies on the side of the tube carrying the mass flux. The heat flux through the tube wall, which changes in axial direction of the tube, can best be modelled with the help of a heat transfer coefficient

$$\dot{Q}_C = -\alpha_W \cdot A \cdot (T - T_W) \tag{4-53}$$

For the PFTR, if the cooling is as strong as it usually is in tube bundle designs the tube wall temperature will approximately be equal to the coolant temperature.

For tubes the ratio of volume to surface area is geometrically fixed and equal to a quarter of the tube's diameter. Taking this into consideration a special definition is obtained for the Stanton number of the PFTR

$$St = \frac{4 \cdot \alpha_W \cdot \tau}{d \cdot \rho \cdot c_P} \tag{4-54}$$

and subsequently a *stationary heat balance of the PFTR* can be derived, which again uses dimensionless numbers and bears a certain analogy to the heat balance of the CSTR:

$$\Phi \cdot L \cdot \frac{dT}{dz} = \Delta T_{ad} \cdot Da_\infty \cdot \Phi(X) \cdot \exp\left(-\frac{E}{R \cdot T}\right) - St \cdot (T - T_0) \tag{4-55}$$

The Heat Balance of the Cooled BR

The equality in reactor behaviour of the stationary PFTR and unsteady BR, which was explained in Section 4.1.5, allows the direct formulation of the heat balance for the cooled BR. If the length of the PFTR is substituted by the characteristic reaction time for the batch process, and if the Stanton number formulation is based on its general definition regarding the overall heat removal mechanism, the *unsteady heat balance of the cooled BR* is obtained.

$$\Phi \cdot t_R \cdot \frac{dT}{dt} = \Delta T_{ad} \cdot Da_\infty \cdot \Phi(X) \cdot \exp\left(-\frac{E}{R \cdot T}\right) - St \cdot (T - T_0) \tag{4-56}$$

The Heat Balance of the Cooled SBR

The cooled SBR has great similarity to the cooled CSTR as far as balancing is concerned. The most important difference is the reaction volume which changes with time.

The SBR is characterized by a continuous feed stream. Consequently the heat balance of the cooled SBR has at least to account for the convective heat flux and the heat transport through the wall.

$$\dot{Q}_{conv} = -\dot{V}_D \cdot \rho \cdot c_P \cdot (T - T_{feed}) \tag{4-57}$$

$$\dot{Q}_C = -U \cdot A \cdot (T - T_C) \tag{4-49}$$

Contrary to reactors with a constant reactor volume, the heat transfer area changes with time due to the feed stream. The safety assessment, however, usually assumes a constant heat transfer area value as a first approximation.

In the case of small volume changes the area wetted by the initial charge and in case of large changes a suitable average value is used for all necessary calculations.

In analogy to the CSTR, the insertion of both heat flux terms into the general heat balance results in the mixing temperature:

$$T_0 = \frac{T_{feed} + \frac{U \cdot A \cdot \tau_D}{V_D \cdot \rho \cdot c_P} \cdot T_C}{1 + \frac{U \cdot A \cdot \tau_D}{V_D \cdot \rho \cdot c_P}} \tag{4-58}$$

provided that the special case of complete absence of any chemical reaction is discussed.

When setting up the mass balance the Damkoehler number was referenced to the final reaction volume, this way enabling an easier comparison with other ideal reactors and a convenient calculation of SBR phase and post reaction batch phase. This shall be adopted for the definition of the Stanton number.

$$St = \frac{U \cdot A \cdot \tau_D}{\left(V_D + V_0\right) \cdot \rho \cdot c_P} \tag{4-59}$$

Making use of this Stanton number as well as the volume increase factor ε, the reference temperature of the SBR is obtained:

$$T_0 = \frac{T_{feed} + \frac{(1+\varepsilon)}{\varepsilon} \cdot St \cdot T_C}{1 + \frac{(1+\varepsilon)}{\varepsilon} \cdot St} \tag{4-60}$$

The two heat flux terms describing the convective transport and the transport through the wall can now be combined to one heat removal term by making use of this reference temperature:

$$\frac{t_{charact.}}{V_R \cdot \rho \cdot c_P} \cdot \sum_{\substack{\text{Sources a.}\\ \text{Sinks}}} \dot{Q} = -\frac{(1+\varepsilon)}{(1+\varepsilon \cdot \Theta)} \left(\frac{\varepsilon}{1+\varepsilon} + St\right) \cdot \left(T - T_0\right) \tag{4-61}$$

When discussing the chemical heat production rate the volume increase has to be accounted for.

$$\frac{t_{\text{charact.}}}{V_R \cdot \rho \cdot c_P} \cdot \dot{Q}_{\text{chem}} = \left(\frac{1+\varepsilon}{1+\varepsilon \cdot \Theta}\right)^2 \cdot \Delta T_{ad} \cdot Da_{\infty} \cdot \Phi(X,\Theta) \cdot \exp\left(-\frac{E}{R \cdot T}\right) \tag{4-62}$$

By inserting all terms derived into the general integral heat balance for cooled ideal reactors, including the thermal inertia Φ, the unsteady state heat balance of the cooled SBR is obtained in a partially dimensionless form:

$$\Phi \cdot \tau_D \cdot \frac{dT}{dt} = \frac{1+\varepsilon}{1+\varepsilon \cdot \Theta} \cdot \left[\Delta T_{ad} \cdot \frac{dX}{d\Theta} - \left(\frac{\varepsilon}{1+\varepsilon} + St\right) \cdot (T - T_0)\right] \tag{4-63}$$

4.2 The Heat Explosion Theory

Before discussing the safety assessment of chemical processes under normal as well as under upset conditions in detail, the classical heat explosion theory shall be treated. The first scientists to investigate the so-called runaway of an exothermic chemical reaction were Semenov and Frank-Kamenetzkii [18,19]. They were the pioneers in investigating and describing the self-heating process of reacting systems up to an explosion-like temperature rise in its dependence on different heat loss conditions to the environment. The criteria they derived are still valid today and form the basis of any safety assessment.

One of the two limiting cases, which was discussed by Semenov, is based on the assumption of a homogeneous temperature distribution within the reacting mass, an assumption that already was underlying to the previous chapter, when the heat balance was set up. This homogeneous temperature field is achieved by very good mixing, as is possible for gases or Newtonian liquids of low viscosity. The heat exchange with the environment is then determined by the heat transfer through the wall only.

Frank-Kamenetzkii, on the other hand, described the other limiting case of a totally unstirred exothermic reacting system. This is also of practical relevance, as this is a good model for particle beds as such exist in drying and storage operations. The main heat transfer resistance prevails within the reaction mass itself. The wall is taken as an infinitely large isothermal reservoir in this case, neglecting all boundary layer effects.

Consequently, a temperature profile develops within the mass which is mainly determined by the substance specific heat conductivity. The temperature profiles of those two limiting cases are presented schematically in Figure 4-7. As the Semenov model is of greater importance to chemical transitions performed in their respective reactors, the following elaboration shall focus on this part of the explosion theory. The other limiting case should be applied when assessing the storage of solid substances with dust explosive or self-reactive properties.

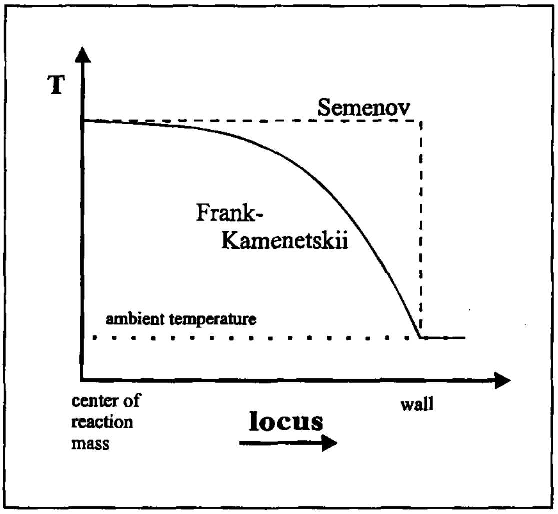


Fig. 4-7. Schematic presentation of the temperature profiles according to Semenov and Frank-Kamenetzkii

It shall be assumed that a simple conversion of A to B shall be performed in a batch reactor. It is further assumed that A is available in a close to infinitive amount, this way allowing the neglection of any consumption of A with progressing reaction time. Such a process may formally be described by a zero-order reaction rate law. The temperature dependence of the reaction rate shall follow the Arrhenius relationship. With these prerequisites the heat production rate of this reaction can be expressed:

$$\dot{Q}_{chem} = V_R \cdot k_\infty^* \cdot (-\Delta_R H) \cdot \exp\left(-\frac{E}{R \cdot T}\right) \tag{4-64}$$

If the rate constant is referred to a reference temperature T_0, which in the case of batch processes is equivalent to the cooling temperature,

$$k^* = k^*(T_0) \cdot \exp\left(-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right) \tag{4-65}$$

and are made the following transformations:

$$k^* = k^*(T_0) \cdot \exp\left(\frac{E}{R} \cdot \frac{(T - T_0)}{T \cdot T_0}\right) \tag{4-66}$$

$$k^* = k^*(T_0) \cdot \exp\left(\frac{E \cdot \Delta T_{ad}}{R \cdot T_0^2} \cdot \frac{(T - T_0)}{\Delta T_{ad} \cdot \frac{T}{T_0}}\right) \tag{4-67}$$

the following expression is finally obtained:

$$k^* = k^*(T_0) \cdot \exp\left(\frac{B_0 \cdot \vartheta}{1 + \frac{\Delta T_{ad}}{T_0} \cdot \vartheta}\right) \qquad \text{with} \quad \vartheta \equiv \frac{T - T_0}{\Delta T_{ad}} \tag{4-68,4-69}$$

Making use of the approximation

$$\frac{\Delta T_{ad}}{T_0} \cdot \vartheta \ll 1 \tag{4-70}$$

Equation (4-71) is obtained

$$k^* = k^*(T_0) \cdot \exp(B_0 \cdot \vartheta) \tag{4-71}$$

and for the heat production rate

$$\dot{Q}_{chem} = V_R \cdot k^*(T_0) \cdot (-\Delta_R H) \cdot \exp(B_0 \cdot \vartheta) \tag{4-72}$$

is yielded. After these considerations it becomes obvious that the thermal reaction number B is not an arbitrary combination of parameters to obtain a dimensionless number, but a safety number which originates from the heat explosion theory.

The exponential dependence of the reaction rate on the temperature dominates the course of the chemical heat production rate with increasing temperature.

The heat removal through the wall can be expressed as

$$\left|\dot{Q}_C\right| = U \cdot A \cdot \left(T - T_0\right) \tag{4-73}$$

This linear temperature dependence of the cooling power and the corresponding exponential dependence of the chemical heat output result in different numbers of operating conditions at which both powers are in equilibrium. The number is influenced by the boundary conditions chosen with respect to the reference temperature and the product of overall heat transfer coefficient and transfer area. This fact is shown graphically in Figure 4-8.

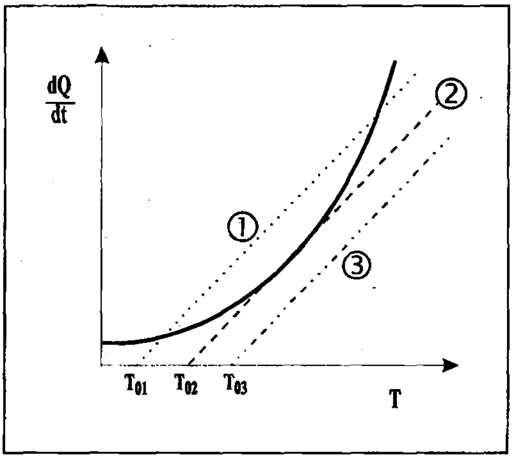


Fig. 4-8. Semenov plot

In addition to the heat production curve of the chemical reaction, three heat removal functions are plotted in this figure, all representing different coolant temperatures. The lower intersection observed with the heat removal line ① shall be discussed first. In the case of an external disturbance of the system which causes a decrease in temperature, the resulting heat production rate is always higher than the corresponding cooling power. Consequently, a self-stabilization is be observed, with the effect that the system returns to the operating condition described by the intersection. In the other case of disturbance leading to a temperature increase the same effect is observed. The self-stabilization is caused by the fact that the cooling power exceeds the reaction power. Due to this self-stabilization this lower intersection is rated *stable*.

A totally different behaviour is observed with the upper intersection of the heat removal line ①. A disturbance resulting in a decrease in temperature leads to a situation in which the cooling power exceeds the reaction power. The system never returns to the upper intersection but is stabilized in the lower intersection. The opposite effect is observed with a disturbance leading to a temperature increase. The reaction power exceeds the cooling power, resulting in a self acceleration or the so-called *runaway*. The upper intersection is therefore rated *unstable*.

A significant shift of the reference temperature to higher values, as it is represented by the heat removal line ③, results in operating conditions which may be called pseudo adiabatic. Each operating point shows runaway behaviour. A comparable situation is obtained if the reference temperature is kept constant but the heat transfer coefficient or area is reduced significantly. Both changes to lower values reduce the slope of the heat removal line with the consequence of an elimination of all intersections.

This elaboration makes it obvious that the heat removal line ② represents a very special case. It describes the limiting case of the first occurrence of an unstable operating point. A mathematical description of this limiting case, which contains all relevant operating and reaction parameters represents the safety technical design limit of this model case. The tangential point of heat removal and heat production function may be described as follows:

$$\dot{Q}_{chem.} = \dot{Q}_C \qquad \text{'und} \qquad \frac{d\dot{Q}_{chem.}}{dT} = \frac{d\dot{Q}_C}{dT}$$

These equations may easily be combined to:

$$\frac{d\ln\dot{Q}_{chem.}}{dT} = \frac{d\ln\dot{Q}_C}{dT} \tag{4-74}$$

The solution to this equation is:

$$B_0 \cdot \vartheta = 1 \tag{4-75}$$

Equ. (4-75) describes a stability condition which can easily be interpreted.

$$\frac{R \cdot T_0^2}{E} \geq T - T_0 \tag{4-76}$$

Based on common operating temperatures ranging from -30 to 200°C as well as typical values for the activation temperature E/R of organic synthesis reactions from

4500 to 12 000 K, the distribution of critical temperature differences as shown in Figure 4-9 can be calculated. It can be seen that on average a critical temperature difference of 20 K should not be exceeded in order to exclude ranges of unstable operating conditions. This statement may be taken as a first rule of thumb for the safety assessment of cooled batch processes as the assumptions on which the Semenov model is based may be regarded as very conservative with respect to actual plant conditions. This is especially true for the assumption of a pseudo zero-order reaction.

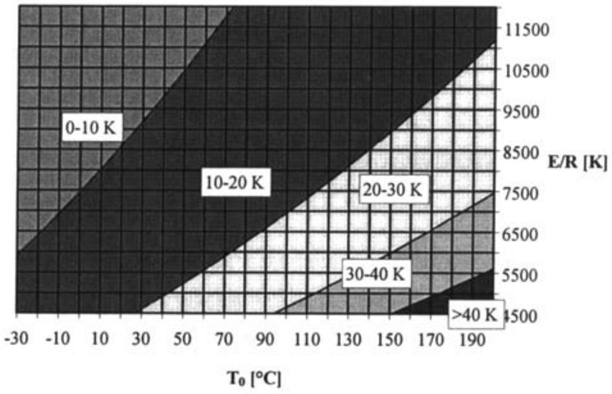


Fig. 4-9. Critical temperature differences ($T-T_0$) for the tangential point according to Semenov

By inserting the solution to Equ.(4-74) expressed in Equ. (4-75) into the equation describing the equality of heat production and removal rate, which is valid at this point of contact, a relationship is obtained fulfilling the requirements of a safety design limit as stated above.

$$\frac{U\cdot A\cdot R\cdot T_0^2}{V_R\cdot k^*(T_0)\cdot\left(-\Delta_R H\right)\cdot E}=\exp(1) \tag{4-77}$$

If this equation is extended in numerator and denominator by the product of density and specific heat, this safety design limit may also be expressed using dimensionless numbers:

$$\frac{St}{Da_0\cdot B_0}=e \tag{4-78}$$

In all cases with a ratio of Stanton number to the product of Damkoehler and thermal reaction number exceeding the natural constant e, the process may be regarded as stable or, in other words, as safe. Based on Semenov's considerations with respect to the heat explosion theory, another rule of thumb for the safety technical assessment of exothermic batch processes can be deduced. The ratio of Stanton to Damkoehler number is that of two time constants. The smaller the value of the time constant of reaction, the faster the reaction proceeds; the smaller the time constant of the cooling, the more intensively and effectively the cooling operates. Using Figure 4.4, which shows the dependence of the thermal reaction number on adiabatic temperature increase as well as on activation temperature E/R, a range for the thermal reaction number may be estimated for moderate exothermic reactions. If values between 5 to 10 are taken as representative for such reactions, Equ. (4-78) can be interpreted in a way the time constant of the cooling has to be 10 to 15 times smaller than the time constant of the reaction in order to ensure safe batch operating conditions. Reversing this interpretation the following may be stated:

> *Cooled batch processes can be operated safely under normal operating conditions only if the reactions are moderately exothermic and proceed slowly. A reaction rate may be regarded as slow if the time constant of the reaction is approximately 20 times higher than the time constant of the cooling.*

The heat explosion theory also is the starting point for another frequently used technical safety data. When exothermic chemical reactions are performed, the cooling becomes extremely important. A standard question to be answered as part of the safety assessment therefore is: How does the system behave in case of a loss of cooling? The heat losses of plant vessels to the environment may be regarded as negligible, at least up to operating temperatures of 150°C. Consequently, the conditions prevailing due to maloperation are close to adiabatic and should be modelled as such. The unsteady heat balance of such a system can be formulated making use of the Semenov boundary conditions:

$$\frac{d\vartheta}{dt} = k^*(T_0) \cdot \exp(B_0 \cdot \vartheta) \tag{4-79}$$

The decisive characteristic of an adiabatic temperature/time-course of a batch process is the enormous self-acceleration of the temperature rise over time. This self-acceleration process is responsible for the fact that corrective action is possible only in the initial maloperation phase. Therefore it is of great importance to have a measure at hand which indicates how long it takes for the adiabatic process to reach a phase of uncontrollable self-acceleration. For this purpose the *adiabatic induction time* τ_{ad} is used. It is defined as the time the system needs under adiabatic conditions to reach the point of highest temperature gradient. In its general form the adiabatic induction time is a function of the adiabatic temperature increase, the activation temperature and the reaction kinetics.

To derive the mathematical equation for the adiabatic induction time the unsteady adiabatic heat balance of the BR is required. If the thermal inertia of the system is neglected, the balance may be obtained from Equ. (4-56), formally setting the heat exchange term equal to zero.

$$t_R \cdot \frac{dT}{dt} = \Delta T_{ad} \cdot Da_\infty \cdot \Phi(X) \cdot \exp\left(-\frac{E}{R \cdot T}\right) \tag{4-80}$$

Dividing this adiabatic heat balance by the mass balance, Equ. (4-33), yields the so-called adiabatic coupling equation:

$$\frac{dT}{dX} = \Delta T_{ad} \tag{4-81}$$

With the boundary conditions for the integration limits $X(T_0) = 0$ and $X(T) = X$, Equ. (4-82) is obtained:

$$X = \frac{T - T_0}{\Delta T_{ad}} \tag{4-82}$$

Under adiabatic conditions $X = \vartheta$ is valid. Substituting the conversion X in the heat balance with the help of Equ. (4-82) results in a formulation, in which the temperature remains the only variable. Integration of this adiabatic heat balance provides the general equation for the determination of the adiabatic induction time:

$$\tau_{ad} = \frac{t_R}{\Delta T_{ad} \cdot Da_\infty} \cdot \int_{T_0}^{T|_{\frac{dT}{dt}\max}} \frac{1}{\Phi\left(\frac{T - T_0}{\Delta T_{ad}}\right)} \cdot \exp\left(\frac{E}{R \cdot T}\right) \, dT \tag{4-83}$$

This equation has the disadvantage of an unknown upper integration limit. For certain simple formal kinetic rate laws the necessary equation may be obtained from the generally valid side condition

$$\frac{d^2T}{dt \cdot dT} = 0 \tag{4-84}$$

in an analytically closed form.

A comparable approach was taken by Frank-Kamenetzkii, limiting the discussion to Semenov's special case of a zero order reaction. In this case,

$$\Phi\left(\frac{T - T_0}{\Delta T_{ad}}\right) = \Phi(\vartheta) = 1 \tag{4-85}$$

may be stated for the dimensionless reaction rate, and at the same time:

$$\frac{t_R}{Da_\infty} = \frac{1}{k_\infty^*} \tag{4-86}$$

Additionally, the upper integration limit is also known, as the temperature increases in a steady and monotone way in this special case. On the other hand, the dimensionless temperature increase ϑ may not become greater than 1 by definition. This way, for the special case of a zero order reaction, the equation for the adiabatic induction time is reduced to:

$$\tau_{ad,0,ord.} = \frac{1}{k_0^*} \cdot \int_0^1 \exp(-B_0 \cdot \vartheta)\, d\vartheta \tag{4-87}$$

which can be solved analytically.

$$\tau_{ad,0.\,ord.} = \frac{1}{k_0^*} \cdot \frac{1}{B_0} \cdot [1 - \exp(-B_0)] \tag{4-88}$$

The exponential term within the brackets is small compared to 1. This allows for another simplification, and the result is called *time to maximum rate* or *TMR*.

$$TMR = \frac{1}{k_0^* \cdot B_0} \tag{4-89}$$

In Section 3.2 this relationship has already been used for the safety technical evaluation of isothermal DTA, respectively DSC, measurements.

4.3 Investigation And Assessment Of Normal Operating Conditions

As long as substances or mixtures are investigated, the small sample amounts limit the variety of possible measuring performances, which is a consciously desired restriction. Consequently the process safety engineers have been forced to develop their own methods of interpretation in order to obtain the desired information from measurements with fixed design and given measured variables. When investigating reactions the situation is much more advantageous. Modern reaction calorimeters allow measurements under conditions which are almost identical to real plant operation. In this situation it is more reasonable to present the theoretical part of the assessment first. Based on this knowledge the requirements on the test design are easily deducible. In a final step it is discussed, which available testing equipment meets the requirements, this way supporting the selection of adequate hardware.

4.3.1 The Safety Technical Assessment Of Normal Operating Conditions

Two questions are mainly asked if a safety assessment of the undisturbed process is required:

1. have the reactor and the auxiliary equipment been correctly designed for a new process?
   or
2. is a new process compatible with the existing equipment?

The basis for the assessment is identical in both cases, namely: the knowledge of all characteristic values of the chemical reaction itself. These are mainly the heat of reaction and the formal kinetics. In the introduction to Section 4.1 it was shown that a variety of different formal kinetic rate laws may be approximated by a power rate law with sufficient accuracy. In these cases the reaction order n has to be interpreted as an effective order with statistical adjustment character. Based on this experience the following discussion will be performed for reactions which can be described with such an n-th order rate law

$$r(X,T) = r_{0,\infty} \cdot (1-X)^n \cdot \exp\left(-\frac{E}{R \cdot T}\right) \tag{4-90}$$

In the subsequent steps the procedures to answer the two questions differ. In the first case, the assessment of a newly designed plant, usually the desired conversion, the optimal process temperature and the required production rate are fixed. Also the mode of operation, such as continuous or discontinuous, is predetermined by demands on selectivity and yield. The safety evaluation now has to assess, whether or not the parameter combination selected from the multi-dimensional space defined by reactor size, initial concentrations, characteristic reaction time as well as coolant and feed temperature can ensure safe operation under normal conditions.

In the second case reactor size and supply temperatures are fixed. In this case the parameter space is restricted either to the selection of suitable initial concentrations or an adequate reaction time for a safe performance. Even in this case of limited degrees of freedom it would not be an economic procedure to simulate and evaluate all conceivable parameter combinations. It is much more advisable to derive and apply generally valid criteria in order to conduct a straightforward safety assessment of process conditions well defined by a certain parameter set.

In an additional step the safety assessment has to include the evaluation of the system's response to the normal variability of all process defining variables. This shall help to exclude the occurrence of severe process deviations leading to uncontrollable upset conditions. Such considerations are also called sensitivity analyses.

4.3.1.1 Safe Normal Operation Of The Cooled CSTR

Steady State Operation

When all start-up effects which are discussed in the following section have leveled off, the cooled CSTR operates in a steady state. The safety assessment has to check whether the cooling capacity is adequate to ensure the removal of all heat produced in such a way that the desired process temperature is not exceeded, as well to evaluate whether sufficient insensitivity regarding normal parameter variability is to be expected. It has turned out to be of advantage to perform this evaluation with the help of diagrams showing either the dependence of the steady state process temperature on residence time for a fixed value of the reference temperature or showing the dependence of this process temperature on the reference temperature for a fixed residence time. Examples of such diagrams are given in Figures 4-10 to 4-13.

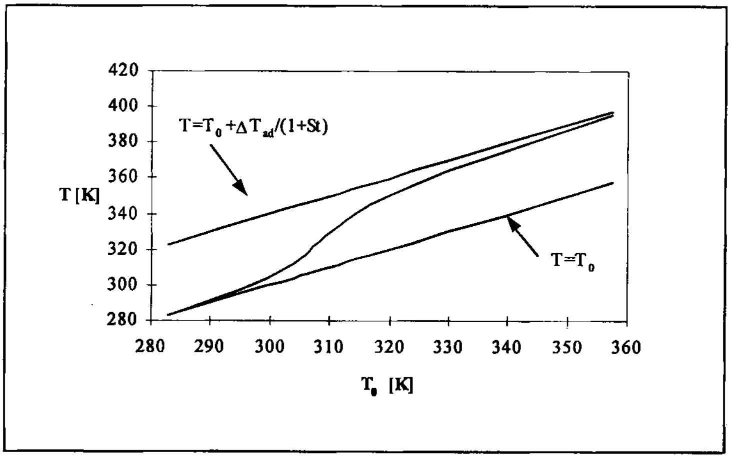


Fig. 4-10. Possible steady state operating conditions for the cooled CSTR
Parameters: $E/R = 10500$ K, $\ln Da_\infty = 32.5$, $\Delta T_{ad} = 100$ K, $St = 1.5$

The easiest way to obtain such plots is to use the so-called coupling equation and the stationary mass balance of the CSTR given in Equ. (4-29). The coupling equation is derived by first transforming the unsteady heat balance of the cooled CSTR into the stationary balance:

$$\dot{Q}_{chem.} = (1 + St) \cdot (T_S - T_0) \tag{4-91}$$

and in a second step by substituting the term

$$Da_\infty \cdot \Phi(X) \cdot \exp\left(-\frac{E}{R \cdot T_S}\right) \tag{4-92}$$

which is part of $\dot{Q}_{chem.}$, by the steady state conversion. The validity of this substitution can be proven by an adequate rearrangement of the corresponding steady state mass balance.

$$X_S = \frac{(T_S - T_0)\cdot(1+St)}{\Delta T_{ad}} \tag{4-93}$$

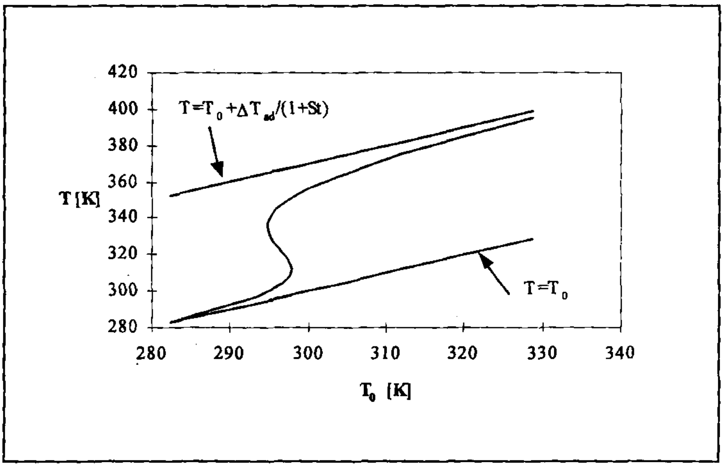


Fig. 4-11. Possible steady state operating conditions for the cooled CSTR
Parameters: $E/R = 10500$ K, $\ln Da_\infty = 32.5$, $\Delta T_{ad} = 175$ K, $St = 1.5$

Figures 4-10 and 4-11 can now be calculated by varying the steady state conversion for a fixed reaction order. The Damkoehler number calculated this way is subsequently used to determine the corresponding steady state temperature using fixed values for the activation energy and Da_∞. From the coupling equation, finally, the corresponding reference temperature is obtained. In order to simplify the later interpretation, two straight lines representing certain border line cases are added. The upper line is the border line for 100% conversion, the lower one for the special case that there is no conversion at all. The sigmoid curve presents all possible solutions. Each point on this curve corresponds to one steady state operating point.

Figure 4-11 shows a peculiarity. Formally interpreted it seems that in a certain range, multiple solutions for the steady state temperature are possible. The main difference in the two processes forming the basis for Figures 4-10 and 4-11 is the significantly higher value of the adiabatic temperature rise in the second case.

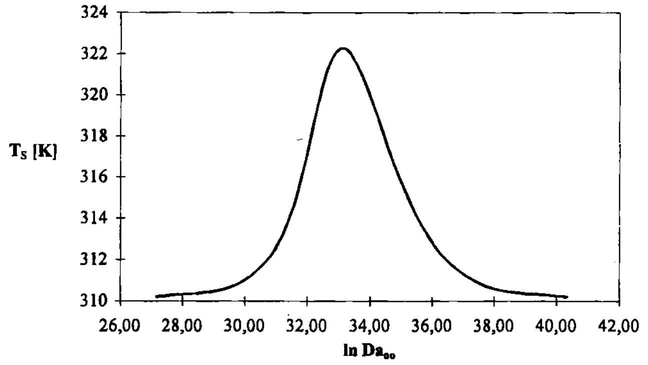


Fig. 4-12. Possible steady state operating conditions for the cooled CSTR
Parameters: $E/R = 10500$ K, $T_0 = 310$ K, $\Delta T_{ad} = 40$ K,
$Da_\infty/St = 4{,}2918 \cdot 10^{14}$, $n = 2$

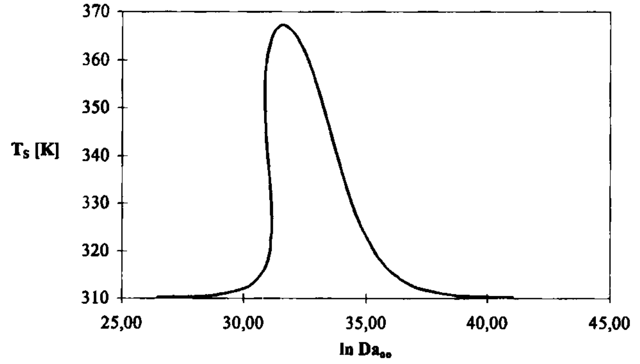


Fig. 4-13. Possible steady state operating conditions for the cooled CSTR
Parameters: $E/R = 10500$ K, $T_0 = 310$ K, $\Delta T_{ad} = 80$ K,
$Da_\infty/St = 4{,}2918 \cdot 10^{14}$, $n = 2$

To enable the calculation of Figures 4-12 and 4-13, an additional step is necessary. The equation for the steady state mass balance as well as the coupling equation of the cooled CSTR each contain a parameter which depends on the residence time: the Damkoehler and the Stanton number, respectively. To eliminate this problem it is best to solve the coupling equation for the Stanton number and to divide the resulting equation by the steady-state mass balance. This way an equation results which is completely independent of the residence time.

$$X_S \frac{St}{Da_\infty \cdot \exp\left(-E/_{R \cdot T_S}\right)} - \frac{\Delta T_{ad}}{\left(T_S - T_0\right)} \cdot X_S \cdot \left(1 - X_S\right)^n + \left(1 - X_S\right)^n = 0 \quad (4\text{-}94)$$

It contains a parameter combination

$$\frac{Da_\infty \cdot \exp\left(-E/_{R \cdot T}\right)}{St} \quad (4\text{-}95)$$

which is of great importance to the safety technical assessment of other reactor types. also, as it is independent of any characteristic reaction time. It has already played a part in the extended interpretation of the heat explosion theory.

If the steady-state temperature is varied and if all kinetic parameters as well as the reference temperature are fixed, Equ. (4-94) can be solved numerically for the corresponding steady state conversion. Attention: in the case of a reverse selection of independent and depending variable, numerical stability problems might be encountered. Using the data couples X_S and T_S, the corresponding Da_∞, which is directly proportional to the residence time, can be calculated from the steady-state mass balance. For certain parameter combinations, multiple solutions may also be observed for one and the same residence time. The difference in the examples given again lies in the degree of exothermicity.

The observed phenomenon is the so-called *ignition-extinction-behaviour*. A close examination of Figure 4-11 will explain this terminology. If one follows the curve of possible steady-state operating points, starting at low reference temperature values, a point is reached at which:

$$\frac{dT_S}{dT_0} = \infty \quad (4\text{-}96)$$

This point is called *ignition point*. A small increase of the reference temperature will lead to a rapid stabilization in a new operating point at a very high stationary process temperature. If, on the other hand, the reference temperature is slowly decreased, another operating point is reached at which condition Equ.(4-96) is again valid. This is the so-called *extinction point*. A further decrease in reference temperature will lead to a rapid stabilization, but this time in an operating point at a very low steady state process temperature. To make the understanding of this phenomenon somewhat easier it is shown again in Figure 4-14. All operating points connected by the dotted line between the lower and the upper branch cannot be realized in practice. **From a safety engineering point of view such ignition-extinction behaviour cannot be tolerated.**

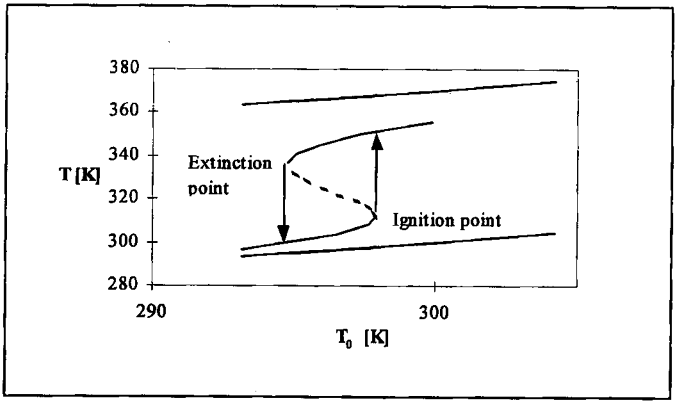


Fig. 4-14. Ignition-extinction behaviour of a cooled CSTR
Parameters: $E/R = 10500$ K, $\ln Da_\infty = 32.5$, $\Delta T_{ad} = 175$ K, $St = 1.5$

It follows that the safety assessment has to focus the evaluation on the sensitivity with which the reactor responds to small deviations in its operating conditions. In this consideration the variability of the reference temperature and its consequences is of somewhat greater significance than that of the residence time. Temperature control of feed tanks and streams is usually less extensively installed than comparable installations for the reactor itself. This can lead to significantly varying feed temperatures. Changes of ± 2 to 3 K are not uncommon in elderly plants, which are not operated with a uniform heating medium.

This *sensitivity* of the steady state process temperature in response to changes of the reference temperature is mathematically expressed in a differential quotient:

$$S = \frac{dT_S}{dT_0} \tag{4-97}$$

This can explicitly be calculated by first extending Equ.(4-97)

$$S = \frac{dT_S}{dT_0} = \frac{dT_S}{dX_S} \Big/ \frac{dT_0}{dX_S} \tag{4-98}$$

and by differentiating of the steady state mass balance and the coupling equation to obtain the required expressions for the numerator and denominator.

$$\frac{dT_S}{dX_S} = \frac{R \cdot T_S^2}{E} \cdot \left(\frac{1}{X_S} + \frac{n}{1 - X_S} \right) \tag{4-99}$$

$$\frac{dT_0}{dX_S} = \frac{dT_S}{dX_S} - \frac{\Delta T_{ad}}{1 + St} \tag{4-100}$$

Inserting these terms leads to the following expression of the sensitivity:

$$S = \frac{1}{1 - \frac{B_S}{1 + St} \cdot \left[\frac{X_S \cdot (1 - X_S)}{1 + (n - 1) \cdot X_S} \right]} \tag{4-101}$$

At the ignition and the extinction point this sensitivity has to become equal to infinity. In other words, the denominator in Equ. (4-101) has to approach zero at these points. This boundary condition allows the exact mathematical description of the ignition-extinction limit:

$$B_\beta = (1 + St) \cdot \frac{1 + (n - 1) \cdot X_S}{X_S \cdot (1 - X_S)} \tag{4-102}$$

which is also called the *static stability limit* of the cooled CSTR. In order to perform the safety technical assessment with respect to the static stability of the process, the reaction order, the Stanton number, and the steady state conversion have to be known. With the help of these parameters, B_β can be calculated and compared with the value for the thermal reaction number of the operating point to be assessed:

$B_{Process} < B_\beta \Rightarrow$ statically stable process
$B_{Process} > B_\beta \Rightarrow$ statically unstable process

This evaluation can also be explained graphically. In the following two Figures 4-15 and 4-16, the corresponding limit curve has been added, which can be calculated for Equ. (4-102) and the coupling equation. Statically unstable operating points always occur, if the area surrounded by the limit curve overlaps the curve of possible steady state operating points. The intersections of the limit curve and the curve of operating points are exactly the ignition and the extinction point.

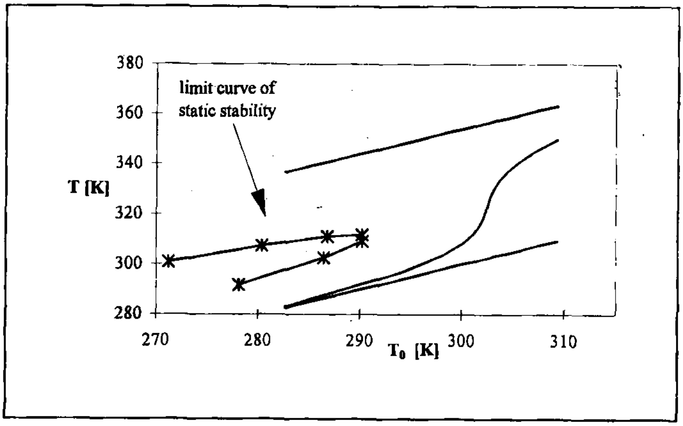


Fig. 4-15. Cooled CSTR with statically stable operating points only
Parameters: E/R = 10500 K, ln Da_∞ = 32.5, ΔTad = 135 K, St = 1.5

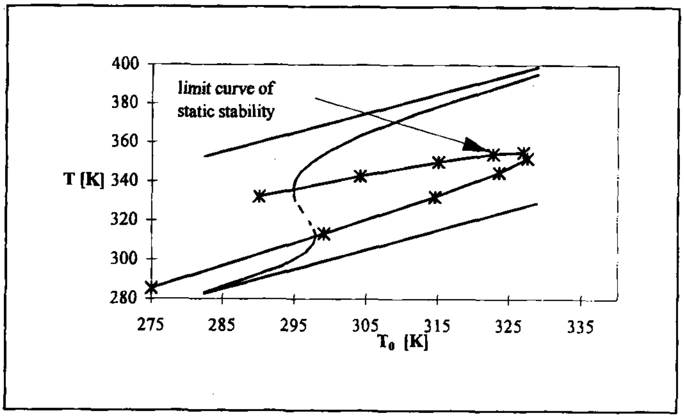


Fig. 4-16. Cooled CSTR with statically unstable operating points
Parameters: E/R = 10500 K, ln Da_∞ = 32.5, ΔT_{ad} = 175 K, St = 1.5

Figure 4-15, however indicates that an exclusion of static instability is not automatically sufficient for the safety assessment of the process under normal operating conditions. In this example operating points with high sensitivity values still exist. They are in the range of medium conversion values. Figure 4-17 shows the corresponding sensitivity values in addition to the previous information.

At the maximum value of sensitivity a variation of 1 K in reference temperature would in consequence lead to a change in process temperature of approximately 14 K! This is hardly tolerable, especially in recognition of van't Hoff's rule that a reaction approximately doubles its rate if the temperature is increased by 10 K. But this problem shall be discussed in detail in the context of the assessment of dynamic sensitivity in a later chapter called „Extended Sensitivity Analysis".

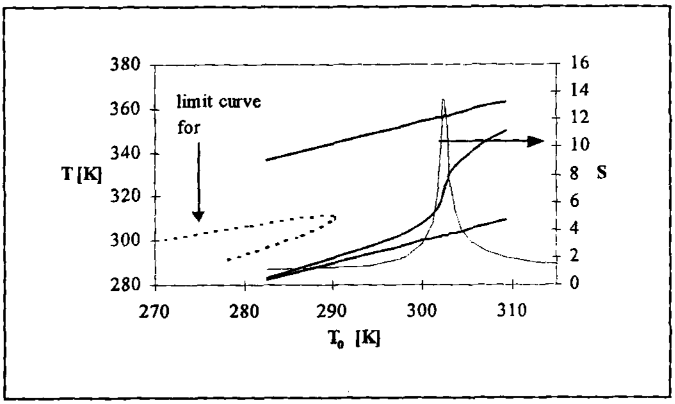


Fig. 4-17. Cooled CSTR with exclusively statically stable operating points
Parameters: $E/R = 10500$ K, $\ln Da_\infty = 32.5$, $\Delta T_{ad} = 135$ K, St = 1.5

This ignition-extinction criterion is applicable in identical form for the evaluation of operating points with a fixed reference temperature but varied residence time.

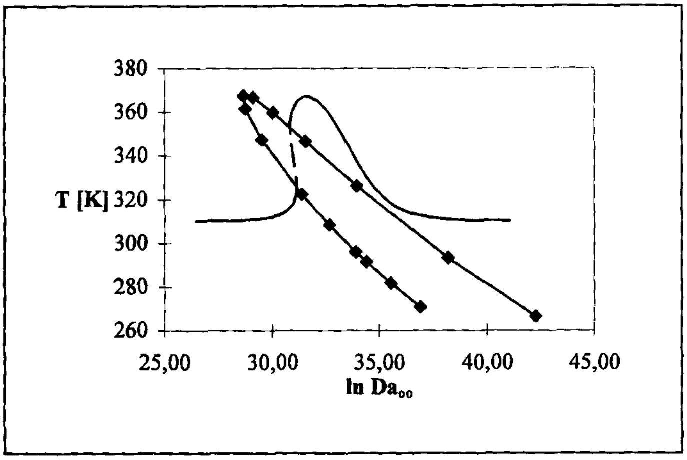


Fig. 4-18. Cooled CSTR with statically unstable operating points
Parameters: $E/R = 10500$ K, $T_0 = 310$ K, $\Delta T_{ad} = 80$ K,
$Da_\infty/St = 4{,}2918 \cdot 10^{14}$, n = 2

When calculating this scenario, special attention has to be paid to the fact that the Stanton number itself depends on the residence time and is not a constant when calculating the limit curve. Again, for clarification purposes, a graphical solution is presented in Figure 4-18.

The Unsteady Operating Behaviour

The safety technical assessment of the unsteady operating behaviour of a cooled CSTR is an important element of the overall evaluation of the normal operating conditions. In the case of the CSTR, a non-steady state behaviour always exists during start-up and shut-down. As these phases turn out to be critical their discussion and interpretation shall be supported graphically.

A process shall be considered with a desired steady state temperature of $T_S = 350$ K and conversion of 0.75. The reaction rate shall follow a second-order formal kinetic law. The exothermicity expressed in terms of the adiabatic temperature increase shall be equal to $\Delta T_{ad} = 120$ K. As a consequence of the residence time chosen and all the other reactor and reaction data, the Stanton number amounts to 7. With the help of all the information given, the reference temperature can be calculated. In the first example the reactor shall be filled with both reactants at a very low temperature, so that in a first approximation no observable conversion takes place:

$$X(t = 0) = 0$$

In the next moment the reaction mixture is heated up very fast to the value of the reference temperature, which this way becomes equal to the starting temperature. This process is shown in Figure 4-19.

A dramatic overshoot of the internal temperature is clearly observed. Temperature levels are reached which are close to 80 K higher than the later steady state temperature. Whether or not the reactor will ever reach this steady state operation is very questionable, as the probability that consecutive and decomposition reactions become so dominant at 400 K and higher that a final runaway will occur is very high. The results from this example can be combined to a first rule for the safe start up of cooled CSTR processes:

> *Strongly exothermic continuous processes must never be started up batch-like by simultaneous addition of both reactants to a quasi empty reaction vessel !*

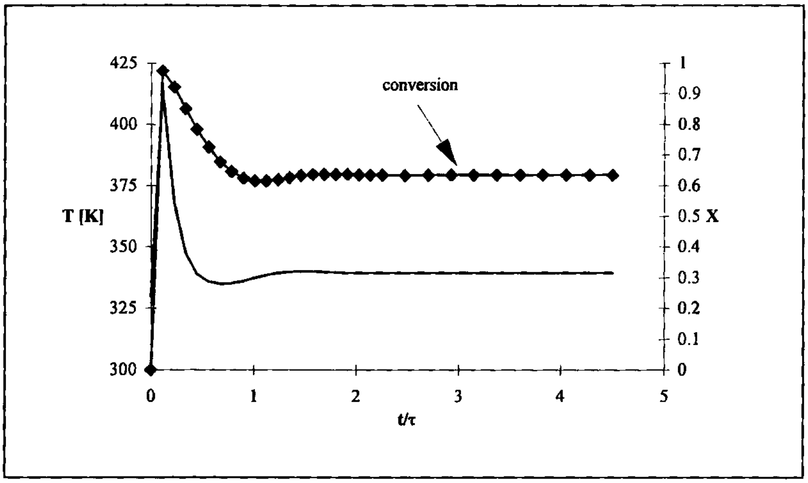


Fig. 4-19. Start-up behaviour of a cooled CSTR -start-up with X=0 and $T=T_0$
Parameters: E/R = 10500 K, $\ln Da_\infty = 32.5$, $\Delta T_{ad} = 120$ K, St = 7

As a first alternative a start-up shall be considered with a reactor filled, either with solvent or with product. The feed of reactants shall be started after the reference temperature has been reached. Formally these conditions correspond to the boundary condition

$$X(t=0)=1$$

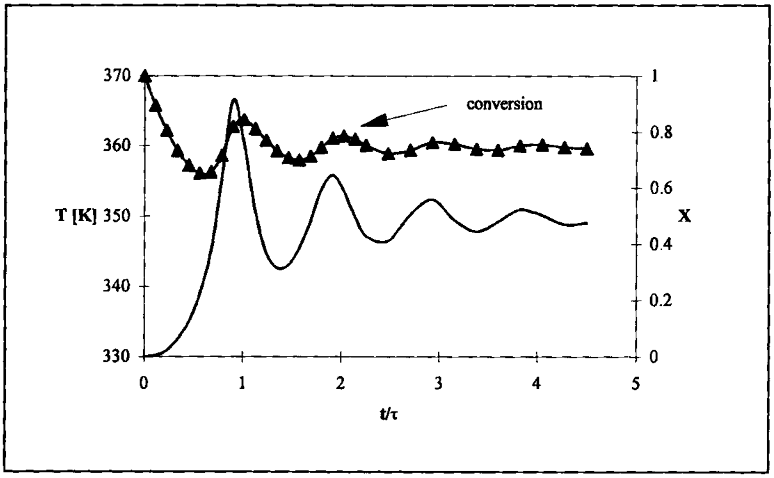


Fig. 4-20. Start up behaviour of a cooled CSTR-start-up with X=1 and $T=T_0$
Parameters: E/R = 10500 K, $\ln Da_\infty = 32.5$, $\Delta T_{ad} = 210$ K, St = 7

The adiabatic temperature increase shall be approximately twice as high as in the first case. The resulting temperature and conversion profiles are shown in Figure 4-20.

Even though the exothermicity has been increased significantly the start-up behaviour has improved to quite some extent. The first overshoot in temperature is still there, but by far not as pronounced as it was observed in the first case. This is especially to be appreciated in view of the absolute value of adiabatic temperature increase, amounting to 210 K. All in all, the start-up phase proceeds as a damped oscillation. The most pronounced first oscillation is caused by the comparably low initial temperature resulting in a low reaction rate and consequently in an accumulation of educts. This effect can be mitigated by increasing the initial temperature (c.f. Figure 4-21).

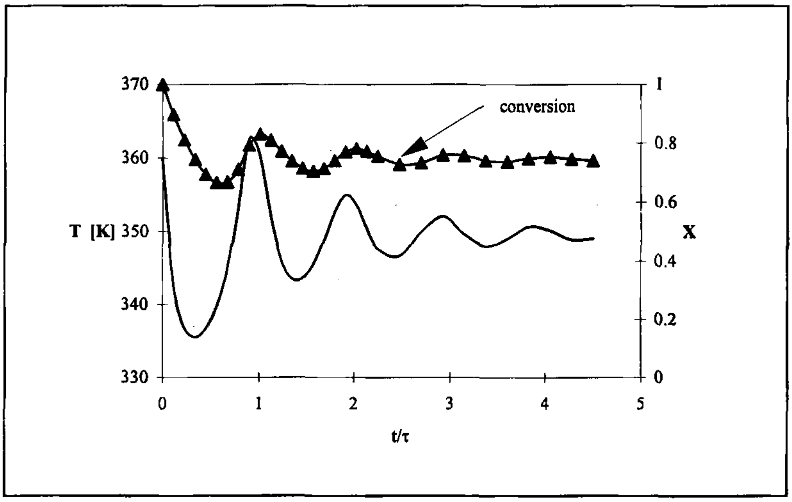


Fig. 4-21. Start-up behaviour of a cooled CSTR-start-up with X=1 and T=360 K
Parameters: E/R = 10500 K, ln Da_∞ = 32.5, ΔT_{ad} = 210 K, St = 7

But even this start-up strategy may be problematic under certain circumstances, as is shown in Figure 4-22. In this case it was assumed that the cooling intensity represented in terms of the Stanton number amounts to only half of the value available for the previous examples.

Under these conditions limit cycle oscillations develop, which are safety technically intolerable.

The safety technical assessment of the start-up conditions has to check on the correct choice of initial temperature and initial conversion, as well as to ensure that the dynamic process does not lead to the development of limit cycle oscillations but to a short transient time with decreasing amplitudes, followed by a steady state.

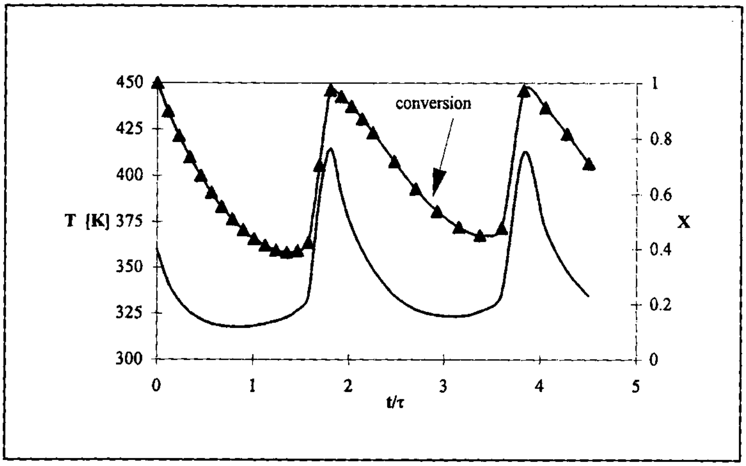


Fig. 4-22. Start-up behaviour of the cooled CSTR – start-up with X=1 and T=360 K
Parameters: E/R = 10500 K, ln Da_∞ = 32.5, ΔT_{ad} = 210 K, St = 3

The necessary procedure can be derived from the classical stability theory for oscillating systems. The unsteady mass and heat balances for the cooled CSTR may be expressed in a very general form

$$\tau \cdot \frac{dX}{dt} = f_1(X,T) \qquad \tau \cdot \frac{dT}{dt} = f_2(X,T) \qquad (4\text{-}103, 4\text{-}104)$$

with the stationary solutions X_S and T_S, which at the same time fulfil the following equations.

$$0 = f_1(X_S, T_S) \qquad 0 = f_2(X_S, T_S) \qquad (4\text{-}105, 4\text{-}106)$$

A steady-state operating point is regarded as stable if the solutions of the two unsteady equations having the initial values

$$X(t=0) = X_S + \Delta X \qquad T(t=0) = T_S + \Delta T \qquad (4\text{-}107, 4\text{-}108)$$

converge in X_S and T_S at a time t which is reached much later than the mean residence time. A prerequisite to this classic treatment according to the stability theory is that the deviations Δ in temperature and conversion are small. This assumption allows for the linearization of the two differential equations in the form:

$$\tau \cdot \frac{d\Delta X}{dt} = a_{11} \cdot \Delta X + a_{12} \cdot \Delta T \qquad \tau \cdot \frac{d\Delta T}{dt} = a_{21} \cdot \Delta X + a_{22} \cdot \Delta T \qquad (4\text{-}109, 4\text{-}110)$$

The terms a_{ij} represent the partial derivatives of the functions f_1 and f_2. The solutions to differential equations of this type are known and have the following form using the chosen symbols:

$$\Delta X = b_{11} \cdot \exp\left(p_1 \cdot \frac{t}{\tau}\right) + b_{12} \cdot \exp\left(p_2 \cdot \frac{t}{\tau}\right) \qquad (4\text{-}111)$$

$$\Delta T = b_{21} \cdot \exp\left(p_1 \cdot \frac{t}{\tau}\right) + b_{22} \cdot \exp\left(p_2 \cdot \frac{t}{\tau}\right) \qquad (4\text{-}112)$$

with

$$p_{1,2} = \frac{a_{11} + a_{22}}{2} \cdot \left[1 \pm \sqrt{1 - \frac{4 \cdot (a_{11} \cdot a_{22} - a_{12} \cdot a_{21})}{(a_{11} + a_{22})^2}}\right] \qquad (4\text{-}113)$$

Following the stability definition, X_S and T_S describe a stable steady state if the deviations ΔX and ΔT approach zero with increasing time. But this can only be the case if the real terms of p_1 and p_2 are less than zero. Based on this logic it follows for the stability condition:

$$2 \cdot \alpha = a_{11} + a_{22} < 0 \qquad (4\text{-}114)$$

$$\beta = a_{11} \cdot a_{22} - a_{12} \cdot a_{21} > 0 \qquad (4\text{-}115)$$

The substitution of the calculated partial derivatives into the stability conditions yields:

$$2 \cdot \alpha = B_S \cdot X_S - \left(2 + St + \frac{n \cdot X_S}{1 - X_S}\right) \qquad (4\text{-}116)$$

$$\beta = (1 + St) \cdot \left(1 + \frac{n \cdot X_S}{1 - X_S}\right) - B_S \cdot X_S \qquad (4\text{-}117)$$

A comparison of Equ. (4-102) and Equ. (4-117) shows that they are identical. The stability limit characterized by the stability parameter β describes nothing other than the static stability limit of ignition and extinction behaviour. This now allows the formulation of the relationship between temperature sensitivity and stability parameter β.

$$S = 1 + \frac{B_S \cdot X_S}{\beta} \tag{4-118}$$

The stability parameter α characterizes the dynamic stability limit, which predicts the occurrence of limit cycle oscillations. The safety technical assessment of the dynamic operating behaviour may follow a comparable procedure to that introduced for the evaluation of static stability. As before, the Stanton number, reaction order, and the steady state conversion have to be known. Using these values, B_α can be calculated applying the equation obtained by setting $\alpha=0$ in Equ. (4-116).

$$B_\alpha = \frac{(2+St)\cdot(1-X_S)+n\cdot X_S}{X_S\cdot(1-X_S)} \tag{4-119}$$

This value is compared with the thermal reaction number of the process to be assessed:

$$B_{Process} < B_\alpha \Rightarrow \text{dynamically stable process}$$
$$B_{Process} > B_\alpha \Rightarrow \text{dynamically unstable process}$$

As has already been demonstrated for the evaluation of static stability, the assessment can also be performed graphically. As an example, Figure 4-23 shows this for the same process of which the static stability was discussed in Figure 4-15 and of which the sensitivity was presented in Figure 4-17.

Now it becomes obvious that the operating points with high sensitivity are dynamically unstable. This, as mentioned before, is not tolerable from a safety technical point of view. It can further be deduced that the exclusion of dynamic instability is the more stringent of the two stability requirements.

This demonstrates the advantage of the graphical over the pure calculation method, which compares the values of two thermal reaction number values only. If the graphical presentation shows no operating point in the relevant range to be enveloped by the limiting curve of dynamic instability, it may also be concluded that all these points are statically stable.

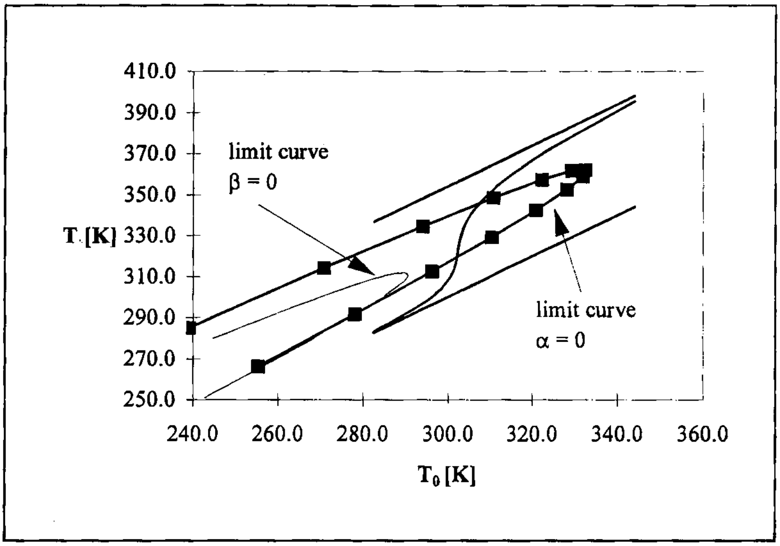


Fig. 4-23. Cooled CSTR with statically stable but dynamically unstable operating points
Parameters: E/R = 10500 K, ln Da_∞ = 32.5, ΔTad = 135 K, St = 1.5

If the purely arithmetical method is applied, both stability limits have to be evaluated in any case, as there are processes with very high values for

$$\frac{\Delta T_{ad}}{1+St}$$

with operating points in the range of small conversion values which are dynamically stable but statically unstable. This can be explained by the fact that operating points with higher conversion values are dynamically unstable, which cannot be seen in the assessment of a single operating point when applying the comparison of the thermal reaction numbers. Such an extraordinary case is shown in Figure 4-24 for demonstration purposes.

The extended sensitivity analysis for the cooled CSTR

In principle, the safety assessment of a process performed in a cooled CSTR under normal operating conditions is fully completed if start-up conditions as well as static and dynamic stability have been evaluated. The assessment performed this way yields unambiguous yes/no statements.

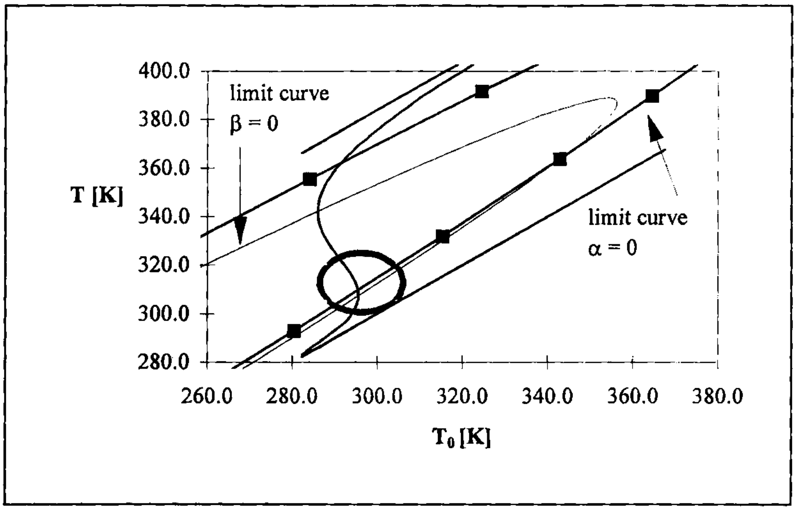


Fig. 4-24. Cooled CSTR with statically and dynamically unstable operating points Parameters: E/R = 10500 K, $\ln Da_\infty = 32.5$, $\Delta T_{ad} = 210$ K, St = 1.

On one hand this is quite a desirable situation as it leaves no room for interpretation. On the other hand it has already been outlined in the context of the discussion of static stability that this restricted yes/no statement provides no information on the overall robustness of the process.

In consequence, the following situation may occur: A process is performed in an operating point which corresponds to a very high steady state conversion. The safety assessment has confirmed that this operating point is statically as well as dynamically stable. After stationary operation for the duration of a single period of mean residence time, one hour in this example, variations in the coolant supply lead to a decrease in reference temperature of 3 K within 12 minutes. Superficially, this seems to be a minor change. But the sensitivity in the original operating point is equal to S = 2.3, resulting in a decrease in operating temperature of approximately 7 K. At this lower temperature, limit cycle oscillations suddenly begin to develop. The parameter plot for this example is given in Figure 4-25, the transient behaviour shown in Figure 4-26.

A more comprehensive safety assessment of an operating condition therefore has to include the whole course of possible steady state solutions as well as their corresponding stability and sensitivity properties. The demand on a safety technically desirable process should therefore be that deviations in operating conditions must neither lead to static nor dynamic instability.

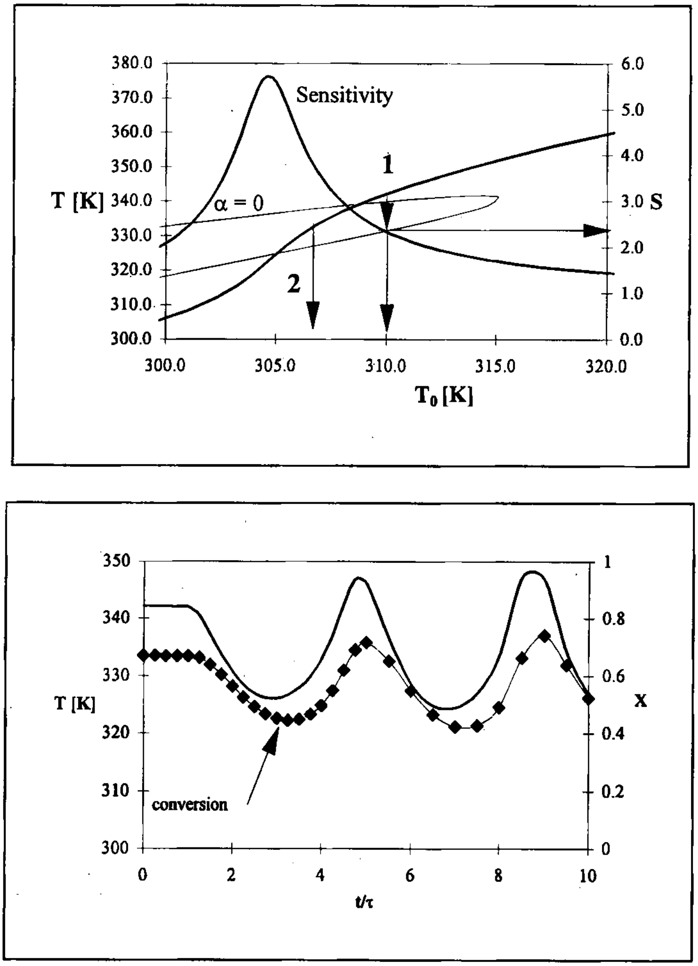


Fig. 4-25 and 4-26. Cooled CSTR : transition from operating point 1 (dynamically stable) to operating point 2 (dynamically unstable) shown as a parameter presentation and as simulated process; occurrence of disturbance at $t/\tau = 1$

Parameters: $E/R = 10500$ K, $\ln Da_\infty = 32.5$, $\Delta T_{ad} = 120$ K, $St = 1.5$

In order to obtain a safety criterion or as equivalent measure to help avoid such a situation, a special case must be considered. It is the point which is characterized by a tangential coexistence of the curves calculated for the possible steady state solutions and the dynamic stability limit. Such a case is shown in Figure 4-27.

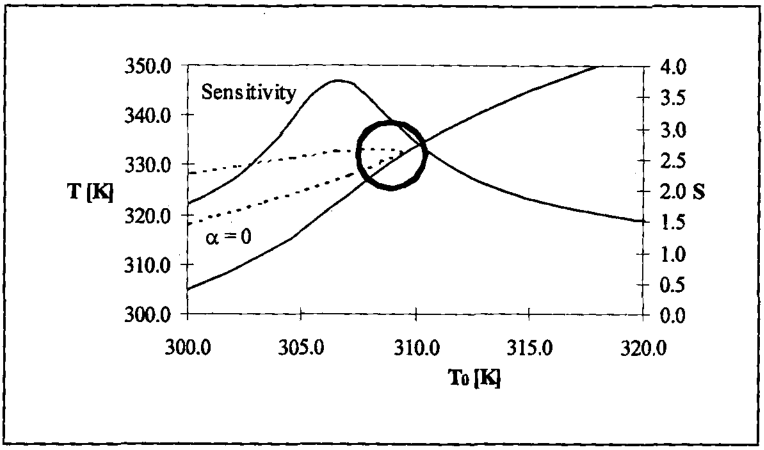


Fig. 4-27. Cooled CSTR with only one tangential point of the curves for steady state solutions and the dynamic stability limit
Parameters: $E/R = 10500$ K, $\ln Da_\infty = 32.5$, $\Delta T_{ad} = 120$ K, $St = 1.809$

This very special operating point has an additional mathematical property. The gradient of the curve for possible steady state solutions in this point is equal to the gradient of the dynamic stability limit curve; this way, both gradients are equal to the sensitivity in this point of operation. The best way to make use of this characteristic is by setting equal the steady state mass balance and the dynamic stability relationship in a suitable parameter presentation (c.f. Equ. 4-120). In a second step the term in the middle and the very right hand term are partially differentiated with respect to the steady state conversion X_S (c.f. Equ. 4-121). This represents the equality of both gradients, as the term dX_S/dT_0, which would have to be calculated to form the total derivative, cancels out.

$$\frac{E}{R \cdot T_S} = \ln(Da_\infty) - \ln\left(\frac{X_S}{(1-X_S)^n}\right) = \sqrt{\frac{E \cdot (2+St)}{R \cdot \Delta T_{ad}}} \cdot \sqrt{\frac{1}{X_S} + \frac{n}{(2+St) \cdot (1-X_S)}} \qquad (4\text{-}120)$$

$$-\left[\frac{1}{X_S} + \frac{n}{1-X_S}\right] = \frac{1}{2} \cdot \sqrt{\frac{E \cdot (2+St)}{R \cdot \Delta T_{ad}}} \cdot \frac{\left[\frac{n}{(2+St) \cdot (1-X_S)^2} - \frac{1}{X_S^2}\right]}{\sqrt{\frac{1}{X_S} + \frac{n}{(1+St) \cdot (1-X_S)}}} \qquad (4\text{-}121)$$

These equations allow for the calculation of stability nomograms. In a first step the parameter

$$P = \sqrt{\frac{E \cdot (2 + St)}{R \cdot \Delta T_{ad}}} \tag{4-122}$$

is calculated by varying the steady state conversion in Equ. 4-121. In a second step the values for P and X_S are inserted into the mass balance to calculate $\ln(Da_\infty)$ for fixed Stanton numbers. This kind of nomogram has to be calculated for each reaction order individually. For a second order reaction the table of values is presented in Table 4-5 and the corresponding nomogram in Figure 4-28.

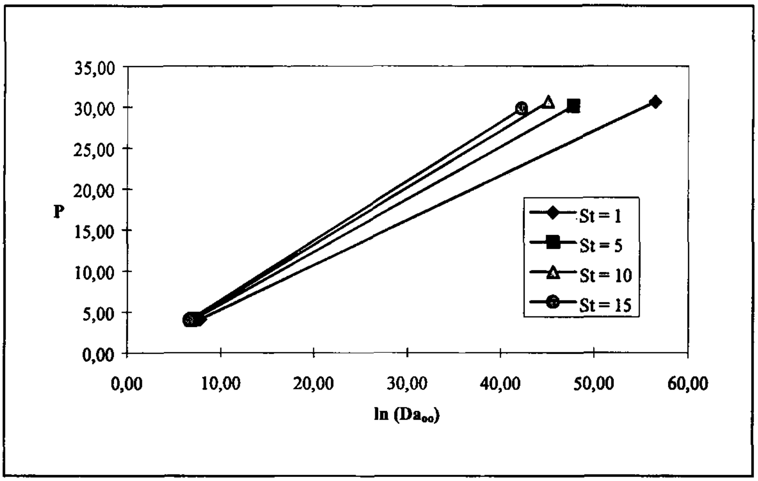


Fig. 4-28. Stability nomogram for a cooled CSTR - n = 2

The safety assessment now follows a procedure which starts with the calculation of the steady state values for $\ln(Da_\infty)$ based on the production requirements for X_S and T_S and the kinetic parameters E/R and n, which must be known. The plausibility of this value may be checked by using the scheduled residence time, the frequency factor and the feed concentration c_{B0}^{n-1} for an alternative determination, which must result in an identical value. This step is followed by the determination of P using Equ. (4-122) and the known process and plant data. If the point defined by P and $\ln(Da_\infty)$ is above the limit curve in the nomogram for the corresponding Stanton number, the operating point is safe under normal operating conditions.

This leaves a last question to be answered: How is a process most effectively stabilized, if it has not been assessed as designed safely? Two different approaches are possible:

- additional implementation of sophisticated measuring and control devices
- process modification

Table 4-5: Table of values (spreadsheet) for the stability nomogram of a cooled CSTR for second order processes

	P				$\ln(Da_{oo})$			
X_S	St = 1	St = 5	St = 10	St = 15	St = 1	St = 5	St = 10	St = 15
0,37	4,05				7,79			
0,38	4,35				8,35			
0,39	4,67				8,98			
0,40	5,04				9,68			
0,41	5,46				10,48			
0,42	5,94	4,10			11,38	7,17		
0,43	6,50	4,33			12,43	7,56		
0,44	7,16	4,58	4,04		13,66	7,98	6,82	
0,45	7,94	4,86	4,24	4,02	15,11	8,44	7,14	6,67
0,46	8,90	5,16	4,46	4,21	16,88	8,94	7,48	6,96
0,47	10,08	5,49	4,69	4,40	19,07	9,48	7,84	7,27
0,48	11,60	5,86	4,94	4,61	21,86	10,08	8,23	7,59
0,49	13,62	6,27	5,21	4,84	25,56	10,75	8,64	7,93
0,50	16,43	6,73	5,50	5,08	30,69	11,49	9,09	8,29
0,51	20,62	7,26	5,82	5,34	38,33	12,33	9,58	8,68
0,52	27,54	7,86	6,17	5,63	50,94	13,29	10,11	9,10
0,53		8,56	6,56	5,93		14,40	10,69	9,55
0,54		9,38	6,98	6,26		15,69	11,33	10,03
0,55		10,35	7,46	6,63		17,21	12,04	10,56
0,56		11,53	8,00	7,03		19,06	12,84	11,13
0,57		13,00	8,61	7,47		21,34	13,73	11,77
0,58		14,87	9,32	7,96		24,24	14,76	12,47
0,59		17,33	10,13	8,52		28,06	15,94	13,25
0,60		20,74	11,09	9,14		33,32	17,32	14,12
0,61		25,77	12,22	9,85		41,07	18,96	15,12
0,62		33,95	13,61	10,67		53,67	20,95	16,25
0,63			15,33	11,63			23,41	17,58
0,64			17,54	12,76			26,55	19,13
0,65			20,46	14,12			30,71	21,00
0,66			24,54	15,79			36,49	23,29
0,67			30,62	17,90			45,10	26,16
0,68				20,65				29,89
0,69				24,39				34,95
0,70				29,78				42,23

The first approach is possible in many cases. On the other hand, the question remains whether it is desirable in every case. The guarantee to be given with the implementation of highly reliable and correct operating devices is an exclusion of the occurrence of any undesirable operating behaviour originating from ignition/extinction or limit cycle phenomena. This is hard to ensure. It presents high demands on availability as well as on the existence of stand-by systems to compensate for failures or fractional dead times of the first system. In most cases these requirements can be met, but the necessary effort and costs should be compared with those which result from a process modification before a decision is made.

A process modification with a stabilizing effect can either be achieved by increasing the heat transfer area or by diluting the feed concentration. The complete assessment procedure including this stabilizing effect for process modification shall be demonstrated in the following example

Example: A continuous process shall be performed at an operating temperature of 323 K. The steady state conversion shall amount to 68%. The start-up is conducted with the product preheated to the initial temperature of 333 K. The adiabatic temperature increase for the scheduled concentrations amounts to 210 K. The reaction rate follows a second order rate law with a Damkoehler number referenced to the frequency factor of $Da_\infty = 8.659*10^{16}$ and an activation temperature of E/R = 12 000 K. The Stanton number of the system is equal to St = 3, with a feed temperature of $T_{in} = 293$ K and a coolant temperature adjustable between 278 and 368 K.

Solution: In a first step the available cooling capacity is checked. With the help of the coupling equation the necessary reference temperature is obtained:

$$T_0 = T_S - \frac{\Delta T_{ad}}{1+St} \cdot X_S = 323\,K - \frac{210\,K}{1+3} \cdot 0.68 = 287.3\,K$$

This allows the determination of the required cooling temperature:

$$T_C = \frac{T_0 \cdot (1+St) - T_{in}}{St} = \frac{287.3K \cdot (1+3) - 293K}{3} = 285.4K$$

which can easily be realized. ✓

This first step may directly be followed by either the simple stability analysis or by the extended sensitivity analysis. In this example both paths shall be pursued. For this purpose $B_{process}$, B_β and B_α are calculated.

$$B_{process} = \frac{E \cdot \Delta T_{ad}}{R \cdot T_S^2} = \frac{12000K \cdot 210K}{323^2 K^2} = 24.15$$

$$B_\beta = (1+St) \cdot \frac{1+(n-1) \cdot X_S}{X_S \cdot (1-X_S)} = (1+3) \cdot \frac{1+(2-1) \cdot 0.68}{0.68 \cdot (1-0.68)} = 30.88$$

$$B_\alpha = \frac{(2+St)\cdot(1-X_S)+n\cdot X_S}{X_S\cdot(1-X_S)} = \frac{(2+3)\cdot(1-0.68)+2\cdot 0.68}{0.68\cdot(1-0.68)} = 13.60$$

An evaluation shows

$B_{Process} < B_\beta \Rightarrow$ statically stable ✓
$B_{Process} > B_\alpha \Rightarrow$ dynamically unstable !!

This process must not be performed due to safety technical concerns. An implementation of additional technical measures or a process modification has to be demanded to ensure the exclusion of possible limit cycle oscillations.

Two alternative process modifications can be proposed. The first possibility is an increase of the parameter P for a fixed value of the Stanton number in the stability nomogram of the extended sensitivity analysis. For the process as proposed, the parameter P amounts to:

$$P = \sqrt{\frac{E\cdot(2+St)}{R\cdot\Delta T_{ad}}} = \sqrt{\frac{12000\,K\cdot(2+3)}{210\,K}} = 16.9$$

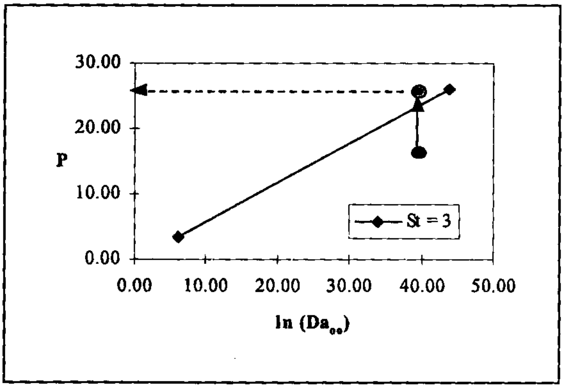


Fig. 4-29. Nomogram for the example

From the nomogram presented in Figure 4-29, it may be deduced that, as a first estimation, P should be equal to P = 27 in order to ensure a safe operation.

With the introduction of a dilution factor κ:

$$c_{A0}^{*} = \kappa \cdot c_{A0} \qquad c_{B0}^{*} = \kappa \cdot c_{B0} \qquad (4\text{-}123, 4\text{-}124)$$

$$\text{ranging from} \quad 0 < \kappa \leq 1 \qquad (4\text{-}125)$$

and the additional prerequisite that standard vessels are used, for which it is usually allowed to assume a constant geometric ratio

$$A \big/ V_R^{2/3} \qquad (4\text{-}126)$$

the critical values to be considered can be expressed in the following form:

$$St^{*} = St \cdot \kappa^{-1/3} \qquad \Delta T_{ad}^{*} = \Delta T_{ad} \cdot \kappa \qquad (4\text{-}127, 4\text{-}128)$$

Consequently P^{*} can be defined

$$P^{*} = \sqrt{\frac{E \cdot \left(2 + St \cdot \kappa^{-1/3}\right)}{R \cdot \Delta T_{ad} \cdot \kappa}} \qquad (4\text{-}129)$$

With the estimated value of $P^{*} = 27$ the dilution factor is determined to be equal to $\kappa = 0.46$ (c.f. Figure 4-30).

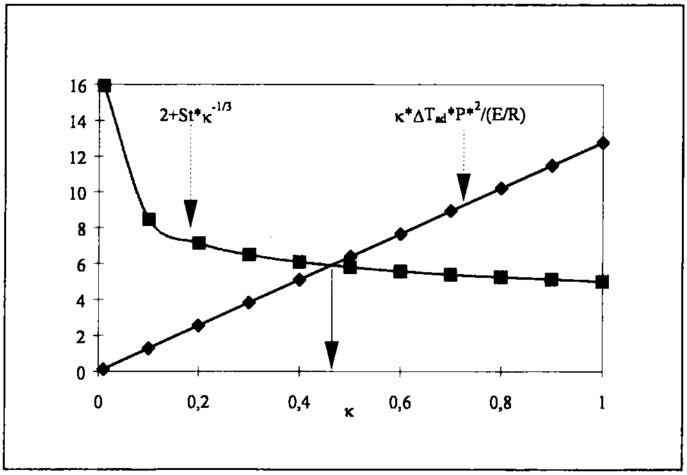


Fig. 4-30. Determination of κ for the example discussed

With κ known the new values for ΔT_{ad} and St can be calculated:

$$St^* = 3.89 \qquad \Delta T_{ad}^* = 96.6$$

In addition, the reactor volume and the volumetric flow rate have to be adjusted if the amount of substance produced per unit of time shall remain the same. For a second order reaction the following relationships are valid:

$$V_R^* = \kappa^{-2} \cdot V_R = 4.73 \cdot V_R \qquad \dot{V}^* = \kappa^{-1} \cdot \dot{V} = 2.17 \cdot \dot{V}$$

Recommendation 1: The proposed process should be modified as follows:

The feed concentrations of the initial components should be reduced to 46% of the originally proposed values. Furthermore, the volumetric flow rate has to be increased by a factor of 2.17. In order to achieve the same production rate, a different reactor has to be used which is 4.73 times larger in volume and which has a Stanton number of St = 3.89 based on the new mean residence time. The cooling temperature should be set equal to T_c = 313.8 K. The start-up procedure proposed may be retained as it is suitable from the point of view of safety.

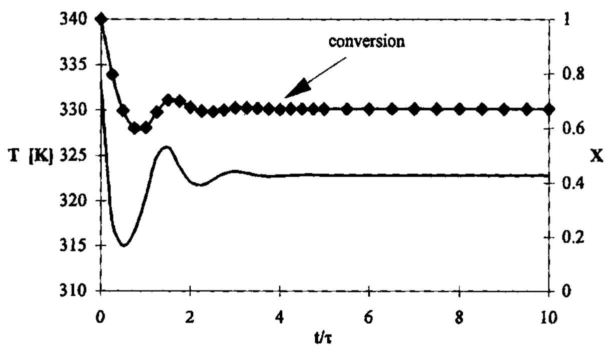


Fig. 4-31. Simulation of the process modified according to the first recommendation

Figure 4-31 shows the result of a simulation of the modified process. A simulation of the original process would have shown that under the start-up conditions chosen, the process would proceed through the ignition/extinction region and would therefore be extinguished completely.

This need not be considered for the modified process as the extended sensitivity analysis already excludes any tangential point with the dynamic stability limit, this way completely excluding any static instability.

The other alternative for a process modification is an increase of the heat transfer area by inserting additional cooling coils into the vessel. Figure 4-32 demonstrates that quite a large increase in heat transfer area is necessary to achieve P values above the corresponding safety limit curves.

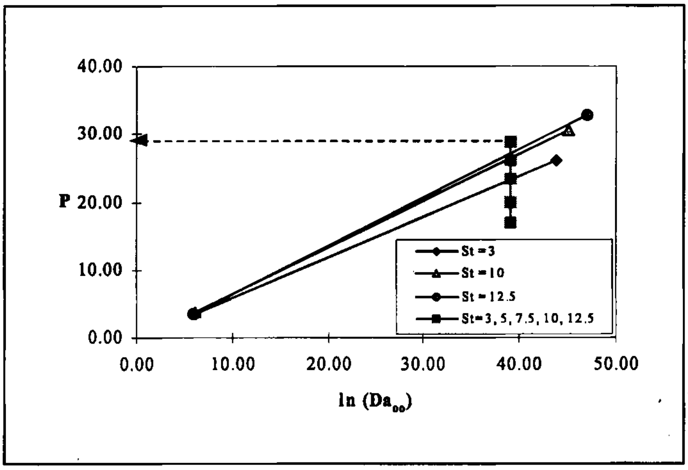


Fig. 4-32. Nomogram for the example - recommendation 2 for process modification

The Stanton number necessary to reach approximately the same distance to the limit curve as in the first recommendation amounts to St = 12.5. From this it follows that the heat transfer area has to be increased by a factor of 4.17 compared to the original design.

Recommendation 2: The proposed process should be modified as follows:

With the help of additionally inserted cooling coils the heat transfer area should be increased by a factor of 4.17. The cooling temperature should be set equal to 314 K. The start-up procedure may be retained as proposed as it is suitable from a safety point of view.

Figure 4-33 presents the simulated profiles for the process modified according to recommendation 2.

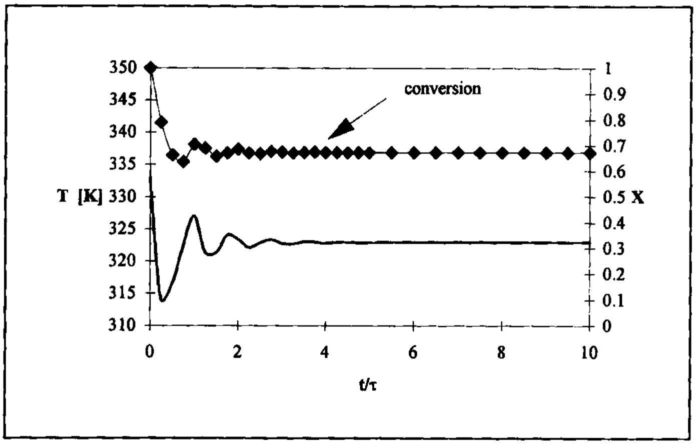


Fig. 4-33. Simulation of the sample process modified according to the second recommendation

Finally a further recommendation for the start-up of cooled CSTR processes shall be given. The oscillating transient behaviour during start-up which was demonstrated here may be avoided if the CSTR is started up as an SBR with constant cooling temperature until the desired operating point is reached. At this time the feed of the second component is then switched on. The design principles to be obeyed for this procedure are discussed in Section 4.3.1.4.

4.3.1.2 Safe Normal Operation of the Cooled PFTR

When discussing PFTR processes under reaction engineering or under safety technical aspects, it has to be discriminated whether the process considered is homogeneous or heterogeneous in character. Heterogeneously catalyzed gaseous reactions are much more commonly performed in cooled tube reactors than homogeneous reactions. The analogy between PFTR and BR may be utilized for the safety technical assessment of homogeneous reactions. Consequently, for such processes it is referred to Section 4.3.1.3, where the guiding principles are presented.

The Cooled Fixed-Bed Tube Reactor

The reaction engineering design of fixed-bed tube reactors is quite a complex task as, besides normal design questions originating from the heat and mass transport involved, problems resulting from momentum transport become significantly important. In other words, fluid mechanics is pivotal to the design of such solid bed tube reactors, as they are called synonymously. However, safety engineering cannot provide special criteria for each individual case. Rather it has to rely on generally applicable criteria which have been derived on the basis of simplified, in the sense of abstracted, models. In order to apply these criteria, however, all simplifying assumptions must be known and present. The following paragraphs shall give an outline on these generally applicable criteria and their deduction.

The cooled fixed-bed reactor is characterized by the simultaneous occurrence of an axial and a radial temperature profile (c.f. Figure 4-34). It is the task of safety engineering to exclude the occurrence of excessive overheating.

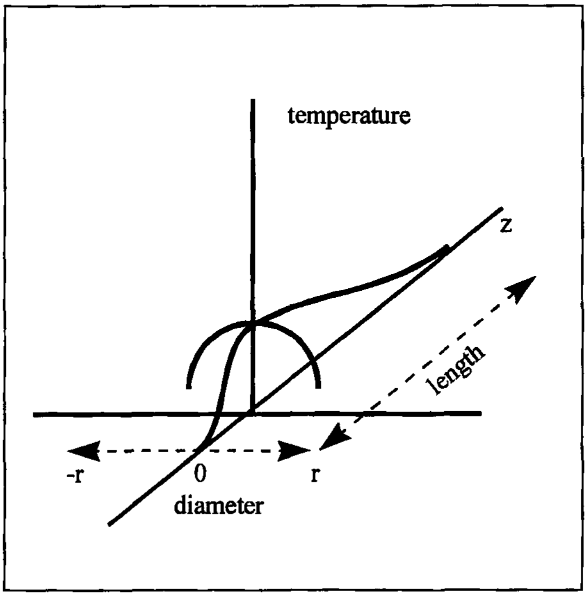


Fig. 4-34. Schematic presentation of the axial as well as the radial temperature distribution in a cooled fixed-bed reactor

The radial overheating towards the middle of the tube depends in its extent mainly on the diameter of the tube. In order to be able to assess this overheating, some assumptions have to be made. The transport mechanism by which the chemically produced heat is led towards the wall determines how pronounced a temperature profile develops. This transport mechanism is more or less solely heat conduction in such fixed-bed reactors. The effective heat conductivity of a solid bed is a combination of rest conductivity and flow dependent conductivity. If the flow velocity through the solid bed is high, which is usually the case in industrial applications, the flow dependent heat conductivity dominates the heat transport. For this case the following basic equation is frequently used:

$$\lambda_S = \frac{C_S \cdot \dot{V}_0 \cdot \rho \cdot c_P}{d} \tag{4-130}$$

C_S is a parameter which characterizes the properties of the solid bed and which is best determined experimentally. If such experimental results are not available, C_S can be estimated with the help of a rough approximation, which correlates this parameter with the mean particle diameter and the pipe diameter.

$$C_S = 0.2 \cdot \frac{d_P}{d} \tag{4-131}$$

Safety engineering now focuses its interest in the most critical spot of the pipe, which corresponds to the site of highest overheating. For this spot a heat balance describing the radial profile can be formulated using cylindrical coordinates.

$$\frac{\lambda_S}{\zeta} \cdot \frac{d}{d\zeta} \cdot \left[\zeta \cdot \frac{dT}{d\zeta}\right] + \left(\frac{d}{2}\right)^2 \cdot \frac{\dot{Q}_{chem.}}{V_R} = 0 \tag{4-132}$$

with

$$\zeta = \frac{2 \cdot r}{d} \tag{4-133}$$

Two approximations allow the solution of this balance. First, the dependency of the reaction rate on temperature shall follow the approximation already used in the discussion of the heat explosion theory. The second step neglects the development of radial concentration profiles.

This second approximation is somewhat problematic as it turns out to be part of an indirect procedure. Its justification is finally given by the safety criterion to be deduced. The application of the latter excludes operating conditions, for which the approximation is invalid. However, this procedure is the only one known so far and which has proven valid in practice.

Making use of these two simplifications allows for the formulation of the reaction power referenced to the reaction volume:

$$\frac{\dot{Q}_{\text{chem.}}}{V_R} = (-\Delta_R H) \cdot r_W \cdot \exp\left(\frac{E}{R \cdot T_W^2} \cdot (T - T_W)\right) \tag{4-134}$$

The reaction rate at the wall is described in its common form:

$$r_W = r_0 \cdot (1 - X)^n \tag{4-135}$$

In this case X is the conversion which is averaged over the cross section and varies in axial direction. The differential equation obtained by the substitution of Equ.(4-134) into Equ. (4-132) can be solved in a closed form for the boundary condition $T(\zeta=1) = T_W$.

$$T - T_W = \frac{2 \cdot R \cdot T_W^2}{E} \cdot \ln\left(\frac{1 + C_1}{1 + C_1 \cdot \zeta^2}\right) \quad \text{with} \quad \frac{8 \cdot C_1}{(1 + C_1)^2} = \frac{d^2 \cdot r_W \cdot E \cdot (-\Delta_R H)}{4 \cdot \lambda_S \cdot R \cdot T_W^2} \tag{4-136, 4-137}$$

The determining equation for C_1 forms the basis of the safety requirements for fixed-bed tube reactors. For an easier understanding of this statement, the left-hand term of Equ. (4-137) is plotted over C_1 in Figure 4-35. This is a reasonable approach to the interpretation of the equations obtained because the right-hand term of the same equation has a fixed value for a certain chemical process to be performed in a certain equipment. The course of the left-hand term over C_1 therefore provides the information of possible operating conditions or, in other words, of allowed values for the right-hand term in Equ.(4-137).

Figure 4-35 shows that the value for this term cannot be larger than two. For small values two solutions seem to exist. This last phenomenon can best be explained in terms of the stability theory. The course of this term over C_1 may be interpreted as a kind of ignition/extinction phenomenon with stable and unstable operating points. In the region where the right-hand term has values larger than two and where no solution exists for C_1, the reactor has ignited in the middle. From a safety point of view this has to be avoided at all events! The solution corresponding to a low wall temperature may be interpreted as extinguished, the other corresponding to a high wall temperature as an unstable operating point.

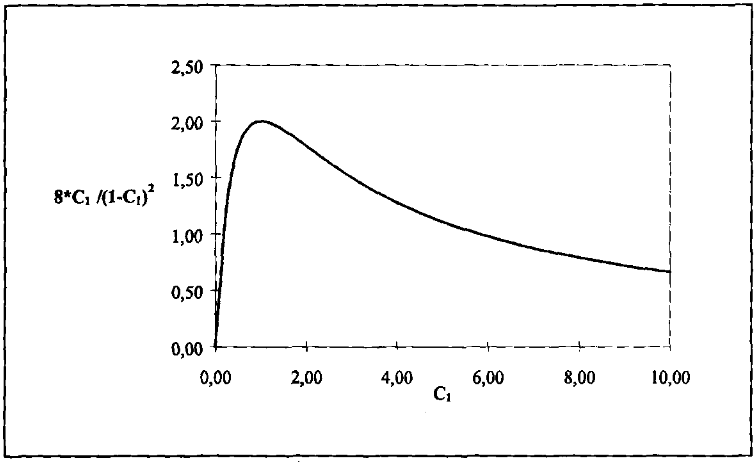


Fig. 4-35. Plot of the dependence of the left-hand term in Equ.(4-131) on C_I

Following these considerations, the boundary condition, stating that the right-hand term of Equ.(4-137) must only have values equal to or smaller than two can be used to express a pivotal safety technical demand:

In order to exclude the ignition of a fixed bed tube reactor in the middle of the pipe reliably, the pipe diameter must be smaller than the critical diameter d_c. This diameter is defined as:

$$d_c = 2 \cdot \sqrt{\frac{2 \cdot \lambda_S \cdot R \cdot T_W^2}{r_W \cdot E \cdot (-\Delta_R H)}} \qquad (4\text{-}138)$$

This safety requirement, however, cannot be applied directly as an assessment criterion, as the exact place along the pipe at which the temperature maximum will occur is not known. This knowledge would be the prerequisite for the determination of the conversion, which itself is required for the calculation of r_{wall}. If r_{wall} were known, it could be used in combination with all other substance and equipment data to calculate the critical pipe diameter and to compare it with the actual diameter. This way the radial temperature profile could be estimated. Figure 4-36 shows a theoretical example.

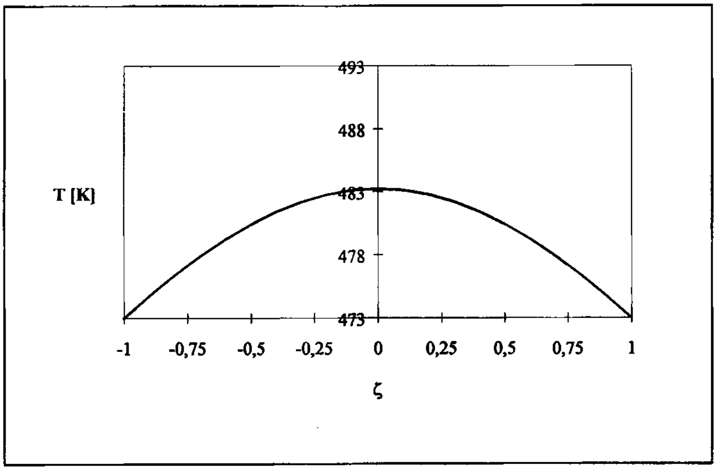


Fig. 4-36. Simulated radial temperature profile of a cooled fixed-bed reactor
Parameters: E/R = 10500 K, T_W = 200°C, d_c = 0.03 m, d = 0.025 m

In order to obtain practically applicable criteria, several further considerations have to be made with respect to the axial temperature profile. First an assumption has to be made regarding all radial temperature profiles along the length of the pipe, which do not satisfy the axial boundary condition

$$\frac{dT}{dz} = 0 \tag{4-139}$$

It is a very conservative assumption that all radial profiles can be described with the solution obtained for the maximum. Formally interpreted this would mean the calculation of conversion for each locus along the pipe length, its insertion into r_{wall} and in consequence a critical tube diameter with changing values along the pipe length. By choosing this approximation for the description of the radial temperature profiles occurring over the total length of the reactor as a basis, the cooled fixed-bed reactor can be reduced to a pseudo-one dimensional system for modelling purposes.

For this pseudo-one dimensional model an auxiliary variable $T^*(z)$ is introduced, which firstly represent a cross-sectional average value for each locus z and secondly complies with two further requirements:

1. T^* must be the value which enables the calculation of the reaction rate over the cross sectional area:

$$r(T^*) = 2 \cdot \int_0^1 r(\zeta) \cdot \zeta \cdot d\zeta \tag{4-140}$$

2. T^* must be accurate enough to allow a formal description of the radial heat transport to the wall by conduction with the help of a heat transfer model.

$$\alpha_W \cdot \left(T^* - T_W\right) = -\frac{2 \cdot \lambda_S}{d} \cdot \left.\frac{dT}{d\zeta}\right|_{z=1} \tag{4-141}$$

Equation (4-134) and (4-136) help to deduce the required relationship for r(ζ), which is required to solve the integral in Equ. (4-140). The solution is:

$$r(T^*) = \left(1 + C_1\right) \tag{4-142}$$

At the same time the simplified Arrhenius temperature dependency has to be fulfilled,

$$r(T^*) = r_W \cdot \exp\left(\frac{E}{R \cdot T_W^2} \cdot \left(T^* - T_W\right)\right) \tag{4-143}$$

leading to conclusion ①:

$$\frac{E}{R \cdot T_W^2} \cdot \left(T^* - T_W\right) = \ln\left(1 + C_1\right) \tag{4-144}$$

At this point it proves to be helpful to make use of the special definition of the Stanton number for cooled tube reactors introduced in Section 4.1, Equ. (4-54), in order to describe the second requirement for T*.

$$T^* - T_W = -\frac{C_2}{4 \cdot St} \cdot \left.\frac{dT}{d\zeta}\right|_{z=1} \quad \text{with} \quad C_2 = 8 \cdot \pi \cdot C_S \cdot \frac{L}{d} \tag{4-145, 4-146}$$

Equ. (4-136) can be used to obtain the differential quotient necessary for further interpretation of Equ.(4-145). This finally yields conclusion ②:

$$\frac{E}{R \cdot T_W^2} \cdot \left(T^* - T_W\right) = \frac{C_2 \cdot C_1}{St \cdot \left(1 + C_1\right)} \tag{4-147}$$

As both conclusions must be fulfilled at the same time, their combination yields a formulation for the necessary cooling capacity in terms of the Stanton number.

$$St = C_2 \frac{C_I}{\left(1 + C_I\right) \cdot \ln\left(1 + C_I\right)} \qquad (4\text{-}148)$$

From a practical point of view this equation is still not very helpful as C_I depends on conversion by being proportional to the critical tube diameter. Sensitivity considerations on the influence of the safe distance between true and critical tube diameter on C_I and on the C_I dependent term of Equ.(4-148), however, show, that a further simplification is justified. These considerations are presented graphically in Fig. 4-37.

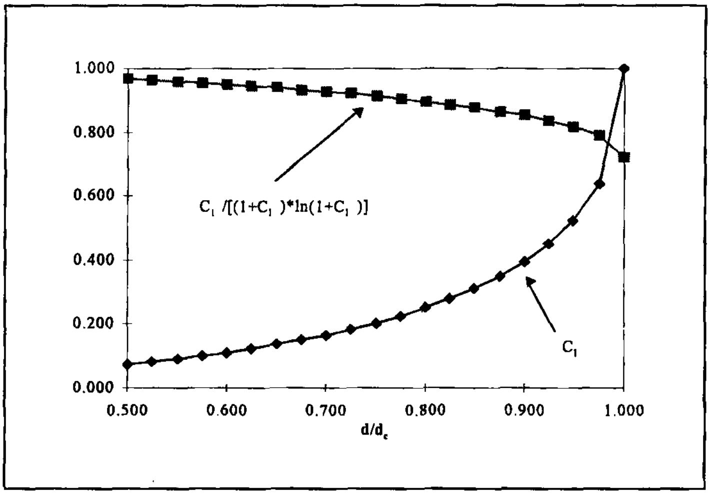


Fig. 4-37. **Presentation of the dependency of C_I and C_I-dependent term of Equ.(4-148) on the ratio d/d_c**

If the true pipe diameter is only 10% smaller than the critical diameter, the C_I-dependent term of Equ.(4-148) already amounts to 0.85, and it approaches 1 if the safety distance is made greater. If a cooling intensity is demanded for fixed-bed reactors which is determined for a fixed value of 1 for the C_I-dependent term, then this can only be advantageous for process safety, especially for a design with close proximity of true and critical tube diameter.

The first safety technical assessment criterion for cooled fixed-bed reactors can now be postulated:

The cooling intensity in terms of the Stanton number must at least meet the requirement

$$\mathrm{St} = \frac{4 \cdot \alpha_W \cdot \tau}{d \cdot \rho \cdot c_P} \geq 8 \cdot \pi \cdot C_S \cdot \frac{L}{d} \tag{4-149}$$

If no experimental value for C_S is available it may be approximated by $C_S = 0.2\ d_P$. From this it follows for the Stanton number:

$$\mathrm{St} = \frac{4 \cdot \alpha_W \cdot \tau}{d \cdot \rho \cdot c_P} \geq 5 \cdot d_P \cdot \frac{L}{d^2} \tag{4-150}$$

A second criterion for the safe operation of a cooled fixed-bed reactor is obtained from Equ.(4-136). If the demand is fulfilled that the true tube diameter must not exceed the critical diameter, then this allows a distinct maximal temperature difference between maximum and wall temperature only. Mathematically this is obtained by setting d equal to d_c resulting in $C_1 = 1$ and inserting this into Equ.(4-136).

$$T_{crit} - T_W = \frac{R \cdot T_W^2}{E} \cdot \ln(4) \tag{4-151}$$

As this critical temperature may not be reached, a safety margin on this exact temperature difference is recommendable. The degree of this margin cannot be given in a compulsory form. Therefore the second criterion can only be given in form of a recommendation:

The maximum driving temperature difference ($T_{process}$ - T_W) should be in compliance with the condition:

$$T_{process} - T_W < \frac{R \cdot T_W^2}{E} \tag{4-152}$$

In conclusion, the two main aspects shall be repeated:

1. When designing cooled solid-bed reactors, a thorough balancing of the three characteristic lengths is necessary.
2. The overheating profile must be kept as low as possible by implementing intense cooling.

The three characteristic lengths are reactor length and diameter and the mean particle diameter of the solid bed. Long and at the same time thin tubes should be given preference. This is not exactly a new finding. It has influenced equipment design already for many years and led to today's design of tube bundle reactors.

4.3.1.3 Safe Normal Operation of Cooled Batch Reactors

The safety technical assessment of cooled batch reactors is based among other things on a recognition which is best understood by a schematic comparison of today's most common modes of operation. These are, as presented in Figure 4-38, isothermal, isoperibolic and partially controlled operation.

In the case of an isothermal process usually one component and solvent are charged initially. This mixture is heated up to the desired reaction temperature. At this point the second component, which has been premixed in solvent and preheated separately, is added in one step and as fast as possible. The jacket temperature is lowered more or less instantly by the controls implemented at this initial moment of reaction. This way the maximum driving temperature difference occurs at the very beginning of the reaction process.

Under isoperibolic operating conditions, i.e. with a constant cooling temperature and an uncontrolled reaction temperature, one reactant and the solvent are again charged initially However, this time the heating up process stops when the temperature level is reached at which the cooling temperature shall be kept constant. The second component is now added all at once. The self-acceleration of the reaction will now lead to an increase of the internal temperature. This will be observed until the heat production rate of the reaction becomes smaller than the cooling power of the reactor. The maximum driving temperature difference will occur some time in the course of the process. With decreasing reaction and heat production rate the internal temperature will then approach the cooling temperature again.

The third case differs from the last only in the phase after the maximum of the reaction temperature has been passed. From this time onwards controls will adjust the jacket temperature in a way that this maximum level is more or less maintained for the remaining process time.

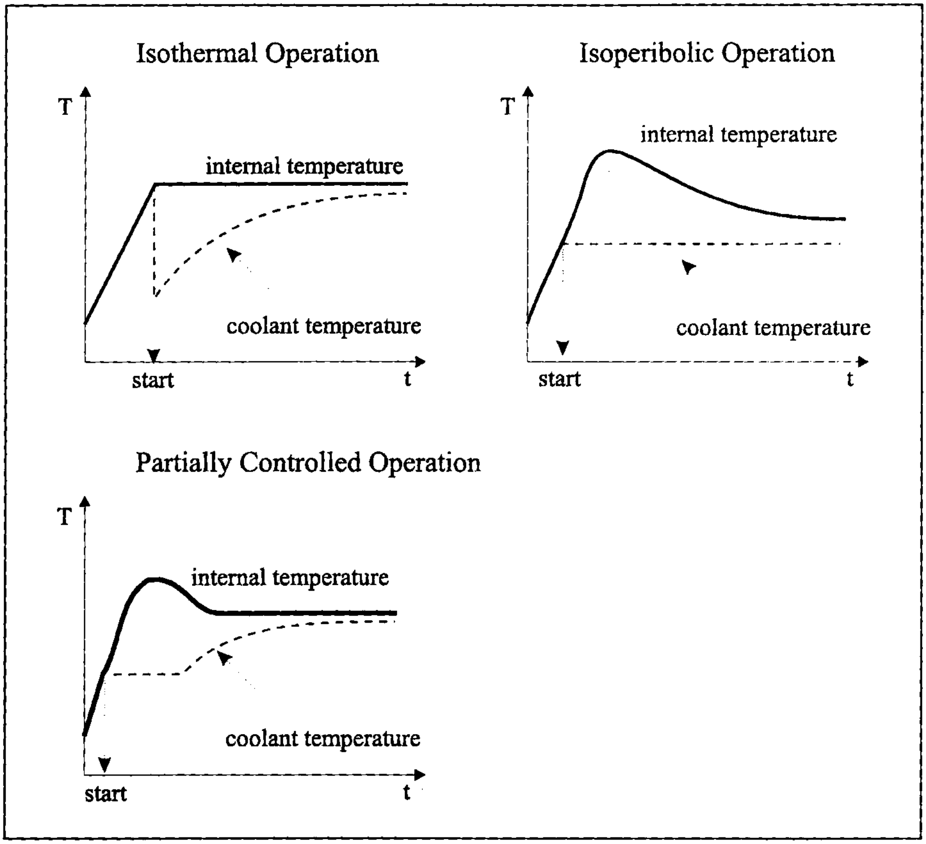


Fig. 4-38. Schematic presentation of temperature/time-profiles for different modes of batch reactor operation

Independent of the mode of operation, the most critical point during the course of the process corresponds to the time at which the maximum driving temperature difference between jacket and reaction mixture temperature occurs. Due to this fact the safety assessment focuses its efforts on the most reliable prediction of this point and its stability. In all three cases this critical point of a batch process is mathematically characterized by the condition $dT/dt = 0$ for the heat balance.

In a first step the isoperibolic and the partially controlled mode of operation shall be investigated more closely because they are common in industrial practice and they have an analogy to a mode of operation for homogeneous cooled tube reactors (c.f. introduction to Section 4.3.1.2). For these two modes the analysis of the heat balance leads to an equation with two unknowns: the maximum reaction temperature and the corresponding value for the conversion.

$$\frac{Da_\infty}{St}\cdot\left(1-X_M\right)^n\cdot\exp\left(-\frac{E}{R\cdot T_M}\right)=\frac{T_M-T_C}{\Delta T_{ad}} \tag{4-153}$$

This problem was overcome by Hugo et al. [48]. They performed more than 6000 simulations of different operating conditions varying all parameters within a range of industrial significance and correlated all values obtained for T_M and X_M empirically. The result was:

$$K\cdot\left(1-X_n\right)^n=\left(1-\sqrt{f}\right)^{0.6\cdot n+0.8} \tag{4-154}$$

with

$$f=\frac{T_M-T_C}{\Delta T_{ad}} \quad \text{and} \quad K=0.822+0.114\cdot B_M^2\cdot f^2 \tag{4-155,4-156}$$

The range of validity for this correlation is:

$$\sqrt{2}\le n\le 2 \quad \text{and} \quad 0.25\le B_M\cdot f\le 3$$

K is a correcting function accounting for residual deviations and minimizes the differences between theoretical and values approximated with the help of the empirical correlation.

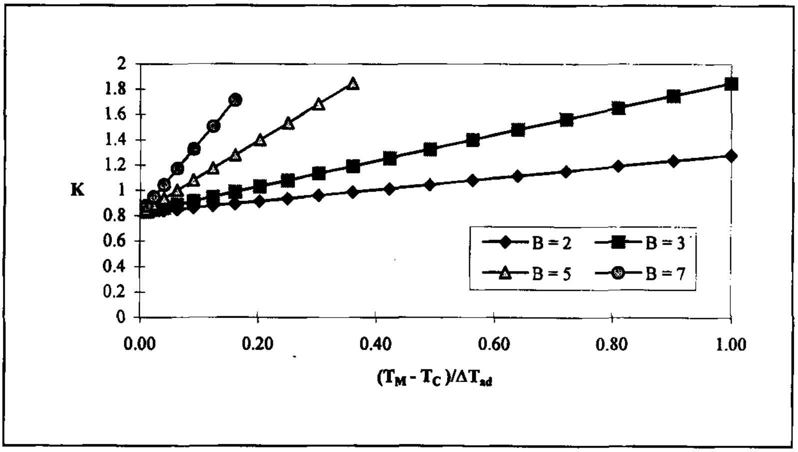


Fig. 4-39. Values of K in dependence on the degree of overheating for different values of the thermal reaction number

However, Figure 4-39 shows that this correction may be neglected if the degree of overheating is small, i.e. $f < 0.4$, and if the value for the thermal reaction number is moderate, i.e. $B < 5$.

This empirical correlation between T_M and X_M now allows the transformation of the exactly valid heat balance, Equ.(4-153), formulated for the extremum, into a relation which depends on T_M only.

$$\frac{Da_\infty}{St \cdot K} \cdot \left(1 - \sqrt{\frac{T_M - T_C}{\Delta T_{ad}}}\right)^{0.6 \cdot n + 0.8} \cdot \exp\left(-\frac{E}{R \cdot T_M}\right) = \frac{T_M - T_C}{\Delta T_{ad}} \qquad (4\text{-}157)$$

Equ. (4-157) is a parameter presentation, which allows, in analogy to the CSTR, the prediction of all maximum driving temperature differences possible for a given reaction, which means that E/R, Da_∞ and ΔT_{ad} are fixed, and for a given reactor system with known volume and cooling capacity. From a mathematical point of view it is advantageous to vary the maximum reaction temperature and to solve for the corresponding coolant temperature. The result of such a study is presented in Figure 4-40.

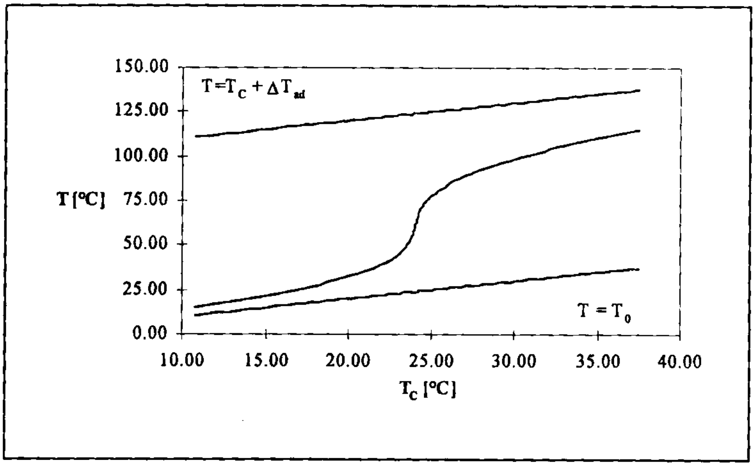


Fig. 4-40. $T_M = T_M(T_C)$ - diagram for the cooled batch reactor
Parameters: $\ln Da_\infty$ ($t_{reaction}$ = 1h) = 24.489, ΔT_{ad} = 100 K,
n = 2, E/R = 7500 K, St ($t_{reaction}$ = 1h) = 3.57

The possible solutions of Equ.(4-157) shown in Figure 4-40 are placed between two parallels. These represent the limit cases either that no reaction takes place and the internal temperature always remains equal to the coolant temperature or that the reaction is performed adiabatically.

The course of the curve representing all possible solutions is in principle very similar to the result obtained for the steady state cooled CSTR. The two additional lines representing the limit cases mentioned help to perceive that in the range of medium sized overheating small changes in the coolant temperature have a great effect on the arising maximum temperature. In this case, the safety technical assessment also has to account for the sensitivity of the operating point in addition to the mandatory check on the sufficiency of the cooling capacity provided.

This sensitivity mathematically expressed, corresponds to the gradient of the curve of possible solutions:

$$S = \frac{dT_M}{dT_C} \tag{4-158}$$

However, it cannot be calculated on the basis of a closed algebraic formulation for the same reason outlined in context with the prediction of the overheating. Also in this case the exact knowledge of both temperature and conversion at the time of maximum overheating would be required.

The only possibility to obtain a helpful tool for the sensitivity analysis as part of the safety assessment of cooled batch processes despite this fact is to apply Equ.(4-158) on the empirical correlation, Equ.(4-157), developed by Hugo, yielding:

$$S = \frac{1}{1 - \frac{2 \cdot B_M \cdot \vartheta \cdot \left(1 - \sqrt{\vartheta}\right)}{2 \cdot \left(1 - \sqrt{\vartheta}\right) + (0.6 \cdot n + 0.8) \cdot \sqrt{\vartheta}}} \tag{4-159}$$

In order to simplify the interpretation of this somewhat complicated looking equation, the special but very common case of a second order reaction shall be considered first. This reduces Equ.(4-159) to:

$$S^{2nd\ ord} = \frac{1}{1 - B_M \cdot \vartheta \cdot \left(1 - \sqrt{\vartheta}\right)} \tag{4-160}$$

Two facts can easily be recognized. The sensitivity of a process with known thermal reaction number depends on the degree of overheating. Furthermore, there are batch processes with a sensitivity formally approaching infinity. In other words, the BR ignites. This is shown graphically in Figures 4-41 and 4-42 for clarification.

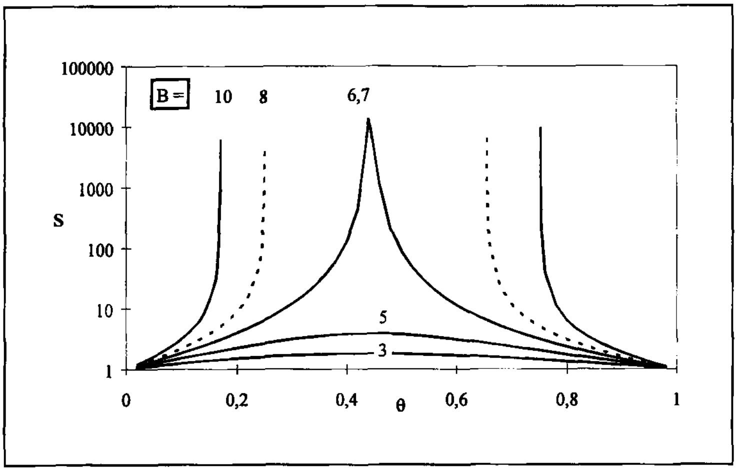


Fig. 4-41. $S^{2nd\ ord}$ in dependence on overheating for different thermal reaction numbers

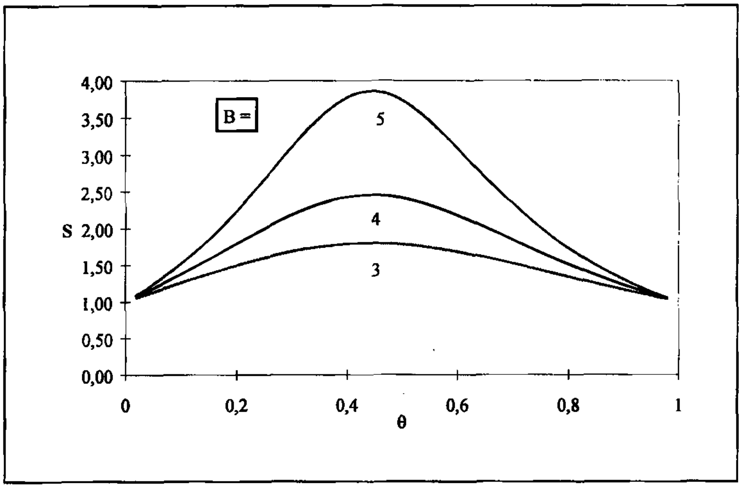


Fig. 4-42. $S^{2nd\ ord}$ in dependence on overheating for small thermal reaction numbers

Safety technically, an ignited state of operation must be avoided for cooled BRs at all events. In consequence the observed singularity must be investigated closer. For this purpose an examination of processes with a small thermal reaction number is helpful. Due to the mathematical character of Equ.(4-159) and (4-160), respectively, the point of maximum sensitivity always occurs for the same degree of overheating.

$$\frac{dS^{2nd\ ord}}{d\vartheta}=\frac{B_M\cdot\left(1-\frac{3}{2}\cdot\sqrt{\vartheta}\right)}{\left(1-B_M\cdot\vartheta\cdot\left(1-\sqrt{\vartheta}\right)\right)^2}=0 \tag{4-161}$$

$$\Rightarrow \vartheta_{crit.}=\frac{4}{9} \tag{4-162}$$

With the help of Equ.(4-160) and (4-162), a limit value diagram can now be developed which allows the determination of the maximum sensitivity in its dependence on the thermal reaction number at the point $\vartheta_{crit.}$. This is shown in Fig. 4-43. All operating conditions with B values which form an intersection with a desired sensitivity below or right of the limit curve can only be conducted safely if the overheating is limited to less than 4/9 of the adiabatic temperature increase. By inserting the value for ϑ_{crit} into the condition for an ignition

$$1=B_M\cdot\vartheta\cdot\left(1-\sqrt{\vartheta}\right) \tag{4-163}$$

the thermal reaction number at the ignition point is obtained:

$$B_{ignit.}^{2nd\ ord}=6.75$$

Processes with thermal reaction numbers higher than the ignition point value must not be performed in cooled batch reactors unless extreme precautions have been undertaken [49].

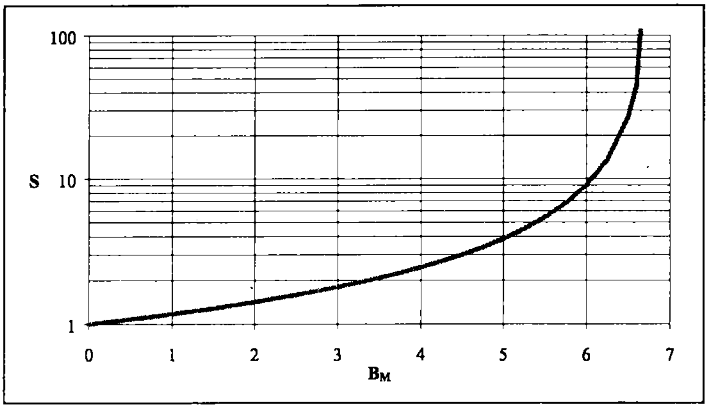


Fig. 4-43. Limit value diagram: $S^{2nd\ ord}$ in its dependence on B_M at ϑ_{crit}

The procedure as shown so far for the interpretation of the sensitivity for the special case of a second order reaction can be performed in an identical way for the complete validity range of the approximation. For ϑ_{crit} and B_{ignit} the following relationships are obtained, which are also graphically presented in Figure 4-44.

$$\vartheta_{crit.} = \frac{\left(0.6\cdot n + 0.8 - 8 + \sqrt{16\cdot(0.6\cdot n + 0.8) + (0.6\cdot n + 0.8)^2}\right)^2}{4\cdot[2\cdot(0.6\cdot n + 0.8) - 4]^2} \qquad \text{for} \quad 1.4 \le n \le 2$$

$$B_{ignit.} = \frac{2 + \sqrt{\vartheta_{crit.}}\cdot(0.6\cdot n + 0.8 - 2)}{2\cdot\vartheta_{crit.}\cdot\left(1 - \sqrt{\vartheta_{crit.}}\right)} \qquad \text{(4-164, 4-165)}$$

Despite the approximately linear dependence of both parameters on the reaction order, as can be seen from Figure 4-44, their range of values is rather restricted. In the sense of chemical process safety it is therefore absolutely justifiable to postulate a safety assessment criterion independent of the reaction order:

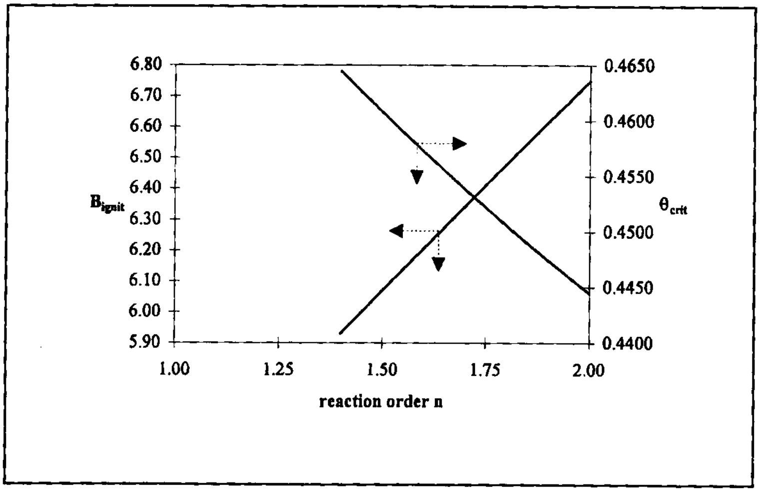


Fig. 4-44. Dependence of the ignition limit of isoperibolically operated BR on the reaction order

Batch processes which are to be performed in isoperibolic mode, and which have a value for the thermal reaction number greater than 6 may only be performed if a cooling capacity is available which ensures a significantly lower degree of overheating than 40% of the adiabatic temperature increase.

In daily practice, a frequently asked question looks for the tolerable value of the thermal reaction number if the maximum sensitivity value is fixed. The background to this situation usually is a given plant with a certain instrumentation and a known variability for the coolant temperature under normal operating conditions. Usually more than 5 K variability in the maximum reaction temperature cannot be tolerated in the production of specialties such as those manufactured in the fine chemicals and pharmaceutical industry. This information fixes the value for the maximum sensitivity.

With the help of Equ.(4-159), a limit value diagram can be calculated which provides information on the maximum tolerable thermal reaction number in its dependence on the degree of overheating. The maximum sensitivity is a parameter in this case. An example is given in Figure 4-45. The operating point in question can be marked and safety technically assessed as being critical or uncritical.

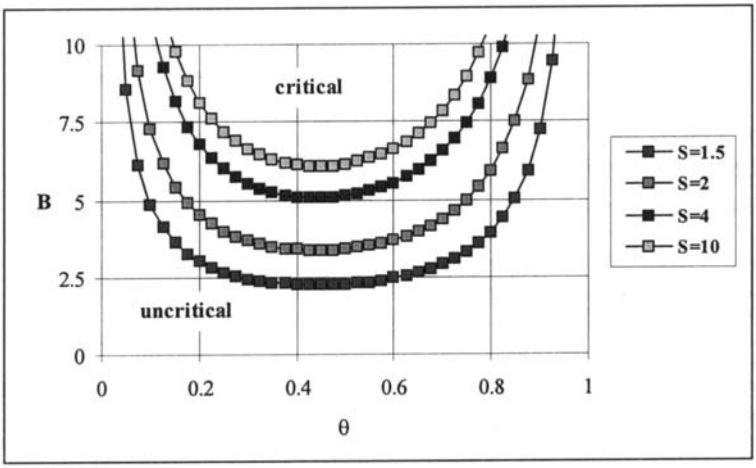


Fig. 4-45. Limit value diagram for n = 2

The curve calculated for a maximum sensitivity of S = 2 may be used to postulate generally applicable guidance for the assessment of isoperibolic batch processes. Such a low sensitivity value poses high demands on the operating technology if the possible variability is not very low. On the other hand, processes with operating points below this curve without modifications in instrumentation and technology may be regarded as safety technically uncritical. This fact shall also be phrased as an assessment criterion:

Batch processes to be performed in isoperibolic mode which

- *either have a thermal reaction number of less than 3, independent of the degree of overheating,*

- *or where the cooling capacity ensures degrees of overheating of less than 15% of the adiabatic temperature increase and which at the same time have a thermal reaction number value of less than 5*

may be regarded as safety technically uncritical with respect to their thermal potential.

Having completed the safety assessment for the isoperibolic batch processes, isothermal batch reactors now shall be considered. The most critical point in the course of process, which is the point of occurrence of the maximum driving temperature difference, is mathematically characterized in this case:

$$T_{isoth} - T_C = \frac{\Delta T_{ad} \cdot Da(T_{isoth})}{St} \tag{4-166}$$

It is an interesting fact that a formally equivalent equation was obtained when discussing the heat explosion theory. At that time a zero-order reaction in a cooled BR was being examined. For the sensitivity the following expression is deduced:

$$S^{isoth} = \frac{1}{1 - B \cdot \vartheta} \tag{4-167}$$

This equation, also shows a singularity. A further examination of this singularity yields a condition which is already known from the heat explosion theory as a rule of thumb

$$\frac{R \cdot T_{isoth.}^2}{E} \geq T_{isoth.} - T_C \tag{4-168}$$

For isothermal batch processes it is an exactly valid safety assessment criterion. The further discussion of the isothermal process can be performed in total analogy to the discussion of the isoperibolic process, except that Equ.(4-167) has to be used. An example of such a limit value diagram for isothermal BR has been calculated and is presented graphically in Figure 4-46.

To compare isothermal and isoperibolic operation the limit curve for S = 2 under isoperibolic conditions has been assumed. It becomes obvious that isothermal processes can only be performed safely and uncritically if the thermal reaction number has a very small value, or, in other words, if the reaction proceeds at low rates and only with moderate exothermicity. If reaction rate and thermal reaction number have higher values, only an isoperibolic mode remains possible. Batch reactors must not be used for fast and strongly exothermic reactions as this would not be acceptable from a safety technical point of view.

The complete assessment procedure including a discussion of the effects of process stabilizing measures shall be demonstrated with the help of the following example.

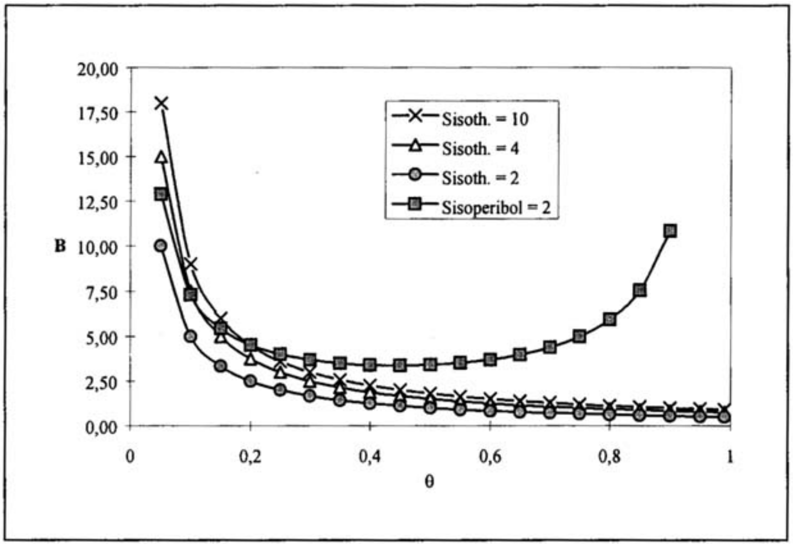


Fig. 4-46. Limit value diagram for an isothermally operated BR

Example: A process shall be performed isothermally in a BR at a process temperature of 383 K. The stoichiometric input concentrations shall be equal to $c_{A0} = c_{B0} = 0.42$ kmol/m^3. The stoichiometric coefficients shall be $|\nu_i| = 1$. The heat of reaction amounts to -150 kJ/mol. The reaction follows a second order rate law with a pre-exponential factor of $k_\infty = 2.778 * 10^5$ m^3/(kmol s) and activation energy of E/R = 7217 K. The reaction shall be performed on a 2 m^3 scale in a reactor with a cooling capacity of 1885 W/K. The value for the product of density and specific heat shall be approximated by a mean value of 1700 kJ/(m^3 K).

Solution: In a first step the available cooling capacity is assessed. For this purpose the adiabatic temperature increase is required.

$$\Delta T_{ad} = \frac{\Delta_R H \cdot c_{A0}}{\nu_A \cdot \rho \cdot c_P} = \frac{(-150) \cdot 0.42}{(-1) \cdot 1.700} = 37\,\mathrm{K}$$

Based on this value it may be stated from a safety point of view that this thermal potential can in principle be controlled. Furthermore, the ratio of Damkoehler to Stanton number can be calculated, which is independent of the reaction time.

$$\frac{Da\left(T_{isoth}\right)}{St} = \frac{k_{\infty} \cdot c_{B0} \cdot V_R \cdot \rho \cdot c_P \cdot \exp\left(-E/_{R \cdot T_{isoth}}\right)}{U \cdot A}$$

$$= \frac{2.778 \cdot 10^5 \, {}^{m^3}/_{kmol \cdot s} \cdot 0.42 \, {}^{kmol}/_{m^3} \cdot 2\,m^3 \cdot 1700 \, {}^{kJ}/_{m^3 \cdot K} \cdot e^{-\frac{7217\,K}{383\,K}}}{1.885 \, {}^{kW}/_{K}}$$

$$= 1.38$$

This ratio of the two characteristic numbers has already been introduced in Section 4.3.1.1, Equ.(4-95). At that time it had already been referred to the safety technical significance of this ratio. This shall now be proven. Besides the adiabatic temperature increase this is the only other parameter which influences the maximum driving temperature differences of batch processes. It is important to recognize at this point that the reaction time does not have any impact on this safety relevant value. The ignition point criterion for isothermal batch processes may also be expressed in a dimensionless form:

$$\frac{T_{isoth.} - T_C}{\Delta T_{ad}} \leq \frac{R \cdot T_{isoth.}^2}{E \cdot \Delta T_{ad}} \Rightarrow \vartheta \leq \frac{1}{B} \qquad (4\text{-}169)$$

At the same time the isothermal heat balance at the critical starting point is valid.

$$\frac{T_{iso} - T_C}{\Delta T_{ad}} = \vartheta = \frac{Da\left(T_{iso}\right)}{St} \qquad (4\text{-}166)$$

For the ignition point, consequently the combination yields:

$$\frac{Da\left(T_{iso}\right)}{St} \leq \frac{1}{B} \qquad (4\text{-}170)$$

When the thermal reaction number was introduced, it was shown that B takes on values greater than 1 (c.f. Figure 4-4 in Section 4.1.4). In conclusion it becomes obvious that isothermal batch processes are safety technically tolerable only if the ratio of Damkoehler to Stanton number is less than 1. In the case of the sample process investigated this is not the case. In concrete terms the value for Da/St should be less than

$$\frac{1}{B}=\frac{R\cdot T_{\text{isoth}}^2}{E\cdot\Delta T_{ad}}=\frac{383^2\ \text{K}^2}{7217\ \text{K}\cdot 37\ \text{K}}=0.55$$

The calculated value for this ratio Da/St amounted to 1.38 and this way by far exceeds the tolerable value of 0.55 !! A performance of this process may therefore not be permitted due to the violation of safety technical criteria.

Two different process modifications can be proposed for stabilization purposes. As alternative 1 a dilution of the input concentrations is suggested. If the dilution factor κ is again applied:

$$c_{A0}^{\bullet}=\kappa\cdot c_{A0} \qquad c_{B0}^{\bullet}=\kappa\cdot c_{B0} \qquad \text{(4-123, 4-124)}$$

$$\text{with} \qquad 0<\kappa\leq 1 \qquad \text{(4-125)}$$

and the use of standard vessels with a constant geometric ratio of

$$A/V_R^{2/3} \qquad \text{(4-126)}$$

is again assumed, the ignition condition yields:

$$\kappa\leq\left(\frac{St}{Da\left(T_{\text{isoth}}\right)\cdot B}\right)^{\frac{3}{7}}\leq 0.67 \qquad \text{(4-171)}$$

This value for κ allows for all necessary adjustments.

Recommendation 1: The proposed process should be modified as follows:

The initial concentration of all educts should be reduced to less than 67% of its original value. This requires an increase of the reaction time by a minimum factor of 1.49 if the conversion is to remain the same. To manufacture the same amount of product a reactor must be chosen which is larger than the original one at least by a factor of 2.23. In addition this reactor must have a Stanton number increased by 14% or more. In this context the changed reaction time has to be accounted for. At the start of reaction it must be possible to lower the coolant temperature to a minimum of 362.9 K or lower. The modification factors describe a process exactly under ignition conditions and therefore must not be used directly for the new manufacturing procedure. The safety assessment procedure should be repeated after the exact dilution factor has been chosen. The following Figure 4-47 shows the simulation result of the process performed directly at the ignition point.

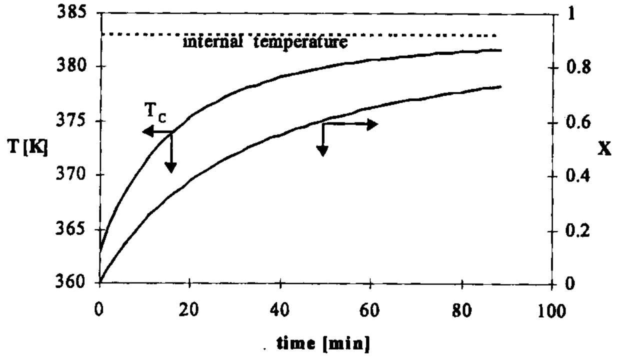


Fig. 4-47. Simulated course of the isothermal process at the ignition point

An alternative would be the modification of the isothermal to an isoperibolic process with the side condition that the internal reaction temperature must not exceed a value of 383 K. The data given can be used to determine the initial temperature with the help of Equ.(4-157). The initial temperature is identical with the coolant temperature if this is kept constant during the process. As the thermal reaction number amounts to the relatively low value of 1.82, the correction function may be set to 1.

$$T_C = T_M - \frac{\Delta T_{ad}}{\left(1+\sqrt{\frac{St}{Da(T_M)}}\right)^2} = 383\text{ K} - \frac{37\text{ K}}{\left(1+\sqrt{\frac{1}{1.38}}\right)^2} = 372.2\text{ K}$$

Now, the dimensionless overheating and the sensitivity of the operating point can be calculated.

$$\vartheta = \frac{T_M - T_C}{\Delta T_{ad}} = \frac{383\text{ K} - 372.2\text{ K}}{37\text{ K}} = 0.29$$

$$S = \frac{1}{1 - B \cdot \vartheta \cdot \left(1 - \sqrt{\vartheta}\right)} = \frac{1}{1 - 1.82 \cdot 0.29 \cdot \left(1 - \sqrt{0.29}\right)} = 1.32$$

The sensitivity of the operating point is very low. The process may be recommended.

Recommendation 2: The proposed process should be modified as follows:

The process mode should be changed to isoperibolic, while retaining all other operating values, such as batch size, concentrations and reaction time as originally proposed. The coolant temperature should have a set value of 372.2 K. This value is identical with the initial temperature. The following Figure 4-48 shows a simulation result of this modified process.

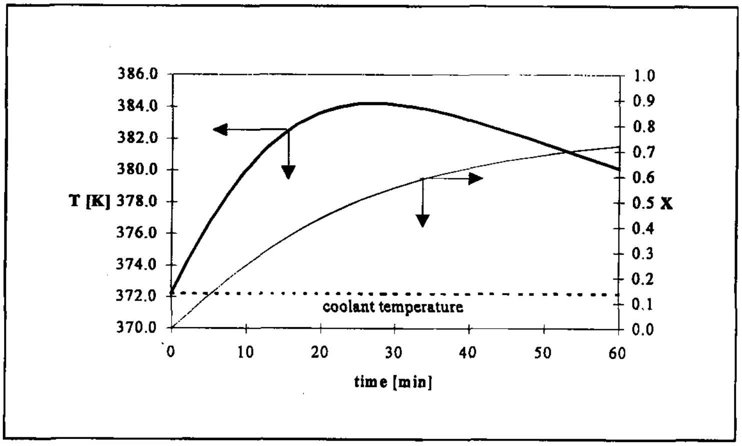


Fig. 4-48. Simulation result of the proposed process performed in isoperibolic mode as described in recommendation 2

4.3.1.4 Safe Normal Operation of the Cooled Semibatch Reactor

The safety technical assessment of the cooled SBR is based on an assumption which has been confirmed by industrial experience. The overwhelming majority of all reactions performed in a SBR can be described with satisfying accuracy with a formal kinetic rate law of second order. This statement is especially valid up to a feed time corresponding to 50 % of stoichiometric addition, but for most reactions it even holds true over the complete feed time. This is extremely helpful as the schematic presentation of industrially common modes of operation, isothermal and isoperibolic, shows, that the critical process phase is limited to the time necessary to add 50 % of the stoichiometric amount. This is shown in Figure 4-49.

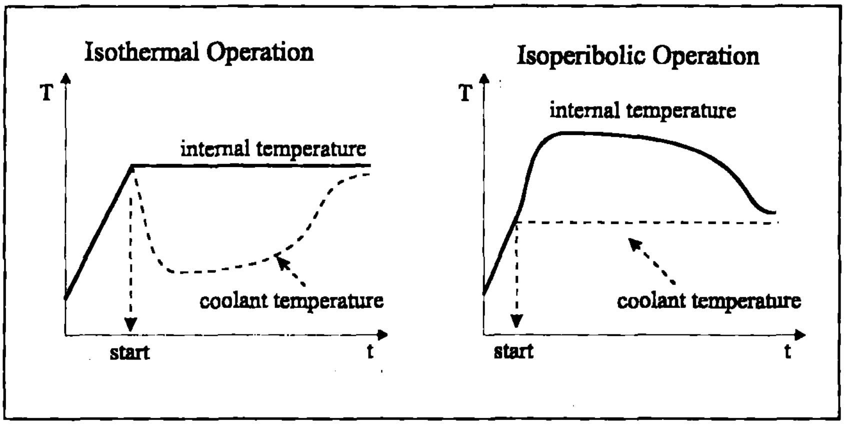


Fig. 4-49. Schematic presentation of temperature/time-profiles for different semibatch reactor modes of operation

In the case of isothermal operation one component with or without solvent is charged initially. The reactor contents are then heated up to the desired temperature. At this point the feed of the second reactant, separately premixed and preheated, is started with a constant rate. The jacket temperature is adjusted in proportion to the heat production rate with the help of controls. The maximum driving temperature difference occurs within the first half of the feed time.

In the case of isoperibolic operation, again, one reactant is charged and if occasion arises premixed with solvent initially. The mixture is this time heated up to the set value of the cooling jacket. Having reached this value the jacket temperature is subsequently kept constant and the addition of the second, separately premixed and preheated component is started. The feed rate, as in the other mode, is kept constant.

The internal temperature will rise in this case due to the self accelerating exothermic reaction. This rise will prevail until the heat removal power exceeds the thermal power of the reaction. In this case, too, the maximum driving temperature difference occurs within the first half of the feed time. The isoperibolic mode shall be treated first.

The basis for the safety technical assessment of isoperibolically performed semibatch processes is obtained from the analysis of extensive simulation results [50,51]. Examples are shown in Figure 4-50a-d.

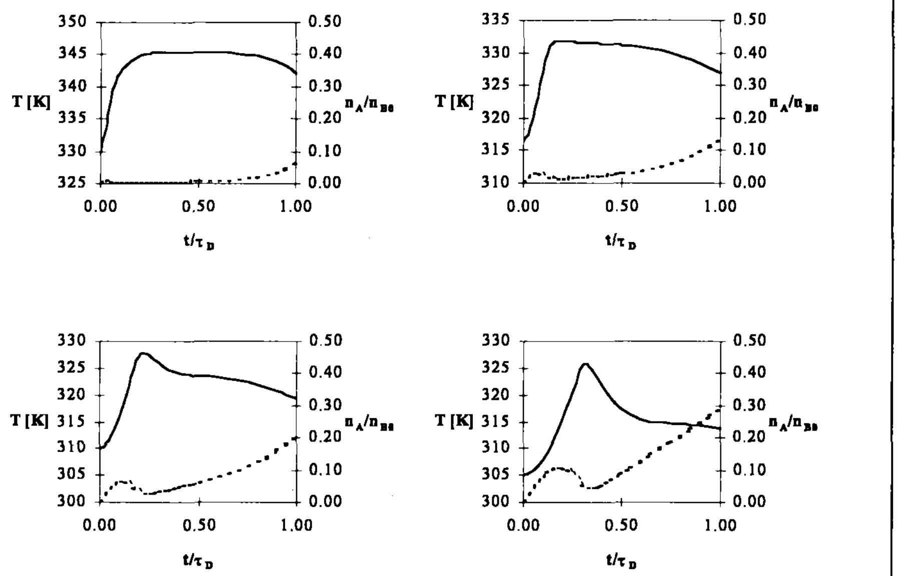


Fig. 4-50a-d. Simulated isoperibolic semibatch processes

upper curve : temperature lower curve: relative amount of added component

Parameters: $\ln Da_\infty = 40$, $E/R = 12000$ K, $n = 2$, $St = 7.5$, $\Delta T_{ad} = 125$ K, $\varepsilon = 1$, $\lambda = 1$

varied: T_0 a: 330 K, b: 316 K, c: 310 K, d: 305 K

The reactor behaviour shown in Figures 4-50a and b is desirable because the reaction proceeds almost isothermally at a temperature level which is reached after a short time of self-acceleration. Only shortly before the end of dosage, which in this sample case corresponds to the addition of the stoichiometric amount, the reaction temperature decreases. A totally different behaviour is observed in the other two cases. Here a strong overheating is observed during the self-acceleration phase and only hereafter the temperature drops to a more or less constant value. From a safety technical point of view the exclusion of such strong overheating has to be ensured, as this could otherwise accelerate side and consecutive reactions in an uncontrollable way, especially if the desired reaction is stronger exothermic than in the example chosen.

The reason for this differing reactor behaviour becomes understandable if the relative concentration profiles of the added component, which are also shown in this figure, are discussed. Cases a and b are characterized by the fact that hardly any accumulation of this component occurs during the first half of the feed phase. In simple terms this means that each amount added to the reactor is converted spontaneously. Only towards the end of the feed time the added component accumulates slightly, reaching its maximum relative concentration at the stoichiometric point.

This is different in the other two cases. There, a significant accumulation is observed in this first half of the feed time. At the moment where this accumulation exceeds a critical amount, a batch reactor-like behaviour takes effect. The cooling cannot cope with the occurring heat production rate, which due to the high reaction rate becomes very high itself. The consequence is the development of a high overheating, which lasts for a short time only. This is accompanied by a nearly complete conversion of the added material. The subsequent lack of reactant leads to a decrease of reactor temperature with a stabilization of the reactor.

This effect of accumulation becomes even more dramatic the lower the reference temperature is chosen. This may lead to an extreme situation like that shown in Figure 4-51. In this case the temperature profile is misleading as it could be interpreted as completely uncritical. In truth this harmless temperature profile is caused by the fact that the reaction hardly proceeds at all and that a dramatic runaway will follow in the batch reactor-like post addition phase.

The analysis shown can be summarized:

> *If the initial reaction rate is too slow in comparison to the feed rate either because the reference temperature was chosen too low or the feed rate too high, a high accumulation of the added component will occur in the reactor followed by a dangerously high overheating.*

A limit separating safe from unsafe reactor behaviour can be deduced by discussing the so-called phase plane set between temperature and relative concentration of the added component. This is shown in Figure 4-52.

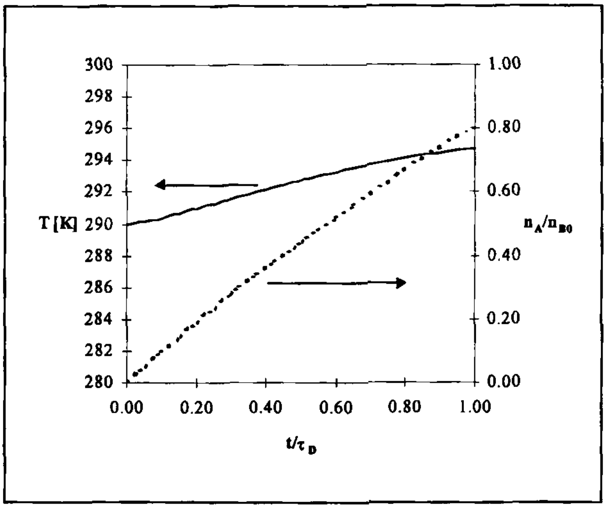


Fig. 4-51. Simulated isoperibolic semibatch process
Parameters: $\ln Da_\infty = 40$, $E/R = 12000$ K, $n = 2$,
$St = 7.5$, $\Delta T_{ad} = 125$ K, $\varepsilon = 1$, $\lambda = 1$, $T_0 = 290$ K

For easier interpretation the temperature scale is transformed into a dimensionless form.

$$\psi = (T - T_0) \cdot \frac{\left(\frac{\varepsilon}{1+\varepsilon} + St\right)}{\Delta T_{ad}} \tag{4-172}$$

It can be seen that the trajectories form a loop in the two safety technically critical processes c and d. They are generated because in the course of time first the maxima of added component and temperature are passed before the concentration of the added component proceeds through a minimum. In the case of the safe process, the two extremes with respect to the added component are passed before the maximum of the temperature is reached. Safe and critical reactor behaviour become separated by the unique case of a singularity formation in the phase plane, characterized by the simultaneous occurrence of mass balance minimum and heat balance maximum. This is represented by case b.

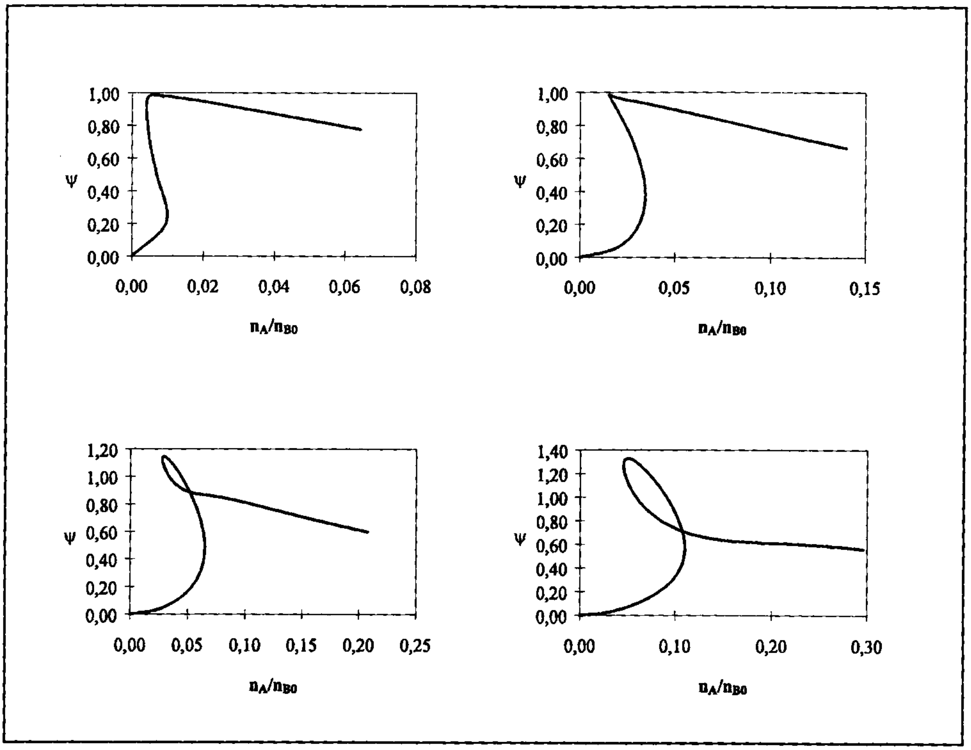


Fig. 4-52a-d. Phase plane presentation of the simulated isoperibolic semibatch processes shown in Fig. 4-50a-d

This special case is further characterized by an additional property . ψ_{max} takes the exact value of 1. In all cases of stable reactor operation ψ_{max} amounts to

$$0.98 \leq \psi_{max} \leq 1 \qquad (4\text{-}173)$$

This will later be used for the predetermination of the maximum temperature difference to be expected in a semibatch operation.

The special characteristic just described unfortunately, cannot be used directly as an assessment criterion. It is possible to deduce immediately the fact that under the boundary condition stated the mass balance at the temperature maximum must have a value of 1, but the only resulting equation

$$Da_\infty \cdot \frac{1+\varepsilon}{1+\varepsilon \cdot \Theta_M} \cdot \left(1 - X_M\right) \cdot \left(\lambda \cdot \Theta_M - X_M\right) \cdot \exp\left(-E/_{R \cdot T_M}\right) = 1 \qquad (4\text{-}174)$$

contains two unknowns, Θ_M and X_M. In consequence one further equation would be required to obtain an exactly valid, algebraically closed description of this selected point.

Process simulation of several thousand operating conditions, covering the technically meaningful and industrially relevant parameter range, was applied to deduce empirically a safety technical assessment criterion.

Cooled semibatch processes may safety technically be rated safe with respect to their thermal potential if they comply with the condition [50]:

$$\frac{1.45 \cdot Da_{\infty} \cdot \exp\left(-E/_{R \cdot T_0}\right)}{\left(\frac{\varepsilon}{1+\varepsilon}+St\right)} \geq 1 \qquad (4\text{-}175)$$

This assessment criterion shows very clearly the fundamental difference between BR and SBR. Especially for the isothermally operated BR the example discussed has shown, that the ratio of Damkoehler to Stanton number should be significantly smaller than 1 to be sure of safe operating conditions. Exactly the opposite is required for the SBR. Semibatch reactors must be operated in an ignited state in order to be able to utilize the degree of heat production rate. Batch reactors have to be operated in the extinguished state with the consequence already outlined in Section 4.3.1.3, that they are suitable for slow and moderately exothermic processes only.

The safety technical assessment of isoperibolic semibatch processes begins with the evaluation of the cooling power. For this purpose the reference temperature is calculated for a given desired maximum temperature using the relationship

$$T_0 = T_M - \frac{\Delta T_{ad}}{\left(\frac{\varepsilon}{1+\varepsilon}+St\right)} \qquad (4\text{-}176)$$

which is obtained from the boundary condition $\psi_{max} = 1$. In a subsequent step the safety criterion Equ.(4-175) is checked for a given feed time. If the process complies with the criterion, then in the last step it remains to be checked whether or not the scheduled feed and coolant temperature result in the corresponding reference temperature.

An additional sensitivity discussion is not necessary in this case. As shown in detail in reference [50], the sensitivity of all operating points which are in compliance with the safety criterion is equal to S = 1.

At this point the remark made in Section 4.1.3.1 about an optimized start-up strategy for the cooled CSTR shall be explained. The safety technical assessment procedure for the cooled isoperibolic SBR has demonstrated that in the case of correct design a prediction of the maximum reaction temperature is easily possible. This can be utilized for the optimization of the start up of the CSTR. The later steady state operating temperature of the CSTR is defined as the set value for the maximum SBR process temperature. In a next step one of the two reactants of the CSTR process is charged initially. Then the reactor is started as a semibatch process by feeding the second reactant. When the maximum temperature is reached, the feed of the initially charged reactant is started, and the feed streams are adjusted in such a way that the Stanton number of the CSTR is established. This way the initial oscillations are elegantly avoided.

The isothermal SBR is much more robust with regard to the thermal safety of operation than all other reactors which have been discussed so far. Actually only two special points remain which have to be observed for the operation of such processes:

1. In very fast SBR processes the controls implemented for the cooling must enable a more or less instant reduction of the coolant temperature down to the level predeterminable with the help of Equ.(4-176). This is comparable to isothermal batch processes. In such cases the heat production rate is directly proportional to the feed rate. Such fast processes are characterized by Damkoehler numbers

   $$Da(T_{isoth}) \geq 100$$

   In consequence of these high Damkoehler numbers the conversion achieved is also very high. An example is shown in 4-53a-b.
2. If the Damkoehler number of isothermal semibatch processes is smaller than 10 the degree of accumulation becomes high. In such cases the reaction rate and thereby the heat production rate is not proportional to the feed rate alone. For such processes a synthesis optimization is recommended which in the last consequence will also benefit the overall process safety. As will be demonstrated in the context of the safety technical assessment of maloperations (c.f. Section 4.4), the reduction of the maximum accumulation is a very decisive factor.

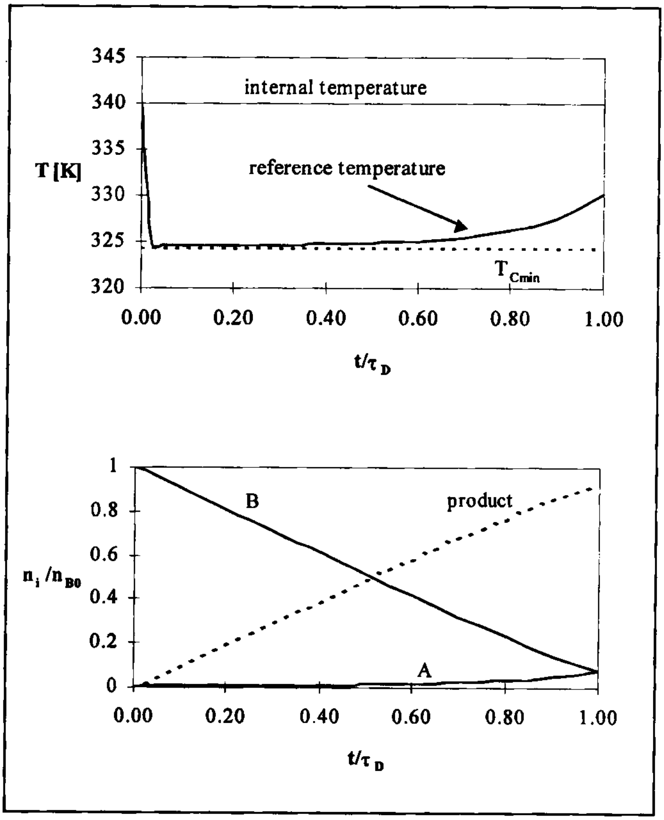


Fig. 4-53a-b. Example for a very fast isothermal semibatch process
Parameters: Da_{isoth} = 110.6, E/R = 12000 K, n = 2, St = 7.5,
ΔT_{ad} = 125 K, ε = 1, λ = 1, $T_{isoth.}$ = 340 K

A good compromise is represented by processes which comply with the safety criterion for isoperibolic processes, if calculated for the minimum coolant temperature. This is a pure recommendation only and not a yes/no criterion for the safety of an isothermal SBR. Two examples of a very slow reaction just in compliance with the criterion are shown in Figures 4-54a-b and. 4-55a-b, respectively.

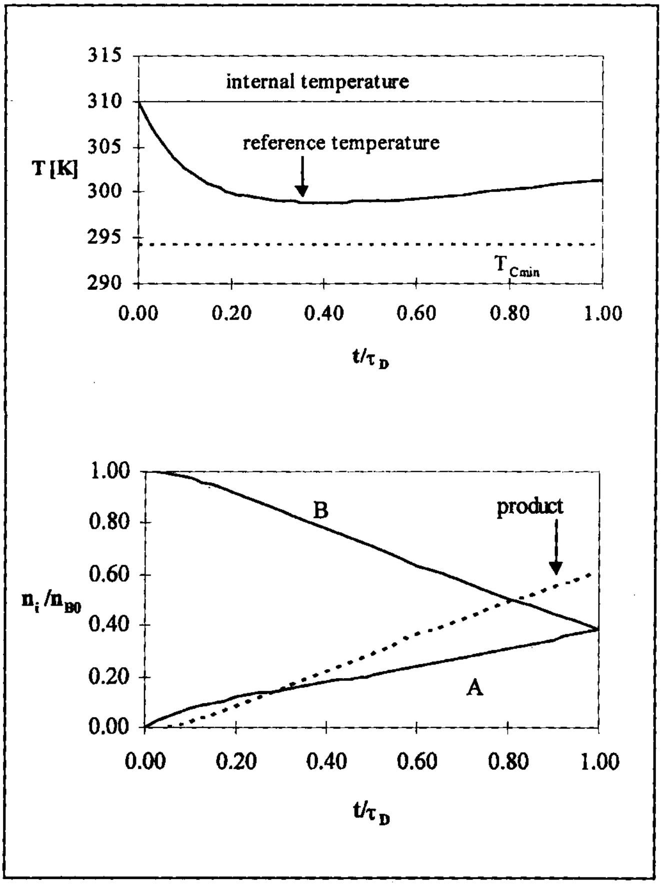


Fig. 4-54a-b. Example of a very slow isothermal semibatch process
Parameters: $Da_{isoth} = 3.63$, $E/R = 12000$ K, $n = 2$, $St = 7.5$,
$\Delta T_{ad} = 125$ K, $\varepsilon = 1$, $\lambda = 1$, $T_{isoth.} = 310$ K

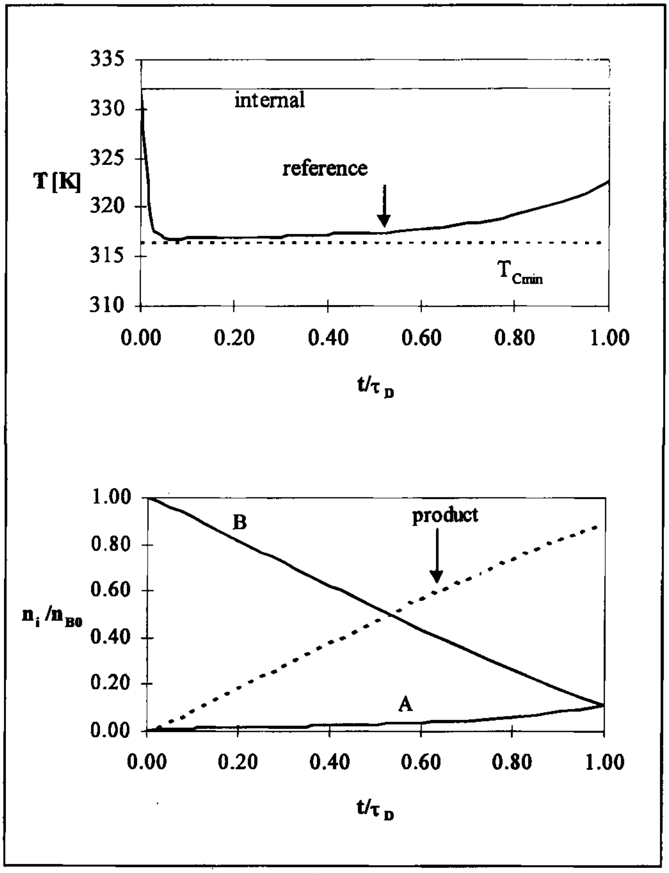


Fig. 4-55a-b. Example for an isothermal SBR which is just in compliance with the safety criterion calculated for T_{Cmin}
Parameters: $Da_{isoth} = 47.6$, $E/R = 12000$ K, $n = 2$, $St = 7.5$,
$\Delta T_{ad} = 125$ K, $\varepsilon = 1$, $\lambda = 1$, $T_{isoth.} = 332$ K

The complete procedure of assessment of the thermal safety of cooled semibatch processes shall be demonstrated with the help of an example:

Example: A reaction shall be performed as an isoperibolic semibatch process on a 20 m^3 scale. 10.43 m^3 shall be charged initially containing B with a concentration of 3.4 kmol/m^3. A stoichiometric amount of A shall be added with constant feed rate. It is available as a premixed solution. The concentration of A amounts to $c = 4.86$ kmol/m^3, its temperature is equal to 25°C. The feed time is scheduled to be 5 hours. The initial reaction temperature shall be equal to the reference temperature and shall have a value of -6°C. The coolant temperature is controlled at a set point of -10 °C. The stoichiometric coefficients are $|\nu_i| = 1$. The heat of reaction shall be equal to -85 kJ/mol. The reaction rate can be approximated with a second order rate law and the parameters $k_\infty = 4.43 * 10^{12}$ $m^3/(kmol\ s)$ and activation temperature E/R = 10450 K. The reactor is characterized by a value of 6000 W/K for the product of heat transfer area and transfer coefficient. The product of density and specific heat capacity amounts to an average value of 1700 kJ/(m^3 K).

Solution: In a first step the volume increase factor and the Stanton number have to be calculated.

$$n_{B0} = V_0 \cdot c = 10.43\,m^3 \cdot 3.4\,kmol \cdot m^{-3} = 35.46\,kmol$$

$$\lambda = 1 \quad \Rightarrow \quad n_A = 35.46\,kmol$$

$$V_D = \frac{n_A}{c} = \frac{35.46\,kmol}{4.86\,kmol \cdot m^{-3}} = 7.3\,m^3 \quad \Rightarrow \quad \varepsilon = \frac{V_D}{V_0} = \frac{7.3\,m^3}{10.43\,m^3} = 0.7$$

$$St = \frac{U \cdot A \cdot \tau_D}{(V_D + V_0) \cdot \rho \cdot c_P} = \frac{6\,kW \cdot K^{-1} \cdot 5\,h \cdot 3600\,s \cdot h^{-1}}{17.73\,m^3 \cdot 1700\,kJ \cdot m^{-3} \cdot K^{-1}} = 3.6$$

With the help of these parameters the given data about the reference temperature can be validated. In all cases the correct value can be determined. It will be required for the calculation of the Damkoehler number Da (T_0).

$$T_0 = \frac{T_{in} + \frac{(1+\varepsilon)}{\varepsilon} \cdot St \cdot T_C}{1 + \frac{(1+\varepsilon)}{\varepsilon} \cdot St} = \frac{298.15K + \frac{1+0.7}{0.7} \cdot 3.6 \cdot 263.15K}{1 + \frac{1+0.7}{0.7} \cdot 3.6}$$

$$= 266{,}6K = -6.5°C$$

The value given for the initial temperature is correct. ✓

In the following step the Damkoehler number can be calculated and evaluated in respect to its compliance with the safety criterion.

$$Da(T_0) = \frac{k_\infty \cdot n_{B0} \cdot \tau_D}{-\nu_A \cdot (V_D + V_0)} \cdot \exp\left(-{E}/{R \cdot T_0}\right)$$

$$= \frac{4.43 \cdot 10^{12}\ m^3 \cdot 35.46\ kmol \cdot 5\ h \cdot 3600\ s \cdot \exp\left(-\frac{10450\ K}{266.6\ K}\right)}{kmol \cdot s \qquad \cdot h \cdot 1 \cdot 17.73\ m^3} =$$

$$= 1.5.$$

$$\frac{1.45 \cdot Da(T_0)}{\frac{\varepsilon}{1+\varepsilon} + St} = \frac{1.45 \cdot 1.5}{\frac{0.7}{1+0.7} + 3.6} = 0.55$$

The safety criterion is not fulfilled !! To confirm this assessment of non-compliance the simulation of the process as proposed is shown in Figure 4-56.

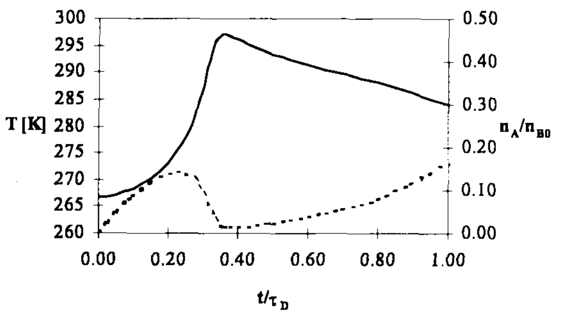


Fig. 4-56. Simulation of the process as proposed
upper curve: internal temperature,
lower curve: relative concentration of the added component A

As in previous examples, measures which could stabilize the process shall be discussed in this case. The most simple measure would be an increase in the reference temperature, provided the thermal stability of all substances and their reaction mixture allows for it. Within a limited temperature range the Stanton number, which forms the major part of the denominator of the safety criterion, may be regarded as independent of temperature. Therefore it is sufficient to approximately double the Damkoehler number in this example. This characteristic number represents the initial reaction rate. Van't Hoff's rule states that an increase in temperature by 10 K roughly doubles the reaction rate. The activation energy in this example is comparatively high, so it may be expected that an increase in temperature by 10 K would even triple the rate. Fixing the coolant temperature 10 K higher at 0 °C yields a reference and initial temperature of 275.5 K or 2.5 °C. With this new value the Damkoehler number now amounts to $Da_0 = 5.4$. The safety criterion now has a value of 1.95.

Recommendation 1: The proposed process should be modified as follows:

The new set point for the controlled coolant temperature should be 273 K. The initial temperature should be increased up to 275.5 K. A simulation of the modified process is shown in Figure 4-57.

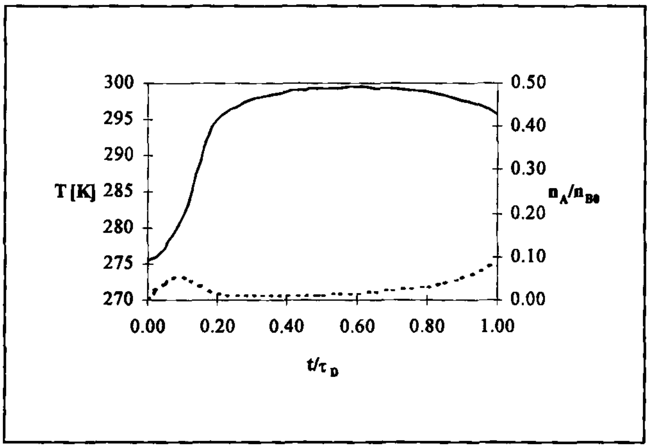


Fig. 4-57. Simulation of the process modified in accordance with recommendation 1, upper curve: internal temperature, lower curve: relative concentration of the added component

As in all other cases another way to stabilize the process is a modification of the input concentrations. Contrary to the BR and the CSTR, in the case of the SBR an increase in input concentration is required in order to speed up the initial reaction rate. In doing so it has to be observed that the significant influence on this initial rate is provided by the pre-charged component.

Applying the dilution factor κ :

$$c_{B0}^{*} = \kappa \cdot \frac{n_{B0} \cdot \varepsilon}{V_D \cdot (1+\varepsilon)} \tag{4-177}$$

$$\text{with} \qquad \kappa > 0 \tag{4-178}$$

and assuming the use of standard vessels with a constant geometric ratio of

$$A \big/ V_R^{2/3} \tag{4-126}$$

all necessary parameters included in the safety criterion can be modified accordingly:

$$Da_0^{*} = \frac{k(T_0) \cdot n_{B0} \cdot \tau_D \cdot \varepsilon \cdot \kappa}{V_D \cdot (1+\varepsilon \cdot \kappa)} \tag{4-179}$$

$$St^{*} = \frac{U \cdot A \cdot \varepsilon \cdot \kappa^{1/3} \cdot \tau_D}{V_D \cdot (1+\varepsilon \cdot \kappa) \cdot \rho \cdot c_P} \tag{4-180}$$

$$\varepsilon^{*} = \varepsilon \cdot \kappa \tag{4-181}$$

In setting up Equ.(4-179) it was neglected that a change in the Stanton number also causes a change in the reference temperature. However, the error which occurs this way is very small. With the equations given the dilution factor, which in this case of increased concentration must be greater than one, can be calculated.

$$\kappa = \left[\frac{\left[k(T_0) \cdot n_{B0} \cdot \tau_D \cdot 1.45 - V_D \right] \cdot \rho \cdot c_P}{U \cdot A \cdot \tau_D} \right]^{-\frac{3}{2}} \tag{4-182}$$

For the example discussed here the calculation yields $\kappa = 2.84$. This value means, a sufficient solubility provided, that 35.46 kmol of component B have initially to be charged in a volume of 3.68 m^3 only. This way the amount produced per batch will also be higher. At the same time it has to be taken into account that the occurring overheating will be much higher because the change in initial concentration also results in a higher adiabatic temperature increase.

$$\Delta T_{ad}^{*} = \Delta T_{ad} \cdot \frac{(1+\varepsilon)\cdot \kappa}{(1+\varepsilon \cdot \kappa)} \tag{4-183}$$

For the discussed example this means explicitly:

$$\Delta T_{ad}^{*} = 100\,\mathrm{K} \cdot \frac{(1+0.7)\cdot 2.84}{(1+0.7\cdot 2.84)} = 161.6\,\mathrm{K}$$

The simultaneous reduction in the Stanton number leads to an overheating of 40 K, which is roughly twice as much as initially planned. However, this can be counterbalanced in a relatively simple way without negative effect on the overall process stability. If the possible gain in productivity due to the changed feed volume is reduced by doubling the feed time, the problem is solved. The Stanton number is directly proportional to the feed time and at the same time the decisive factor in the denominator of Equ.(4-176), which is used to calculate the overheating, therefore doubling the feed time cuts the overheating by half at the same time. This elongation has nearly no effect on the overall process safety, because the safety criterion in a simplified form reduces to the ratio of Damkoehler to Stanton number, which is independent of the feed time. A summary of the above can now be phrased as a second recommendation.

Recommendation 2: The proposed process should be modified as follows:

The amount of reactant B charged initially should be increased to 61.39 kmol per batch in 6.36 m^3 volume. It is assumed that the solubility is as high as required. Instead of the proposed 7.3 m^3 of the solution to be added, 12.63 m^3 should be prepared. The concentration of A in this solution remains as unchanged with 4.86 $kmol/m^3$ as the feed temperature with 25 °C. The feed time is adjusted to 10 hours. Coolant and initial temperature also remain unchanged. The expected maximum temperature amounts to 18.5 °C. The space/time-yield or overall productivity will reach roughly 90% of the initially proposed process. A simulation of the modified process is shown in Figure 4-58.

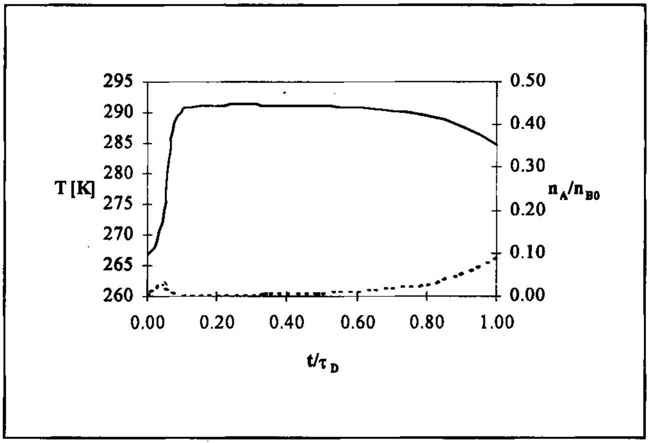


Fig. 4-58. Simulation of the sample process modified according to recommendation 2, upper curve: internal temperature, lower curve: relative concentration of the added component

4.3.2 Special Problems In The Assessment Of Normal Operating Conditions

Two quite frequently occurring questions regarding the safety technical assessment of chemical reactions cannot be placed directly into the order presented here so far. The first case is the evaluation of reactions performed under reflux conditions. The safety assessment of such processes does not depend primarily on the general mode of operation, which in most cases is either discontinuous or semi-continuous, but on the peripheral installations to the reactor itself. In industrial practice, numerous designs can be found. Consequently the discussion here has to focus on two examples to outline the general assessment procedure. If these examples demonstrating the fundamental approach to the assessment of processes under reflux are combined with the assessment criteria presented so far, the basis is provided to perform the safety evaluation for any other unique design as required.

The other special case is the assessment of polymerization processes. These are characterized by extremely high heat production rates, accompanied by enormous changes in viscosity. Polymerization reactions are performed in many different ways. Examples are polymerization in bulk, in solution, in suspension or emulsion. The general assessment criteria which have been presented in the previous sections can in principle be applied to polymerization processes accordingly. However, it must be observed that quite a number of parameters which are considered to have constant values when performing conventional reactions become dynamically changing in this case. In the following, certain recommendations shall be provided in order to assist the safety technical treatment of such phenomena.

4.3.2.1 Safe Normal Operation of Reactions Under Reflux

Despite the fact that this mode of operation may be regarded as one of the most elegant because, simply expressed, it has its own cooling integrated, only very limited information can be obtained from the literature which can be used for the safety assessment. For quite some time it was even questioned in general by the experts whether reactions under reflux can pose a safety problem at all. It is only since a dissertation was written on behalf of the CIBA-Geigy, Basle, safety department that possible problems arising from such processes have become more known [52]. An industrial working group of safety experts then compiled the most important questions concerning such reactions as well as the corresponding safety technical recommendations for normal as well as upset operating conditions [53].

In assessing normal operating conditions, two points have especially to be investigated:

1. Has the volume increase due to the heat expansion of the liquid, which accompanies the temperature increase from the initial temperature, usually room temperature, to the boiling point, as well as the liquid swell caused by the bubble formation due to boiling been sufficiently accounted for in the process design ?
2. Has the condensation capacity of the succeeding condenser been calculated adequately ?

Especially the first-mentioned phenomenon of thermal liquid expansion is often neglected when reactions are performed under reflux. But it is responsible for a significant reduction of the free volume in the reactor dome. If this effect is increased by the additional liquid swell caused by the bubble formation prevailing under reflux conditions, it may occur that more liquid is carried away in the vapour stream. In the worst case it may even happen that the reactor dome becomes completely filled with the boiling liquid. In both situations a two-phase stream enters the vapour tube, which should be avoided at all events. Figure 4-59 shows how thermal liquid expansion leads to a cut in free volume by half if a 8 m^3 reactor, initially filled with 6.5 m^3 of either toluene or ethyl acetate, is heated up from room temperature to the corresponding boiling point.

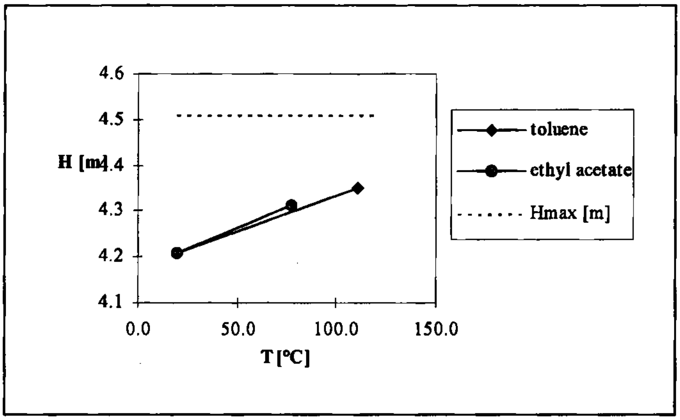


Fig. 4-59. Demonstration of the filling level increase due to the heating up of the reactor contents to the boiling point
- $V_{R0} = 6.5\ m^3$, nominal volume = 8 m^3, H/D = 3

The safety technical recommendation has to account for the thermal expansion as well as all the other effects mentioned and therefore reads:

> *The filling level under reflux conditions, $H_{B.P.}$, should not exceed 80% of the height which corresponds to the filling level of the nominal volume. If the process includes a dosage, the critical level has to be calculated under consideration of the total volume to be added.*

In order to be able to apply this rule in practice, it must be possible to precalculate both the level under reflux conditions and the initial level. Besides other alternative models the so-called Wilson correlation provides a possibility. This model correlates system specific substance data and the relative free board level α.

$$\alpha = \frac{H_{B.P.} - H_0}{H_{B.P.}} \tag{4-184}$$

$$\alpha = K \cdot \left(\frac{\rho_V}{\rho_L - \rho_V} \right)^{0.17} \cdot D^{*-1} \cdot u_V^{*\,a} \tag{4-185}$$

D* symbolizes the dimensionless reactor diameter and u_V^* the dimensionless maximum vapour velocity in the reactor.

$$D^* = \frac{D}{\sqrt{\frac{\sigma}{g \cdot (\rho_L - \rho_V)}}} \qquad u_V^* = \frac{u_V}{\sqrt{g \cdot \sqrt{\frac{\sigma}{g \cdot (\rho_L - \rho_V)}}}} \tag{4-186, 4-187}$$

K and a are correlation parameters, defined as follows:

$K = 0.68$ and $a = 0.62$ for $u_V^* < 2$ and $K = 0.88$ and $a = 0.4$ for $u_V^* \geq 2$

While the dimensionless reactor diameter is directly accessible as the substance data and geometry of the reactor are known, the maximum vapour velocity in the reactor can only be calculated if the maximum heat production rate is available. In most cases this has to be determined experimentally. If this value is known, the maximum vapour velocity can be calculated.

$$u_V = \frac{\dot{Q}_{chem,max}}{\Delta_V h \cdot \rho_V \cdot A_{R,cross\ section}} \tag{4-188}$$

The necessary calculations shall be performed for the example of a reaction in boiling toluene in order to demonstrate their significance. The reaction to be assessed shall be performed in batch mode in a reactor of 8 m^3 nominal volume. The reactor diameter shall be 1.5 m. The initial volume amounts to 6 m^3 per batch. With these data the critical level under reflux conditions and the initial level at room temperature can be calculated. They are:

$$H_{B.P.} = 0.8 \cdot \left(\frac{8m^3 \cdot 4}{\pi \cdot (1.5m)^2} \right) = 3.6m \qquad H_0(6m^3) = \frac{6m^3 \cdot 4}{\pi \cdot (1.5m)^2} = 3.4m$$

Figure 4-60 shows the maximum allowable level at room temperature calculated for different maximum specific heat production rates and a total batch volume of 6 m^3.

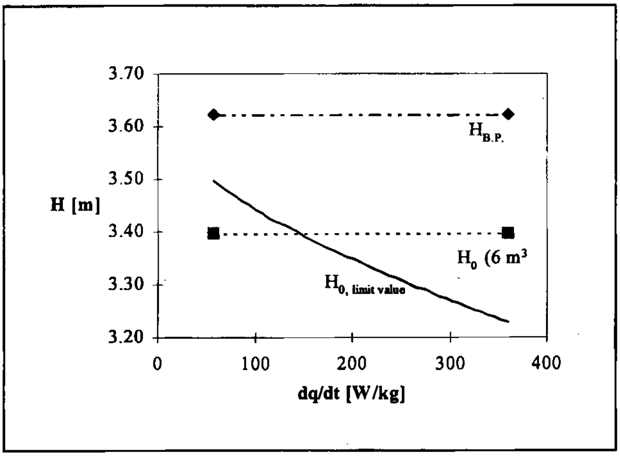


Fig. 4-60. Limit value diagram for reactions under reflux in toluene; nominal volume: 8 m^3, total volume per batch at room temperature: 6 m^3

The Figure 4-60 shows that only reactions with maximum specific heat production rates of less than 130 W/kg are safety technically acceptable if the batch size amounts to 6 m^3. If the maximum specific power output is expected to be higher, the batch size has to be reduced. The limit curve has to be recalculated for each batch size because the maximum vapour velocity in the reactor directly depends on this batch size. For the sample process considered, Figure 4-61 additionally provides the curves for a 5 m^3 batch size. It can be seen that in the case of this reduced total batch volume, maximum reaction power outputs up to 400 W/kg could be tolerated.

The second safety recommendation deals with the condenser connected to the vapour tube. In this case a relative high safety margin is included in the recommendation as the importance of having sufficient condensation capacity is very obvious:

> *It is recommended that in the case of reactions performed under reflux the condenser should be designed for a capacity approximately 1.5...2 times larger than the maximum heat production rate of the chemical reaction.*

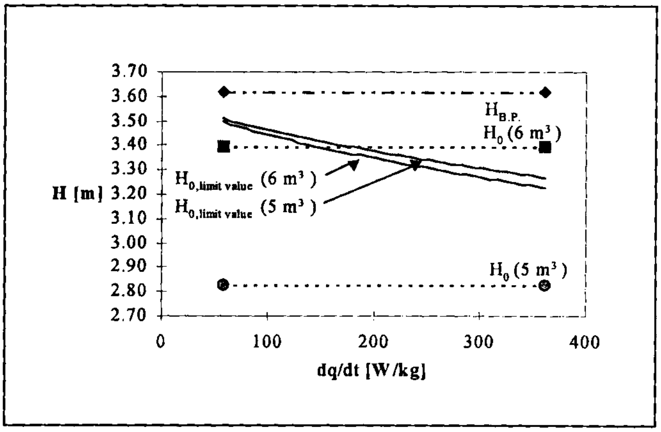


Fig. 4-61. Limit value diagram for reactions under reflux in toluene; nominal volume: 8 m^3, total volume per batch at room temperature: 6 and 5 m^3 resp.

4.3.2.2 Safe Normal Operation of Polymerization Reactions

Polymerization reactions are classified in two categories, which discriminate different chain propagation mechanisms: propagation by monomer combination and such by polymer combination. The latter is represented by polyaddition and polycondensation reactions, while the classical representative of the former is radical polymerization.

All polymerization reactions with monomer combination, as well as polyadditions are characterized by very high specific heats of reaction. Some examples, supplemented by the resulting adiabatic temperature rises, are given in Table 4-6.

These heats of reaction become perceptible in practice in high heat release rates, which is of safety technical significance. But two further special effects have to be accounted for in polymerization reactions. These are on one hand an extraordinary dynamics in the thermal power, which means very strong time dependent changes in the second derivative of the total heat output with respect to time, and on the other hand an enormous dynamic change in the physicochemical properties of the reaction mixture in the course of the reaction. The reaction system has to be adequately designed and safety technically evaluated in respect to both effects.

Table 4-6: Examples of heats of reaction for polymer reactions with monomer combination according to Brandrup and Immergut [54]

monomer	state of aggregation [monomer/polymer]	specific heat of reaction [kJ/kg]	ΔT_{ad} [K]
Ethylene	g,c	3620	1810
Propene	l,c	2000	1000
Butadiene	l,c	1350	676
Isoprene	l,c	1100	559
Acrylamide	s,s	1147	574
Acrylnitrile	l,c'	1423	721
Acrylic Acid	l,c	930	465
Methylmethacrylate	l,c	550	277
Vinyl Acetate	l,c	1022	511
Vinyl Chloride	l,c	1135	542
Styrene	l,c	672	336
Ethylene oxide	l,c'	2145	1073

g = gaseous, l = liquid, s = in solution, c = condensed amorphous, c' = crystalline or partially crystalline

The example of radical polymerization, which represents processes of greatest industrial relevance, shall be used to outline some of the fundamentals and to help with the understanding of these effects. Radical polymerization can be described as a series of elementary reactions. These are:

- radical formation,
- initiating reaction,
- propagation,
- terminating reaction,
- transfer reaction (occasionally).

Radicals can be formed by quite different ways. The most common pathways are chemical, thermal and photochemical radical formation. In industrial practice, mainly so-called initiators are used, which, depending on the temperature range, have an inherent thermal instability. Most common initiators are azo compounds, such as azobis-iso-butyronitrile (AIBN), peroxides and hydroperoxides, such as benzoyl peroxide or tert.-butyl hydroperoxide, peresters and peracids.

Initiator decomposition reactions usually follow a first order kinetic rate law, which allows the following formal kinetic description of radical formation:

$$I \xrightarrow{k_D} 2\,R^* \qquad r_D = k_D \cdot c_I \qquad (4\text{-}189, 4\text{-}190)$$

Besides this thermally triggered decomposition of the initiator, radical formation can also be achieved with the help of a reaction with a solvent or other compounds added on purpose. This so-called induced radical formation is worth mentioning because it may proceed like an explosion. Amines such as dimethylaniline are known to have this effect.

Alternatively, as mentioned, radical formation can also be obtained quite differently, for example by combination of reducing agent, peroxide and metal ions or metal carbonyls with organic halides, or by use of certain redox systems, such as peroxodisulfate and a mercaptane, and, not least photochemically by irradiation.

The initiation reaction which follows describes the addition of a monomer to the radical, resulting in a polymer radical.

$$R^* + M \xrightarrow{k_{St}} P^* \qquad r_{St} = k_{St} \cdot c_M \cdot c_{R^*} \qquad (4\text{-}191, 4\text{-}192)$$

The concentration of the primary radical c_{R^*} is characterized by the fast establishment of a steady-state value. Applying Bodenstein's quasi-steady-state principle to this concentration yields the following description of the initiating reaction:

$$r_{INI} = 2 \cdot k_D \cdot c_I \qquad (4\text{-}193)$$

Especially if radical formation processes are used which result in two radicals per initiator molecule, effects may be observed which lead to the situation, that not all primary radicals start a polymer chain. This is accounted for by the introduction of a radical yield factor f, which in most cases takes values between 0.5 and 1. The complete reaction rate law for the initiation reaction finally takes the form:

$$r_{INI} = 2 \cdot f \cdot k_D \cdot c_I \qquad (4\text{-}194)$$

The actual chain propagation reaction is characterized by the addition of a further monomer to the polymer chain.

$$P_n^* + M \xrightarrow{k_P} P_{n+1}^* \qquad r_P = k_P \cdot c_M \cdot c_{P^*} \qquad (4\text{-}195, 4\text{-}196)$$

The concentration of polymer chain radicals c_{P^*}, which forms one factor of the kinetic rate law for the chain propagation reaction, has to be interpreted as the result of a summation over all radical concentrations with different chain length.

The termination of a chain reaction mainly follows one of the two following mechanistic pathways:

- by recombination: two polymer radicals with chain lengths n and m, respectively, form a polymer molecule of the length n+m
- by disproportionation: a proton transfer from a polymer radical which has a chain length n to one with a chain length m results in an unsaturated polymer molecule P_n and a saturated one P_m.

The formal kinetic rate law describing the termination reaction is the same in both cases. For both mechanisms the following is valid:

$$P_n^* + P_m^* \xrightarrow{k_{T,R}} P_{n+m} \qquad \text{or} \qquad P_n^* + P_m^* \xrightarrow{k_{T,D}} P_n^= + P_m \qquad (4\text{-}197, 4\text{-}198)$$

$$r_T = k_T \cdot c_{P^*}^2 \qquad (4\text{-}199)$$

In the case that both mechanisms occur at the same time, however, the two different rate constants both have to be considered. The termination constant in this case is equivalent to the sum of the two specific rate constants $k_{T,R}$ and $k_{T,D}$.

A special mechanism of termination is frequently observed if a radical is transferred to a monomer under proton exchange with the boundary condition, that the resulting unsaturated monomer is stabilized by resonance in such a way that it does not undergo any further chain reaction. Chemically such a precondition is given in case of allylic monomers. The formal kinetic rate law for this termination step is as follows:

$$P_n^* + M \xrightarrow{k_T} P_{n+1} + M^* \qquad r_T = k_T \cdot c_M \cdot c_{P^*} \qquad (4\text{-}200, 4\text{-}201)$$

In some cases a so-called transfer reaction can additionally either be observed or purposely initiated. This transfer reaction is a reaction of the growing polymer radical with either initiator, polymer molecule or a deliberately added foreign substance, terminating the chain growth and transferring at least the radical to the reaction partner. These modifiers, as these added substances are commonly called because of their influence on the properties of the product, are often mercaptanes. Kinetically this reaction is of very limited significance.

The easiest approach to developing a gross reaction rate law for the polymerization process in total is to make use of the monomer consumption.

$$r_{gross} = r_{INI} + r_P \tag{4-202}$$

The polymer radical concentration c_{P*}, which is part of the propagation rate, can be obtained by applying the Bodenstein quasi-steady state principle.

$$c_{P^\bullet} = \left(\frac{2 \cdot f \cdot k_D}{k_T}\right)^{0.5} \cdot c_I^{0.5} \tag{4-203}$$

From this it follows for the gross reaction rate law:

$$r_{gross} = 2 \cdot f \cdot k_D \cdot c_I + k_P \cdot \left(\frac{2 \cdot f \cdot k_D}{k_T}\right)^{0.5} \cdot c_I^{0.5} \cdot c_M \tag{4-204}$$

In general the monomer concentration c_M by far exceeds the initiator concentration c_I and the rate constant of the termination reaction k_T is much higher than the rate constant of the decomposition k_D. This allows the formulation of the gross reaction rate with the help of the following approximation, which is still of satisfying accuracy:

$$r_{gross} = k_P \cdot \left(\frac{2 \cdot f \cdot k_D}{k_T}\right)^{0.5} \cdot c_I^{0.5} \cdot c_M \tag{4-205}$$

Finally the temperature dependence of the reaction rate may be estimated. The gross activation energy is a combination of:

$$E_{gross} = \frac{1}{2} \cdot E_D + E_P - \frac{1}{2} \cdot E_T \tag{4-206}$$

In almost all cases the activation energy of the decomposition reaction is significantly higher than those of the other two elementary steps. Consequently, in a first approximation, the gross activation energy amounts to roughly half the value of the activation energy of the decomposition reaction.

The Gel- or Trommsdorf Effect

Even a close look at the equations deduced for the formal kinetic description of the gross reaction does not provide any indication that an extraordinary process behaviour is to be expected. However, it is very typical for radical polymerizations, that the heat production rate, which is directly proportional to the reaction rate, exhibits an almost spontaneous increase when a certain monomer conversion has been reached. Schematically this effect is shown in Figure 4-62.

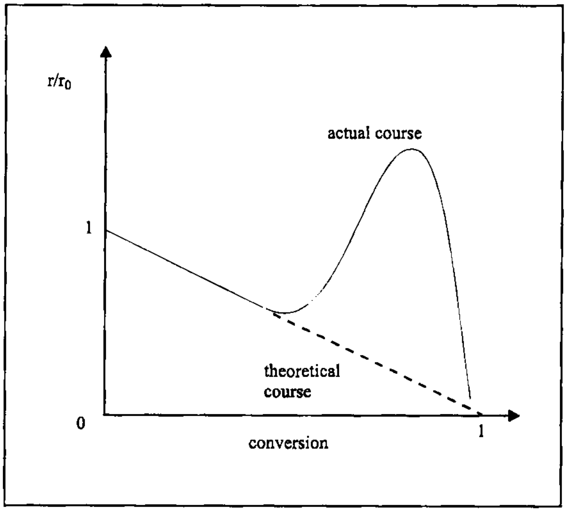


Fig. 4-62. Schematic presentation of the gel- or Trommsdorf effect

The cause is explained by the different mobility of the reactive species. Comparatively small monomer molecules take part in primary radical formation and chain propagation. These small monomer molecules maintain an almost unchanged mobility almost throughout the complete reaction time despite increasing viscosity. The reactions are entirely kinetically controlled. Only when the so-called glass point is reached does the monomer lose its mobility, and the polymerization reaction rate diminishes to zero. For long polymer chains an entirely different behaviour is observed. In the beginning those long chains, too, can perform translational as well as oscillating and rotational movements.

Both ways to move, however, become more and more restricted with increasing degree of polymerization. The entanglement of the chains leads to a situation where their mobility becomes limited to oscillatory and rotational movement, a situation also called segment diffusion. The termination reaction, independent of its mechanism, requires a close approach of the reactive centers of two polymer radical chains. Consequently, with increasing conversion the termination reaction becomes more and more mass transfer controlled. If the rate constant of the termination reaction becomes smaller with increasing conversion, and if, at the same time, the rate constants of decomposition and propagation remain approximately constant, it becomes unavoidable that the gross reaction rate increases again despite the increasing degree of monomer conversion. Only just before the glass point is reached the reaction rate will decrease again.

The above, however, makes it very obvious that the strength with which the gel effect occurs can best be influenced by the polymer and the initiator concentration. From a safety point of view it remains necessary to state:

> *In radical polymerization processes the exact time of occurrence of this gel effect and the degree of its strength have to be determined experimentally for each manufacturing recipe. The cooling capacity of the plant has to be designed to be able to cope with the maximum heat production rate set free shortly before the glass point. The most effective way to reduce the strength of the gel-effect is to perform the process with a higher degree of dilution.*

The central role of the change in viscosity

In the introduction to this section it was already referred to the massive change in properties of the reaction mixture with proceeding reaction time as an extraordinary characteristic of polymerization processes. The viscosity is the most significant property. This substance property has an influence on, or interacts with, so many parameters included in the balance equations and other factors that a graphical presentation seems to be the only appropriate form to explain this (c.f. Figure 4-63).

From a safety technical point of view the viscosity has a decisive influence on two parameters:

- the overall heat transfer coefficient of the reaction mixture
- the increasing heat input by stirring

In polymerization reactors equipped with cooling jackets, the conductively removed heat flow can be described in an identical form to that introduced in Section 4.1.7 for normal synthesis reactions.

$$\dot{Q}_C = -U \cdot A \cdot (T - T_C) \qquad (4\text{-}49)$$

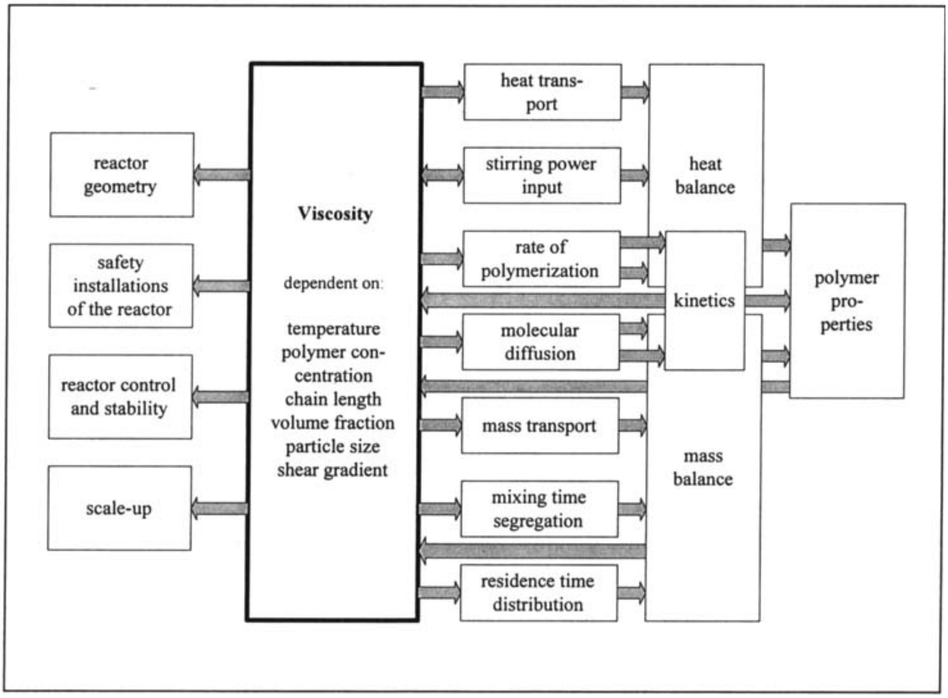


Fig. 4-63. Influence of the dynamic viscosity on the polymerization process according to Moritz [55,56,57]

According to the so-called Peclet-Equation, the overall heat transfer coefficient results from the summation of the following individual heat transfer resistances:

$$\frac{1}{U} = \frac{1}{\alpha_{react}} + \frac{d_{wall}}{\lambda_{wall}} + \frac{1}{\alpha_{coolant}} \tag{4-207}$$

The heat transfer coefficient on the side of the reaction mixture α_{react} strongly depends on the flow conditions which themselves depend on the viscosity, among other things. If the viscosity of the reaction mixture increases during the course of the reaction, this leads to an increase in thickness of the laminar film. In consequence, the film heat transfer coefficient decreases and the heat removal by conduction is reduced.

While this change in viscosity is relatively small in conventional reaction systems, which justifies the assumption of a more or less constant overall heat transfer coefficient, it may reach several orders of magnitude in the case of polymerization processes. To describe the connection between change in viscosity and reduction in inner heat transfer coefficient, the form common in process engineering is used, which has been deduced from the similarity theory.

$$\mathrm{Nu} = f\left(\mathrm{Re}, \mathrm{Pr}, \frac{\eta}{\eta_W}, \frac{D}{d}\right) \qquad (4\text{-}208)$$

The Nusselt number Nu is the relevant dimensionless number which is directly proportional to the film heat transfer coefficient, in this case of the reaction mixture.

$$\mathrm{Nu} = \frac{\alpha_{\mathrm{react}} \cdot D}{\lambda} \qquad (4\text{-}209)$$

The viscosity has an influence on the dimensionless parameters

$$\mathrm{Re} = \frac{n \cdot d^2 \cdot \rho}{\eta} \qquad \text{Reynolds number,} \qquad (4\text{-}210)$$

which describes the ratio of inertial to shear force and this way characterizes the flow condition induced by agitation, and

$$\mathrm{Pr} = \frac{c_P \cdot \eta}{\lambda} \qquad \text{Prandtl number,} \qquad (4\text{-}211)$$

describing the heat dispersion. In addition, it has a direct part in the calculation in form of the viscosity number η/η_W. The viscosity number characterizes the temperature gradient which develops with changing degree between the bulk reaction temperature and the temperature directly at the wall depending on the laminar film thickness. In case of turbulent flow conditions the following relationship has proved very suitable to describe the heat transport in stirred vessels:

$$\mathrm{Nu} = C \cdot \mathrm{Re}^{2/3} \cdot \mathrm{Pr}^{1/3} \cdot \left(\frac{\eta}{\eta_W}\right)^{0.14} \qquad (4\text{-}212)$$

Turbulent flow conditions may be assumed in stirred vessels with baffles if Re > 200. If no baffles are installed, Re has to be greater than 50 000. The proportionality constant C mainly depends on the type of agitator used. For fast rotating agitators, the proportionality factor has values between 0.3 and 1, in the case of slow types C takes values between 1 and 5, in exceptional cases even up to 10.

At this point, however, it is of less importance to assess the accuracy with which the heat transport can be described for a certain system by choosing the correct value for the proportionality constant. Instead, the phenomenological discussion should be continued. Figure 4-64 shows a typical plot for a representative data set of the Nusselt number change depending on viscosity.

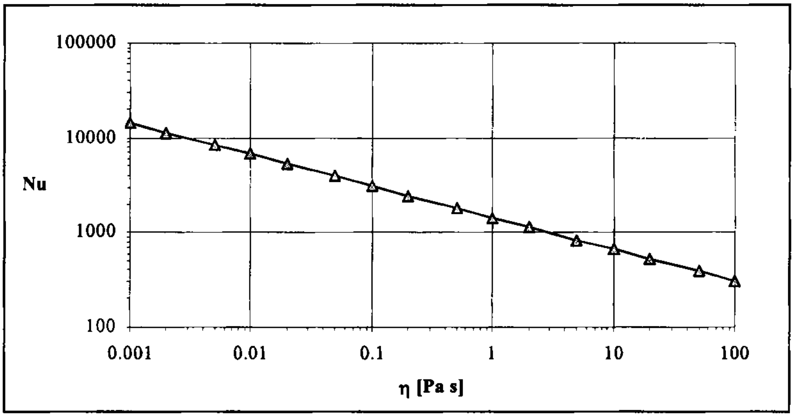


Fig. 4-64. Dependence of the film heat transfer on viscosity; 8 m^3 vessel with baffles, H/D = 2.5, $\lambda = 0.2$ W/m K, $c_P = 2$ kJ/kg K, $\rho = 900$ kg/m^3

If polymerizations are conducted in bulk, the viscosity may easily reach values of 100 Pa s and more, but even if performed in solution 1 Pa s is not uncommon. This corresponds to a change in viscosity of at least two orders of magnitude, sometimes even three.

With the help of the correlation given for the Nusselt number the following proportionalities may be deduced:

$$\mathrm{Re} \propto \eta^{-2/3} \quad \text{and} \quad \mathrm{Pr} \propto \eta^{1/3} \tag{4-213, 4-214}$$

They have the following consequences for the film heat transfer on the side of the reaction mixture:

$$\mathrm{Nu} \propto \alpha_{\mathrm{react}} \propto \eta^{-1/3} \tag{4-215}$$

and furthermore for the overall heat transfer coefficient

$$U(t) \propto U(t=0) \cdot \frac{\alpha_{\mathrm{react}}(t)}{\alpha_{\mathrm{react}}(t=0)} \propto U(t=0) \cdot \left(\frac{\eta(t)}{\eta(t=0)} \right)^{-\frac{1}{3}} \tag{4-216}$$

A change in viscosity by a factor of 100 or, in other words, by two orders of magnitude, reduces the overall heat transfer coefficient to approximately 1/5 of its original value. This dramatic effect is shown graphically in Figure 4-65 for the relevant range of possible viscosity changes.

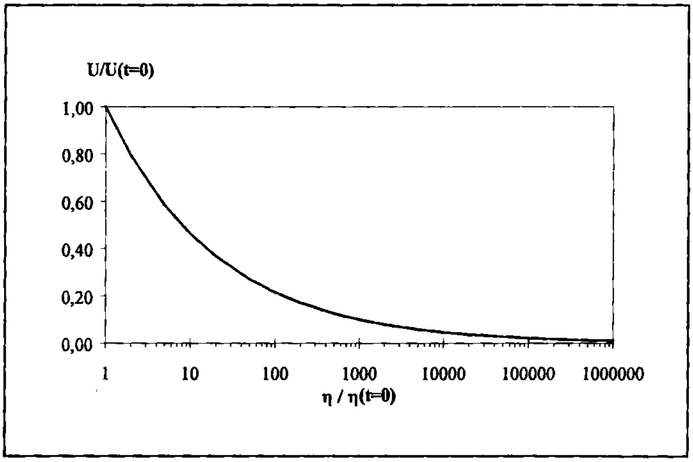


Fig. 4-65. Effect of viscosity changes on the overall heat transfer coefficient under turbulent flow conditions in a stirred vessel

Even in the case of a semi-continuous operation this loss in cooling capacity cannot be compensated by the increase of the wetted heat transfer area. Under these operating conditions a decrease of the heat removal power to 1/3 of its original value, again, is not uncommon.

As previously shown, the gel effect is a result of increasing viscosity, too, leading to higher heat production rates. In consequence it must be understood, that both effects amplify each other. The heat production rate may rise easily by a factor between two and three due to the gel effect, while at the same time the accompanying removal power is diminished to 1/3 down to 1/5 of its original value. Therefore the cooling must be designed in such a way that it can remove 6 to 10 times the power initially necessary to ensure isothermal operation.

In terms of practical consequences this for example means, that the driving temperature difference between internal and jacket temperature should initially not exceed 5 K in order to be increased to 30 up to 50 K at a later time in the course of the process.

All elaborations made stress the necessity to characterize polymerization reactions on small scale with the help of reaction calorimetry and with simultaneous registration of the conversion dependent changes in viscosity before any first performance on production scale.

The problem of effective heat removal when conducting polymerization reactions

In theory it should be possible to improve the heat removal from polymerization processes by increasing the agitator speed. This should help to keep the laminar film thickness small even if the viscosity of the reaction mixture becomes higher. In addition, it should help to prevent the formation of a polymer coating on the reactor wall, which is quite frequently observed with such processes and which forms an additional heat removal resistance:

$$\frac{1}{U}=\frac{1}{\alpha_{\text{react}}}+\frac{d_{\text{coating}}}{\lambda_{\text{polymer}}}+\frac{d_{\text{wall}}}{\lambda_{\text{wall}}}+\frac{1}{\alpha_{\text{coolant}}} \qquad (4\text{-}217)$$

However, as Moritz has outlined in great detail, just the opposite effect may occur [56]. The increase in stirrer speed definitely results in a stronger dissipation of stirring power and may also reduce the convective mixing time. But the first consequence mentioned may lead to a heating up of the total system by this external influence. The second can result in an increase in gross reaction rate and thereby in heat production rate. The effective cooling power without latent heat of evaporation due to boiling can be expressed as:

$$\dot{Q}_C=\dot{Q}_{\text{cond}}-P_{\text{stirrer}} \qquad (2\text{-}218)$$

with

$$P_{\text{stirrer}}=Ne\cdot n^3\cdot d^5\cdot\rho \qquad (2\text{-}219)$$

Ne, the so-called Newton number, is tabulated in the standard literature for numerous types of agitators [58,59]. The revolution rate of the stirrer determines to the first power the conductive heat removal rate and to the third power the dissipated stirring power, respectively.

Based on this analysis it follows that the selection of the agitator itself as well as the choice of the stirrer speed is subject to optimization. In a phenomenological form this optimization problem is shown graphically in Figure 4-66. It shows schematically the course of the total cooling power in its dependence on the number of stirrer revolutions per unit time, each for a constant value of viscosity.

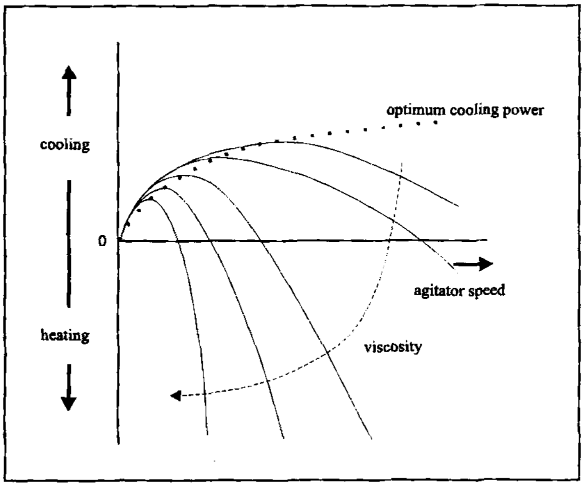


Fig. 4-66. Schematic presentation of the interactions between cooling power, viscosity and revolution rate of the stirrer

The dotted line marks the optimum curve for a system with a conversion dependent change in viscosity. According to this analysis it actually becomes necessary to reduce the number of revolutions per unit time for the stirrer in order for the cooling not to undergo the transition to a heating.

From a safety point of view this especially means:

- already at the time of experimental characterization of the reaction it has to be ensured that the heat dissipated by agitation is registered accurately, because the thermal signal for the determination of the true gross heat production rate due to the chemical reaction has to be corrected for this contribution,
- the production scale plant conditions must sensible be accounted for in the assessment procedure, because type of stirrer, its geometry and power may vary individually from one reaction apparatus to the other.

4.3.3 Investigation Methods for the Characterization of Normal Operating Conditions

A good experimental characterization is the prerequisite to any application of the safety technical assessment criteria for normal operation. If the opportunity is lacking, the safety assessment must remain superficial. The only information which under certain circumstances may be accessible without experimental work is the heat of reaction and the deduced value of the adiabatic temperature increase. But it must expressly be warned against relying only on calculated values if plant scale process are discussed.

The probability that the desired reaction is accompanied by a number of undesired processes is very high. Synthesis optimization activities may improve the selectivity, but a value of 1 with respect to the desired reaction is seldom achieved. A calculated heat of reaction can account for these side reactions only if they are definitely known. Otherwise the calculated value has to be regarded as a net value which corresponds to the desired reaction only and which may significantly be wrong with respect to the process in total.

The most important target information of an experimental characterization is the course of the chemical heat production rate. The integration of this curve over time yields the gross heat of reaction, which means the integral value including all simultaneously progressing reactions and physical processes. A major source of error for this method of determining the gross heat of reaction lies in the assumption on the conversion achieved within the limits of integration.

In most cases the heat flow signal approaches the base line almost asymptotically. If the upper integration limit is fixed at a time value which does not coincide with the moment at which the reaction has reached completion, because the signal cannot clearly be distinguished from base line noise anymore, the value determined for the gross enthalpy of reaction will be too small. Some reactions will never achieve complete conversion under the conditions proposed for the process. Possible reasons for such a situation may be, for example, chemical equilibria, pH-value dependent inhibitions, or solubility limits.

This initial error in the determination of the heat of reaction may propagate if it is attempted in a subsequent step to determine thermokinetic data from these experimental results. This will be explained with the help of an example in Section 4.3.3.3.

The most simple and most recommendable method to avoid this error is the application of a classical analytical technique on a sample taken by the experimentor at a time at which the reaction signal cannot be distinguished from base noise anymore. This moment then also becomes the upper integration limit for the determination of the heat of reaction. With the help of this analytically determined extent of reaction this total heat output can be extrapolated to the heat of reaction value which corresponds to full conversion.

Another piece of information can directly be gathered from the curve for the heat production rate measured: the maximum value of specific reaction power. According to the German TAA guideline this value is recommended for comparison with the maximum available cooling power (also c.f. Section 2.1).

All further-reaching assessment criteria and sensitivity analyses become possible only if an additional kinetic evaluation of the experiments can be performed. At this point a further-going safety assessment is often refused with the argument that the determination of kinetic parameters poses a disproportionate expense considering the complexity with which chemical reactions proceed. If one follows a fundamental physicochemical approach to solve this problem, then this argument cannot be denied. However, if a modified approach is chosen, which relies on the same basis of model reduction as was applied to the concept of formal kinetics, this argument is not valid anymore. This modified approach is called: **thermokinetics**.

4.3.3.1 Fundamentals of Thermokinetics

The basis to thermokinetics is formed by a modified consideration about the relative conversion. Thermokinetic conversion is defined as the fraction of the total energy output of the process which has been released between the start of reaction and the time currently considered. The total energy output results as integral value over all simultaneously progressing chemical reactions within the time interval of process start and the moment of reaching full conversion with respect to the desired reaction X_P.

$$X = \frac{\int_0^t \dot{Q}_{chem,gross} \cdot dt}{\int_0^{t(X_P=1)} \dot{Q}_{chem,gross} \cdot dt} \qquad (4\text{-}220)$$

This procedure has many advantages, but it is also accompanied by boundary conditions, which especially have to be observed in those cases where formal kinetic rate laws are used which have been determined with the help of this thermokinetic conversion.

The main advantage lies in the easy access to all values necessary for the calculation. If the heat production rate due to the chemical process has been measured with the help of a reaction calorimeter, such as those described in the next section, then this power signal is exactly the gross value required for the calculation of the thermal conversion. Without any classical kinetic investigations, which rely on analytical measuring techniques, it is not possible to interpret the measured signal regarding the power fractions set free either by the desired reaction or by n side reactions at a certain point in time. The signal remains in any case a gross value. The integration necessary does not pose any problem considering the latest developments in computers.

Another advantage lies in the application of this thermal conversion to determine the accumulation potential. The safety technical significance of the accumulation has already been outlined when discussing the normal operating conditions of a cooled SBR, and it will be of even greater importance in the discussion of maloperation.

$$Y_{accu} = \frac{t}{t_{charac.}} - X \tag{4-221}$$

The limitations and boundary conditions of this concept, which were mentioned in the introduction, mainly refer to the question of extrapolation of the results obtained. The application of this concept remains comparatively simple as long as the process to be safety technically assessed belongs to the group of homogeneous liquid phase reactions. In heterogeneous processes, the thermal conversion obtained reflects the flow conditions of the measuring apparatus. Here, special care has to be taken in the experimental design in order to obtain results which, under full observation of all rules of the similarity theory, may be used for plant scale assessment.

In addition it must be observed that the thermal conversion obtained is specific for the manufacturing recipe in question. This means that a formal kinetics determined with the help of thermal conversion-time data sets must not be used for the assessment of a process modified either with respect to the mode of operation or the stoichiometric input ratio.

Further limitations and rules for the application of thermokinetic conversion data are given in Section 4.3.3.3 in the context of thermokinetic evaluation methods.

4.3.3.2 Reaction Calorimetry

Modern reaction calorimetry is the method of choice for the experimental characterization of normal operating conditions. Today, such measuring devices are available commercially as well as self-made in many different designs and their description can be found in the literature [e.g. 60,61,62,63]. The key input to this development was given by Regenass 1979, when he developed the first so-called bench-scale calorimeter [64].

The fundamental measuring set up is almost identical for all calorimeters today. The core of the calorimeter is a jacketed reaction vessel usually with 2 liters volume.

The material this vessel is made of depends on the technical range of application. If reactions are to be investigated, which are performed in the pressure range of 0 to 1 bar abs., then the vessels are usually made out of glass. If elevated pressure is required for the experimental characterization, medium pressure vessels withstanding up to 6 bar abs. still manufactured out of a special glass are available. For even higher pressure, stainless steel autoclaves withstanding up to 60 bar abs. can be used.

The jacket is filled with a circulating coolant or heating medium, respectively, those temperature is adjusted to the required value, which will depend on the chosen mode of operation, with the help of a separately installed thermostat. The key point, which enables a fast response to a major change in the set point value of the required jacket temperature, is the use of two separate reservoirs in this thermostat unit, which are stored one at a very high, the other at a very low temperature. The quality of the calorimeter, is then determined, among other things, by the measuring and control devices installed, which achieve a mixing of the two volume flows, coming from these separate reservoirs, to one coolant stream in such way that the temperature required at this very moment is realized.

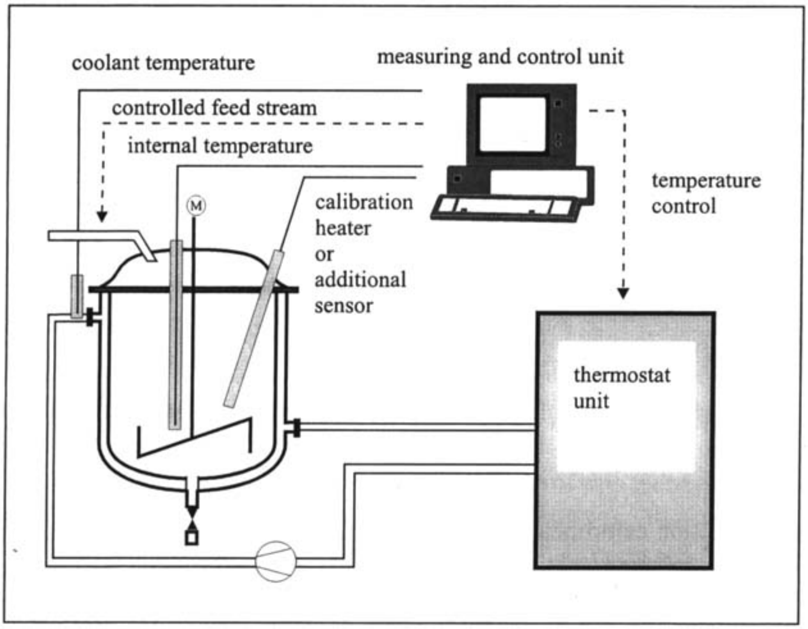


Fig. 4-67. Schematic drawing of the measuring set up of a modern reaction calorimeter

The modern calorimeters can be equipped with numerous additional installations enabling a number of different feed modes, other processes control strategies, such as pH-value dependent, or the simultaneous measurement of additional properties, such as density, viscosity or permanent gas generation rates. Furthermore, sophisticated reflux condenser systems are available, allowing the investigation of reactions under reflux as well as the so-called single vessel processes with intermediate distillation steps and many more. A schematic drawing of the measuring set-up is shown in Figure 4-67.

The individual calorimeters may be distinguished on one hand by the number of possible modes of operation and on the other hand by the way the heat flow signal is determined. An overview is provided in the following Table 4-7.

Table 4-7: Overview on calorimetric measuring and evaluation methods
⊕ = possible

heat balancing	mode of operation		
	Isothermal	isoperibolic	isothermal under reflux conditions
conductive through the vessel wall	⊕	⊕	
convective over the coolant circuit	⊕		⊕ at the reflux condenser
with heat compensation principle	⊕		

Isothermal Calorimetry

The isothermal mode is the most demanding with respect to measurement and control, as has already been stated for plant scale operation. Consequently the devices that allow this mode of operation are expensive to purchase. Their big advantage is the possibility to run classical kinetic investigations in parallel. The evaluation of the isothermal measurement with respect to the power of the process depends on the chosen calorimetric principle.

A very elegant method is the so-called *compensation calorimetry*. With this method the not yet reacting mixture is thermally equilibrated by establishing a constant coolant temperature which is much lower than the scheduled isothermal test temperature. An electrical heater is placed in this mixture to compensate for this overcooling. At a constant voltage, the current is adjusted in such a way that, after some time, the temperature of the mixture equilibrates at the desired measuring temperature. If the second reactant is added now, initiating the chemical heat release, the current is automatically adjusted by the controls in such a way that the internal temperature remains constant throughout.

The ability of such a measuring device to maintain isothermal conditions for the reaction mixture strongly depends on a large initial temperature difference, in order to be able to compensate for strongly exothermic processes, as well as on the capability to increase the electrical heating power significantly if the process to be investigated should surprisingly show an endothermic behaviour.

The superiority of this technique, especially in comparison to the so-called heat flux calorimetry, which still remains to be described, lies in the fact that the measured signal is completely independent of the size of the heat transfer area, which may change due to a feed process, or of any other substance properties of the mixture, such as density or viscosity. These properties determine the heat transfer on the side of the reaction mixture or, in other words, the film heat transfer coefficient, as is well known from process engineering.

The measured power signal

$$P(t) = -U_{\text{heating}} \cdot \left(I_0 - I(t)\right) \tag{4-222}$$

is directly equivalent to the heat production rate of the desired process, provided any material added has previously been pre-heated to the desired measuring temperature. Otherwise the signal measured has to be corrected for this convective heat flux due to the dosage.

The most frequently applied method is the so-called *heat flow calorimetry.* With this technique, the thermal power generated by the process is determined by that driving temperature difference between the mean coolant temperature in the jacket and the temperature of the reaction mixture which is necessary to maintain a constant internal temperature.

$$\dot{Q}_{\text{cond.}} = -U \cdot A \cdot \left(T_R - \overline{T}_C\right) \tag{4-223}$$

In this case the coolant temperature is adjusted by the controls. The measured conductive power signal has to be corrected for the convective heat removal due to the dosage and the conductive heat loss to the environment.

$$\begin{aligned}\dot{Q}_{\text{chem.}} &= -\left(\dot{Q}_{\text{cond.}} + \dot{Q}_{\text{conv.}} + \dot{Q}_{\text{env.}}\right) \\ &= -\dot{Q}_{\text{cond.}} + \dot{m}_D \cdot c_{PD} \cdot (T_R - T_{in}) - \dot{Q}_{\text{env.}}\end{aligned} \tag{4-224}$$

Furthermore, when determining the heat production rate of the process it has to be observed that the product of heat transfer area and overall heat transfer coefficient is, at least for the time being, an unknown and system specific value. The heat transfer area may dynamically change either because of a feed process or because the reaction is accompanied by a significant change in volume. The value of the overall heat transfer coefficient may vary significantly due to changes in the physicochemical properties of the reaction mixture such as may occur with polymerization reactions.

In order to overcome this problem, this kind of calorimeter provides experimental phases which can be used for the calibration of this product of heat transfer area and coefficient. For this purpose of calibration an electrical heater is commonly used which puts into the system a defined power over a fixed time interval.

The evaluation of such a phase can best be explained for the case that this calibration is performed in the isothermal mode and in the absence of any chemical reaction. Such phases always occur at the beginning of the calorimetric measurement when only the solvent and possibly one reactant have been charged to the test vessel, but not the second. A second such phase occurs towards the end of the measurement, when the power signal has become very small and almost constant. The product of heat transfer area and coefficient can be calculated as follows:

$$U \cdot A = \frac{P_{\text{heating}} \cdot \left(t_{\text{end of calib.}} - t_{\text{begin of calib.}}\right)}{\int\limits_{\text{begin of calib.}}^{\text{end of calib.}} \left(T_R(t) - \overline{T}_C(t)\right) \cdot dt} \qquad (4\text{-}225)$$

Such calibrations can also be performed on temperature ramps or while chemical reactions are still in progress, provided that the correct, generally valid unsteady-state heat balance corresponding to the mode of operation is used for their evaluation. In these cases, however, it becomes crucial that in the period of time shortly before and shortly after the calibration heater is in use no significant dynamic effects occur, as these times are used to determine initial and final state of the system. The course of a typical experiment including the calibration phases is shown in Figure 4-68.

Most of today's commercially available reaction calorimeters have an automatic registration of inputs of reactants and auxiliary materials, which is used to correct the wetted heat transfer area for these changes. This way specific data couples of heat transfer area and coefficient are stored for each calibration. If the heat transfer coefficient does not change too strongly between two calibrations, its value may be interpolated by linear regression. In the case of more severe changes either more calibrations must be performed or the interpolation model has to be changed in such way that the proportionality of this change in heat transfer coefficient and conversion or any other relevant property, such as density or viscosity, is used for the calculation between the boundary values.

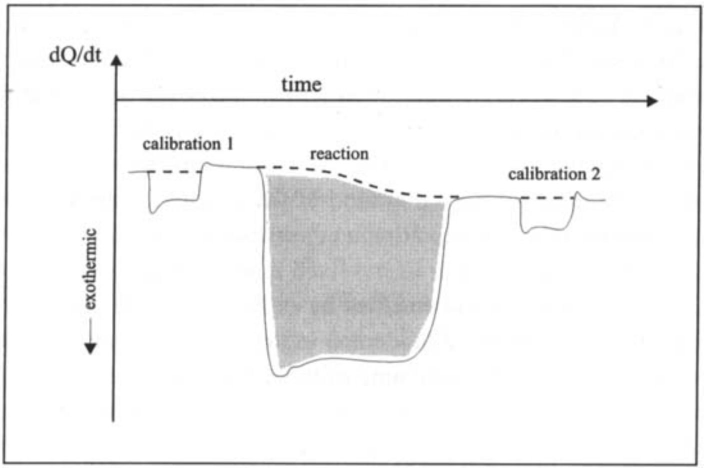


Fig. 4-68. Presentation of a typical result of an isothermally performed reaction calorimetric experiment

Nonetheless, exactly this fact that deficiencies in the modelling of strongly varying products of heat transfer area and coefficient may lead to intolerable errors in the determination of the reaction power and the heat of reaction has to be regarded as the main weakness of this technique. Under circumstances where such strong changes occur, this calorimetric principle is not recommendable, unless a great amount of experience in calorimetric measuring is available.

Another frequently occurring problem can be seen quite clearly in Figure 4-68. The levels of the power signals before and after the reaction are often not identical. This makes the definition of a correct baseline very difficult. But exactly this correctness is vital for the determination of the true value for the heat of reaction. A course of the baseline iteratively determined and proportional to the increasing thermal conversion has often proved suitable in such cases.

The main advantage of this calorimetric principle lies in the frequently large driving temperature difference between internal and mean jacket temperature. For example: in a semibatch reaction with an adiabatic temperature increase of ΔT_{ad} = 120 K, which releases 85% of its total heat output within four hours and which is performed with a batch size of 1,8 liters in a jacketed glass vessel, the average driving temperature difference amounts to five Kelvin. This temperature difference roughly corresponds to a power output of 15 W/kg. Modern Pt-100 resistance thermo-sensors combined with their converters allow a resolution of this temperature difference down to 1/10 Kelvin relatively easy. This corresponds to a power output of approximately 0,3 W/kg. This sensitivity confirms that reaction calorimeters with this specification may be regarded as sophisticated devices for safety technical investigations.

The third calorimetric method is called ***heat balance calorimetry***. This is actually not a very well chosen name, because the evaluation of measurements according to the previously described calorimetric methods are based on the heat balance in absolutely the same way as this method is. However, this name has established itself world-wide.

This calorimetric principle makes use of the fact that the heat produced by the process must be equivalent to the heat accumulation in the coolant circulating in the jacket in order to ensure a constant internal temperature.

$$\dot{Q}_C = -\dot{m}_C \cdot c_{PC} \cdot \left(T_{C,out} - T_{C,in}\right) \tag{4-226}$$

In this case also, the heat flow measured must be corrected for convective heat removal due to a feed process and conductive heat losses from the cooling jacket to the environment.

$$\begin{aligned} \dot{Q}_{chem.} &= -\left(\dot{Q}_C + \dot{Q}_{conv.} + \dot{Q}_{env.}\right) \\ &= -\dot{Q}_C + \dot{m}_D \cdot c_{PD} \cdot (T_R - T_D) - \dot{Q}_{env.} \end{aligned} \tag{4-227}$$

The great advantage of this kind of evaluation of the heat balance is its complete independence of changes of the physicochemical properties of the reaction mixture. Consequently it is preferred for reaction systems for which this kind of changes in properties is known or to be expected. Especially polymerization reactions belong to this group. At the same time this calorimetric principle is independent of the product of heat transfer area and coefficient.

However, also this calorimetric principle is not without weaknesses. Equ.(4-226) shows that the exact knowledge of the coolant mass flow is pivotal to the overall accuracy of the measurement. Today's commercially available calorimeters are equipped with pumps for the coolant like those known in type from thermostats. They are not able to provide a fully constant mass flow rate, especially not if the experiment lasts several hours. Furthermore, the preinstalled mass flow meters usually are rotameters of quite a simple type.

On the other hand, the calibration presumes a constant value for the product of coolant mass flow and specific heat capacity. The purpose of the calibration this time is twofold. For one, the proportionality of the difference in temperature between coolant inlet and outlet and the power input shall be calibrated. This way, $\dot{m}_C\ c_{P,C}$ becomes a calibration constant. Practice has shown, however, that this procedure allows an evaluation of the power output of the investigated process only to a limited extent of validity. It is much more recommendable to install a precision mass flowmeter in the coolant circuit, which allows the continuous registration of the measured signal throughout the experiment. This way this pivotal information becomes available for the complete evaluation of the experiment including the calibration phases.

The second task of the calibration is the determination of an offset to compensate for heat losses of the system to the environment.

Another critical point about this method is the absolute value of the coolant mass flow rate. It must be high enough to ensure a sufficient cooling capacity within the jacket in order to avoid an increase of the internal temperature due to the heat of reaction released and this way to maintain isothermal measuring conditions. This high mass flow rate at the same means a comparatively small residence time of the coolant in the jacket and this way a very small temperature difference between inlet and outlet coolant temperature. This may lead to technical measurement problems. This shall be explained with the help of an example.

When discussing the sensitivity of heat flow calorimetry a representative example was chosen of a reaction releasing 27 W/batch on average when performed in a 2 liters glass vessel. A frequently found value for the coolant mass flow rate of a heat balance calorimeter amounts to 70 l/hour. Assuming a specific heat capacity of the coolant of 2600 J/kg K, this reaction power is transferred into a temperature difference between coolant inlet and outlet of 0,54 K. If the heat balance calorimeter and the heat flow calorimeter are to be of equal sensitivity, it follows that a resolution down to 1/100 K is required for the temperature difference.

If isothermal experiments are to be used for the safety assessment of a process, a number of points should be observed. In general, a safety assessment should never be based on a single measurement, provided enough input sample material is available. An evaluation of the sensitivity to small variations in the quality of the input material can only be performed if the experiment is repeated at least once, better more often, without any changes to the recipe or any other variable parameters. In addition to these runs, experiments should be performed at temperature levels 10 to 20 K higher than the scheduled reaction temperature, because without these measurements a possibly different reaction behaviour caused by increasingly occurring simultaneous reactions will remain undetected. Such effects, however, may easily be observed on plant scale, as the controls implemented in calorimetric devices are often of higher quality than those in production units, resulting in deviations from the ideal isothermal reactor behaviour in plant operation.

Isoperibolic Calorimetry

The isoperibolic mode of operation can technically be carried out much more easily, because in this case exclusively the jacket temperature has to be maintained constant with the help of controls. Furthermore, significant temperature differences between coolant in- and outlet must be avoided. In technical terms, this last requirement calls for high coolant mass flow rates in the jacket and a thermostat with a high capacity, which can be realized more easily the greater the coolant reservoir is designed.

The only evaluation method in this case is the *heat flow calorimetry*, which already has been explained.

$$\dot{Q}_{\text{cond.}} = -U \cdot A \cdot \left(T_R - \overline{T}_C\right) \tag{4-223}$$

The great advantage of this kind of calorimetry lies in the opportunity to detect simultaneous reactions and their hazard potential for plant operation very easily. Temperature dependent changes in the mechanism of a reaction process, as they frequently occur with heterogeneous systems, are easy to identify in most cases.

But the fact that the calorimetric experiment should be performed as close as possible to the actual plant conditions is of much greater importance. If the process shall be performed isoperibolically on plant scale, then the safety investigation should apply an identical mode of operation. If effects are observed, such as strong changes in the physicochemical properties of the reaction mixture, it has to be recognized that these effects can be observed very well *qualitatively*. *Quantitative* interpretation, however, requires extensive experience and is possible with certain reservations only. In such cases it turns out to be helpful to perform an isoperibolic experiment and several additional isothermal measurements spread over the temperature range covered by the reaction temperature in the isoperibolic run. Those isothermal runs may be conducted either according to the balance or to the compensation principle. A very careful and detailed evaluation of the isothermal experiments often allows a good quantitative differentiation of several effects contributing to the isoperibolic experimental result.

Reflux Calorimetry

Reflux calorimetry represents a very complex form of reaction calorimetry. This is partly due to the way these experiments are performed, partly a consequence of the physicochemical properties of the investigated reaction system and to some extent a question of the measuring devices used.

At least two different modes of operation can be discriminated:

- measurements under quasi-steady-state reflux conditions
- measurements with reflux conditions reached dynamically, either by making use of the self-acceleration of the reaction system or by applying external heating, and then steadily maintained.

In the first case a solvent and possibly one reactant are charged to the vessel initially at a temperature well below the boiling point. In a next step the reactor content is heated up until boiling conditions are reached. A steady state is then established by setting a fixed temperature difference between jacket and boiling temperature. After a calibration phase the reaction is started by the addition of one or both reactants. The fixing of the overheating with the help of a suitable control causes all heat produced by the chemical reaction to be transferred to an intensified evaporation power. This is propagated to a higher condensation power in the reflux condenser connected to the vessel. This can finally be measured in the form of an increased temperature difference between inlet and outlet of the coolant of the condenser. The run is completed by a final calibration phase. With the help of these two calibration phases it is possible to evaluate the measurement by calculating the reaction power from this increased temperature difference between coolant inlet and outlet of the reflux condenser.

In the second case the reaction is performed below the boiling point initially. The jacket temperature is either controlled to follow the increasing temperature of the reaction mixture, which is caused by the exothermicity of the process, or is distinctly increased at a fixed heating rate. In both cases the boiling point will be reached eventually and the remaining heat of reaction is released and transferred into heat of evaporation. Calibration phases are of very limited use in this case as they are performed under steady-state conditions and hardly provide any information for the transition range before boiling. In general, quantitative evaluation of the measurements anyhow remains restricted to those cases which were obtained from runs with well defined heating ramps. For such trials it is more recommendable to repeat the heating up process with the final product mixture in order to obtain a baseline for both the change in internal temperature and in the temperature difference at the condenser. The difference between the temperature profiles obtained from the reaction experiment and the post-reaction run with the product mixture can then be attributed to the chemical heat release. But this kind of experiments and their evaluation requires extensive practical experience.

Independent of the mode chosen for the investigation of a reaction under reflux conditions, as mentioned, other facts may add to the difficulties which are caused either by changing physicochemical properties of the reaction mixture or by the device used.

It is known from thermodynamics that the boiling point at constant pressure depends on the purity of the more volatile component. The majority of chemical reactions under reflux conditions are performed in a solvent for the reactants. Due to the change in composition of the reaction mixture, changes in the boiling temperature may be observed. In the case of irreversible reactions, this change in composition will occur until the limiting component has been consumed or until the equilibrium conversion has been reached. This fact usually results in differing calibration factors determined before and after the chemical process. An interpolation which iteratively takes into account the increasing conversion should be preferred in comparison to a simple linear calculation.

A great error can be made in the evaluation of the calorimetric heat balance if one reaction product turns out to be a permanent gas and if this is not accounted for correctly. Such gases irreversibly withdraw heat from the system.

Severe sources of error originating from the design of the device can be heat losses through the reactor lid and badly insulated connecting tubes to and from the reflux condenser. Great care should be taken regarding these possible deficiencies.

All these effects have been investigated in great detail by Nolan and Nomen [65,66]. The work of the two scientists provides numerous alternatives for the solution of these problems and gives extensive reference to further primary literature of relevance.

General Remark In Respect To Reaction Calorimetry

In the last few paragraphs the describing adjectives were selected with care: *suitable, reliable*, but never *correct, exact* or *true*. The reaction calorimetry as applied in safety engineering must not be mistaken for the classical calorimetry known from physical chemistry. Most of the measurements are conducted with comparably highly concentrated solutions and consciously using material directly obtained from the plant or development laboratory. Many theoretical approaches of physical chemistry, however, are valid only if the experiments are conducted in very diluted systems. Especially the heat of reaction, which, as has already been mentioned several times, must be looked upon as a gross value in those safety related experiments, is a property extremely sensitive to the presence of impurities or similar influences.

The presentation of a heat of reaction, measured with one of the methods described here, accurate to the tenth part of a Joule is the presentation of a virtual accuracy only. An expectation with respect to reproducibility of less than 5% difference in reaction enthalpy values determined expresses an unrealistic demand on the presented techniques.

4.3.3.3 Thermokinetic Evaluation of Reaction Calorimetric Measurements

Before the procedure for the evaluation of reaction calorimetric measurements regarding thermokinetics is explained, some fundamental remarks have to be made. Thermokinetic data can be of tremendous value if certain boundary conditions are observed closely for their determination and their use. On the other hand, they can be dangerously misleading if these boundary conditions are ignored. Therefore, the observance of the following fundamental rules, which have been compiled by Hugo and which are presented here in a short form, is essential [67]:

- *A reasonable thermokinetic evaluation is possible only if it has been ensured with the help of other techniques that reactions running parallel to the desired one are of absolutely minor importance only.* In practical terms this requirements means that it has to be ensured with the aid of e.g. classical analytical methods that within the evaluated interval the process of interest can be described in terms of a mass balance with sufficient accuracy with a single gross conversion equation.
- *Processes which take place within homogeneous liquids phases process are the preferred reaction systems for thermokinetic descriptions.* In heterogeneous systems, which can be modelled with the help of macrokinetic formal rate laws, thermokinetic evaluation is possible, too, but only if additional information on the properties of the two phases is obtained in parallel.
- *It is fundamental to have at least two, if possible three or more, measurements available which must differ in their initial temperature in order to be able to perform a reasonable thermokinetic evaluation.* This demand can be justified by the fact that the measuring result of interest, the thermal reaction power, contains all thermokinetic parameters in combination. The mathematical rules of algebra call for at least n linear independent equations if n unknowns are to be determined. Even if the experimental runs have all been started with different initial temperatures, the resulting heat production rate curves, thinking in a certain analogy, remain „linearly dependent“. The determination of thermokinetic parameters remains a statistical adjustment to a model, which results in very good agreement of measurement and model prediction. Other parameter combinations may solve the problem equally adequately, as long as the values are not physicochemically meaningless. However, the confidence interval for each individual thermokinetic parameter is significantly improved if several measurements with different initial temperatures are evaluated.

- *An extrapolation of the operating behaviour to process conditions which are outside the range covered by the measurements used to determine the thermokinetic parameters is not permitted.* Naturally, the results obtained may be used for process simulation and in this sense to get estimates on quite different operating behaviour. But if critical states regarding plant safety, which demand special protective concepts, are identified this way, then the thermokinetic model should be validated for these conditions by additional experiments before it is used for the design of such systems. This rule should especially be observed if changes in the substance input ratios are considered.

The result of a calorimetric experiment at least consists of data for the experimental time, the internal temperature and the power signal. The first step in the evaluation is the determination of the total heat output either per mole of limiting component or per kg batch. This is determined by the integration of the power signal over the experimental time. It has to be emphasized that only the integral from the start of reaction to the point of full conversion corresponds to this total heat release. The point in time at which this total conversion is achieved, however, can only be determined with the help of additional, e.g. analytical methods. The same is true for any other conversion value which corresponds to the time chosen for the upper integration limit. The importance of this shall be demonstrated. Figures 4-69 and 4-70 show simulations of three isoperibolic batch experiments. The reaction enthalpy for this example was chosen to be $\Delta_R H$ = -80 kJ/mol. The time axis of the power signal plot has been reduced with respect to the individual experimental time of each run.

The experimental time was obviously sufficiently long that for the heat generation to have come to an end towards the end of the simulated experiment. A reliable indicator for having achieved full conversion?

The simple integration of the measured power curves without having additional information at hand yields the following values for the gross total heat release:

	$T_{initial}$ = 288 K	$T_{initial}$ = 280 K	$T_{initial}$ = 273 K
$\Delta_R H$ [kJ/mol]	-67	-50	-44

The value used for the simulation amounted to $\Delta_R H$ = -80 kJ/mol. In the experiment exhibiting the slowest reaction rate, the underdetermination is close to 50%. This error cannot be tolerated any more.

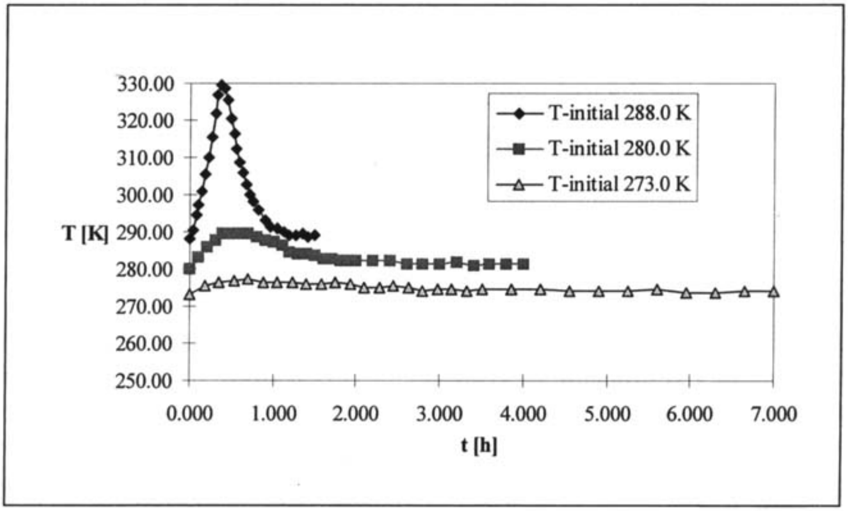


Fig. 4-69. Simulated temperature profiles of three isoperibolic calorimetric batch runs

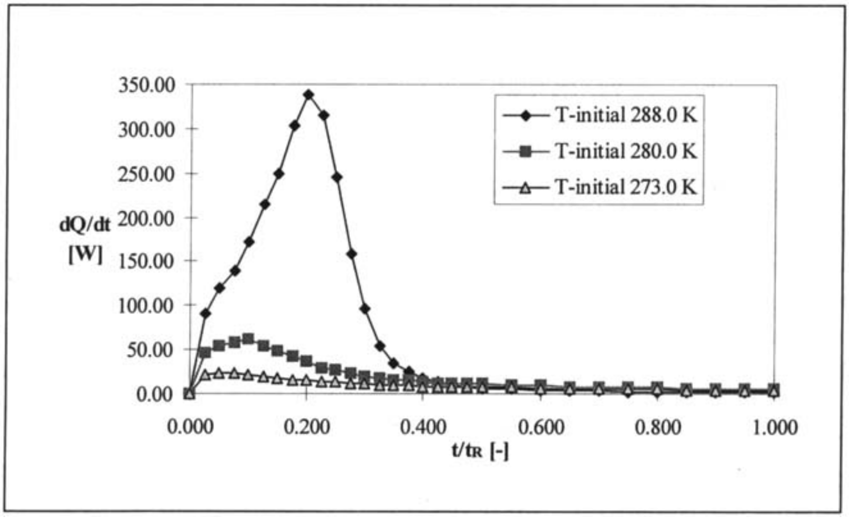


Fig. 4-70. Reaction power signals calculated from the simulated isoperibolic calorimetric batch runs

The difference in the values obtained is much greater than 5%. This is an indicator that the evaluation is erroneous . The conversion at the end of the experimental run has by no means been complete. It shall now be assumed that with the help of classical analytical methods the conversion at the end of each run has been determined:

	$T_{initial} = 288$ K	$T_{initial} = 280$ K	$T_{initial} = 273$ K
X_{end}	0.83	0.64	0.57

With this additional information the following gross heats of reaction are obtained:

	$T_{initial} = 288$ K	$T_{initial} = 280$ K	$T_{initial} = 273$ K
$\Delta_R H$ [kJ/mol]	-80	-78	-77

or on average:

$$\Delta_R H = -78(,3) \text{ kJ/mol}$$

The mean deviation of the single results from the average is equal to 1,4% and the deviation of this average from the true value amounts to -2,1%, a very good result.

The task of the next step is the calculation of the thermal conversion for each of the experiments with the help of Equ.(4-220), which has already been introduced.

$$X = \frac{\int_0^t \dot{Q}_{chem,gross} \cdot dt}{\int_0^{t(X_P=1)} \dot{Q}_{chem,gross} \cdot dt} \tag{4-220}$$

The result is shown graphically in Figure 4-71.

At this point the true kinetic evaluation begins. It is important always to have in mind that at least three parameters have to be adjusted based on rather limited information:

- the activation temperature E/R
- the pre-exponential factor k_∞, or more advantageously, $Da_\infty = -\nu_A \cdot r_{0,\infty} \cdot t_{charact.} / c_{A0}$
- the reaction order n

and in the case of more complex formal kinetic systems even more parameters. The determination of kinetic parameters from thermoanalytical measurements has been in the focus of research for several decades now. Probably the best-known methods were developed by Borchardt and Daniels, Freeman and Caroll, and Coats and Redfern [68,69,70]. In this context, however, a method shall be presented which has been developed only recently. The method has advantages over the older ones for several reasons. *UVTHERK*, universal evaluation of thermokinetic measurements, was developed theoretically and was experimentally validated in the years 1990 to 1995 by Hugo, Gnewikow, Wagner and Leonhardt, and is now available as a PC based software [71,72,73].

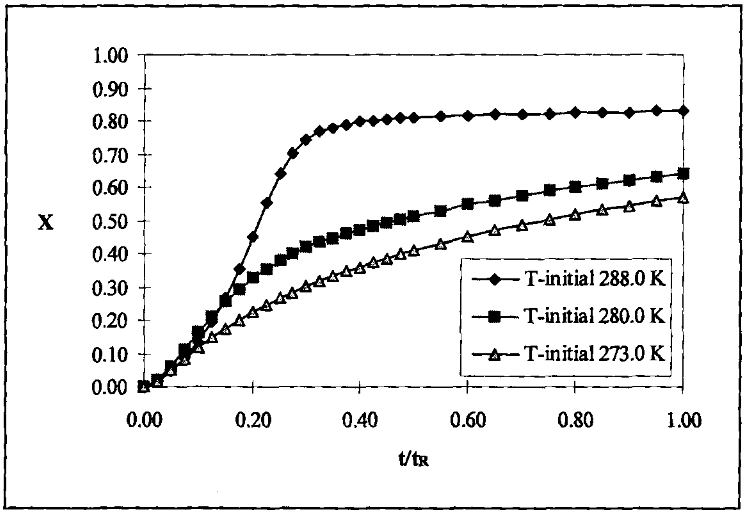


Fig. 4-71. Thermokinetic conversion profiles calculated from the power signals of the simulated isoperibolic calorimetric batch experiments

The superiority of the method results from

- the consequent application of the concept of formal kinetics
- the requirement that it is applicable only if several measurements with different initial temperature are available
- the ability to use results simultaneously in the same evaluation which have been gathered from different measuring techniques, such as DSC or reaction calorimetry, as well as different modes like isothermal, adiabatic or isoperibolic operation.

The evaluation has its basis in the individual mass balance, which is the mass balance of the batch reactor for the example currently considered,

$$\frac{dX}{dt} = \frac{-v_A}{c_{A0}} \cdot r(X,T) \qquad (4\text{-}228)$$

and the formal kinetic description of the reaction rate, which allows the split into one conversion and one temperature dependent term (see also Sec. 4.1).

$$r(X,T) = r_{0,Tref} \cdot \exp\left[\frac{E}{R} \cdot \left(\frac{1}{T_{ref}} - \frac{1}{T}\right)\right] \cdot \Phi(X) \qquad (4\text{-}229)$$

In this equation, T_{ref} is a reference temperature which should be chosen in such a way that it is representative for the temperature range covered by the measurements.

The pivotal step,

- which allows for the simultaneous evaluation of several measurements from different measuring modes and methods as well as initial temperature conditions,
- and only this way enables the fulfillment of the most important requirement regarding the applicability of thermokinetics, namely the use of more than one measurement with different initial temperatures,

is the introduction of an equivalent isothermal reaction time h(t).

$$h(t) = \int_0^t \exp\left[\frac{E}{R} \cdot \left(\frac{1}{T_{ref}} - \frac{1}{T}\right)\right] \cdot dt \qquad (4\text{-}230)$$

In the case of an isothermal mode of operation for a measurement and provided that the reference temperature is identical with the isothermal test temperature, this equivalent reaction time automatically becomes identical with the true reaction time. In the case of a none-isothermal mode of operation or the choice of a reference temperature which does not correspond to an isothermal test temperature, all thermal conversion data X(t) are plotted over h(t). In order to obtain the different h(t) data, a first estimation of the activation temperature has to be made. If the activation temperature was correctly chosen and if, at the same time, the process can be described with a single gross reaction equation with sufficient accuracy, then all the different data sets plotted over h(t) must take an identical course. The first estimate on the activation temperature can be obtained from the slope of the linearized functional relationship

$$\ln\left(\frac{dX}{dt}\right)\bigg|_{X=0.5} = \ln\left(\frac{(-\nu_A) \cdot r_{0,\infty}}{c_{A0}} \cdot \Phi(X)\big|_{X=0.5}\right) - \frac{E}{R} \cdot \frac{1}{T}\bigg|_{X=0.5} \qquad (4\text{-}231)$$

by selecting data from different experiments for a constant thermal conversion, in this example 50%, which are evaluated with the help of a linear regression algorithm. For the example considered here the first estimate for the activation temperature amounts to E/R = 6940 K. Figure 4-72 shows the resulting plot of the different X(t) data over the calculated h(t) data.

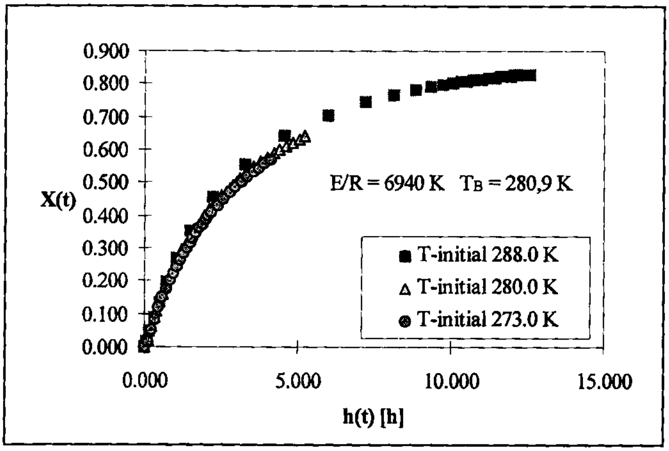


Fig. 4-72. Result of the transformation of the three simulated isoperibolic batch experiments to equivalent isothermal runs at a reference temperature of 280.9 K

- 1st estimate -

The curves are already very close together, but they are not yet completely congruent. In order to develop a feeling for the quality of this first estimate on the activation temperature, it is best to repeat the calculation arbitrarily with a significantly wrong value for E/R. Just for clarification purposes this has been done with a value of E/R = 5500 K. The result is shown in Figure 4-73. The curves differ in a dramatic way from each other.

In a next step the result obtained with the help of the first estimate on E/R is optimized by trial and error. The assessment of the degree of congruence achieved can either be performed with optical control or with the help of statistical methods which are used to characterize variability. For this example, the highest degree of congruence of the curves obtained from the transformation to equivalent isothermal experiments was reached with a value of E/R = 7300 K (c.f. Figure 4-74).

This kind of experimental evaluation automatically yields very reliable estimates on the thermokinetic parameter E/R, because, simply said, the value obtained describes quite differing individual experiments with equal quality. Quite consciously the input value for the simulation has not been mentioned thus far.

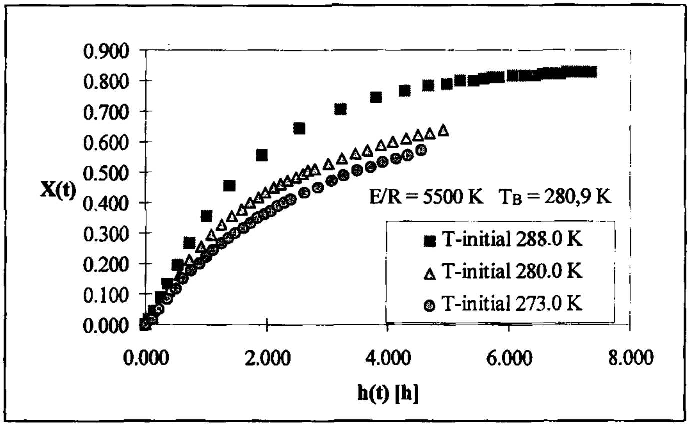


Fig. 4-73. Result of the transformation of the three simulated isoperibolic batch experiments to equivalent isothermal runs at a reference temperature of 280.9 K

- arbitrarily wrongly chosen value for E/R -

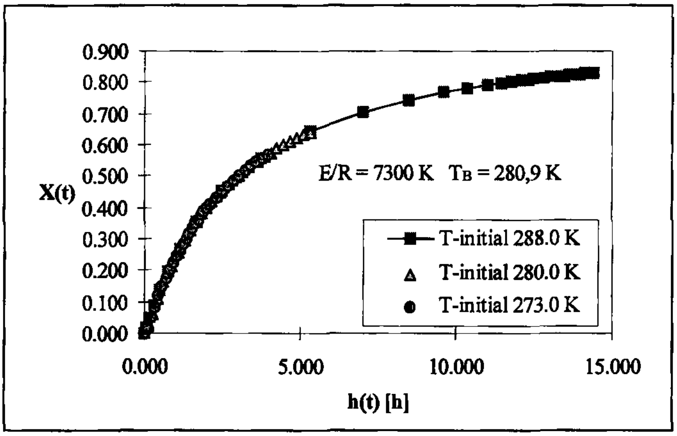


Fig. 4-74. Result of the transformation of the three simulated isoperibolic batch experiments to equivalent isothermal runs at a reference temperature of 280.9 K

- optimized E/R value -

Today's data collection methods allow the registration of a great number of data and this simultaneously with a high time density. In consequence, numerical differentiation of a progressing value described by numerous discrete data points can be performed without making significant errors. Such a differentiation of the congruent X(h) curves of all three experiments with respect to the equivalent isothermal reaction time yields dX/dh. If Equ.(4-228) to (4-230) are combined in a suitable way, it can be deduced that the following relationship is valid.

$$\frac{dX}{dh} = \frac{(-\nu_A) \cdot r_{0,ref}}{c_{A0}} \cdot \Phi(X) \qquad (4\text{-}232)$$

At the time t = 0 it is known for the batch reactor that the dimensionless reaction rate $\Phi(X)$ exactly takes the value of one. If the curve of dX/dh over h(t), which has just been obtained with the help of the previous calculation, is now numerically fitted to a spline function of the first or second order, then the initial gradient dX/dh at h(t) = 0 can be determined by extrapolation. This initial gradient exactly corresponds to:

$$\left.\frac{dX}{dh}\right|_{h(t)=0} = \frac{(-\nu_A) \cdot r_{0,ref}}{c_{A0}} \qquad (4\text{-}233)$$

With the help of the previously determined activation temperature, k_∞ or Da_∞ can be calculated very easily. Following this procedure, one obtains for the discussed example:

$$Da_\infty(t_R = 1 \text{ hour}) = 6.49 \cdot 10^{10}$$

Another very important advantage of this evaluation method becomes obvious now. Already two parameters have been determined without any necessity to make a statement about the reaction order n or any other mechanistic assumption.

By applying Equ. 4-232 and using the parameters identified so far, all discrete values of the dimensionless reaction rate $\Phi(X)$ can be calculated for each individual conversion data point. In a last step the data set couples $\Phi(X)$ and X have to be fitted to a formal kinetic rate law. It is recommendable to begin this fitting procedure with the most simple model, the power law, first.

$$\Phi(X) = (1 - X)^n$$

If the fit cannot be achieved in a satisfactory form, the other models, which have been introduced in Sect. 4.1.2, should be tested with increasing complexity. In the worst case, spline models can be used, which, however, have no physicochemical meaning anymore.

In this example a fit to the power rate law is successful. The quality can be seen in Figure 4-75.

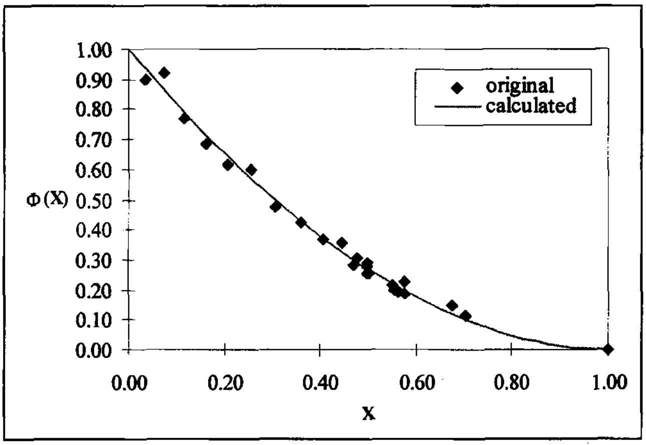


Fig. 4-75. Fit of the dimensionless rate data transformed into isothermal equivalence data to a power rate model
- n = 1.9 -

Table 4-8 provides a comparison of the kinetic put into data to the simulation with those obtained from the evaluation according to the UVTHERK procedure. In order to receive a more realistic situation from the simulation, a noise of (-1...+1) * 0.5 K generated with the help of a random number generator was superimposed on the theoretically calculated temperature signals.

Table 4-8: Comparison of the kinetic parameters used and obtained in the calorimetric example

	E/R [K]	Da_∞ (t_R = 1 hour)	N
input	7500	$1.31 \cdot 10^{11}$	2
determined	7300	$6.49 \cdot 10^{10}$	1.9
Δ%	-2.67	-50.5	-5

The deviation in the pre-exponential factor, represented here by the Damkoehler number Da_∞, seems to be quite severe. But this is a superficial judgement only. For numbers of this magnitude, deviations in percentages are always very large although the realistic assessment comes up with moderate differences. It becomes easier to evaluate the quality of the data determined, if they are used in a new simulation and if this result is compared with the original simulation. This is presented in Figures 4-76 to 4-78.

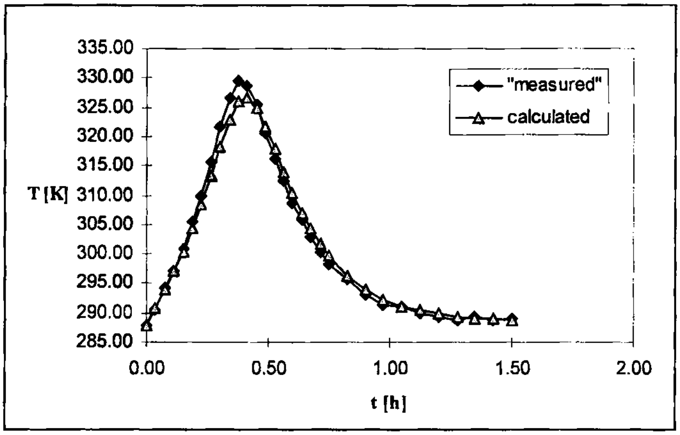


Fig. 4-76. Comparison of the simulated measurement and of the simulated profile obtained with the thermokinetically determined parameters
T-initial = 288 K

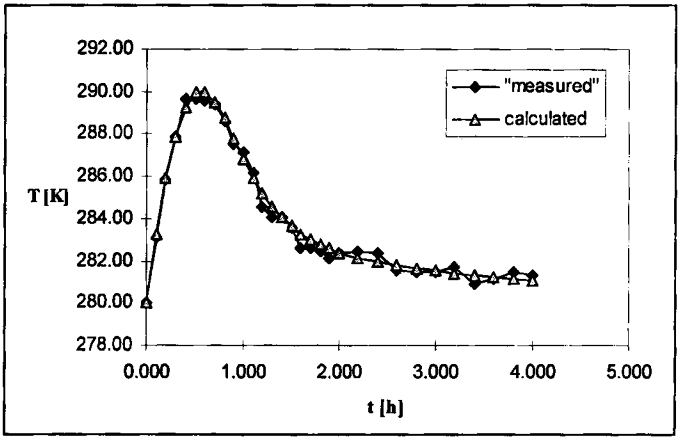


Fig. 4-77. Comparison of the simulated measurement and of the simulated profile obtained with the thermokinetically determined parameters
T-initial = 280 K

This demonstrates convincingly how well the measurements can be reproduced with the adjusted parameters. At the same time, however, it becomes obvious again that the characteristic numbers determined here remain adjustment parameters of an algebraically underdetermined system, of which several combinations can describe the system with comparable quality due to compensating effects. This becomes particularly clear upon looking at the reaction order, which, with a value of 1.9, has no physicochemical meaning any more, but at the same time compensates all other differences with its deviation from the exact input value of 2. The evaluation becomes more significant the more the individual measurements differ from each other.

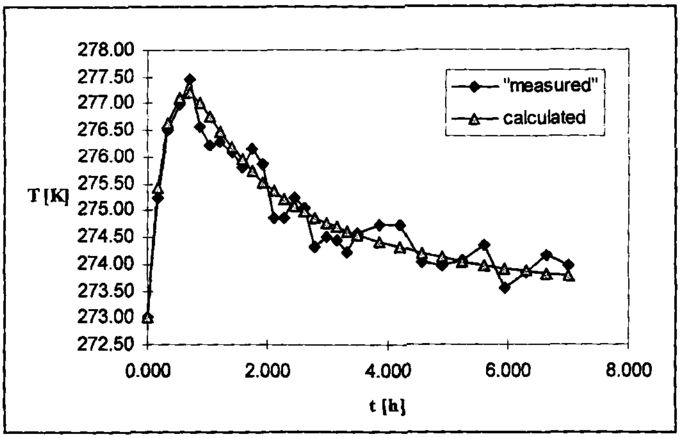


Abb. 4-78. Comparison of the simulated measurement and of the simulated profile obtained with the thermokinetically determined parameters
T-initial = 273 K

4.4 Investigation And Assessment Of Upset Operating Conditions

4.4.1 The Safety Technical Assessment Of The Process Design For Upset Operating Conditions

The systematic analysis of possibly occurring maloperations and process deviations as well as the assessment of their consequences is quite a demanding task, which must be solved in process safety engineering. The problem arises because of the close to infinite multitude of possible influences exerted on the process, either by technical or human procedures. The problem loses all objectivity when it comes to discussing the question of the number of simultaneously occurring errors or erroneous handlings. The systematic methods of identification used in most cases today including their advantages and disadvantages will be presented in detail in Chapter 6.

Plant technological safety concepts, which means measures taken in consequence of the above-mentioned analysis in order to prevent damage to human beings and the environment, will be discussed in form of selected examples in Chapter 7.

At this point only one selected question shall be considered more closely, which is the adequacy of thermal design of the chemical process in response to process deviations. In order to clarify the restriction made an example shall help. A chemical manufacturing process is strongly exothermic, uses a highly flammable solvent and is further characterized by the formation of a highly corrosive permanent gas as a side product. The complete Chapter 4 deals with the chemical reaction and its plant technical conduction. Following this line the discussion remains limited to the safety assessment of deviations which have an influence on the thermal and kinetic process behaviour. A malfunction of the inertization of the vessel, which as a potential hazard may cause the formation of an explosible atmosphere due to the use of a flammable solvent, or the malfunction of a waste gas scrubber, which may cause the undesirable release of the highly corrosive gas to plant areas not intended for such an exposure, are not going to be discussed here.

In positive terms, this restriction means that recommendations shall be provided for the assessment of deviations which influence either the chemically generated thermal reaction power or the plant specific cooling capacity installed. A simplification of this problem results from the fact that the effects of such deviations on factors determining both powers mentioned act in the same direction. The following Table 4-9 shall give proof to this statement by providing some selected examples.

This very general assessment does not consider the loss of a batch when rating an effect „harmless“. However, an operating temperature at too low a level due to the disturbance or another change in recipe will cause the production of a batch out of specification. In the same way, a rating „dangerous“ does not consider the degree of hazard of the possible consequences. It is much more the aim of this table to demonstrate that almost all conceivable „dangerous“ disturbances will have an effect on both powers determining the thermal reactor behaviour, which causes the internal temperature and possibly the pressure to rise.

Table 4-9: Selected deviations influencing reaction and cooling power and their consequences

Selected deviations influencing the thermal reaction power

Disturbed or influenced value	Kind of influence	Effect	Consequence	Assessment
concentration of educts	higher	$\dot{Q}_{chem.}$ rises	T and poss. p rise	dangerous
	lower	$\dot{Q}_{chem.}$ drops	T and poss. p drop	harmless
concentration of catalyst	higher	$\dot{Q}_{chem.}$ rises	T and poss. p rise	dangerous
	lower	$\dot{Q}_{chem.}$ drops	T and poss. p drop	harmless
mix-up of substances	more reactive	$\dot{Q}_{chem.}$ rises	T and poss. p rise	dangerous
	more inert	$\dot{Q}_{chem.}$ drops	T and poss. p drop	harmless
mass flows	faster	a) $\dot{Q}_{chem.}$ rises at once	T and poss. p rise	dangerous
		b) $\dot{Q}_{chem.}$ remains equal at first, but rises later	T and poss. p rise	dangerous
	slower	$\dot{Q}_{chem.}$ drops	T and poss. p drop	harmless
internal temperature (if controlled)	higher	$\dot{Q}_{chem.}$ rises	T and poss. p rise	dangerous
	lower	$\dot{Q}_{chem.}$ drops	T and poss. p drop	harmless

Selected deviations influencing the cooling power

Disturbed or influenced value	Kind of influence	Effect	Consequence	Assessment
circulating or conveying pump	more	$\dot{Q}_C$ rises $\dot{Q}_{chem.}$ drops	T and poss. p drop	harmless
	less	$\dot{Q}_C$ drops $\dot{Q}_{chem.}$ rises	T and poss. p rise	dangerous
stirrer	on	Undisturbed		
	off	$\dot{Q}_C$ drops $\dot{Q}_{chem.}$ rises	T and poss. p rise	dangerous
coolant inlet temperature	higher	$\dot{Q}_C$ drops $\dot{Q}_{chem.}$ rises	T and poss. p rise	dangerous
	lower	$\dot{Q}_C$ rises $\dot{Q}_{chem.}$ drops	T and poss. p drop	harmless

The increase of the internal temperature has to be regarded as critical because temperature ranges could be reached at which secondary reactions could become perceptible up to a dangerous extent. Such secondary reactions are often combined with a strong gas generation. In parallel, the vapour pressure of the volatile compounds will rise. Alone or in combination, these effects may cause an intolerable pressure rise even in so-called open systems. If the vessel is not suitably protected against overpressure, it may rupture, initiating a variety of possible further effects.

The aim of the safety technical assessment of the thermal design with respect to its response to possible maloperation is

- to determine and evaluate the maximum internal temperature which can be reached due to a disturbance; this corresponds to the MTSR defined in Section 2.3
- to determine and evaluate the time available for corrective action before any undesirable effects occur
- to determine alarm levels, respectively to check them
- either to determine counter-measures or to evaluate them regarding their efficiency
- to determine data for the design of safety installations, such as bursting disks or emergency relief valves

Independent of the mode of reactor operation it is of tremendous importance to stop any further addition of fresh reactants to the system, once a maloperation has occurred. This should be ensured technically, whenever possible. In elderly plants, organizational measures can be sufficient, provided they are of very good quality. The interruption in supplies ensures that the hazard potential related to the maloperation remains restricted to the substance amount present in the reactor at the time of process disturbance. All further elaborations assume this effective interruption in supplies.

The safety technical assessment of continuous CSTR processes and discontinuous processes performed in batch or semibatch reactors is of special importance. In the case of reactions conducted in tube reactors the amount of substance is comparatively smaller. On the other hand, reactions performed in such tube reactors are often very complex catalytic equilibrium processes, which need an individual evaluation for an adequate safety assessment. Generalizations are hardly possible.

The cooling failure shall be taken as a representative example for the numerous possible maloperations with an influence on the thermal stability of the process. For the moment, the cause of this failure remains more or less unimportant. A breakdown of the coolant supply pump and a stirrer defect have comparable effects. In consequence the reactor behaviour will be close to adiabatic, which means that there will be no heat removal from the system to the environment anymore.

At the moment at which the disturbance occurs, the reactor is characterized by the operating temperature T_P and the current accumulation potential Y, which has been defined in its general form in Section 4.3.3.1. With the help of this information and the adiabatic temperature increase of the desired reaction, the MTSR can be calculated directly

$$\mathrm{MTSR} = T_P + \Delta T_{ad} \cdot Y \tag{4-234}$$

It is recommendable in general that the MTSR should be as low as possible, because if higher values are reached the risk of triggering decomposition reactions increases. But Equ.(4-234) also shows that this requirement cannot easily be fulfilled. The MTSR takes low values if either the desired process temperature is low itself or the accumulation potential at the time of maloperation is small. The accumulation potential, however, depends on the extent of reaction just achieved and on the mode of operation. If the process temperature is chosen very low, then the achievable conversion is also small and the accumulation potential will be very high. This indicates an optimization problem.

A closer examination has shown that this optimization potential is not available to all processes [74]. The boundary condition which predicts the availability of an optimal design is obtained from the condition for the MTSR to take a minimum value.

$$\frac{d\,\mathrm{MTSR}}{dT_P} = 1 + \Delta T_{ad} \cdot \frac{dY}{dT_P} = 0 \tag{4-235}$$

This equation can be rearranged with the help of the equation defining the degree of accumulation, Equ.(4-221):

$$\frac{d\,\mathrm{MTSR}}{dT_P} = 1 - \Delta T_{ad} \cdot \frac{dX}{dT_P} = 0 \tag{4-236}$$

The conversion, as shown in Section 4.1.5, has a functional relation to the Damkoehler number which has a special form for each type of reactor and kinetic rate law. But in a general formulation the following is valid:

$$\frac{dX}{dT_P} = \frac{dX}{d\,\mathrm{Da}} \cdot \frac{d\,\mathrm{Da}}{dT_P} = \mathrm{Da} \cdot \frac{dX}{d\,\mathrm{Da}} \cdot \frac{d\ln(\mathrm{Da})}{dT_P} = \mathrm{Da} \cdot \frac{dX}{d\,\mathrm{Da}} \cdot \frac{E}{R \cdot T_P^2} \tag{4-237}$$

If this equation is substituted into the one describing the minimum condition, the following requirement with respect to the thermal reaction number is obtained. This must be fulfilled in order to have an optimization possibility regarding the lowest MTSR available.

$$B > \frac{1}{Da} \cdot \frac{d\,Da}{dX} \qquad (4\text{-}238)$$

In consequence, the task of a safety assessment of the process behaviour upset by a cooling failure may have two quite different forms:

- if changes in the manufacturing recipe are possible:
  check whether the process can be optimized in such a way that the MTSR takes the lowest value possible and that this value itself is uncritical

- if the manufacturing recipe must remain unchanged:
  check whether the expected MTSR has an uncritical value

The methodology to assess the second situation is independent of the type of reactor. Therefore it shall be treated first.

For this purpose the adiabatic induction time, which has been deduced in Section 4.2 and mathematically defined in Equ.(4-83), shall be used as an assessment criterion. Similarly to the procedure explained for the TMR, which is used for the interpretation of isothermal DTA results, a minimum time is also defined when evaluating maloperation scenarios, which must be available for corrective action to the disturbance. As in the case of the TMR, this minimum time should amount to 24 hours. This value may be adjusted in both directions based on a company specific justification. The methodology calls for the calculation of the temperature which corresponds to this response time and its comparison with the temperature expected to be reached in case of maloperation. The latter usually corresponds to the MTSR. It is now checked whether this temperature reached in case of a disturbance is higher than that corresponding to the minimum response time or not. In the special case that the temperature exactly corresponds to a 24 hour response time, it is called ADT24 (temperature, at which the adiabatic induction time to decomposition exactly amounts to 24 hours). The assessment criterion now says:

> *If the ADT24 or a value equivalent in its meaning is higher than the temperature expected to be reached in the case of process deviation, such a disturbance may be regarded as uncritical.*
>
> *If the ADT24 or a value equivalent in its meaning is lower than the temperature expected to be reached in the case of a process deviation, then this disturbance must be regarded as critical and incident preventing measures have to be defined.*

The other kind of assessment situation shall be presented specifically for each type of reactor.

4.4.1.1 Assessment Of The CSTR Under Upset Operating Conditions

When performing the safety assessment of a CSTR which has deviated from normal operating conditions due to a cooling failure, it may be assumed that the reactor was previously been operated in a steady state. This state is characterized by the desired set conversion X_S. For the CSTR the following is valid:

$$t = t_{\text{charact.}} = \tau \tag{4-239}$$

and consequently

$$Y = (1 - X_S) \tag{4-240}$$

For the CSTR, the MTSR can be calculated according to

$$\text{MTSR} = T_S + \Delta T_{ad} \cdot (1 - X_S) \tag{4-241}$$

The further procedure shall be explained for the sample case of a second-order reaction. For this case the steady state mass balance of the isothermal CSTR is equal to (see also Table 4-4 in Section 4.1.5):

$$\text{Da} = \frac{X_S}{(1 - X_S)^2} \tag{4-242}$$

Now Equ.(4-238) can be solved specifically for this case.

$$B > \frac{1 + X_S}{X_S \cdot (1 - X_S)} \tag{4-243}$$

This result is presented graphically in Figure 4-79.

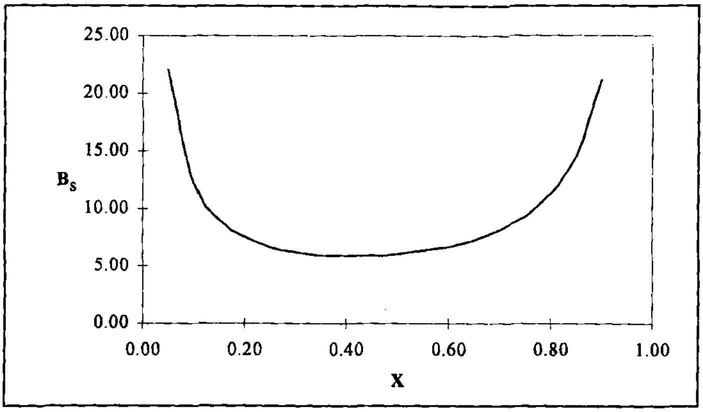


Fig. 4-79. CSTR-limit curve for second-order reactions with optimization potential regarding the MSTR

For all operating conditions below the limit curve the MSTR rises monotonously with the process temperature; above the curve the MSTR passes through a minimum. An example of a second-order reaction with optimization potential regarding the MSTR is shown in Figure 4-80.

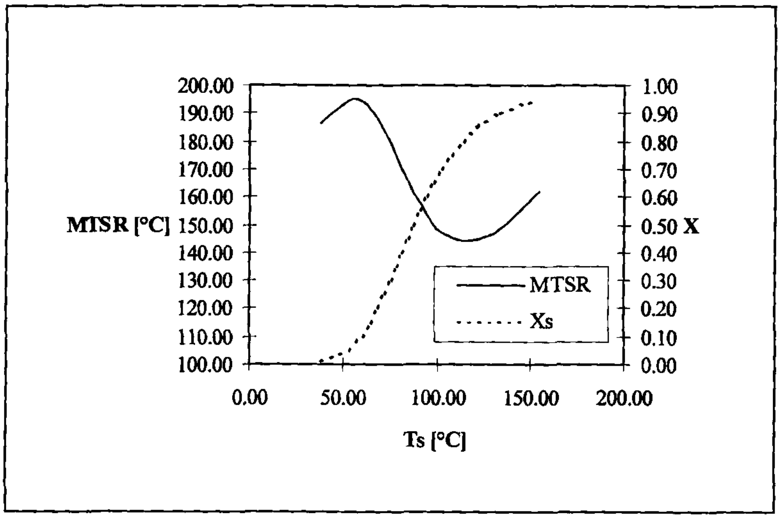


Fig. 4-80. Dependency of the MTSR on the process temperature in the case of a cooling failure

Parameters : E/R = 12 000 K, $Da_\infty = 5{,}83 \cdot 10^{14}$, $\Delta T_{ad} = 150$ K, n = 2

If in course of the assessment it has been determined, for example, that temperatures above 155°C have definitely to be avoided in the case of any maloperation, then it can be seen from Figure 4-80 that this can be ensured by choosing a process temperature of 120°C without any need for additional protecting installations. Such a design can be regarded as step towards an inherently safer process design.

However, if selectivity or quality aspects demand a performance of the process at much lower temperatures, this raises the question which parameters should reasonably be changed to lower the MTSR curve.

One possible solution is to reduce the space/time-yield at fixed reactor size. If the reaction system is diluted and the residence time simultaneously prolonged, so that the product of $c_{B0} \cdot \tau$ remains constant, then the Damkoehler number and thereby the conversion are left unchanged, but the adiabatic temperature increase is lowered. Due to such a change in the manufacturing recipe, naturally, the amount of product manufactured per unit time is reduced. Such a measure and its effect is shown in Figure 4-81 for the example.

This procedure, which for the example considered results in a solution, that the reactor responds inherently safely to a cooling failure for almost all process temperatures, can be performed in a complete analogical way for any other kinetic rate law.

The same concept can also be transferred to any other maloperation scenario. For instance, the same diagram can be supplemented by a curve representing the effect of a different concentration and the additional occurrence of a cooling failure. For this purpose the corresponding MTSR curve must be calculated for a different Da_∞-value and the related adiabatic temperature increase value and subsequently compared with the original curve.

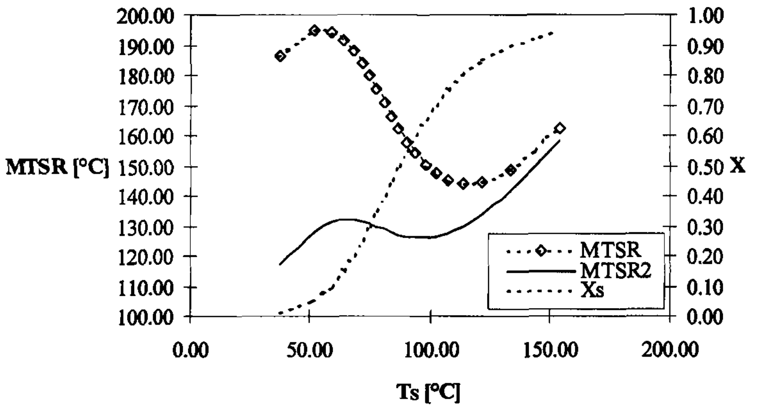


Fig. 4-81. Dependency of the MTSR on the process temperature in the case of a coolant failure Parameters : $E/R = 12\ 000$ K, $Da_\infty = 5{,}83 \cdot 10^{14}$, $n = 2$, MTSR : $\Delta T_{ad} = 150$ K, MTSR2 : $\Delta T_{ad} = 80$ K

4.4.1.2 The Assessment Of The SBR Under Upset Operating Conditions

Again, the example of a second order reaction shall be regarded. In the safety assessment of a SBR under upset operating conditions due to a cooling failure, it has to be observed that the accumulation potential is a time dependent value because of the unsteady operation. For the SBR the following is valid:

$t_{\text{charact.}} = \tau_D$ and in consequence $Y = \left(\frac{t}{\tau_D} - X\right)$ (4-244, (4-245))

In the case of the SBR the MTSR is calculated according to

$$\text{MTSR} = T_P + \Delta T_{ad} \cdot \left(\frac{t}{\tau_D} - X\right) \tag{4-246}$$

Investigations performed for reactions following a formal kinetic rate law of the second-order have shown that in the case of the SBR the accumulation reaches its maximum, independent of isothermal or isoperibolic mode of operation, at that point in the feed time, at which a stoichiometric amount has been added [47]. The maximum temperature to be reached under adiabatic conditions with this maximum accumulation can be precalculated with the help of the following relationships.

$$X_{St} = 1 - \sqrt{\frac{2}{\pi \cdot Da}} \tag{4-247}$$

$$\text{MTSR} = T_P + \Delta T_{ad} \cdot \left(1 - X_{St}\right) \tag{4-248}$$

The error which occurs by applying Equ.(4-247) to isoperibolic processes due to the fact that the relation is exactly valid only for the isothermal SBR may be neglected if the quasi-steady state maximum temperature is used for the process temperature.

As a special solution to Equ.(4-238), the following requirement regarding the thermal reaction number is obtained, which must be fulfilled to have an optimization potential available in respect to the MTSR:

$$B > \frac{2}{1 - X_{St}} \tag{4-249}$$

The course of this limit curve separating processes with and without the possibility to optimize the MTSR is shown graphically in Figure 4-82. All operating points with an optimization potential are above the limit curve. The minimum value is B = 2.

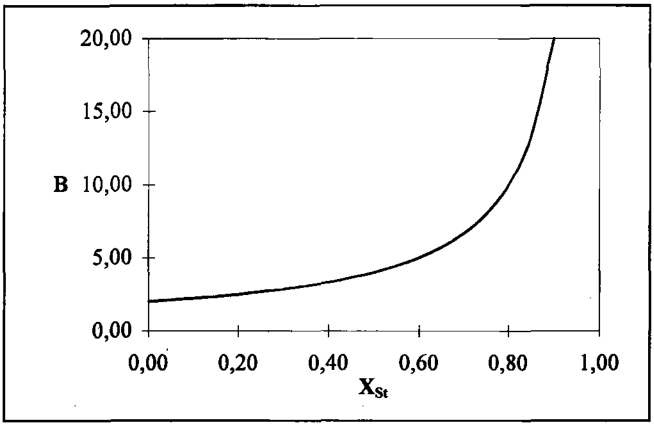


Fig. 4-82. SBR limit curve for second-order reactions with optimization potential regarding the MSTR

An example of a second-order reaction which can be optimized in respect to the MSTR is shown in Figure 4-83. The value for the optimum process temperature approximately amounts to 125°C. Hazardous secondary effects, which would become perceptible only above temperatures of 170°C, would be excluded inherently safely.

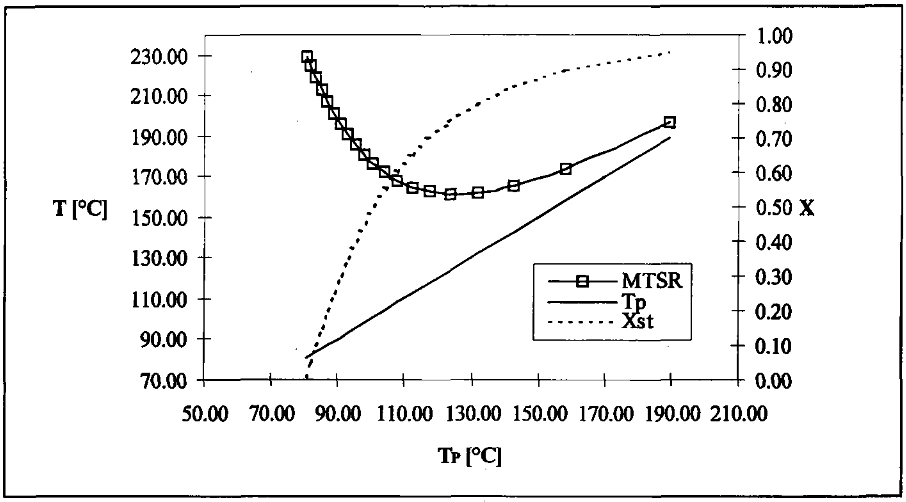


Fig. 4-83. Dependency of the MTSR on the process temperature in the case of a cooling failure; Parameters : E/R = 9000 K, $Da_\infty = 7{,}2 \cdot 10^{10}$, ΔT_{ad} = 150 K, n = 2

For the SBR, too, the MTSR curve can be moved to lower temperature values by reducing the adiabatic temperature increase. A corresponding example is shown in Figure 4-84.

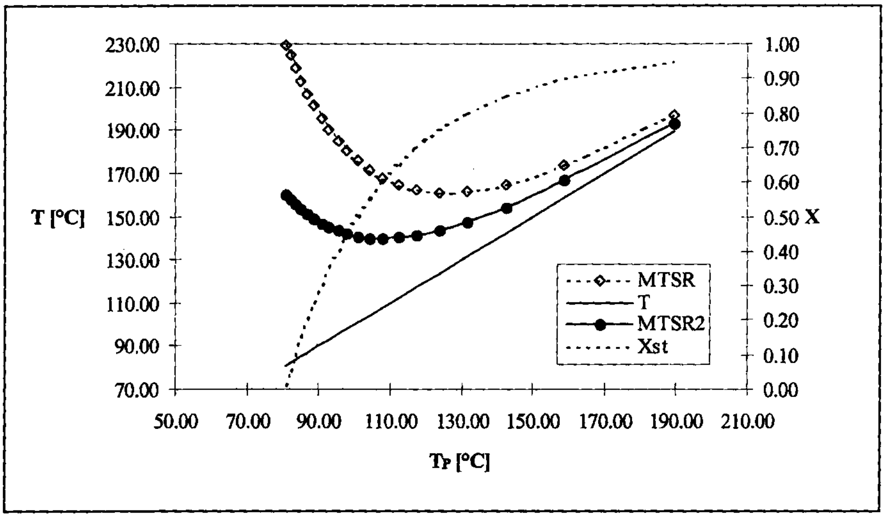


Fig. 4-84. Dependency of the MTSR on the process temperature in the case of a cooling failure; Parameters : E/R = 9000 K, $Da_\infty = 7{,}2 \cdot 10^{10}$, n = 2, MTSR : $\Delta T_{ad} = 150$ K, MTSR2 : $\Delta T_{ad} = 80$ K

4.4.1.3 The Assessment Of The BR Under Upset Operating Conditions

Applying the worst case principle, it must be assumed that the cooling failure occurs at the very beginning of the process. At this point in time the maximum accumulation potential is present.

In the case of the BR it is helpful for the evaluation of the cooling failure scenario to discuss four temperature levels and their interactions, as was first developed by Stoessel [75]:

- the process temperature, which corresponds to the initial temperature in a maloperation scenario - **a** -
- the temperature to be reached under upset conditions, e.g. the MTSR - **b** -

- the temperature at which the adiabatic induction time of a possible decomposition reaction falls below a company specific limit value, ADT24 or equivalent limit value- **c** -
- the boiling point of the reaction mass - **d** -

The possible different positions of the temperature levels relative to each other are presented in Figure 4-85, sorted by increasing degree of hazard.

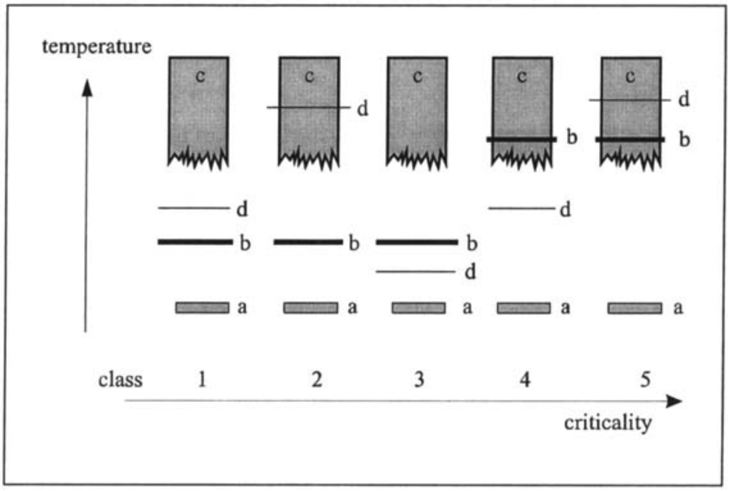


Fig. 4-85. Classes of maloperation scenarios for the BR with increasing criticality according to Stoessel [75]

In a class 1 scenario, neither the boiling point of the mixture nor the dangerous region in which the decomposition reaction becomes effective within a critical time is ever reached. Such processes may be regarded as inherently safe with respect to the process deviation evaluated.

Also in the second case, which differs from the first by the absence of the boiling point barrier between temperature levels b and c, the process may be regarded as safe.

In the third class, the boiling point with its latent heat of evaporation may be looked upon as a safety barrier, provided the condenser is adequately designed. If the process is performed in a closed system, the apparatus must be designed for the maximum expectable overpressure or be equipped with a pressure relief device.

Scenarios with class 4 characteristics must be evaluated as to whether or not the evaporation capacity provides sufficient safety. If this is not the case, additional organizational or technical measures have to be implemented. Should the operation be performed in a closed system, then the temperature corresponding to the relief valve's set pressure may not be much higher than the level of d.

The fifth class must in any case be rated problematic. Plant and/or process modifications usually cannot be avoided in such situations.

This very plausible and easy to follow approach to an evaluation of a cooling failure scenario for the batch reactor can in numerous ways be transferred to other reactor types as well as the assessment of the consequences of other maloperation scenarios.

4.4.2 Methods For The Investigation Of Upset Operating Conditions

A disturbance affecting a parameter which itself has an influence on the reaction or the cooling power may, as presented in Table 4-9 of Section 4.4.1, in the worst case lead to a runaway (see also Section 4.2). Therefore, it must be the aim of the experimental characterization to simulate the disturbed process situation as well as possible by adiabatic experiments. In order to define the requirements for such experimental devices in a more concrete form, the effects possibly to be observed shall be presented and comprehensively discussed again in a phenomenological way.

Figure 4-86 shows the most important runaway scenarios. As a consequence of the assumed cooling failure, an adiabatic temperature rise will be observed which is identical to the reacting accumulation potential of the desired reaction. The maximum temperature reached corresponds to the MTSR, which has been discussed in the previous section.

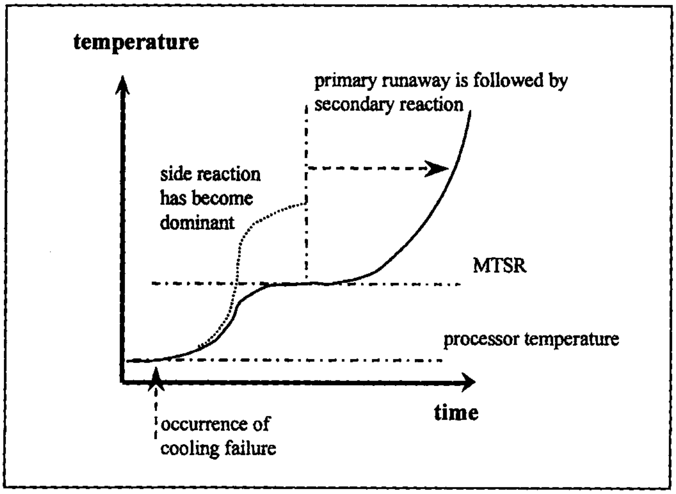


Fig. 4-86. Schematic presentation of runaway scenarios

But already at this early stage, surprises may happen if side reactions suddenly become dominant. This possibility is often underestimated. Very easily a side reaction may proceed with quite an insignificant rate at normal operation, but at elevated temperatures the situation reverses completely.

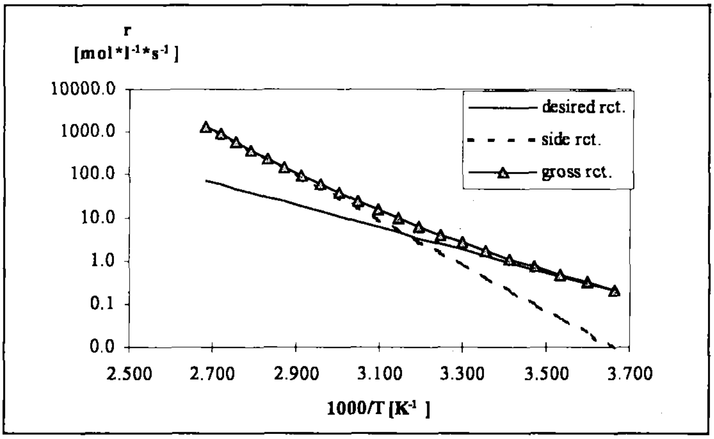


Fig. 4-87. Explanation of kinetic effects of side reactions
E/R (desired reaction) = 6000 K, E/R (side reaction) = 12 000 K

It is a precondition to this scenario, that the activation temperature of the side reaction is much higher than that of the desired reaction. To make this situation clearer it is presented in Figure 4-87 as an Arrhenius type diagram.

A first indication of such a situation is obtained if the precalculated adiabatic temperature increase, derived from the gross heat of reaction measured under normal operating conditions, is by far exceeded in the adiabatic experiment. An analytical examination of the final reaction mixture will provide the final proof.

It should be possible with the help of the same experiment to find out the time after which the secondary processes become perceptible and their character. The latter means, the degree of exothermicity and possibly the strength of an accompanying gas generation. When performing such experiments, it has to be observed whether evaporation prevents a runaway of the reaction. If this turns out to be the case, a closed test system should be available for the measurement. In a closed system the evaporation would be suppressed by the rising internal pressure.

Additional information can be deduced from the shape of the measured temperature profile. Reactions which follow an n-th order formal kinetic rate law show a sigmoid pattern in a more pronounced way than autocatalytic reactions. An example demonstrating this effect is shown in Figure 4-88 for two reactions with approximately equal initial reaction rate.

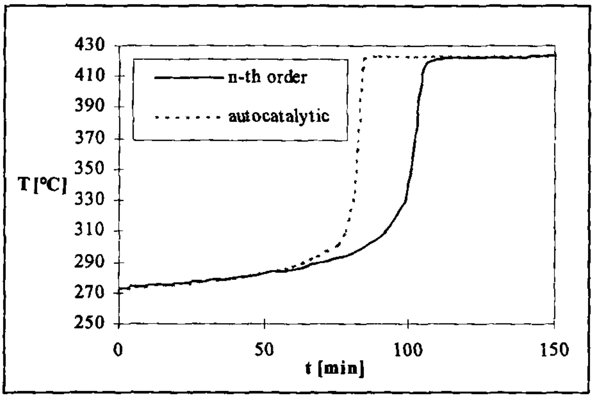


Fig. 4-88. Influence of the formal kinetics on the course of adiabatic reactions

In summary, the following minimum requirements can be stated which have to be met by a measuring device suitable for the characterization of process deviations:

- registration of the temperature and, if possible, of the pressure/time history under adiabatic conditions
- conduction of the experiments in open as well as closed set-up
- registration of the presence of hazardous secondary processes and their observation at least in the initial phase

Furthermore, at least the following information must be obtainable from such measurements:

- the adiabatic temperature increase due to the reacting accumulation potential of the desired reaction
- the maximum pressure reached due to this first runaway
- the time the system needs to reach this first temperature rise
- the adiabatic induction time of the secondary effect
- an information on the consequences to be expected from this secondary effect

If, based on such experiments, a pressure relief device is to be designed as a protective system to prevent the occurrence of intolerable overpressures in the reactor, then further information must be deducible.

At the moment five well-known devices are commercially available, and one setup is easily self-made from common laboratory equipment. These are the ARC™, the

VSP™, the PHI-TEC II™, the RSST™ and the Chilworth™ stainless-steel dewar, as well as the self-made types. On top of these there are several other measuring set-ups, which are more or less modified versions of those mentioned. The general discussion of adiabatic calorimetry shall be conducted on the basis of the general dewar technique as a comparative study of the commercially available devices is not the subject of this book.

Before describing adiabatic dewar calorimetry in detail, some more fundamental considerations shall be made. As has been outlined, the basic requirement to such an experiment is its performance under adiabatic conditions. This can never be achieved if the demand is taken to be absolute. It is inherent to all measuring devices that they lose some heat to the environment. What differs is the degree of this loss. Grewer has compiled some data on the heat loss characteristics of different sample vessels [15]. They are shown in Table 4-10.

The half-time tabulated shall be defined as the time which passes by until the temperature has dropped to 50 % of the initial temperature present in the vessel due to filling it with a hot organic liquid. Well-manufactured dewar vessels show heat loss fluxes which are about two magnitudes smaller than those from any other sample vessel mentioned here.

Table 4-10: Typical heat loss characteristics of sample vessels according to Grewer [15]

Sample vessel	Volume [cm^3]	Heat loss coefficient U*A/V [KW/m^3 K]	Half-time $t_{1/2}$ for organic solvents [min]
Carius tube	10	5.83	3
glass beaker	100	2.33	8
jacketed glass vessel	200	0.83	24
dewar	200	0.08	240
dewar	500	0.04	470

The higher those heat loss fluxes are, the more it becomes important and necessary to correct the pseudo-adiabatically obtained data for true adiabatic conditions with the help of model-based mathematical correcting functions. The more severe the necessary corrections are, however, the greater is the risk involved that those data corrections become data manipulations. Practical experience, backed up by theoretical considerations, has shown that no corrections are necessary as long as the measuring time is shorter than the half-time described above. But it remains extremely important to characterize each measuring device individually regarding its heat loss characteristics, and to account for these results in a suitable form for each evaluation of a measurement.

The second fundamental topic deals with the thermal inertia Φ of the measuring device, which was first introduced in Section 2.3. This property, unfortunately, is often mixed up with heat losses due to a lack of adiabaticity in the context of adiabatic calorimeters, but it is something entirely different. To put it simply, thermal inertia is a measure for the total heat „absorbed“ by the vessel wall, the sensor, the stirrer, possibly by other installations, or in short, by the complete system due to its own heat capacity. The heat capacity of plant equipment usually is smaller than that of the reaction mixture. In the case of small sample containers, like those used for the DTA, the heat capacity of the device is larger than that of the sample mixture. The higher the heat capacity ratio of the system to the reaction mixture, the less sensitive is the measuring method, the more necessary are model-based mathematical corrections to the measured data. If the value of thermal inertia is very high, as is the case for DTA devices, such a correction of data for the theoretical value of $\Phi = 1$ is not permitted. If a new measuring device is to be set up which allows the collection of data in such a good way that their correction becomes unnecessary, it must be attempted to keep the value of thermal inertia as close as possible to 1. In any case the thermal inertia of a measuring system has to be determined experimentally and accounted for in the evaluation of test runs.

The comment about the commercially available systems shall be limited here to the following remarks. In the case of the RSST™ a correction of the measured data is absolutely necessary with respect to the heat exchange with the environment because the system works with a superpositioned external heater. On the other hand, the thermal inertia may be neglected, as values close to $\Phi = 1.04$ are reported. The reverse is true for the ARC™. In this case the heat exchange with the environment is successfully suppressed, but the thermal inertia must be accounted for because this can take high values due to the use of stainless steel sample bombs. Each measuring system must be analyzed individually for both phenomena.

In the following, dewar calorimetry shall be discussed in greater detail. A schematic drawing of the measuring set-up is shown in Figure 4-89.

Dewar tests can be set up for measurements under normal pressure as well as under elevated pressure. The two best-known examples for calorimetry under elevated pressure are the stainless steel dewar and the so-called pressure-heat-storage test apparatus [76,77]. If the dewar is placed into an oven which is equipped with a control device ensuring the oven temperature to follow the temperature of the reaction mixture, then the heat exchange with the environment may be regarded as reduced to a negligible amount.

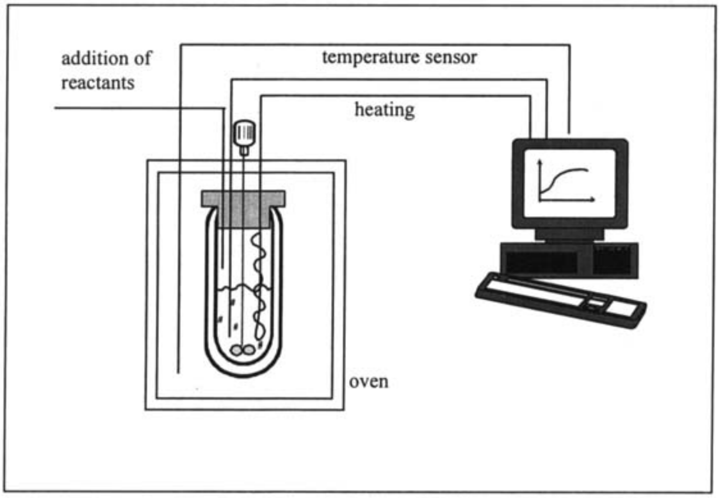


Fig. 4-89. Schematic set-up of an adiabatic dewar calorimeter

The special property of very good, which means rather thin-walled, highly evacuated dewar flasks is that they have a heat loss characteristic which is directly comparable to that of uncooled process vessels up to 10 m^3 in reaction volume. This fact, first investigated and documented by Rogers, is presented graphically in Figure 4-90 [78].

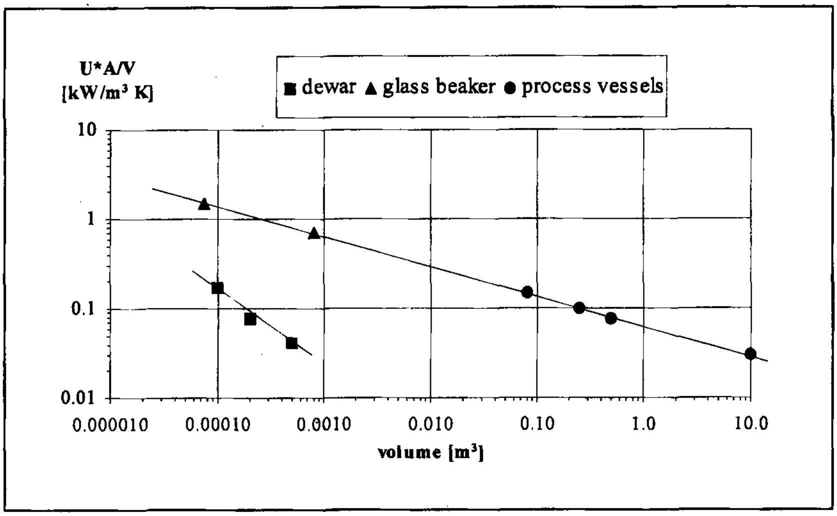


Fig. 4-90. Presentation of heat loss characteristics of different vessels with varying volume according to Rogers [78]

The measuring results, even if obtained from dewar tests without a controlled oven, can directly be taken, without any model-based mathematical modification, as representative for the behaviour of plant vessels. This fact makes dewar techniques superior to all others.

The direct results from adiabatic measurements are:

- the adiabatic temperature increase from the maximum temperature rise observed and corrected for the thermal inertia
- the maximum pressure, provided a pressure sensor is installed and the device was operated as a closed system
- the adiabatic induction time
- formal kinetic parameters

Examples of three simulated temperature profiles are shown in Figure 4-91.

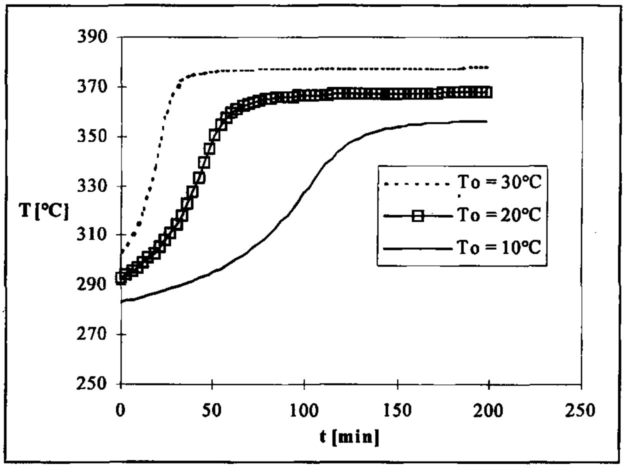


Fig. 4-91. Simulated temperature profiles of three adiabatic batch dewar tests

With respect to the adiabatic temperature increase observed, it has to be checked whether the final temperature truly is a consequence of the complete consumption of all educts, or whether it is an artificial final value because evaporation has prevented the temperature to rise any further. If all runs are started from different initial temperature levels, which is recommendable anyhow, then the dependency of the adiabatic induction time on temperature can directly be seen. For this purpose the measured temperature curve are differentiated once with respect to time and the resulting gradient profile is evaluated. For the above example this is shown in Figure 4-92.

If the adiabatic induction time thus determined is plotted in semilogarithmic scale over the reciprocal value of the initial temperatures in degrees Kelvin, then the ADT24 or any other induction time corresponding to a temperature of interest can be determined graphically. This is shown in Figure 4-93 for clarification purposes.

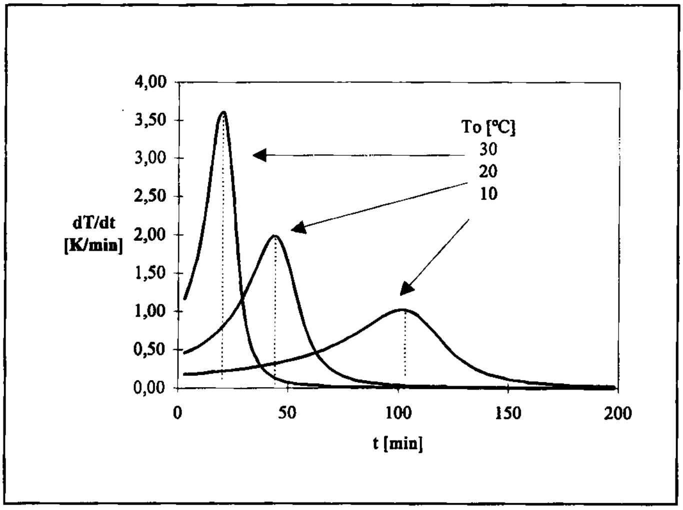


Fig. 4-92. Determination of the adiabatic induction time

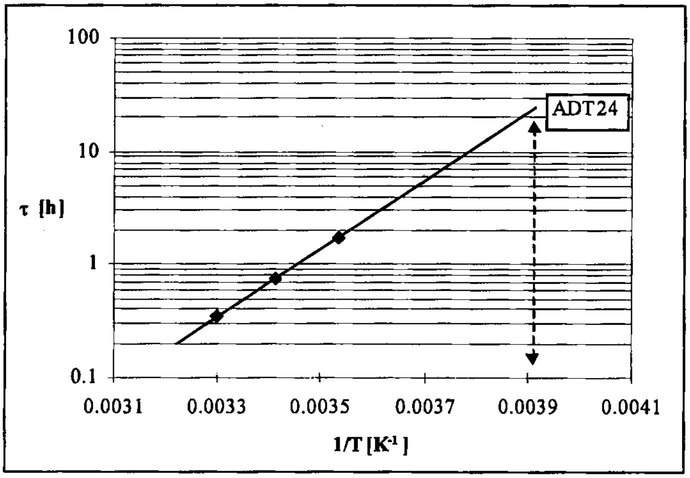


Fig. 4-93. Determination of the ADT24 based on measured adiabatic induction times

In determining the ADT24 it has to be observed that it must not be attempted to obtain this value by a thermokinetic evaluation of a single experiment. This would be an extremely dangerous and intolerable procedure. All elaborations made in Section 4.3.3.3 about a responsible application of the thermokinetic concept have to be observed even more stringently in the case of adiabatic calorimetry. Temperature profiles from adiabatic batch measurements respond very insensitively to assumed reaction orders. This reaction order, contrary to the procedure described in Section 4.3.3, would have to be postulated first when trying to evaluate a single measurement. Figure 4-94 shows two different evaluations of the simulated measurement initiated at the middle of the three temperatures in an Arrhenius plot. One is obtained for a first-order, the other for a second-order formal kinetic rate law.

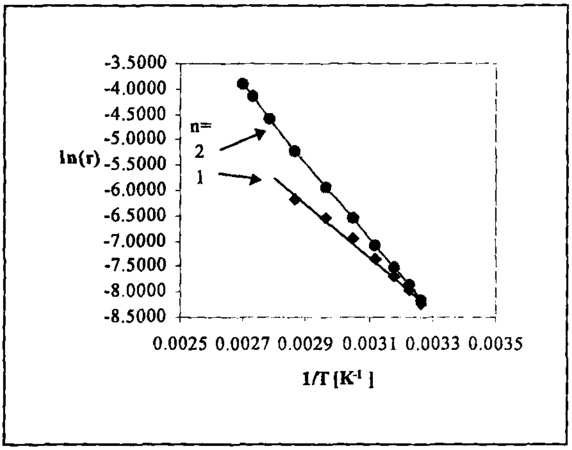


Fig. 4-94. Thermokinetic evaluation of a single adiabatic experiment assuming different reaction orders

As can easily be seen, two quite different values for the activation energy and the pre-exponential factor would be determined resulting in significantly differing predictions of the ADT24. If the evaluation is looked upon very carefully, a slightly curved profile can be identified in the Arrhenius plot for the evaluation assuming a first order kinetics, indicating that this evaluation might be erroneous. But this effect is much less pronounced if the data do not originate from simulations but from real experiments.

However, if the thermokinetic evaluation procedure is applied, which was explained in Section 4.3.3.3, very reliable kinetic models can be obtained from adiabatic measurements. The parameters thus determined can reliably be used for the prediction of the reactor behaviour in other maloperation scenarios. In a first approximation, other adiabatic induction times may be estimated with the help of the following equation

$$\tau_{ad} \cong \frac{t_{react.}}{Da_0 \cdot (B_0 - n)} \tag{4-250}$$

Safety Assessment for Chemical Processes
by. Jörg Steinbach

5 Dust Explosions (Milling, Mixing, Drying)

5.1 Fundamentals Of Dust Explosions

The handling of powdered or dust-like substances, is an activity, which has been known for more than two hundred years to require a careful safety technical assessment and evaluation in order to prevent major accidents. The hazard potential related to handling such substances is their affinity to decompose either in form of a combustion or an explosion. This affinity becomes ever stronger with decreasing particle diameter.

The literature is filled with reports on dust explosion incidents, some of them with disastrous consequences. In his book „Explosions“, Bartknecht provides a short historical outline of first reports describing dust explosions and milestones of their research [79]. According to this survey, one of the first reports dates back to 1785 and describes the destruction of a flour storage building. In general, most accidents occurred in either the food or the mining industry. In 1844 Faraday discovered, that coal dust is explosible.

The systematic scientific investigation of the basic mechanisms and phenomena underlying dust explosions, supplemented by industrial practice, has led to methods for their investigation, to assessment criteria and to recommended protective measures. Their general international acknowledgement finally resulted in their documentation in technical regulations. In Germany the major regulations to be mentioned are VDI-2263 and VDI-3673 [80,81]. These technical regulations are supplemented, among others, by monographs written by Bartknecht, Field, and Eckhoff, which are highly recommended for a more detailed pursuit of this special area of process safety engineering [79, 82, 83]. The following presentation shall just provide a very comprehensive overview on the main fundamentals.

There is a special reason for treating this topic of process safety engineering here despite the existence of extensive literature. It is necessary to reduce the risk, which is involved in focusing entirely on the control of the chemical transition process and simultaneously neglecting the hazards related to the accompanying physical unit operations. Drying, milling, sieving, as well as mixing and granulation, are examples of such unit operations which are related to the handling of powders and dusts.

The basic requirement for the occurrence of an explosion is the simultaneous presence of a fuel, an oxidizing agent and an ignition source with sufficient energy content. This relationship is often called the explosion triangle (c.f. Figure 5-1).

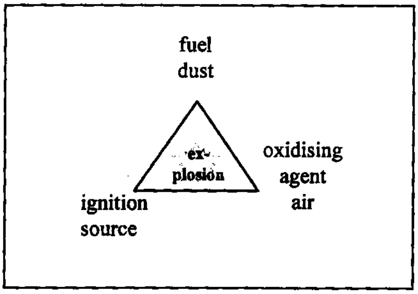


Fig. 5-1. The explosion triangle

However, this is a necessary but not a sufficient condition. In addition, fuel and oxidizing agent have to be mixed intensively and the fuel must have a certain concentration in this oxidizing agent. All these statements are independent of the fact whether the fuel is a gas, a liquid or a solid.

An oxidizing decomposition reaction and an explosion differ mainly in the reaction rate. Explosion processes proceed so fast that the combustion energy becomes visible in form of a flame. The warming of the environment due to heat radiation will lead to a pressure rise in closed systems with all possible damaging consequences.

In the special case that the fuel is a dust, there are a number of substance properties which influence the affinity and course of the explosion. The most important substance property in this context is the particle size. In the sense of a safety technical rule of thumb it may be stated in simplified terms that every substance will become dust explosible provided it is micronized sufficiently. This is mainly an effect which has to be attributed to the enormous rise in specific surface area accompanying the decreasing particle diameter. The other way round, the probability of dust explosibility becomes rather restricted if the mean particle diameter exceeds 500 μm.

Other parameters are humidity of the material and, not least, the chemical constitution. Furthermore, dust explosions require a much higher ignition energy than vapour/air mixtures to trigger the event.

Another phenomenological characteristic of dust explosions is the occurrence of secondary explosions. Swirled dust is a consequence of the existence of settled dust. If a dust explosion happens, the so-called primary explosion, it will cause settled dust to be whirled up. This is ignited by the propagating flame front of the first explosion. These secondary explosions often show more severe consequences than the primary events.

Settled dust can also decompose, following the same chemical reaction. However, the reaction rate will be much slower because the dust and the oxidizing agent are not well mixed. The reaction progresses as a so-called dust combustion.

5.2 Relevant Technical Safety Data

Safety technical numbers as well as the corresponding experimental methods for their determination are required in order to enable an assessment of the risk related to handling powders and dust. In the evaluation the different reaction mechanisms, namely dust combustion and dust explosion, have to be accounted for.

The following safety technical numbers are commonly used for the characterization of the dust explosion risk or, in other words, for the characterization of hazards related to handling dust:

- dust explosibility (yes/no statement)
- maximum explosion pressure
- maximum pressure rate, respectively the K_{St}-value
- explosion limits
- minimum ignition energy
- ignition temperature
- oxygen limit concentrations

In the determination of all these safety numbers, a number of demands on the sample must be observed. Thus it is recommended, as it has already been mentioned in the general discussion of Chapter 3 on safety investigations of substances and mixtures, to pay special attention to the representativeness of the sample regarding the material later to be handled in the plant. Especially if a dust is to be assessed, the degree of humidity of the test material must be determined and a drying of the sample prior to testing is recommended. The German Technical Regulation VDI-2263 further suggests to perform a sieving analysis in order to separate the fine dust fraction. The tests should be conducted only with the fraction containing particles with diameters of less than 63 µm. The reason for this recommendation is the fact that this fine dust fraction determines the hazardous properties of the material. If only this special fraction is used for the safety tests, then possible variations in the particle size distribution of the later plant material become safety technically irrelevant.

The description of the different experimental test methods shall be limited here to three somewhat more prominent ones, as all the methods for the determination of the relevant safety data are described in great detail in the cited literature. These are:

- the modified Hartmann tube
- the 20 l sphere
- the method to determine the minimum ignition energy

The modified Hartmann tube is used to obtain a yes/no answer to the question of dust explosibility. The method belongs to the group of screening tests, as no protective measure can be designed on the basis of its test result.

The modified Hartmann tube consists of a Pyrex glass cylinder. This cylinder is charged with dust samples of 36, 120, 240 and 600 mg individually for each test. In the base of this device there is an air pressure chamber of 50 ml volume which is under a pressure of 7 bars.

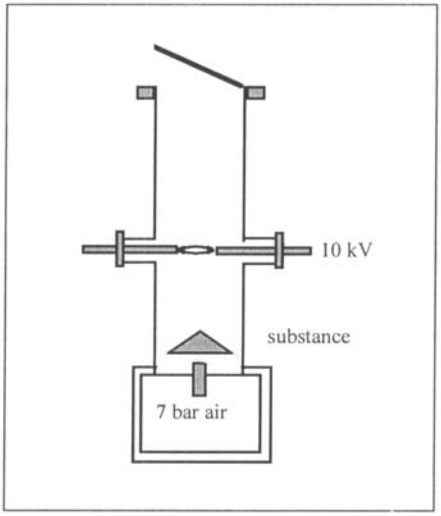


Fig. 5-2. Schematic set up of a modified Hartmann tube

By opening this pressure chamber the dust sample is finely dispersed and blown past an inductive spark discharge. The dust concentrations approximately amount to 30, 100, 200 and 500 g/m^3. The tube is closed by a spring-loaded lid. If a dust explosion takes place, the lid is opened to a varying degree depending on the strength of the explosion. An indicator discriminates two positions besides the closed position, namely 1 and 2. If one of these open positions is registered in at least one out of three tests per initial weight, then the substance is rated dust explosible. Schematically this device is presented in Figure 5-2.

The second test apparatus mentioned is used to determine the maximum explosion pressure and the maximum pressure rate. It is a spherical stainless steel autoclave of 20 liters volume. Dust samples of up to 40 g per trial, covering a concentration range of up to 2 kg/m^3, are blown into the sphere through special ring nozzles. The dispersed dust is ignited with varying delay time. The pressure/time-history is measured. The maximum pressure rate observed is transferred into the safety number K_{St} value with the help of the so-called cubic-root-law.

$$K_{St} = \left(\frac{dp}{dt}\right)_{max} \cdot \sqrt[3]{V} \tag{5-1}$$

This K_{St} value is used to classify dust in dust classes. Both the K_{St} value and the dust class provide a characterization of the hazard potential. The attribution of K_{St} values to dust classes is shown in Table 5-1.

The maximum explosion pressure is also measured in this test, but is of comparatively limited importance, because the degree of damage to be expected is mainly determined by the pressure rate. The maximum explosion pressure can be predicted quite reliably to amount to 10 bars in the case of organic materials and approx. 15 bars in the case of metal dusts when having started the test at ambient pressure.

Table 5-1: Classification of dust

K_{St} value $[\mathrm{bar} \cdot \mathrm{m} \cdot \mathrm{s}^{-1}]$	dust class
0	St 0
0 - 200	St 1
200 - 300	St 2
> 300	St 3

It is more important in this context that one should never rely on a single measurement. A dust sample is never fully identical with the next, because a solid substance can never be homogenized in such a way that an ideally mixed system with identical humidity and particle size distribution in each sample is achieved. If possible, up to 20 measurements should be performed.

In addition, caution is indicated when comparing results obtained at different laboratories. If one of the laboratories has modified the standard set-up one or the other way, significantly different results may be the consequence. Investigations have shown that the results from 20 l sphere trials are influenced by any modification of the degree of turbulence in the apparatus as well as by the placing of the ignition source and a number of other factors.

The third method, the determination of the minimum ignition energy, has a prominent meaning because its result characterizes the affinity of a substance to undergo an explosion and this way, in the widest sense, provides a probability of the dust explosion risk. This minimum ignition energy can be determined in both devices, the 20 l sphere as well as in an adjusted Hartmann tube. Again, the degree of turbulence and the ignition source influence the results. The standard method applies an inductive spark discharge.

It is important to acknowledge that a minimum ignition energy is almost unpredictable. In the sense of a first mark it may be stated that the majority of solid substances can be ignited only with minimum ignition energies greater than 10 mJ, a value which is much higher than the value for vapour/air-mixtures. On the other hand, quite a number of micronized substances with minimum ignition energies of less than 1 mJ are known. In such cases, special explosion preventing measures are called for. If the minimum ignition energy of a substance amounts to less than 10 mJ, the substance is to be rated highly ignitable.

The characterization of a dust combustion risk, which means the assessment of hazards related to handling substances in the presence of settled dust, is commonly based on the following safety technical numbers:

- the burning number
- the smouldering temperature
- the self-ignition temperature
- characteristic values for an exothermic decomposition

Partially, the necessary test methods have already been described in detail in Chapter 3, partially they are explained in the relevant technical regulations. One further calorimeter shall be mentioned here. A specific problem related to drying substances is the determination of the allowable thermal stress. The uncertainties inherent to the deduction of critical temperature limits with the help of screening tests have been discussed in detail at the relevant points.

With the help of the so-called TAM^{TM} (thermoactivity monitor), critical heat fluxes can be measured directly under isothermal conditions in a temperature range from +5 to +90 °C [84]. The measuring technique utilizes semiconductors in a particular way which allows the detection of a thermal power of a few μW/kg. With the help of the heat explosion theory according to Frank-Kamenetzky it is possible to deduce the critical mass or, in the case of a fixed mass, the critical temperature for storage or drying directly from the measured data.

5.3 Protective Measures Against Dust Explosions

When speaking about explosions, preventive and constructive measures are discriminated. This is also done in the case of protection against dust explosions. When discussing the preventive measures which have the task to eliminate the chance of a possible event actually occurring, the question of substance substitution is the first to be asked. If a dust explosible substance can be replaced by one which does not have this property, this substitution is the most effective measure. The probability that this exchange is possible in practice is, however, comparatively low.

In most situations it remains necessary to rely on other alternatives. The most recommendable method to prevent the occurrence of dust explosions is inertization. Some details to be observed in its application will be presented in Section 7.4. At this point, some general remarks shall just be made. The highest allowable oxygen concentration is substance specific. Experimental methods for the determination of this limit concentration are well known. In a first approximation it may be assumed, however, that the oxygen limit concentration for organic powders and dusts will not be lower than 8%. For metal dusts this value has to be halved.

It must further be observed that inertization is acknowledged as a protective measure only if it is continuously supervised by measurements. A vacuum purge inertization of an apparatus repeated once or twice without any subsequent supervision cannot be accepted as a preventive protecting measure.

A further decisive factor determining the efficiency of this measure is to safeguard the absence of a substance which decomposes without the presence of oxygen, as such a process would render an inertization absolutely useless.

Another measure is vividly discussed regarding its efficiency: the elimination of ignition sources. Today's view of experts supports any attempt pursued to eliminate ignition sources but denies it the quality to be sufficient as a single measure on which to base the safety of a process or a plant. This very critical assessment of the measure is the result of the negative experience that incidents have become known which took place after supposedly full elimination of ignition sources. It is more responsible to act on the premise that the possible formation of an explosible atmosphere provides enough reason to implement effective countermeasures or incident preventing measures because the critical ignition source may always be overlooked.

In order to be able to fight ignition sources at all, the most important ones must at least be known. A few shall be enumerated without claiming any comprehensiveness (c.f. Table 5-2).

Table 5-2: Important ignition sources for dust/air-mixtures

open flames
hot surfaces
strongly exothermic reactions
welding and cutting sparks
friction heat and sparks
impact sparks
electrical sparks
electrostatic discharges
smouldering pockets

Special attention should be paid to hazards resulting from electrostatics. The correct identification of unintentionally built in capacitors requires experience and very good knowledge on material properties, in order to find hidden insulators.

With respect to constructive measures the following alternatives are available:

- pressure resistant design
- pressure impact resistant design
- explosion pressure relief
- explosion suppression
- explosion barriers

The first alternatives are well documented in the relevant technical regulations. Detailed information on the design of dust explosion relief systems can be found in the German VDI-3673, the British guide on dust explosion venting HSE 1977 and the US standard NFPA 68.

Explosion suppression can be a very elegant method to prevent dust explosions. This method utilizes the faster propagation of the pressure wave in comparison to the flame front. The vessel to be protected is equipped with containers comparable in size and design to fire extinguishers. They are filled with a substance which suffocates the fire in a comparable way to powder extinguishers.

If a dust explosion happens, the pressure wave propagates in all directions with sonic velocity. Depending on the design, either the pressure wave destroys a membrane, causing the extinguishing substance, which itself is stored under high pressure, to disperse towards the approaching flame front, or it is registered by a pressure sensor, which then initiates the release of this extinguishing substance. This method is good and reliable if an expert has determined the number of necessary extinguishers and the location of their installation carefully.

Explosion barriers should always be installed if two coupled process units are to be separated in such a way that a dust explosion cannot propagate from one unit to the other.

With respect to all further considerations and the actual design, as well as the attribution of safety numbers to types of dryers and mixes, it is referred again to the literature mentioned.

Safety Assessment for Chemical Processes
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6 Methods For The Identification Of Deviations And Their Assessment

One of the most important steps of a safety technical assessment of a plant or a process is the systematic identification of possible disturbing influences, their initiating events and effects. The character of the method applied can be quite different. In consequence the quality of the result of this identification procedure also will be different.

The selection of the method should depend on the aim of the study. If the aim is a purely qualitative evaluation focusing on a very small balance volume, the checklist methods will be sufficient in most cases, as they have been developed to quite a degree of maturity for such a purpose. If the character of a system is more strongly addressed and if the mostly complex interactions of different functional units are to be investigated with regard to possible malfunctions, then significantly more sophisticated methods have to be applied.

The necessary effort becomes largest when a quantitative risk assessment is to be performed. Besides identification techniques, quantitative consequence modelling methods and procedures to determine the event probability of the incident being considered must be applied.

The following discussion can only provide a very rough overview of the methods mainly used in the chemical industry today, briefly mentioning their strengths and weaknesses. The order of presentation contains a rating only in so far that first the qualitative methods are described, followed by the quantitative methods. Besides this, there is not the **one and only** method. In many cases it is even recommendable to apply a number of methods in combination in order to meet the goal as well as possible.

It must especially be emphasized that studying the pure description of a method does not make anyone an expert in its application. For some of those explained here, it is extremely recommendable to attend educational and training courses, which are offered by several institutions. This should be supplemented by accompanying experienced users to collect further practical experience. The proverb: a method can only be as good as its user is seldom found to be as true as it is with the techniques for the identification of maloperation to be presented here.

6.1 Qualitative Methods For The Identification Of Deviations

6.1.1 Checklists [85]

The application of checklists is one of the most popular methods for the identification of process deviations and their effects. The reason lies in their broad and very simple applicability as well as in the usually relatively limited effort required. Checklists can be compiled for quite different aims of a safety technical assessment. Special lists can be developed and applied for

- design of a plant
- construction of a plant
- check-up prior to first operation
- safety audits
- introduction or transfer of new processes
- plant modifications
- process modifications
- start-up and close-down processes
- etc.

The development requires only a limited number of expert personnel in most cases, who evaluate lists published in the literature, general publications of relevance and reports on experiences [e.g. 4, 9]. The German guideline on identification and control of exothermic chemical processes contains a simple checklist of possible deviations with negative effect on the progress of the desired process, which can be used as a basis for the development of one's own lists [8].

As mentioned before, their advantage lies in their simple applicability and the limited requirements regarding the qualification of their users and the necessary manpower. One of their important disadvantages is the fact that only those hazards and disturbances are addressed which have been compiled in the list. It is not a creative method in this sense. The quality of the method can only be improved by establishing a good feed-back system on experiences gathered in the operational practice.

Related to this is the second major disadvantage. It is the psychological effect of wrongly deducing absolute safety from the fact that all checklist requirements have been complied with. In the worst case the method degrades to the process of mechanically ticking off all questions without any critical reflection of the answers received. The dangerous aspects must be known to the user of the method in order to respond to them successfully.

6.1.2 Preliminary Hazard Analysis [86]

This method is applied in the industry under quite different headings. The name used here refers to an established American technology, PHA, which was initially developed for military use.

The aim of a preliminary hazard assessment is the dedicated analysis of the following areas of interest at a very early design stage:

- reactivity of educts as well as intermediate and final products
- parts of a plant or installation
- interaction of plant units
- plant surroundings
- inspection and maintenance
- site services
- safety installations

in order to identify problematic points in the design which can be eliminated either completely by modifying the concept or by implementing countermeasures during the project phase of detail engineering.

The efficiency of the method is mainly influenced by the amount of information available at the time of application. The effort is usually rather limited. The user, however, should have a good training in process safety engineering in order to be able to apply this kind of evaluation in a more flexible way than the pure checklist method. Furthermore, it is highly recommended to include the later user of the plant into this analysis. This actually is a recommendation which is not limited to this method, but valid for numerous other methods described in the following.

6.1.3 „What if“ Method

This method is also frequently applied, although not much has been published about it in the literature. The reason for this fact most probably is that it does not belong to the systematic methods.

It investigates certain hazards which are more or less obvious due to substance properties or process conditions. Examples are the handling of highly flammable liquids, process steps under vacuum or, the reverse, under high pressure. A group of co-workers, which at all events should be interdisciplinary, tries to anticipate all possible process or plant conditions in a kind of brainstorming approach by asking the „what if“ question. Then the team evaluates the effects.

The quality of the method depends almost totally on the practical experience and training of the individual members of the team. If experienced operators and representatives of the different technical faculties of interest belong to the team and they are already familiar with the technique, then it can be of tremendous value. It is the first of the methods mentioned so far which allows for the consideration of interactions of numerous components in the complexity of a system. This way complete event paths may be analyzed.

Another advantage of this method lies in the fact that it may also be applied to existing plants or processes. The effort for its use is somewhat larger than for checklists and depends individually on the number of possible hazards to be covered.

6.1.4 HAZOP Analysis [87, 88]

This procedure used for the identification and assessment of hazards is most probably the best-known and most widely acknowledged of the qualitative methods. While the full German name for this method, „prognosis, identification of the cause, estimation of consequences, deduction of countermeasures - PAAG“, emphasizes its safety technical application, it seems that the English name gives the more precise description of the method, „hazard and operability study“.

The method is based on the following procedure:

1. definition of the set function to be analyzed
2. application of the n th guidance word to the set function ⇒ disturbed set function
3. identification of possible causes
4. estimation of possible consequences
5. determination of countermeasures
6. application of the (n+1)th guidance word to the set function ⇒ disturbed set function
7. loop back to 3.

The guidance words and their interpretation are compiled in Table 6-1.

Table 6-1: HAZOP guidance words and their interpretation
set function for the example:
pump conveys substance Z from A to B at a rate of X l/s

No	Guidance word	Interpretation	Example
1.	no or not	does not do what is intended	pump does not convey
2.	less	does less than intended	pump conveys less
3.	more	does more than intended	pump conveys too much
4.	partially	does it, but not as well as intended	pump sucks in air
5.	as well as	does the intended, but also something else	pump conveys Z from A to B, but also to C
6.	reverse	does the opposite to what was intended	pump conveys Z from B to A instead of from A to B (wrong installation)
7.	other than	does something totally different	is being inspected

This way very many deviations of the desired operation are identified, which are not necessary relevant to safety, but which may cause the manufacture of a product out of specification. This is the „operability" part of this analytical method.

This method is very systematic and reaches a high degree of completeness with respect to the identification of possible process deviations if it is applied in an experienced and consequent manner. The most important facts to be observed in the application of this technique are

- a clever choice of the set function
- team composition
- quality of the team leader

These points need some explanation.

The prerequisite to the conduction of a HAZOP analysis is the existence of a thorough process description including detailed information on design and process data as well as complete piping and installation diagrams, P&IDs. Then the study analyzes all set functions which are conceivable on the basis of these P&IDs and in context with the operational unit(s) considered. For each set function a certain compromise between very simple and very comprehensive becomes necessary when it is established. For a very simple set function, the application of the guidance words and the discussion of the resulting disturbed function becomes relatively easy, but at the same time the value of the study remains rather limited because interactions with adjacent elements remain unconsidered. If a very comprehensive set function is phrased quite complex units linked to process operation can be evaluated in their interactions. Because some effects demand the simultaneous occurrence of several maloperations, however, the cause/consequence determination frequently becomes so obscure and so diverse, that in consequence a logical assessment is not possible anymore. A suitable selection of a set function requires experience and a high qualification of the team leader.

The composition of the team determines the success of the method to quite some extent. The team should be interdisciplinary and represent a balance between specialists and experienced operators. All members must identify themselves with the procedure and the aim of the study. All efforts of the willing team can be blocked by a single destructive member.

It is not mandatory that the team leader is a safety specialist. But he must be a very good discussion chairman. He must repeatedly ask for the necessary attention and discipline of the team without limiting its creativity, postpone the determination of detail solutions to other meetings, assess correctly the ability of the team to concentrate and sometimes finish a meeting in time and finally focus the general discussion on the actual task again whenever required. Otherwise the whole enterprise may get out of control due to long-lasting discussions on operability problems and possibly even fail completely.

The necessary effort may become extremely high for complex plants and is already quite significant for smaller units. Experience has shown that one of the other techniques should be used to identify a problem of special safety relevance and then to conduct a HAZOP study on this limited balance volume. This has turned out to be the best solution.

6.2 Quantitative Methods For The Identification Of Process Deviations

As an introductory remark to this section it must be emphasized that all methods described in the following paragraphs are mainly used for quantitative evaluations as part of risk analysis, but that they may be applied qualitatively also in a first approach.

6.2.1 Fault-Tree Analysis [89]

Fault-tree analysis is one of the most important methods to clarify the logical connection of a disturbance and the events which may have caused it.

The construction of a fault tree always begins with the top event. Its consequences are evaluated in another step. Having identified this top event, the immediate causes which will lead to it are searched for. For example, a top event may be a substance release through an emergency valve. The state of the system immediately causing the opening of the emergency relief valve is that of a fast pressure rise. It is important to notice the emphasis on the term *immediately*. Thus, the breakdown of a coolant circulation pump is neither the immediately preceding event nor state of system. On the contrary. A direct connection of the malfunction of the pump and the top event would shorten the chain of causes so tremendously that a lot of safety technical information of relevance would get lost.

A continuation of this process of asking reversely directed questions aiming for each immediately preceding event or state, yields a variety of possible initiating events, the so-called basic events. In doing so some rules have to be observed:

- if a certain position of the fault tree is a direct consequence of a component failure, then this is preceded by a logical „or“ connection (the breakdown of the heat removal out of the system is either caused by a malfunctioning coolant pump or an agitator failure)
- if a certain position of the fault tree is a direct consequence of a state of the system, then this is preceded by a logical „and“ connection (the temperature rise is caused by the simultaneous occurrence of a breakdown of the heat removal system and the performance of an exothermic reaction)

This way it can easily be recognized whether or not a basic event directly causes the top event, because then the logical chain contains „or“ connections only. If this is the case, then the error chain must be interrupted safety technically with high availability, possibly with the help of redundant installations depending on the severeness of the consequences to be expected. If there is at least one „and“ gate on the way from the basic event to the top event, connecting two independent error pathways, then the fault tree helps to identify those places along the line where incident preventing measures are best implemented in order to ensure that each single cause is not able to trigger the top event alone.

This kind of plant design is also called single error forgiving or error tolerating design. For this purpose of identifying the error propagating pathways this qualitative use and evaluation of a fault tree analysis is especially suitable.

Figure 6-1 shows a schematic example. The basic event BE 1 represents the case of an initiating event with „or“ gates only on the way to the top event, while all other basic events represent inputs to „and“ gates. On the other hand, if the initial events BE 2 and BE 3 occur at the same time, then the top event will occur even without additional occurrence of the basic event B 1.

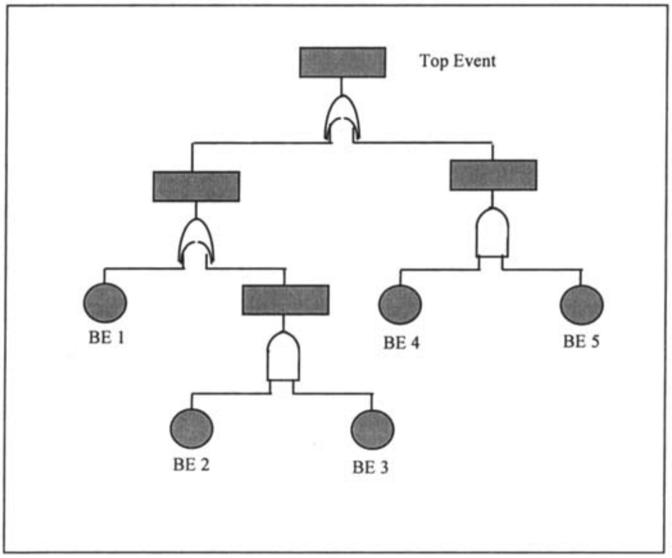

Fig. 6-1. Example of a simple fault tree

In order to use fault trees for the quantitative determination of the probability of occurrence of the top event, probabilities and frequencies are attributed to the individual states and malfunctioning components. But also in this case certain rules must be obeyed:

- all input values to an „and“ gate are to be multiplied
- no more than one input value to an „and“ gate may be a frequency; the second and any further value must be a probability, which means that it has to be dimensionless
- all input values to an „or“ gate must be added up; the exact mathematical rule demands A+B-A*B, but the product of A*B can be neglected in comparison to the sum of A+B
- the input values to an „or“ gate must either all be probabilities or frequencies

The construction of fault trees is by far not a trivial task, but requires a lot of expert knowledge and experience. The quantification of fault trees is for the time being extremely problematic, because the available databases for the determination of unreliability data of components and other probability data need significant further development. However, the existing databases and subjective estimated values may be used if two different plant designs are to be compared with each other, as the absolute values at the end of the calculation are not of interest but, instead, their relative comparison.

The effort related to the construction and calculation of fault trees depends on the complexity of the individual plant or process.

6.2.2 Event Tree Analysis [90]

In simple words, an event tree analysis begins at the point at which the fault tree ends. Its primary application is the determination of priorities with respect to consequence modelling.

This shall be explained with the help of the example for a top event used in the previous section, a release of substance. If the substance considered is a flammable gas, then an ignition can occur either spontaneously or after a time delay. In the case of a heavy gas, the probability of a delayed ignition will be rated higher than in the case of a neutral buoyant gas. Probabilities are attributed to the single steps towards possible events. The final probabilities of the individual event effects are calculated by multiplying the probabilities attributed to the single steps. Such analyses are extremely helpful in order to identify event paths which require mitigating measures to a greater extent.

The requirements and estimations on efforts necessary are comparable to those for fault tree analyses.

6.3 Special Methods

All elaborations made cannot and shall not claim to be exhaustive in any form. There are numerous other methods, such as the failure mode and effect analysis, which is preferably applied to the investigation of signal processing devices, or the human error analysis.

Especially the last-mentioned is currently undergoing tremendous development. For certain other branches, for example the aviation and space industry, it is already well developed. But in respect to the chemical process industry its development is still in a very initial phase.

Further semi-quantitative methods are the so-called index methods. Examples are the DOW-Fire and Explosion Index and the Mond-Hazard Index. They allow a relative scaling of different plants and process in quite a rigorous way concerning their hazard potential.

Safety Assessment for Chemical Processes
by. Jörg Steinbach

7 Plant Technical Safety Concepts

The variety of plants and processes in the chemical industry makes it almost impossible to describe all existing safety concepts with the necessary detail. But this intellectual approach in itself would be a mistake, because especially with respect to process related safety concepts nearly each represents a unique solution. The reason lies in the variety of parameters which must be determined. To name just a few: number of employees, qualification of the staff and internal as well as external properties of the site. Especially these parameters mentioned are hardly ever identical for two different plants or processes.

On the other hand there are parts of the complete safety concept characterized by a unified approach, which has been developed due to systematic research and industrial experience. In consequence, some have become standardized in technical regulations or have at least become state of the art of process safety engineering.

At this point three aspects of plant technical safety concepts shall be explained here, which have been selected because of their frequent application in the chemical process industry:

- emergency venting of chemical reactors
- safe disposal and containment of emergency venting streams
- protection against explosion by inertization

7.1 Design Of Emergency Relief Systems

The majority of chemical processes is performed in pressure vessels. As has been outlined in Section 4.4 in detail, the heat release due to a chemical reaction may lead to a strong temperature increase if it is not adequately controlled. In the case of volatile substances this rise in temperature results in a significant vapour pressure increase. In some cases a higher permanent gas generation rate due to a decomposition reaction may additionally occur. One or both will cause a strong pressure rise if the process is performed in a closed system. Therefore the pressure vessel must be protected against intolerable overpressure by the installation of either bursting disks or a safety relief valves.

The design of emergency relief systems for chemical reactors has been investigated by expert for many years now. Two relief scenarios are generally distinguished, which differ in the character of the relief stream:

- single phase flow of gas/vapour or liquid
- two phase flow of gas/vapour and liquid

Other multi-phase systems, like they can occur due to the additional presence of solids, are not covered by any broad and widely accepted theory so far, but must be treated and assessed individually.

The extreme difficulties in the treatment of such systems is mainly caused by the fact that the so-called *direct scaling* must not be applied. This term means the direct transfer of experimentally obtained results to the actual plant conditions respecting the rules of geometric similarity. For example, if it is assumed that a vent diameter of 0.1 m would be sufficient on a 6 m^3 reaction vessel, then the ratio of vent to reactor diameter amounts to approximately 1:15,6. If one tries to realize this ratio in a laboratory device with 0.1 l volume, then the emergency vent diameter would be close to 2,6 mm, this way comparable to the diameter of a steel capillary. However, the particle diameter of a solid with its corresponding distribution cannot be scaled down in an equivalent way. In consequence, the solid particles will block this vent capillary or significantly less solid material will be vented. If this solid is one of the reactive partners, this will cause a greater energy potential to remain within the laboratory reactor, and the behaviour observed in the laboratory experiment will have nothing to do with the later plant scale behaviour.

For the emergency relief design case of single phase venting all necessary design rules are published in technical regulations [91, 92, 93, 94]. In the case of incompressible fluids the necessary vent area is determined with the help of the following equation, which includes the assumption of one-dimensional, isentropic flow without phase transition:

$$A_0 = 0{,}6211 \cdot \frac{\dot{m}}{\alpha_w \cdot \sqrt{\Delta p \cdot \rho}} \tag{7-1}$$

In the case of compressible fluids the necessary vent area is determined using the same assumptions described for incompressible fluids, except that the resulting equation includes an additional flow function ψ:

$$A_0 = \frac{\dot{m}}{\psi \cdot \alpha} \cdot \sqrt{\frac{v}{2 \cdot p}} = 0{,}1791 \cdot \frac{\dot{m}}{\psi \cdot \alpha \cdot p} \sqrt{\frac{T \cdot Z}{M}} \qquad (7\text{-}2, 7\text{-}3)$$

In an emergency relief situation releasing compressible media, critical and subcritical pressure and flow conditions must be discriminated. The gas flow rate is limited to a maximum value of sonic velocity. This flow is called critical. In order to insert the correct flow function into Equ.(7-2/3), the critical pressure ratio between internal pressure, existing in the vessel to be vented, and the counter pressure, which in most cases is equivalent to ambient pressure, has to be evaluated:

$$\text{if } \frac{p_{\text{counter}}}{p} > \left(\frac{2}{\kappa+1}\right)^{\frac{\kappa}{\kappa-1}} \Rightarrow \text{subcritical pressure ratio}$$

Depending on the result of this evaluation of critical conditions, either the flow function ψ for subcritical conditions

$$\psi = \sqrt{\frac{\kappa}{\kappa-1}} \cdot \sqrt{\left(\frac{p_a}{p}\right)^{2/\kappa} - \left(\frac{p_a}{p}\right)^{(\kappa+1)/\kappa}} \qquad (7\text{-}4)$$

or for critical pressure conditions:

$$\psi_{\max} = \sqrt{\frac{\kappa}{\kappa+1}} \cdot \left(\frac{2}{\kappa+1}\right)^{1/(\kappa-1)} \qquad (7\text{-}5)$$

has to be inserted.

The design of emergency relief systems for two-phase flow, as is often observed in consequence of a runaway, is somewhat more complex. Especially the 10 years of intensive research conducted by DIERS, Design Institute for Emergency Relief Systems, [95, 96], the succeeding activities of the so-called DIERS-User Group, the pioneer work by Friedel in Germany [97, 98, 99], and the increasing number of available experimental data [100, 101] has resulted in an increasing understanding of the hydrodynamic processes involved in a pressure relief situation. While several years ago the design of emergency relief systems was entirely based on models of single phase adiabatic gas expansion, in its wider sense it has become the state of the art today to apply models accounting for two-phase flow, as it frequently occurs in reality. While 10 years ago all model experiments were still performed with non-reacting systems, such as Freon, it is possible today to investigate reacting systems experimentally.

Provided that the necessary amount of physicochemical substance data as well as kinetic and thermodynamic reaction data has thoroughly been obtained experimentally, one can choose today whether to base the vent design for a monoproduction process on either a steady model or on a simulation of the dynamic reactor behaviour with the help of specifically developed computer codes, such as e.g. SAFIRE^{TM} and RELIEF^{TM}.

In most cases it is sufficient, however, to perform the design with the help of steady state models. Before a possible procedure is presented in detail, a classification of reactions considered as well as pressure relief scenarios must be conducted.

7.1.1 General Fundamentals Of Two-Phase Pressure Relief

With respect to the type of reaction, at least three classes are generally distinguished, differing in the composition of the gaseous phase during the venting process. This system is shown in Figure 7-1. The left branch represents all cases which are characterized by a gas phase consisting of evaporated solvent only, neglecting the very small amount of nitrogen present, which is used for rendering the vessel inert.

All further considerations shall remain limited to pure vapour phase systems, because the design of hybrid and gas generating systems requires the additional information of the individual permanent gas generation rate. Such systems must each be characterized experimentally before the first run on the plant. This must be followed by the second step of assessing the compatibility of process and plant design.

In the investigation of vapour phase systems it is assumed that the reactor operates as a closed system and that the total pressure in the reactor corresponds to the vapour pressure at all times, which itself is related to the current temperature. The relationship between vapour pressure and temperature may be described with the simplified Antoine-relation

$$\ln p = j_1 - \frac{j_2}{T} \tag{7-6}$$

Vapour pressure systems have the advantage of reaching and passing through the pressure and temperature maxima at the same time. At the begin of relief the system is in a state of overheating with respect to ambient pressure. If the relief system was

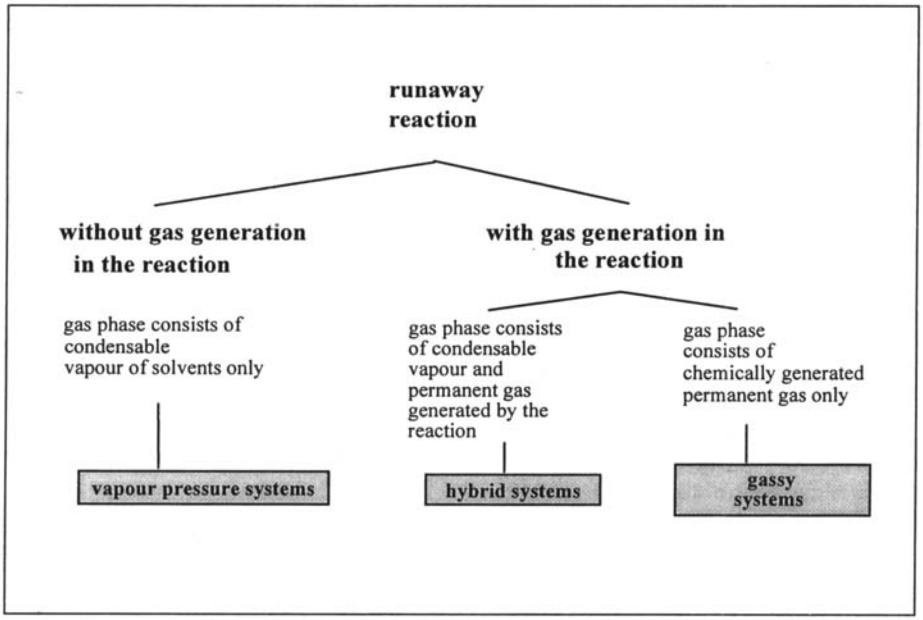

Fig. 7-1. Classification of runaway reactions in respect to the composition of the with gas phase released during an emergency venting

adequately designed, temperature and pressure will not increase further once the device has opened because all remaining heat of reaction will be fully transformed into latent heat of evaporation. Due to this effect vapour phase systems are also called ***tempered systems.***

From a construction point of view ***top or bottom venting*** are discriminated. In the majority of cases top venting with the help of a bursting disk or a safety valve installed on the reactor lid is preferred. This is the only alternative, which in principle provides the chance of a single phase vapour flow relief situation, e.g. if the filling level is low and if at the same time the system is not foaming. This kind of relief situation requires the smallest effective vent area. All further descriptions refers to the top venting situation only.

7.1.2 Design According To Leung's Equilibrium Model

The modified homogeneous equilibrium rate model according to Leung [101] is probably the most widely accepted model for the design of emergency relief situations for vapour phase systems. The attribute „homogeneous" in this case refers to the phase velocities of vapour and liquid in the relief stream. Using this term it is assumed that both phases move at an identical velocity and they are in thermodynamic equilibrium. This shows itself in the use of a homogeneous density for the description of the fluid.

$$\rho_{lg} = \frac{1}{v_{lg}} = \frac{1}{\dfrac{x}{\rho_g} + \dfrac{1-x}{\rho_l}} = \frac{1}{x \cdot v_g + (1-x) \cdot v_l} \tag{7-7}$$

The variable x in Equ.(7-7) refers to the vapour mass fraction of the fluid passing through the emergency vent area. The exact knowledge of this variable represents by far the greatest hurdle that has to be overcome in the design of emergency relief systems. The vapour mass fraction depends on numerous factors, among others on the flushing behaviour in the reactor.

For this reason, in a first step this flushing behaviour must be evaluated and it has to be examined whether a two-phase venting can be expected to occur or not. Figure 7-2 schematically shows the boiling phases.

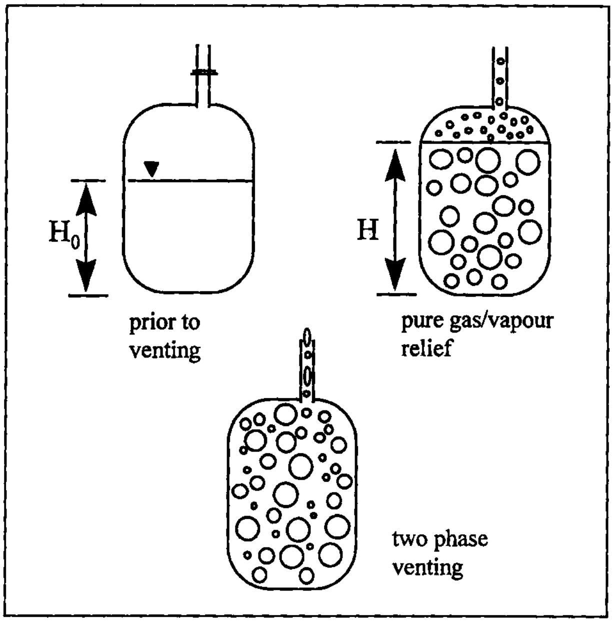

Fig. 7-2. Schematic presentation of the boil-up behaviour during pressure venting

Prior to venting the reaction mixture occupies a certain filling level H_0. The system is in equilibrium. With the opening of the relief device the liquid is in an overheated state. At first, just pure gas is vented and the flashing of the liquid begins. The vapour bubbles formed occupy more and more volume, causing the reaction mixture to boil up. The liquid level reached this way strongly depends, among other things, on the viscosity of the reaction mixture, which itself influences the mean bubble size. Usually two flushing flow patterns are distinguished: bubble flow, which occurs with higher viscous systems, and churn turbulent flow for lower viscous systems. The velocity of the rising bubbles amounts to approximately 5 to 10 cm/s in the first case and 15 to 25 cm/s in the case of churn turbulent flow.

The optical impression of a bubble flow system is characterized by a great number of finely dispersed small bubbles, while in the case of the churn turbulent flow a growing bubble size is observed on its way to the liquid surface.

A measure of the strength of the ebullience to be expected is the ratio of the vapour velocity based on the net cross sectional area u_{pipe} to the velocity of the rising bubble u_{bubble} for the two individual flow pattern. The vapour velocity based on the net cross sectional area is obtained from the volumetric vapour generation rate referenced to the cross-sectional area of the reactor. If this velocity and the viscosity of the reaction mixture are known for the relief conditions, then the liquid level occupied due to the boil-up may be estimated with the help of one of the flow models (c.f. Figure 7-3).

If this estimation shows that the free board volume is not completely filled with the boiling reaction mixture because the liquid level prior to venting was very low, the design for single phase venting may be conducted.

In the other case the vapour mass fraction at the relief device entrance must be estimated taking into account the flushing flow hypothesis. This allows the calculation of the so-called entropy parameter ω, which is required for the determination of the critical mass flow density G^*.

$$\omega = x \cdot \rho_{lg} \cdot (v_g - v_l) + \left[\frac{(v_g - v_l)}{\Delta_V h}\right]^2 \cdot c_P \cdot \frac{T}{v_{lg}} \qquad (7\text{-}8)$$

$$G^* = \sqrt{\rho_{lg} \cdot p} \cdot \left[0.6055 + 0.1356 \cdot \ln\omega - 0.0131 \cdot (\ln\omega)^2\right] / \sqrt{\omega} \qquad \text{for } \omega > 4 \qquad (7\text{-}9)$$

$$G^* = \sqrt{\rho_{lg} \cdot p} \cdot 0.66 / \omega^{0.39} \qquad \text{for } \omega \le 4 \qquad (7\text{-}10)$$

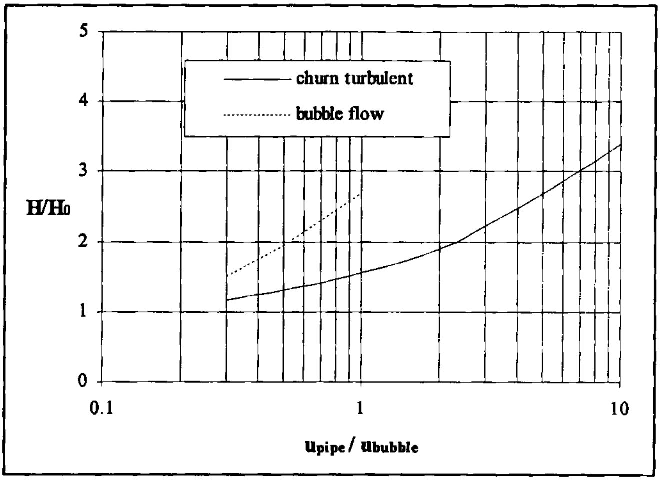

Fig. 7-3. Assessment of the boiling behaviour during emergency venting

A common prerequisite to the application of all these equations is the evaluation whether the ratio of set pressure of the relief device to the counterpressure is high enough to ensure critical flow conditions in the vent area.

For the majority of reactions performed in organic solvents with a low viscosity, it may be assumed that the vapour mass fraction of the fluid will be very small. This can be explained by the dependence of the volumetric vapour fraction ε on the vapour mass fraction. Figure 7-4 shows this relationship for four solvents at 6 bars absolute pressure.

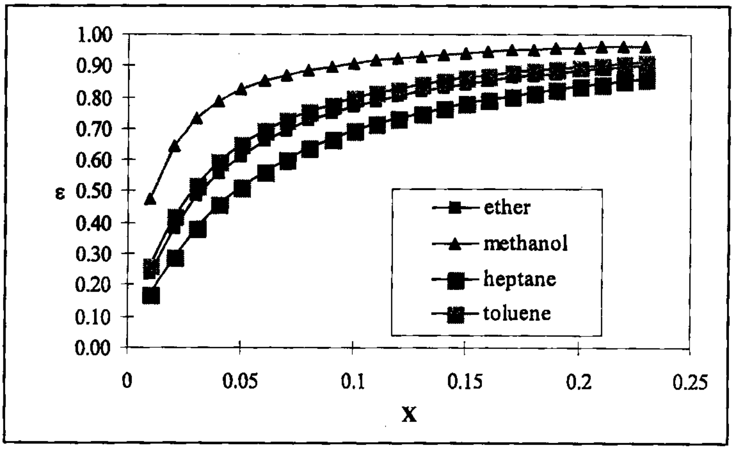

Fig. 7-4. Dependence of volumetric vapour fraction on vapour mass fraction for four different organic solvents at 6 bar

From this diagram it can be seen that 5% vapour mass fraction already correspond to 65% of volumetric vapour fraction on average. Actually this value of 5 % may be regarded as a good first estimate if a rigorous design is acceptable. For such cases, with a low vapour mass fractions the critical mass flow density may be approximated with the help of the following equation.

$$G^{*} = 0.9 \cdot \left(\frac{\Delta_V h}{v_{lg}} \right) \cdot \frac{1}{\sqrt{T_{set} \cdot c_P}} \tag{7-11}$$

This critical mass flow density G^{*} has to be corrected with a flow correction value α, as was the case for single phase flow. The model uncertainties, which are still inherent to all two-phase flow models, are arbitrarily compensated by this parameter. Therefore a range for α of

$$0.9 \le \alpha \le 0.95 \tag{7-12}$$

is recommended in context with the design according to Leung's model. For the critical mass flow density it follows

$$G = G^{*} \cdot \alpha \tag{7-13}$$

The necessary vent area can be calculated from:

$$A = \frac{\dot{m}}{G} \tag{7-14}$$

with the mass flow $\dot{m}$

$$\dot{m} = \frac{m \cdot \dot{q}}{\left(\left(\frac{V}{m} \cdot \frac{\Delta_V h}{v_{lg}} \right)^{0.5} + \left(c_p \cdot \Delta T \right)^{0.5} \right)^{2}} \tag{7-15}$$

The term $\Delta_V h/v_{lg}$ is obtained by substitution of the term $T_{set} * (dp/dT)$ with the help of the Clausius-Clapeyron equation.

A great number of investigations performed in the past have shown that permitting a slight further pressure increase above the set pressure during venting results in a significant reduction of required vent area. But this advantageous effect is limited to approximately 25% Δp referring to the set pressure. Above these 25 % the effect becomes negligible.

The temperature difference ΔT of Equ.(7-15) exactly corresponds to the difference between the maximum temperature, which is achieved due to this permitted overpressure, and the temperature at this set point.

$$\Delta T = T_{max} - T_{set} \tag{7-16}$$

The specific thermal reaction power is calculated by arithmetically averaging the specific powers corresponding to the maximum and set temperature, respectively.

$$\dot{q} = \frac{\dot{Q}}{m} = \frac{1}{2} \cdot c_p \cdot \left[\left(\frac{dT}{dt} \right)_{set} + \left(\frac{dT}{dt} \right)_{max} \right] \tag{7-17}$$

Provided that the course of the temperature gradient in its dependence on temperature under upset conditions has successfully been determined by adiabatic calorimetry, which has been described in Section 4.4, and if the set temperature is known from the set pressure and the vapour pressure relation, then the minimum vent area can be calculated applying the equations as presented.

7.1.3 Design For Multi-Purpose Plants - A Special Problem -

The procedure described in the previous section is only applicable, if the reaction vessel considered is used for just one single process. In this case all necessary substance and system data can be obtained experimentally at a reasonable expense. In the fine chemicals and pharmaceutical industry, however, multipurpose plants are preferred. They are required in order to be able to respond adequately to the fast changing development activities and the continuously changing mass demands. During project engineering activities for such a plant the problem may arise that several hundred different syntheses are expected to be performed on this plant, of which may be half are known chemically due to current activities.

As escalating process deviations can never be fully excluded, these reaction vessels also have to be equipped with emergency relief devices. The experimental characterization of all processes, even of the known ones, is not possible in the extent necessary for vent design.

In the following a procedure is presented which leads a way out of this problem and allows the necessary design of multi-purpose plants without an exact knowledge of the chemistry to be performed later on this plant.

It must be emphasized again at this point that it is a *procedure* which is going to be presented here. The data used are only sample data and must specifically be defined for each company in case of application.

7.1.3.1 The Concept Of The Credible Worst Case

Pressure relief systems represent the last level of measures taken to protect the plant and its environment. As this is world wide acknowledged practice, the state of the art demands a design of these systems for the worst possible case. This phrase has guaranteed endless discussions ever since it was first coined.

Those responsible for the project engineering of such a plant, who often have access to less than 50 % of the information on the chemistry to be performed later due to the reasons mentioned, can come up with only one recommendation if they seriously wish to meet the demand for a design for the worst possible case: leave the lid off the reactor. The lack of practicability of this proposal, not least due to the violation of other process safety engineering principles, does not need to be elaborated any further.

Experts in the Anglo-Saxon world deal with this problem in a more reasonable semantic way. They discriminate between the terms possible worst case and credible worst case [6]. The terminology of a credible worst case now opens the space to interpretation without leaving the worst case philosophy.

The chemistry which is to be performed in this new plant belonging to a certain branch of the company usually can be characterized and classified with respect to certain boundary conditions. An example for one of these boundary conditions could be the fact that all reactions are going to be performed in a quasi-open system. A quasi-open system shall be defined as a vessel, which is connected to at least one condenser, and which is operated under a pressure-controlled inert gas atmosphere. Looking at the definition of vapour pressure systems, their definition can be looked upon as a first step towards a credible worst case design. They are regarded as systems operated in a closed form with an increasing pressure following the vapour pressure curve up to the set pressure.

Furthermore it is highly probable that the majority of specialty chemicals are manufactured in feed controlled processes. If the pressure relief design assumes that the maximum potential comes into effect in the batch process, then this corresponds to the assumption of a complete dosage failure, at least for the majority of processes. This procedure on one hand covers all exceptions which are designed as batch processes, and on the other side contributes to the definition of a credible worst case for all semibatch processes.

All further assumptions for the design are based on a cooling failure scenario without specifying any of the causes leading to it. Thus it is assumed that at least two independent failures occur simultaneously:

1. the break-down of the cooling independent of its causes
2. the closed, instead of quasi-open, operation of the vessel

and for the majority of chemical processes that even a third independent maloperation occurs:

- the coming to effect of the total potential in form of a batch process due to a dosage failure.

Finally a fourth boundary condition shall be valid to support the worst case character of the procedure. The reaction order necessary for the formal kinetic description of a process has a severe influence on the pressure/time and respectively the temperature/time-profiles to be expected. Industrial experience has shown that approximately 90% of all processes conducted in either batch or semibatch reactors can be described with a second order formal kinetic rate law. But it remains uncertain whether this statement, which is related to isothermal or isoperibolic operation with a rather limited overheating, remains valid if the reaction proceeds adiabatically and if side reactions contribute to the gross reaction rate at a much higher degree. In consequence, it shall be assumed for a *credible worst case* evaluation that the disturbed process follows a first order kinetics. Any reactions occurring in reality will almost certainly proceed at a much lower rate.

Figure 7-5 shows the dependence of the isothermal conversion on the Damkoehler number for reactions of the first and second order performed in a batch reactor. If the expected conversion is equal to 90%, then the first order reaction will be four times faster than the second order reaction.

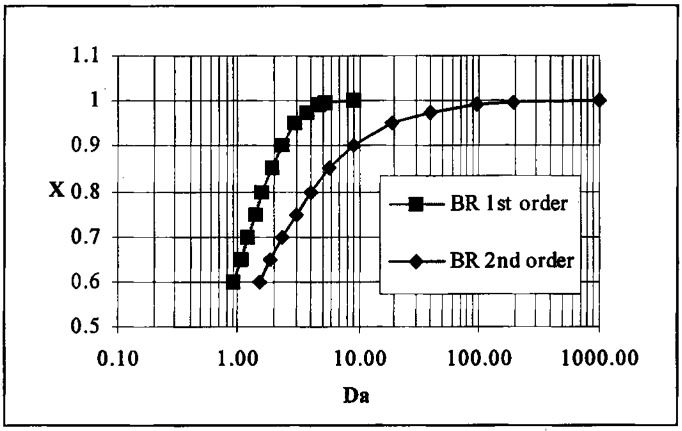

Fig. 7-5. Dependence of conversion on Damkoehler number for first and second order reactions performed in an isothermal batch reactor

This philosophy presented here, which naturally must be adapted from case to case, for example, if low-temperature reactions or high-pressure hydrogenations are to be performed, allows for the development of a truly credible worst case. It cannot be compared with a possible worst case scenario constructed with unlimited imagination. But it still has a quality which justifies its title of a worst case. A factor of simultaneously occurring independent errors of 3 and the additional formal kinetic constraint add up to a process deviation from normal operation, which may be called dramatic with quite some confidence.

7.1.3.2 The Procedure

The starting point to all further calculations is defined by a very limited amount of plant as well as substance data. All plant data necessary are in general restricted to the following, copied from a sample spreadsheet.

vessel volume	V [m^3] = 7.080
batch size	V_l [m^3] = 6.0
maxim. allowable overpressure	Δp [%] = 20.0
safety valve	d [mm] = 80.0
	d-inlet [mm] = 100.0
	d-outlet [mm] = 150.0
	A [m^2] = 0.005
	friction flow factor α = 0.9

All data given for the safety valve refer to the inlet and outlet diameter as well as the smallest cross sectional area. The friction flow factor α was fixed in accordance with the recommendations given for Leung's model.

An easy way to obtain substance data is to look at the organic solvents which are expected to be used. In many cases a selection can be made containing those which cover the operational range by their boiling points under standard pressure and at the maximum relief set pressure. Figure 7-6 shows such a selection for the example used to help understand the presented procedure.

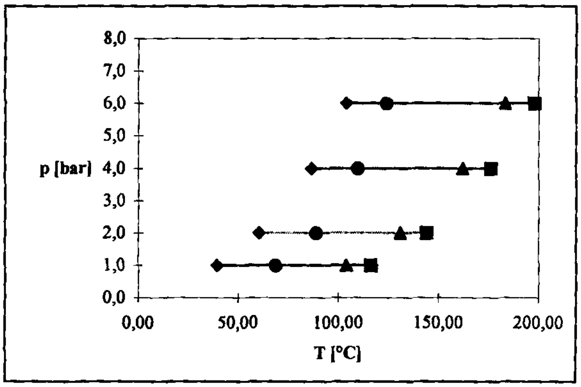

Fig. 7-6. Presentation of a temperature range covered by four organic solvents
◆ = ether • = methanol ▲ = heptane ■ = toluene

With the help of the substance property data, which are well known for these common solvents, and the plant data listed above, the mass flow which can be relieved safely by the planned safety valve can be calculated applying the equilibrium model according to Leung. For the sample calculations presented in Table 7-1, a vapour mass fraction of 5 %, an allowable overpressure during relief of $0.2 \cdot p_{Set}$ and the simplified model for the determination of the critical mass density have been assumed.

The sample solutions presented for methanol, as given in Table 7-1, can easily be calculated for all other solvents. In a next step it is necessary to find the thermodynamic and kinetic parameters of reactions which in the case of maloperation produce exactly the mass flow just determined due to their energy release, if they are started at a temperature below the boiling point at standard conditions of the solvent they are performed in.

Table 7-1: Sample solutions for the determination of the relief mass flow possible in the plant described - solvent : methanol -

p	c_p	Δvh	v_g	v_f	v_{lg}	m	G	G*α	m/t	q	dT/dt
[bar]	[kJ/kgK]	[kJ/kg]	[m³/kg]	[m³/kg]	[m³/kg]	[kg]	[kg/m² s]	[kg/m² s]	[kg/s]	[W]	[K/s]
1	2.783	1102	0.699	0.001264	0.697818	4746.0					
3	3.260	1022	0.250	0.001402	0.248598	4746.0	3352.4	3017.1	15.2	658163	0.0425
4	3.380	996	0.185	0.001422	0.183578	4746.0	4291.4	3862.3	19.4	985780	0.0615
5	3.490	974	0.148	0.001400	0.146600	4746.0	5122.4	4610.2	23.2	1330652	0.0803
6	3.580	953	0.130	0.001455	0.128545	4746.0	5595.5	5036.0	25.3	1574309	0.0927

7.1.3.3 "The Trick"

All assumptions made so far correspond to two known equations, which describe the reactions to be performed:

- the unsteady-state heat balance of the adiabatic batch reactor for first-order chemical reactions

$$\frac{dT}{dt} = \Delta T_{ad} \cdot k_\infty \cdot (1 - X_{ad}) \cdot \exp\left(-\frac{E}{R \cdot T}\right) \tag{7-18}$$

- the adiabatic coupling equation

$$T - T_0 = \Delta T_{ad} \cdot X_{ad} \tag{7-19}$$

Analysis of these two equations shows that at least two more linear independent equations must be found in order to be able to describe the system completely.

The trick to solve this problem consists of two steps. In the first step it is postulated, that the maximum adiabatic temperature gradient is reached at the set pressure.

Based on this postulate a first decisive equation can be obtained which describes the relation between the activation temperature E/R and the adiabatic conversion X_{ad} at the set point.

$$\frac{d^2T}{dt \cdot dT} = 0 \quad \Rightarrow \quad \frac{E}{R} = \frac{T_{Pset}^2}{\Delta T_{ad} \cdot (1 - X_{ad,Pset})} \tag{7-20}$$

If the adiabatic conversion X_{ad} in the adiabatic coupling equation is substituted with the help of Equ.(7-20), the following relationship is obtained:

$$T_0 = T_{Pset} - \Delta T_{ad} + \frac{R \cdot T_{Pset}^2}{E} \tag{7-21}$$

Now only one further information about E/R is missing in order to be able to calculate all relevant values. This missing information can be obtained from one of the oldest rules of physicochemistry. Van't Hoff's rule makes a statement about the acceleration of a reaction if the process temperature is increased by 10 K. Based on the knowledge about the chemistry usually conducted in a plant, such a company specific acceleration factor can be defined. For the example discussed here the following shall be valid:

- at the normal operating process temperature, which corresponds to T_0 in the case of a maloperation, all reactions shall follow van't Hoff's rule and on average double their reaction rate if the temperature is increased by 10 K.

If this acceleration factor is regarded too low, then it can be set equal to 3 or any other specific value. In any case this application of van't Hoff's rule helps to obtain another equation for the determination of E/R:

$$\left.\frac{d \ln k}{dT}\right|_{T_0} = \frac{E}{R \cdot T_0^2} = \frac{\ln 2}{10} = 0.069 \tag{7-22}$$

If T_0 is substituted in Equ.(7-22) with the help of Equ.(7-21), an equation of the third degree is obtained to determine E/R. This equation contains the term RT^2/E, which is much smaller than 1 and which may therefore be neglected in a first approximation. With this simplification the following equation for the calculation of E/R is obtained:

$$\frac{E}{R} = \left(T_{Pset} - \Delta T_{ad}\right)^2 \cdot 0.069 \qquad (7\text{-}23)$$

Now a parameter array can be opened, containing all valid solutions which have the maximum temperature gradient at the set pressure as calculated from plant data on the basis of Leung's model, and which this way just generate the maximum allowable relief stream. One possibility for the calculation of this array is to vary E/R within a reasonable range, for example between 5000 and 15 000 K, and then to calculate the corresponding adiabatic temperature increase with the help of Equ.(7-23) for each solvent and the corresponding set temperatures. Only those solutions are physically meaningful which are greater than 0. With these data, the corresponding initial temperatures in case of a maloperation, T_0, can be obtained from Equ.(7-21). Only those solutions are permitted, which have initial temperatures lower than the standard state boiling point of the solvent considered. The adiabatic coupling equation may now be used to calculate the adiabatic conversion, which may not exceed a value of one by definition. With the help of the heat balance the last missing value can be obtained, which is the preexponential factor belonging to each parameter combination.

If all parameter sets calculated in accordance with the procedure just described are evaluated, it turns out that, due to the principle of corresponding states, they form a net. All reactions characterized by a three-dimensional parameter combination positioned under this net may be performed in this vessel because, in the case of a failure scenario, they will produce mass flows which are smaller than the maximum allowed mass flow. All reactions with a parameter combination positioned above the net must not be performed in this plant except if the protecting safety concept has been adequately modified. A three-dimensional plot of the columns which carry the net for a set pressure of 6 bars is shown in Figure 7-7 for the example discussed here.

Now it is only a small step to develop 2-dimensional nomograms based on this three-dimensional presentation which can be used to assess the compatibility of each synthesis with the vessel they have been calculated for. Figure 7-8 shows the relation between $k(T_0)$ and T_0. It can be seen that all values which connect different activation temperatures at constant boiling temperature for a given set pressure can be approximated by a linear relationship. At the same time it can be seen that the different solvents form a systematic order on the curve of constant activation temperature. If this last mentioned curve at constant activation temperature is scaled, then the other curves of arbitrary boiling temperatures for a given set pressure can also be calculated. The relation between ΔT_{ad} and T_0 can be treated in exactly the same manner. The resulting nomograms are shown in Figures 7-9 and 7-10.

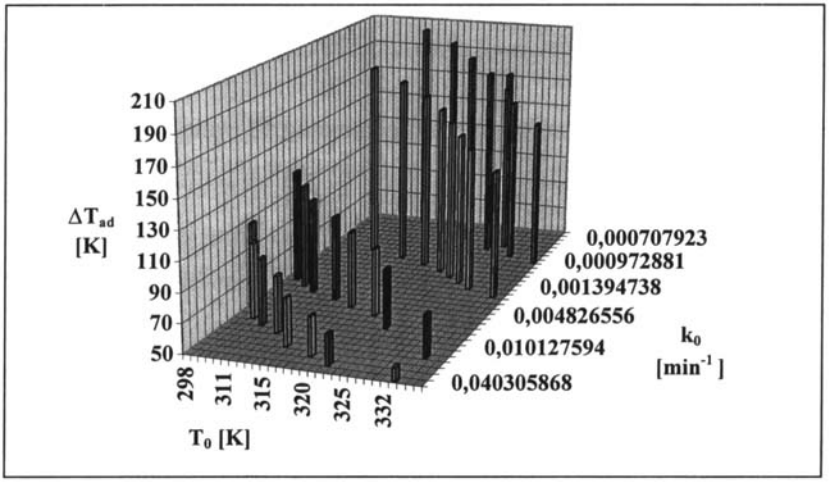

Fig. 7-7. Presentation of the columns supporting the net for a set pressure of 6 bars

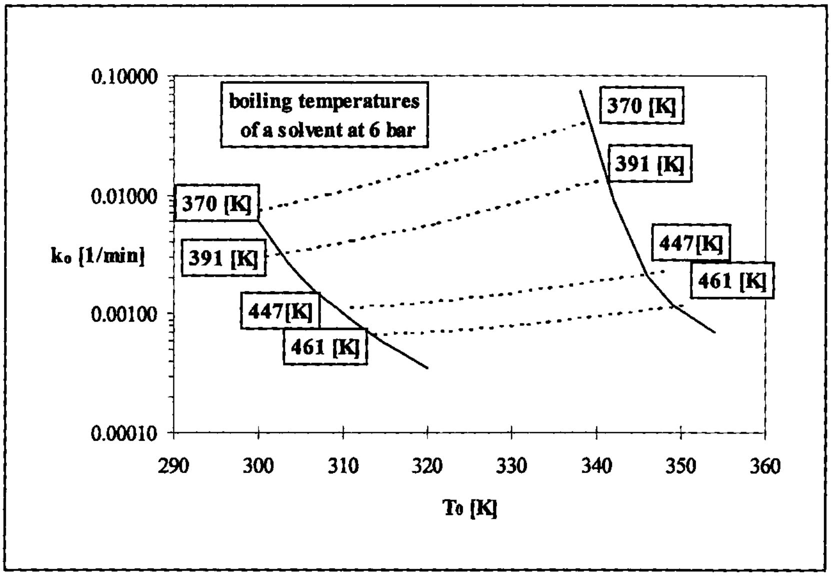

Fig. 7-8. Presentation of curves at constant activation temperature (full line) and at constant boiling temperatures (dotted line) for a given set pressure of 6 bars absolute

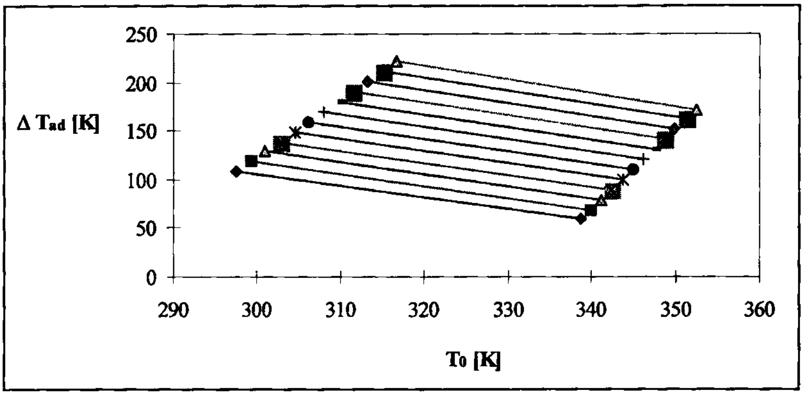

Fig. 7-9. Nomogram 1 for the safety assessment of chemical reactions, valid for the vessel described in the example
set pressure 6 bar absolute - lines at constant boiling temperatures starting at 370 K (bottom line) in 10 K intervals

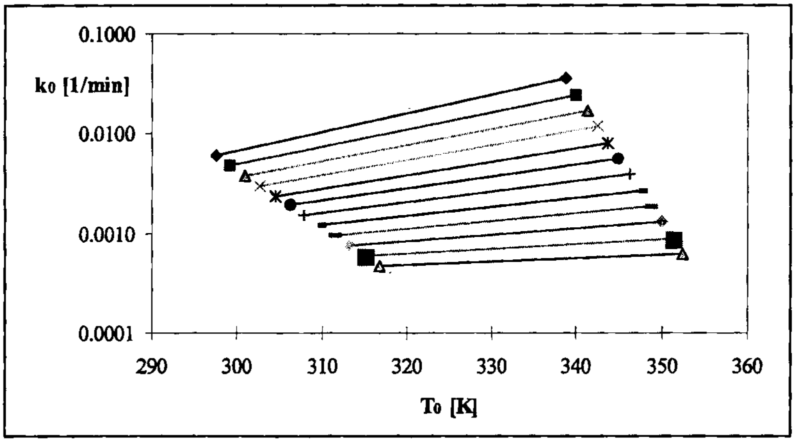

Fig. 7-10. Nomogram 2 for the safety assessment of chemical reactions, valid for the vessel described in the example
set pressure 6 bar absolute - lines at constant boiling temperatures starting at 370 K (top line) in 10 K intervals

This closes the design of emergency relief systems for vapour phase systems, which have been considered here exclusively. If the adiabatic temperature rise which will be observed in case of a cooling failure is known, and with the knowledge of the boiling point of the solvent at the set pressure, in this example 6 bars, nomogram 1 can be used to evaluate whether the process temperature under normal operating conditions is lower than the value obtained by constructing a line perpendicular to the x-axis. The maximum allowable T_0 value obtained by the intersection of this line perpendicular to the x-axis and the axis itself is used as input value to nomogram 2, which is used to assess whether the reaction rate constant under normal operating conditions is lower than the maximum allowable value. This maximum value for the rate constant is obtained by constructing a line perpendicular to the y-axis. Finally, organizational measures must be implemented to ensure that no process which is not in compliance with the boundary conditions of this procedure, for example gas generating reactions, receives a permit to operate without an individual assessment.

7.1.4 Summary

It was the aim of this section to present and deduce the main procedures which allow a responsible design of emergency relief systems. The concept is based on the definition of a "*credible worst case*" and the utilization of reaction engineering principles in a suitable combination.

But it must be emphasized again, that bursting disks and safety valves should always represent the last resort only. Instead, one should work towards a synthesis development which takes care of a significant distance between true reaction data under desired conditions and those limit values which correspond to the individual designs of relief systems. Such designs in the sense of safety barriers support the attempt to allow the performance of thermally inherent safer processes only. This way relief systems could be reduced in their purpose to what they actually should be: a formally required installation to a vessel, which should never have to prove its efficiency.

7.2 Safe Disposal And Containment Of Emergency Relief Streams

Chemical reactors and pressure vessels must be protected against an intolerable pressure rise by the installation of safety devices. If measuring and control devices are not sufficient to control a runaway reaction, then the only remaining protective measure is, as discussed in the previous section, to provide a pressure relief system, such as a bursting disk or safety valve.

In a next step a safe disposal of the relief stream has to be taken care of. Finally, substances with extremely hazardous properties must either be collected in a catch tank or further conveyed to a suitable treatment system for their final disposal.

The following paragraphs will list criteria to be assessed in order to ensure the correct design of all relevant pipes as well as present the fundamental design recommendations for a few kinds of catch systems.

7.2.1 Assessment Of Vent Line Design To And From Relief Devices

The assessment of the adequate vent line design to and from the relief device has the task to ensure the required operability especially of the emergency relief valve. For this purpose it must be checked that there is only a limited pressure drop in both vent lines.

The permitted distinct values for the maximum allowable pressure drop depend, among other things, on the exact design of the valve. It is common practice to limit the maximum permitted pressure drop for the inlet pipe to 10% of the set pressure. For the outlet vent line from a balanced bellows safety relief valve a 30% pressure drop with respect to the set pressure is regarded as permissible. The manufacturers of relief valves provide the exact limit values. Therefore the data given here should be looked upon as recommendations without any mandatory character.

In the following some equations shall be provided which allow a fast estimation on the pressure drop to be expected in the case of two-phase pipe flow. Exact calculations, especially for very long pipes with changing cross-sectional area, are very extensive and can be performed correctly only by a few experts. However, the equations presented here are sufficient to estimate the pressure drop if the purpose is to compare the calculated values and the given limit values.

In principle, the classical Fanning-equation can be used to calculate the frictional loss in pressure

$$\Delta p = \left(4 \cdot f \cdot \frac{L}{d_{pipe}} + \sum_i n_i \cdot \xi_i \right) \cdot \rho \frac{u^2}{2} \qquad (7\text{-}24)$$

except, that all parameters included must account for two phase flow. The following relation is obtained by some rearrangements of the above expression:

$$\Delta p = \left(4 \cdot f \cdot \frac{L}{d_{pipe}} + \sum_i n_i \cdot \xi_i\right) \cdot \frac{G^2_{c.s.-pipe} \cdot v_{lg}}{2} \tag{7-25}$$

The critical mass flow density is referenced to the cross-sectional area of the pipe in this case. In order to be able to calculate the friction factor f for the pipe, the Reynolds-number must be known. For the special case of a homogeneous two-phase pipe flow, this can be calculated according to:

$$Re_{lg} = \frac{G_{c.s.-pipe} \cdot d}{\eta_l} \tag{7-26}$$

The friction factor can now be calculated with the help of one of the numerous correlations known from process engineering, e.g. the correlation by Churchill

$$f = \frac{1}{\left(3.6 \cdot \log \frac{Re}{7}\right)^2} \tag{7-27}$$

The total pressure drop finally results from the sum of frictional and hydrostatic pressure losses.

7.2.2 Catch Tank Design (Knockout Drums)

The relieved vent stream enters the catch tank at one end, the gas phase is separated from the liquid phase, the liquid phase remains in the catch tank and the gas leaves it at the other end. Such catch tanks working according to the gravity separator principle are widely used in industry, because they are applicable for many substances. Another advantage is the capacity to contain large volumes and the fact that they may be placed quite a distance away from the reaction vessel.

Their design can be performed according to technical regulation API 521 [103]. The aim of the assessment regarding the design is a comparison of the length of the tank and the necessary distance the droplets need to settle.

In a first step the settling of the droplets in the tank is calculated.

$$u_d = 1.15 \cdot \sqrt{\frac{g \cdot d_{droplet} \cdot \left(\rho_l - \rho_g\right)}{\rho_g \cdot C}} \tag{7-28}$$

If the boundary condition is made that only those droplets may leave the catch tank again which are smaller in diameter than $d_{droplet} < 150\ \mu m$, then this equation becomes simplified to:

$$u_d = 0.0441 \cdot \sqrt{\frac{\left(\rho_l - \rho_g\right)}{\rho_g \cdot C}} \tag{7-29}$$

C is a dimensionless factor representing a drag coefficient, which may be calculated by the following approximation

$$C = \exp(-2 + \exp(2.16095 + 0.15567 \cdot \ln C(Re)^2)) \tag{7-30}$$

with

$$C(Re)^2 = \frac{119 \cdot 10^{-10} \cdot \rho_g \cdot (\rho_l - \rho_g)}{\eta^2} \tag{7-31}$$

In a next step the geometrical data of the catch tank must be determined or fixed. With these data the fraction of the cross-sectional area is calculated, which is wetted by the liquid caught back. In doing so, it is assumed that the complete inventory vented is caught back as a liquid.

$$S_l = \frac{V_l}{L} \tag{7-32}$$

In the succeeding step the non-wetted cross-sectional area is required,

$$S_g = \frac{\pi \cdot D_{tank}^2}{4} - S_l \tag{7-33}$$

in order to calculate the heights H_l and H_g at the front side of the tank. By combining the free height H_g, which is proportional to the non-wetted area, and the settling velocity of the droplets, the liquid drop-out time can be calculated.

$$t = \frac{H_g}{u_d} \qquad (7\text{-}34)$$

This time is required, finally, for the determination of the minimum length of the catch tank.

$$L = u_V \cdot t \qquad (7\text{-}35)$$

The last remaining unknown is the vapour inlet velocity, which may be obtained from the mass flow rate leaving the vent pipe and the non-wetted front area.

$$u_V = \frac{\dot{m} \cdot v_g}{S_g} \qquad (7\text{-}36)$$

Finally this minimum length and the true length of the tank are compared. If the actual length is greater than the calculated length, the assessment is finished, if not, the tank must be changed or a different system selected.

7.2.3 Cyclone Separator With Separate/Integrated Catch Tank

The cyclone separates liquid and gas phase, and the liquid settles in a separate container. In the case of a high gas phase volume fraction, it is recommendable to design the cyclone with an integrated catch tank to collect the liquid. The advantage of a cyclone is its lower space requirement compared to horizontal knockout drums. Cyclones are widely used in the chemical process industry as their range of operation is very large. It may be used for low as well as high gas velocities, low as well as highly viscous liquids and under elevated pressure. Its disadvantage is the fact that it has to be installed rather close to the reaction vessel.

Grossel gives design recommendations as shown in Figure 7-11 [104]. The necessary cross-sectional area is calculated according to

$$A = \frac{\dot{m}}{G_V} \qquad (7\text{-}37)$$

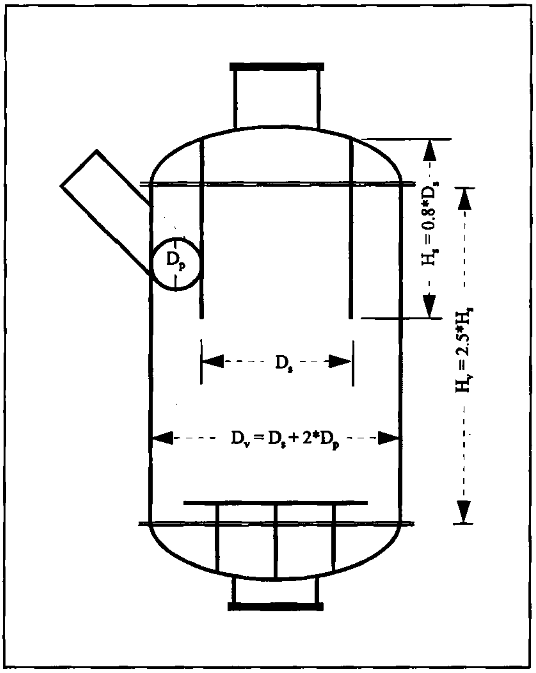

Fig. 7-11. Design of cyclone separators according to Grossel

In the case of an integrated design the length of the vessel must be enlarged to enable a containment of the maximum liquid inventory to be relieved.

Muschelknautz gives the following additional design recommendations [105]:

1. The volume of the separator must be so large, that the separation process is not negatively influenced by the accumulation of liquid material at the bottom. As a first recommendation, the vessel volume should be 1.5 times larger than the maximum liquid inventory relieved and to be contained.
2. The liquid separation and settlement are enhanced by an inlet pipe, which is installed in with a slightly negative slope and in such a way that a tangential inlet flow is ensured. This at the same time enables the connection of a second vessel to this separator. The angle of the negative slope should approximately lie between 15° and 20°.
3. A cyclone separator suitable for to pressure venting scenarios should be very robust in design, because in the case of a high liquid entrainment in the vent stream the resulting momentum forces exerted on the structure can be strong.

The major design data according to Muschelknautz are presented in Figure 7-12 and the relations to follow.

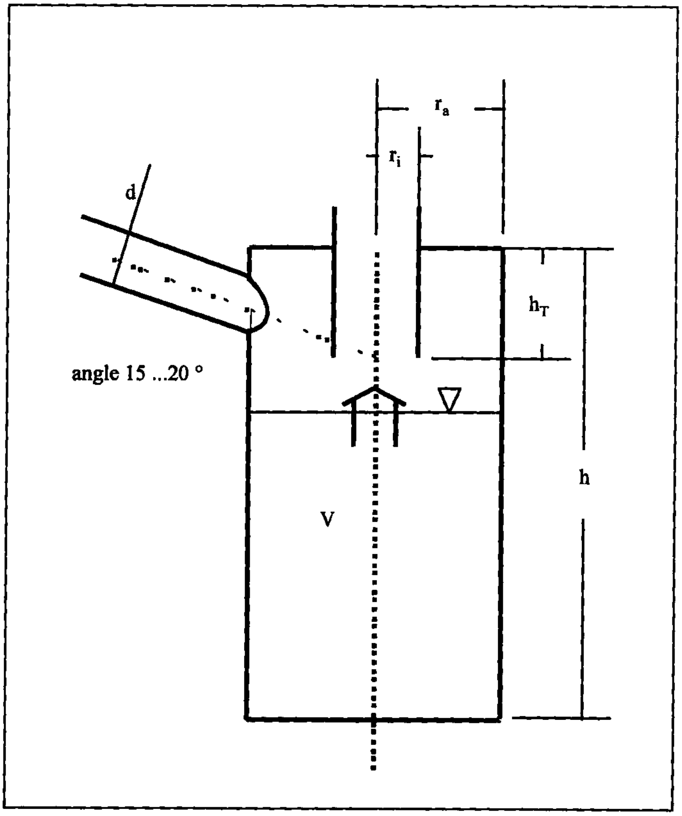

Fig. 7-12. Design of a cyclone according to Muschelknautz [105]

$\frac{\dot{V}_{Gas}}{\pi \cdot r_c^2} = 3...6$ [m/s]	with the radius r_c of the catch tank [m]
$r_c \geq 1{,}5d$	with d = vent line diameter [m]
$h \geq 3r_c$	with h = height of the tank [m]
$r_i = 0{,}3...0{,}6r_c$	with r_i = radius on the outlet pipe of the cyclone [m]
$h_T = 0{,}3...0{,}6r_c$	with h_T = height of the dip tube [m]
$V = 1.5 \cdot V_l$	with V = catch tank volume [m^3]

7.3 Protection Against Explosions By Inertization

By definition, an explosion is a very fast proceeding oxidation reaction. Prerequisites are the prevalence of a concentration of the flammable substance within specific explosion limits, a high dispersion of the fuel in the oxidizing medium and the presence of an effective ignition source.

An explosible atmosphere is defined as a mixture of flammable gases, vapours, mists or dusts and air or another oxidizer under atmospheric conditions in such a ratio that the reaction, once ignited, proceeds self-sustained, accompanied by increases in temperature and pressure.

These are the most important definitions. Before the detailed presentation is given on how the suitable addition of a chemically inert gas can convert an explosible atmosphere into one which does not hold this risk any more, some general hints shall be provided regarding the assessment strategy of an explosion risk.

7.3.1 Description Of The Assessment Procedure For Explosion Risk

All installations and functional units which come into operational contact with flammable material, have to be examined as to whether an explosible atmosphere may be present under normal operating conditions. These include times of inspection and maintenance as well as situations of minor process deviations. In a new plant this evaluation should be performed for the first time during process engineering activities and be available in documented form for the detail engineering.

The assessment of an explosion hazard has to include the close vicinity of the installation or functional unit. In the case of in-house installations the complete room has to be considered. If an existing plant is evaluated, explosion protection measures already installed may not be accounted for in this analysis of an explosion hazard. If they were selected adequately in former times, then the result of the study will reconfirm their necessity.

After the localization of places and areas with the possibility of a formation of an explosible atmosphere, the resulting hazard must be assessed. Corresponding to the probability of formation of an explosible atmosphere, which represents the endangerment, these localized areas are attributed „zones“. Within a building the boundaries of a zone are defined at concrete walls. The zone classification still in use in Germany was first published by the BG-Chemie. Some changes to this system are to be expected due to European legal harmonization activities. Consequently, the individual zone definitions are not repeated here. But the general principle of the application of a zone system will remain unchanged also in the future.

The result of this zone classification has to be documented in suitable maps, such as concession or set-up maps. If a new plant is being built, these activities should at the latest be part of the detail engineering.

7.3.2 Classification Of Protection Measures Against Explosions

The main underlying principle behind the protection against explosions says that the higher either the probability of formation or the duration of existence of an explosible atmosphere is, the higher are the demands on protective measures.

As has already been outlined in Section 5.3, *preventive* and *constructive* protective measures are discriminated. The preventive measures among other things comprise:

- the prevention or limitation of formation of an explosible atmosphere within a device by substitution or limitation of the inventory of flammable material
- supervised inertization
- limitation of concentration
- the prevention or limitation of the formation of an explosible atmosphere in the vicinity of a device by using a closed system

The elimination of ignition sources such as hot surfaces, flames, hot gases, mechanical sparks, electrical installations, static electricity or exothermic reactions, is looked upon as preventive to a limited extent only. In former times this measure was rated secondary.

Constructive measures comprise pressure resistant design, pressure impact resistant design, explosion venting, explosion suppression and decoupling.

Preference should be given to primary or preventive measures wherever possible. Due to this, inertization, as the most frequently applied technique, shall be considered more closely.

7.3.3 Fundamentals Of Inertization

Some important terms shall be introduced and defined prior to the detailed description of inertization techniques.

- *Inertization* is defined as the replacement of air/oxygen by a non-reactive gas within an apparatus.
- *inert gases* are substances, which will not form an explosible atmosphere with a fuel or which act as phlegmatizers, if a sufficient amount is added to the mixture.
- *maximum allowable oxygen concentration* is defined as the concentration which must not be exceeded if a sufficient desensitization shall remain ensured.
- *degree of inertization* characterizes the oxygen concentration in the device to be protected.
- *partial inertization* is the reduction of the oxygen concentration down to a value which leaves the atmosphere no longer explosible independent of the amount of fuel added.
- *total inertization* defines a concentration ratio of inert gas to fuel which cannot be turned into an explosible mixture independent of how much air/oxygen is added.

The following paragraphs describe steps to follow in designing or assessing an inertization.

Definition of the inertization concept

In defining the concept the following points must be addressed:

- method of inertization: vacuum purging or sweep-through purging
- degree of inertization
- type of inert gas: nitrogen, argon, carbon dioxide
- demands on availability and supervision of inertization

Methods of Inertization

A very common method to reduce the oxygen concentration is to draw vacuum to the apparatus or container and then to relieve it with an inert gas. This procedure is commonly called *pressure purging* and is repeated a number of times until the desired degree of inertization has been achieved. A condition for the application of the vacuum purging method is that the system is designed to withstand vacuum. If the method is applied, it is necessary to check whether the apparatus or vessel is leak-proof prior to each time the inertization is required. The following Table 7-2 provides the oxygen concentrations achievable with this method in dependence on the frequency of vacuum draws and reliefs as well as on the degree of vacuum realized.

Table 7-2: Achievable degree of inertization by the vacuum purging method

vacuum operations	remaining contents after 1, 2 and 3 repetitions					
	0.5 bar		0.3 bar		0.1 bar	
	oxygen %(v/v)	nitrogen *	oxygen %(v/v)	nitrogen *	oxygen %(v/v)	nitrogen *
1x vacuum drawn and relieved with inert gas	11	0.5	6.5	0.7	2.5	0.9
2x vacuum drawn and relieved with inert gas	5.5	1	2.3	1.4	0.7	1.8
3x vacuum drawn and relieved with inert gas	3	1.5	1.1	2.1	0.5	2.7

* multiples of volume of the individual apparatus

Another method of inertization is the so-called *sweep-through purging* method with an inert gas. This sweep-through purging method is especially suitable for the inertization of pipelines and devices not designed to withstand vacuum. If the device is not completely leak-proof, special attention has to be paid to possible adverse effects to health by the inert gas and possible oxygen deficiencies in close proximity to the apparatus. Necessary countermeasures are to be implemented. The TLV-TWA of CO_2 is equal to 5000 ppm and a suffocating effect of nitrogen is observed above a fraction of 84 % (v/v) in air.

The degree of inertization achievable with the help of the sweep-through purging method strongly depends on the flow conditions and the geometry of the apparatus. Special attention has to be paid to inbuilt devices and dead zones. During the purging process, a slight overpressure should be maintained. Figure 7-13 shows an approximate calculation of the required nitrogen volume, expressed in multiples of the volume of the apparatus, to achieve certain degrees of inertization.

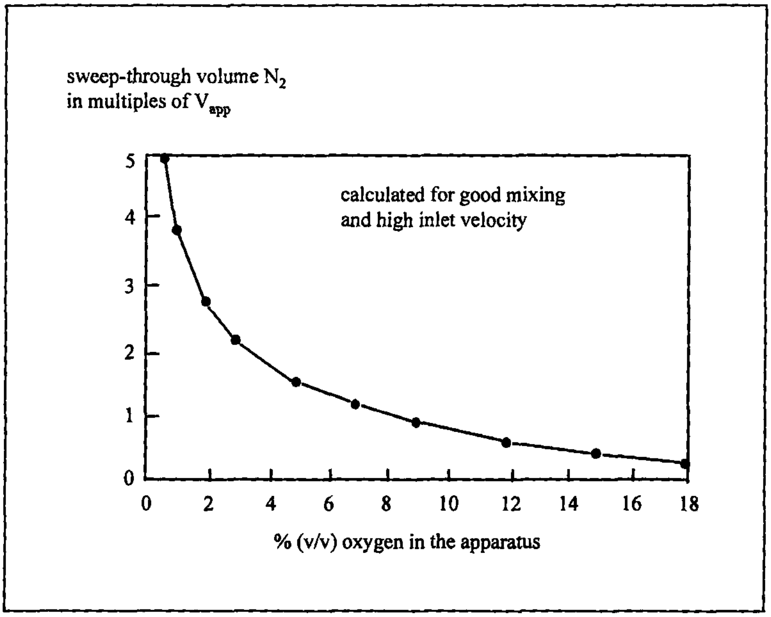

Fig. 7-13. Sweep-through volume of inert gas in dependence on the oxygen concentration

A prerequisite to achieve the desired degree of inertization is a very good mixing, which can be improved by a high inlet velocity. In the case of electrically non-conducting gases electrostatic charging effects have to be taken into account at the inlet and outlet openings. Thus, when CO_2 was used, highly charged carbon-dioxide snow crystals have been observed. Inlet and outlet should be placed diagonal to each other. The differences in density between inert gas and the air to be replaced have to be observed, but can be utilized. CO_2 is approximately 50 % heavier than air and therefore settles at the bottom of the container. In contrast, nitrogen is about 5% lighter than air.

Degree of Inertization

All substances which form an explosible atmosphere with air, do so only within a certain range of concentrations. The degree of inertization should be established and maintained during the process in such a way that the concentration of the fuel does not lie within the flammable region. This flammable region is limited by the lower and upper flammability limits, LFL and UFL. The concentration of the gaseous fuel is so high between the lower and upper flammability limit that an explosion can be triggered in the presence of sufficient oxygen and an ignition source. These concentration limit values are specific for each substance and, unless they are known, must be determined experimentally. If these specific values cannot be determined, then it is recommended to ensure that the maximum oxygen concentration is 7 %. In this context it has to be taken care to avoid any local variations in concentration within the apparatus. If the inertization is monitored, the maximum allowable oxygen concentration must not be exceeded during the dead time between malfunctioning and taking effect of an emergency measure. If this cannot be ensured, higher degrees of inertization should be established. The explosible regions of flammable gases are commonly presented in triangular diagrams as shown in Figure 7-14.

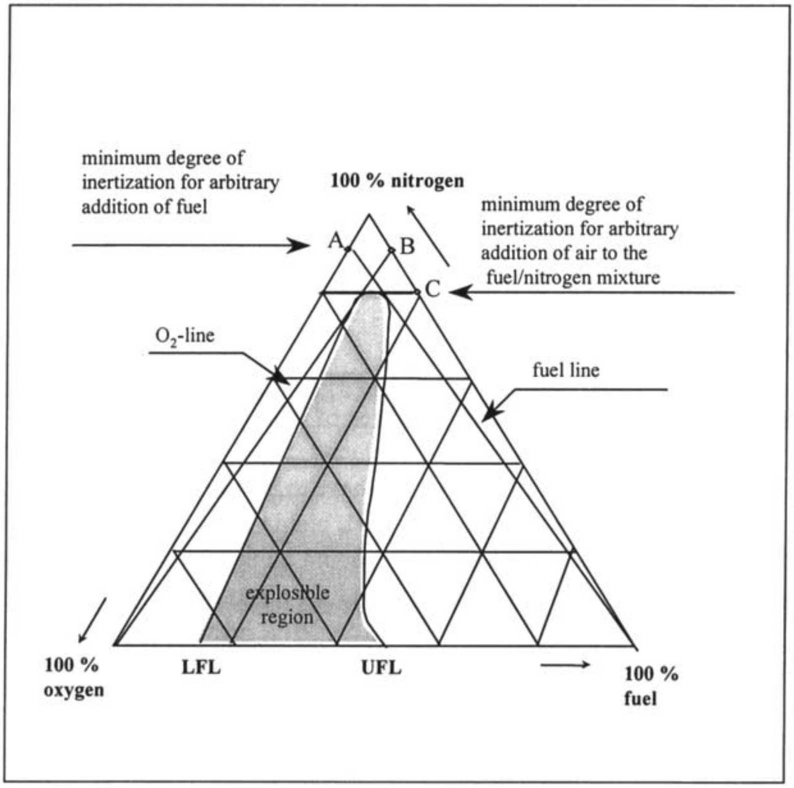

Fig. 7-14. Triangular diagram for explosion

Each point in this diagram corresponds to a certain composition of this three-component system. The edges describe two-component mixtures. Point A in this figure, for example, represents the minimum degree of inertization to be established in a device at the beginning of the process prior to charging the fuel, in order not to pass through the flammable region later in the process independent of the amount of fuel added. The line A-100% - fuel describes this course in concentration. Most gases are not flammable any more if the oxygen content amounts to less than 10 % (v/v) in the mixture at room temperature and normal pressure. As has been mentioned before, if no substance data are known, the oxygen contents should be reduced to 7 % (v/v). Exceptions are necessary in some individual cases. For example, hydrogen and CO require a reduction to 4 % (v/v).

Hybrid explosible mixtures can be composed of substances which on their own are not flammable dust-fuel for example. In general, the strength of an explosion increases and the minimum ignition energy decreases in relation to the single explosible substance. The following is true for all hybrid systems:

- the maximum explosion pressure rises with increasing initial pressure; therefore, the strength of an explosion decreases, if the operating pressure is reduced

If the operating pressure amounts to less than 70 mbar, an explosion becomes highly unlikely. In the case of aerosol formation it must be observed that in many cases these aerosols are already flammable at temperatures below the flash point of the gas of the same substance.

Demands on the inertization

Inertization with its installations belongs to the class of safety devices for which supervision is mandatory. The following requirements have generally to be fulfilled: the degree of inertization has to be maintained and supervised throughout the duration of an explosion endangerment. An inspection and maintenance programme geared to the installation has to be established and documented. In the case of a new implementation of an inertization device only those with proven reliability under operating conditions may be used.

An inertization is regarded as supervised either if the oxygen concentration is measured discontinuously or if the volume flow is measured continuously. In the case of a deviation from the pre-fixed set point an alarm must be trigged and correcting measures, which must have been defined previously, must be initiated. A breakdown of an inertization system must be treated like a disturbance signal. In fixing the alarm levels safety margins must be included, which account for local variations in concentration, time delay in response to the alarm, deviating conditions with respect to pressure and/or temperature as well as the accuracy of the supervising technique.

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8 Concluding Remark

Personal responsibility should be the guiding principle behind any activity concerning the safe operation of processes. A process can always be performed safely if the underlying mechanisms have been understood. The major fundamentals to achieve this understanding have been provided here.

Any activity should not primary be focussed on laws and regulations, but on one‘s own expert knowledge. Processes and plants will remain safe if there is an awareness that energy-rich, reactive substances are handled. They are controllable if their potential is identified and evaluated correctly. The facts and considerations about test methods and assessment criteria presented here should provide all the necessary aid.

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Literature Index

[1] DIN 31000, Beuth Verlag Berlin, 1987

[2] Bundesimmissionsschutzgesetz, BGBl. I, 1990

[3] US – OSHA *Process Safety Management of Highly Hazardous Chemicals, Explosives and Blasting Agents; Final Rule*, 29 CFR Part 1910.119, Federal Register, **57** (36), US Dept. Of Labor, OSHA, Washington D.C. 1992

[4] Barton, J., Rogers, R. L.: *Chemical Reaction Hazards*, IchemE, Rugby 1993

[5] CCPS: *Guidelines For Chemical Reactivity Evaluation And Application To Process Design*, AIChemE, New York 1995

[6] CCPS: *Chemical Process Quantitative Risk Assessment*, AIChemE, New York 1989

[7] Gibson, N.; *Conference on Chemical Reaction Hazards*, IBC Ltd., London 1993

[8] TAA: *Leitfaden zur Erkennung und Beherrschung exothermer chemischer Reaktionen*, TAA-GS-06, GRS Köln 1994

[9] CCPS: *Technical Management of Chemical Process Safety*, AIChemE, New York 1989

[10] Gygax, R.: ISCRE 10, *Chem. Eng. Sci.* 1988, **43** Nr. 8

[11] Bretherick, L.: *Handbook of Reactive Chemicals Hazards*, 4.ed., Butterworths, London 1990

[12] Sanderson, R.T.: *Chemical Bond and Bond Energy*, Academic Press, New York 1971

[13] Craven, A.D.: *IChemE Symp. Ser.* **102**, 1987

[14] Hemminger, W.F., Cammenga, H.K.: *Methoden der thermischen Analyse*, Springer Verlag, Heidelberg, Berlin 1989

[15] Grewer, T.: *Thermal Hazards of Chemical Reactions*, Elsevier, Amsterdam 1994

[16] Berthold, W., Löffler, U.: *IChemE Symp. Ser.* **82**, 1983

[17] Hofelich, T.C., Thomas, R.C.: *Int. Symp. on Runaway Reactions*, CCPS, AIChE, New York 1989

[18] Semenov, N.: *Z. Physik* 1928, **48**

[19] Frank-Kamenetskii, D.A.: *Diffusion and Heat Transfer in Chemical Kinetics*, 2nd ed. Plenum Press, New York 1969

[20] Grewer, T., Klusacek, H., Löffler, U., Rogers, R., Steinbach, J.: „*Determination And Assessment Of The Thermal Stability Of Chemical Processes*", J. Loss Prev. Proc. Ind., **2**, 1989

[21] Gibson, N., Rogers, R., Wright, T.K.: *IChemE Symp. Ser.* **102**, 1987

[22] System Technik AG, CH-8803, Ruschlikon

[23] Lütolf, J.: *Staub, Reinh. Luft* 1971, **31** Nr. 3

[24] VDI 2263 Anhang 1 „*Untersuchungsmethoden zur Ermittlung von sicherheitstechnischen Kenngrößen von Stäuben*", VDI-Verlag GmbH Düsseldorf, 1990

[25] DIN 51755 Beuth Verlag Berlin 1974

[26] DIN 51758 Beuth Verlag Berlin 1985

[27] DIN 51376, Beuth Verlag Berlin 1972

[28] „*Verordnung über Anlagen zur Lagerung, Abfüllung und Beförderung brennbarer Flüssigkeiten zu Lande (VbF)*", BGBl. 1, 1980

[29] Germar, N., Steinbach, J.: *APC89*, internal report of the Schering AG Berlin, 1989

[30] Nabert, K., Schön, G.: *Sicherheitstechnische Kennzahlen brennbarer Gase und Dämpfe*, 2. Auflg., Deutscher Eichverlag, Braunschweig 1980

[31] Schubert (Hrsg.): *Verfahrenstechnische Berechnungsmethoden Teil 7 Stoffwerte*, VCH, Weinheim 1988

[32] Chemsafe™, Dechema e. V. Frankfurt

[33] Magdanz, H.: Flammpunkte von Mischungen II., *Plaste und Kautschuk* 1978, **25** Nr 12

[34] DIN 51794, Beuth Verlag Berlin 1978

[35] Amtsblatt der Europäischen Gemeinschaft L383-A98 Annex 9

[36] DIN/VDE 0165: *Errichten elektrischer Anlagen in explosionsgefährdeten Bereichen*, Beuth Verlag Berlin 1969

[37] Koenen, H., Ide, K.H.: *Explosivstoffe*, 1955, **3**

[38] Koenen, H., Ide, K.H.: *Explosivstoffe*, 1956, **4**

[39] Yoshida, T.: *Safety of Reactive Chemicals*, Elsevier, Amsterdam 1987

[40] Grewer, T., Klais, O.: *IChemE Symp. Ser.* **102**, 1987

[41] personal communication from Dr. M. Steensma, AKZO

[42] Gibson, N.: *Intern. Symp. on Dust Explosion Risks*, Karlovy Vary 1972

[43] United Nations: *Recommendations on the Transport of Dangerous Goods, Tests and Criteria*, New York 1990

[44] Westerterp, K.R., van Swaaij, W.P.M., Beenackers, A.A.C.M.: *Chemical Reactor Design and Operation*, John Wiley and Sons, New York 1984

[45] Baerns, M., Hofmann, H., Renken, A.: *Chemische Reaktionstechnik*, G. Thieme Verlag, Stuttgart 1987

[46] Wright, A.: *Proceedings of the First Conference on Scale-up of Batch Processes*, Brighton 1994

[47] Hugo, P.: *Chem. Ing. Tech.* 1981, **53** Nr. 9

[48] Hugo, P., Konczalla, M., Mauser, H.: *Chem. Ing. Tech.* 1980, **52** Nr. 8

[49] Steinbach, J.: *„Theoretische Untersuchungen reaktionstechnischer Probleme in der Syntheseoptimierung und der chemischen Sicherheitstechnik"*, Habilitation Thesis, TU-Berlin, 1994

[50] Steinbach, J.: *„Untersuchung zu thermischen Sicherheit des indirekt gekühlten Semibatch-Reaktors"*, Dissertation, TU-Berlin 1985

[51] Steinbach, J.: *Dechema Monographie 107 „Fortschritte der Sicherheitstechnik I"*, VCH, Weinheim 1987

[52] Jacques Wiss, Dissertation Nr. 92 MULH0250 Ecole Nationale Superieure de Chimie, F - 68093 Mulhouse

[53] Personal communication with the industrial working group: „Exchange of experiences on hazardous chemical reactions – test methods", chair Dr. M. Steensma, AKZO

[54] Brandrup, J., Immergut, E.H.: *Polymer Handbook*, Wiley-Interscience, New York 1989

[55] Moritz, H.-U., Reichert, K.-H.: *Comprehensive Polymer Science*, eds. Sir G. Allen and J.C. Bevington, Pergamon Press, Oxford, 1989, **3** Part I

[56] Moritz, H.-U.: *Chem. Eng. Technol.* 1989, **12**

[57] Moritz, H.-U.: *Sichere Handhabung chemischer Reaktionen*, Praxis der Sicherheitstechnik Nr. 3, Dechema e.V., Frankfurt 1995

[58] VDI-Wärmeatlas, 7. Auflage, VDI-Verlag, Düsseldorf 1994

[59] Zlokarnik, M.: *„Rührtechnik"* in Ullman Encyklopädie der technischen Chemie, 4. Auflage, VCH, Weinheim 1972

[60] Wright, T.K.: *IChemE Symp. Ser.* **102**, 1987

[61] Lambert, P.: Proceedings *„Chemical Reaction Hazards"*, IBC, Amsterdam 1990

[62] Moritz, H.-U.: *„Rechnergestützter Laborreaktor zur Emulsionspolymerisation von Vinylacetat"*, Habilitation Thesis, TU-Berlin 1988

[63] Mauser, H.: *„Detaillierte und modellreduzierte Beschreibung der chemischen Wärmeentwicklung am Beispiel der Oxidation von Acetaldehyd mit Salpetersäure"*, Dissertation, TU-Berlin 1984

[64] Regenass, W: *Am. Chem. Soc. Symp. Ser.* **65**, 1979

[65] Nolan, P., Steel, C.H.: *Int. Symp. on Runaway Reactions*, CCPS, AIChE, New York 1989

[66] Nomen, R.: *Thermochimica Acta* 1993, **225** Nr. 2

[67] Hugo, P.: *Chem. Ing. Tech.*, 1993, **65**

[68] Borchardt, H.J., Daniels, F.: *J. Am. Chem. Soc.*, 1957, **79**

[69] Freeman, E.S., Caroll, B.: *J. Phys. Chem.*, 1968, **62**

[70] Coats, A., Redfern, J.P.: *Nature*, 1964, **201**

[71] Gnewikow, T.: *Theoretische und experimentelle Untersuchungen zur Bestimmung der Reaktionskinetik mit Methoden der Differenzthermoanalyse (DTA bzw. DSC)*, Dissertation, TU-Berlin 1990

[72] Hugo, P., Gnewikow, T., Wagner, S.: *Thermochimica Acta* 1993, **225** Nr. 2

[73] Hugo, P., Leonhardt, J., Wagner, S.: *Sichere Handhabung chemischer Reaktionen*, Praxis der Sicherheitstechnik Nr. 3, Dechema e.V., Frankfurt 1995

[74] Hugo, P., Steinbach, J., Stoessel, F.: ISCRE 10, *Chem. Eng. Sci.* 1988, **43** Nr. 8

[75] Stoessel, F.: *Chem. Eng. Prog.* 1993, **89** Nr. 10

[76] Rogers, R.: *Int. Symp. on Runaway Reactions*, CCPS, AIChE, New York 1989

[77] BASF: *„Prüfen bringt Sicherheit"*, Merkblätter für Umweltschutz und Arbeitssicherheit Nr. 10, Ludwigshafen, 1994

[78] Rogers, R., Wright, T.K.: *IChemE Symp. Ser.* **97**, 1986

[79] Bartknecht, W.: *Explosionen*, Springer-Verlag Berlin, Heidelberg 1993

[80] VDI 2263 *„Staubbrände und Staubexplosionen, Gefahren-Beurteilung-Schutzmaßnahmen"*, VDI-Verlag GmbH, Düsseldorf 1986

[81] VDI 3673 *„Druckentlastung von Staubexplosionen"*, 1. Gründruck, VDI-Verlag GmbH, Düsseldorf 1992

[82] Eckhoff, R.K.: *Dust Explosions in the Process Industries*, Butterworths, London 1991

[83] Field, P.: *Dust Explosions* (Vol. 4 of Handbook of Powder Technology), Elsevier ISSN 0167-3785

[84] Chemisens Ltd., Stockholm Schweden

[85] CCPS: *Guidelines for Hazard Evaluation Procedures*, AIChemE, New York 1985

[86] Department of Defense, Military Standard System Safety Program Requirements, MIL-STD-882B, Washington, D.C., 1984

[87] Internationale Vereinigung für soziale Sicherheit: *„Der Störfall im chemischen Betrieb (PAAG)"*, BG Chemie, Heidelberg 1980

[88] Knowlton, E.: *„Creative Checklist Hazard and Operability Studies"*, Chemical Manufacturers Association, Process Safety Management Workshop, Arlington, Virginia 1985

[89] Fussell, J.B.: *„Fault Tree Analysis: Concepts and Techniques"*, Generic Techniques in System Reliability Assessment, 1976

[90] Lees, F.P.: *Loss Prevention in the Process Industries*, Butterworths, London, 1980

[91] AD-Merkblatt der Arbeitsgemeinschaft Druckbehälter A1 *"Berstscheiben"*, Beuth Verlag, Berlin 1980

[92] AD-Merkblatt der Arbeitsgemeinschaft Druckbehälter A2: *"Sicherheitsventile"*, Beuth Verlag, Berlin 1980

[93] DIN 3320, Teil 1 *"Sicherheitsabsperrventile"*, Beuth Verlag, Berlin 1984

[94] TRD 421 *"Sicherheitseinrichtungen gegen Drucküberschreitung (Sicherheitsventile) für Dampfkessel"*, Beuth Verlag, Berlin 1990

[95] Fauske, H.K., Leung, J.C.: *Plant/Opns Prog.* 1987, **6** Nr. 2

[96] Fischer, H.G.: *Chem. Eng. Prog.* 1985, Nr. 8

[97] Friedel, L.: *Dechema Monographie 107 „Fortschritte der Sicherheitstechnik I"*, VCH, Weinheim 1987

[98] Friedel, L., Kißner, H.-M.: *Dechema Monographie 111 „Fortschritte der Sicherheitstechnik II"*, VCH, Weinheim 1987

[99] Friedel, L.: Proceedings *„Chemical Reaction Hazards"*, IBC, Amsterdam 1990

[100] Rogers, R.: Proceedings *„Chemical Reaction Hazards"*, IBC, Amsterdam 1990

[101] Singh, J.: *Chem. Eng.* 1990, Nr. 8

[102] Leung, J.C.: *AIChE J.* 1986, 32 Nr.10

[103] API RP 521: *„Guide for pressure relief and depressuring systems"*, API-Institute, New York 1969

[104] Grossel, S.: *Plant/Opns Prog.* 1986, 5 Nr. 3

[105] Muschelknautz, S., Klug, F., Ruppert, K.A.: *Chem. Ing. Tech.* 1994, **66** Nr. 2

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