TECHNICAL COMMITTEE FOR PLANT SAFETY (TAA)

at the
German Federal Ministry of Environment, Nature Conservation and Nuclear Safety

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Guide

for the

Identification and Control of Exothermic Chemical Reactions

Status as of April 1994

Adopted at the 5th Meeting of the TAA on 12 April, 1994

The Technical Committee for Plant Safety (TAA) is a committee constituted at the German Federal Ministry of the Environment, Nature Conservation and Nuclear safety under Section 31a of the Federal Immission Control Act.

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Identification and Control

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Rough English Translation

Note: This rough translation of the document "Leitfaden - Erkennen und Beherrschen exothermer chemischer Reaktionen" (TAA-GS-05) has been prepared for the convenience of participants at the EU Seminar on the Safety of "Runaway Reactions" to be held at Frankfurt-am-Main on 7th and 8th November 1994. For the exact contents of the document, reference should be made to the German original. The translation was prepared on behalf of the European Process Safety Centre, and then revised by Neil Mitchison of the European Commission's Joint Research Centre, Ispra, with the aid of comments from Dr. Pilz and Dr. Schacke of Bayer AG and Mr. H.A. Duxbury of the EPSC. Mr. Mitchison is responsible for any errors in the final text.

TAA = Technischer Ausschuß für Anlagensicherheit beim Bundesministerum for Umwelt, Naturschutz und Reaktorsicherheit (Technical Committee for Plant Safety of the Federal Ministry of the Environment, Nature Conservation and Reactor Safety)

GUIDE

Identification and control of exothermic reactions

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This guide was prepared by a study group on behalf of the Technical Committee for Plant Safety (TAA) of the Federal Ministry of the Environment.

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A. Introduction and Problem description

Chemical plant needs to be operated safely, both during operation as intended, and when there are deviations from the prescribed process and plant parameters. Chemical reactions in such plant can only become a hazard for man and the environment, if pressures or temperatures rise beyond the design parameters of an installation during processing, for example because of a reaction going out of control. For example, an inadmissible pressure increase can arise when the heat removal from an exothermic process is insufficient, or in the case of reactions producing gas, such as decomposition. The potential hazards caused by such chemical reactions are generally determined by the energy generated or released, the volume of gas and/or the nature and quantity of the substances involved. These hazards arise from the interaction of the properties of individual substances and mixtures, the process and operating parameters and other relevant variables, with the timing of the reactions also requiring consideration.
For a processing concept which is satisfactory in terms of safety and the environment, it is first necessary to identify the hazards associated with the process and then to assess them. Following the assessment it is necessary to define to what extent safety measures are required.
The discussion below is confined to reactions in the true sense of the word, i.e. reactions between substances. However, the spirit of the points made is applicable to other process engineering operations, e.g. physical processes such as drying and distillation.

B. Safety assessment of reaction during normal operation

A chemical reaction can generally be described by reaction equations, from which the substances involved can be immediately determined, and which also provide information about intermediate products and by-products and in certain cases gas released.
In order to identify the possible hazards produced by the exothermic nature of chemical reactions, a number of physico-chemical parameters of the substances concerned and the equipment used are applied. The following are the most important:

1. The reaction enthalpy ΔH_R both for the reaction concerned and for potential secondary reactions (e.g. decomposition)
2. The possible gas evolution M and the rate of gas evolution (dM/dt) (or corresponding derived parameters) from the reaction or the possible decomposition
3. The rate of heat production (dQ_R/dt, reaction power), where appropriate as a function of temperature
4. The total heat removal capacity of the system (dQ_K/dt)
5. The limit temperature T_{exo} for the thermal stability of the substances concerned and the reaction mixtures under process conditions[1]

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[1] The temperature T_{exo} is not substance-specific alone, but is essentially determined by the interaction of (dQ_R/dt) and (dQ_K/dt). For this reason it is not clearly defined by a single measuring method for a given substance. It can be obtained in different ways, depending on the process and the plant, and different values may be obtained for T_{exo}. Depending on individual circumstances, use can be made either of measuring systems which simulate the specific plant conditions (or which can be extrapolated to obtain them), or of adiabatic measuring methods. In practical examples, the following alternative determinations have proven satisfactory:

a) the temperature at the beginning of the exothermic reaction after screen DTA (heating rate 1...10°K/min.), reduced by 100°K
b) the temperature for an adiabatic induction period (up to maximum turnover) of 24 hours ("AZT 24"), reduced by 10°K
c) the temperature at which the heat reduction from the system reaches 0.1 W/kg, reduced by 10°K.

This procedure is based on typical residence times and parameters for reactions and process engineering operations. Conditions which vary substantially from these, such as the storage of materials and mixtures of materials over a prolonged period of time and with very large inventories should be taken into consideration accordingly when determining T_{exo}.

The above parameters need to be considered not only for the reaction in accordance with the intended application, but also for possible deviations (see section C). Measuring methods for determining material characteristics, e.g. differential thermal analysis ("DTA"), calorimetry, and adiabatic experiments, and their possible uses and applications have been described in detail in the literature /1, 2, 3, 4/.
Substances and substance mixtures which are capable of deflagration or detonation occupy a special position. In these, the rate of heat and gas production is no longer a function of the process temperature, so that measures to control an exothermic process based for example on this parameter are not effective. This mainly concerns explosive substances, organic peroxides, and spontaneously decomposing substances (classes 1, 5.2 and 4.1 of the German regulations for the transport of hazardous goods). In general, to control reactions in which such substances and their intermediary reaction mixtures /5/ are involved requires additional measures which are beyond the scope of the present study. Criteria and test methods for the assessment of such substances can be found, for example, in the UN test manual /6/ and other relevant regulations. However, this guide can be applied in the appropriate context to the other properties to be considered.

One major precondition for the safety assessment of exothermic reactions is also a knowledge of the boundary conditions under which reactions should take place. This includes in particular

- control of the reaction, e.g.
  - continuous/intermittent, with batch/semi-batch operation (controlled by metering)
  - added components/metering rate
  - temperature/pressure range
  - aggregate state during the reaction

- plant engineering parameters, e.g.
  - reactor vessel size
  - technical equipment
  - heat removal capacity of equipment

The next page shows a schematic diagram (schema 1) used to determine the hazard potential and to perform a safety assessment.

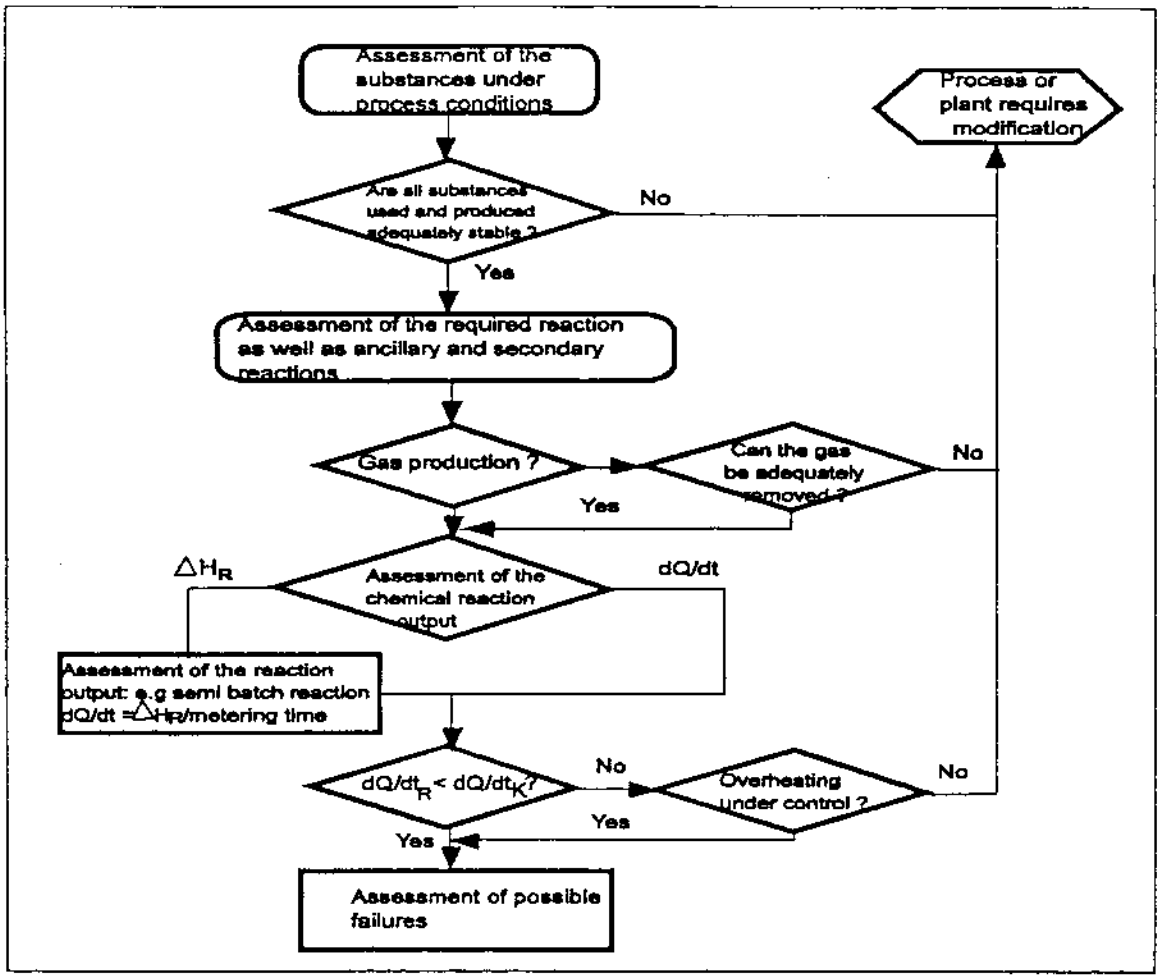
The assessment starts with an inventory of the initial materials. The question to be answered is whether all initial materials involved can be regarded as thermally stable at the intended temperature range and for the intended period of time. Information about the thermal stability of substances and mixtures can be obtained using relatively simple means. It is known that when certain functional groups are present, there is an increased probability of exothermic decomposition. A list of noteworthy radicals and substances will be found in the annex (section G 1).

Beyond this purely theoretical analysis, experimental screening methods are generally needed to determine the hazard potential associated with the handling of the material or mixture. See the literature /7,8/ for the possible applications and limitations of these screening methods. The first objective of these screening methods is to obtain information about stability in the intended temperature range. If there are significant thermal effects in the temperature range concerned further investigations must be carried out, such as adiabatic tests or comparable techniques, to determine the question of stability over time, bearing in mind the reaction time and the mixtures produced.

If the investigations performed show adequate stability of all starting substances involved in the reaction, then the next step is to assess the reactions required in normal operation, including side and ancillary reactions. One important basis is the stoichiometric equation of the reactions concerned. If this equation shows the formation a gas as a reaction product, then the plant has to be engineered to dispose adequately of the resulting mass of gas.

A further key element in the assessment of the reaction is the thermal evaluation. A preliminary decision for the assessment of the safety of normal operation can be derived from knowing the heat of reaction ΔH_R. This makes it possible to determine the adiabatic temperature ΔT_{adiab}.

Schema 1: Iterative assessment strategy for normal operations



If the adiabatic temperature increase is known, then the following assessment applies to the intended process:

- If the adiabatic temperature increase of the reaction in normal operation is less than 50°K, and if no thermal instability of the starting material, the reaction mixture or the products is found in a temperature range ($T_{process} + \Delta T_{adiab}$), then normal operation may be regarded as safe. The same applies in the event of a secondary decomposition reaction, provided this produces so little heat that, together with the heat of reaction, it does not lead to an adiabatic temperature increase of more than 50°K.

- If there is thermal instability of the starting material, the reaction mixture or the products within a temperature range ($T_{process} + \Delta T_{adiab}$) and this thermal instability, together with the heat of reaction, leads to an adiabatic temperature increase of more than 50°K, then the evolution of heat production over time needs to be properly evaluated, especially of the intended reaction.

- In certain cases the system may be regarded as adequately safe even for $\Delta T_{adiab} > 50°K$, provided that the boiling point of the system lies in the interval $T_{process} \leq T_{boil} < T_{process} + 50°K$ and, because of the system properties and the design of the installation, there is a reasonable degree of certainty that the boiling point and the rate of heat production at the boiling point cannot be increased to an inadmissible extent.

Direct experimental determination of the evolution of heat production over time, for example using reaction calorimetry, is a great help in assessing the power of an exothermic reaction. Alternatively, it is possible to estimate the reaction power, as a first approximation, from the reaction enthalpy together with other measurements and observations. An essential precondition for such an estimation is knowing the

approximate reaction mechanism. If the reaction can be defined by a kinetic equation (effective order of reaction ≥ 1), then, for metered operation for example, it is possible to determine the heat production from the quotient of reaction enthalpy and metering time. However, an essential precondition is a reaction speed sufficient to prevent hazardous reactant accumulation. Similar considerations apply for continuous methods, when the residence time is used. (This method is no longer permitted for autocatalytic behaviour!). In the case of heterogeneous systems, the effect of the phase conditions needs to be taken into consideration as well.

One critical point of a chemical process is the point of maximum heat production. This maximum value should be compared with the entire, predetermined maximum heat removal capacity. If this capacity is sufficient for the safe removal of the maximum heat production, then the reaction under normal operation may be considered as safe. For more precise analysis see the literature /9, 10, 11/.

The assessment process is completed by an assessment of the thermal stability of the substances produced during the reaction over the predetermined temperature and time range, including any interactions with the materials used. Here the methods are the same as those described above for the assessment of the starting material. However, it is necessary to emphasize that here it may not be sufficient to analyse the pure reaction products alone; representative samples of the reaction mixture may need to be assessed with different types of reaction.

In all cases in which the questions to be answered in the flow diagram cannot be clearly answered, it is necessary either to perform further investigations, or to modify the process or the plant. The overall assessment of the process should continue as the next step to determine the effect of possible deviations and failures. If the assessment of possible failures leads to plant and process modifications, then it is necessary to reinvestigate the normal operation iteratively.

C. Safety assessment of the reaction in the case of deviations

When analysing chemical processes, it is necessary to consider conceivable deviations and failures, and their possible effects on the reaction enthalpy ΔH_R, the gas volume M produced and the rate of gas production (dM/dt), the heat flow balance $(dQ_R/dt) - (dQ_K/dt)$ and the limit temperature T_{exo} for thermal stability under the processing conditions concerned, starting with the operation of a process and a plant as intended. Failures can be divided into two categories, and their effects can be assessed on the basis of the following tables[2]:

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2 Notes on the use of the tables:
The grid fields are not data fields which require the insertion of numerical values. They are intended as a framework indicating what points require consideration, and which assessment parameters are affected by certain failures, and to what extent. Where necessary, relevant fields should be ticked after appropriate consideration and investigation. (For the preparation of checklists, see e.g. /12/).

Table 1: Effects due to deviations of chemical processes

Failure caused by	ΔH_R	dM/dt	$(dQ_R/dt)-(dQ_K/dt)$	T_{exo}	Δn Subst.*
Starting materials (specification, nature, properties), e.g.: - contamination with catalytic effect - increase/decrease of concentration - residues from previous use - decomposition of activators/ inhibitors (e.g. as a result of extended storage)					
Presence of starting materials/ auxiliary materials, e.g.: - solvent used - solution promoter - activator - inhibitor					
Metering, e.g.: - wrong substance - wrong quantities/ratios - changed metering sequence - wrong metering rate					
Reaction conditions, e.g.: - change in pH value - temperature increase/decrease - pressure increase/decrease - reaction/residence time - delayed reaction start - increase of by-products/residues					
Mixing, e.g.: - inadequate agitation - separation of solids/catalyst					

*Δn Subst: Formation of new unwanted products or by-products which lead to an increase in the reaction enthalpy or gas formation or reduction of the limit temperature T_{exo}.

Table 2: Effects due to deviations in the operation of plant

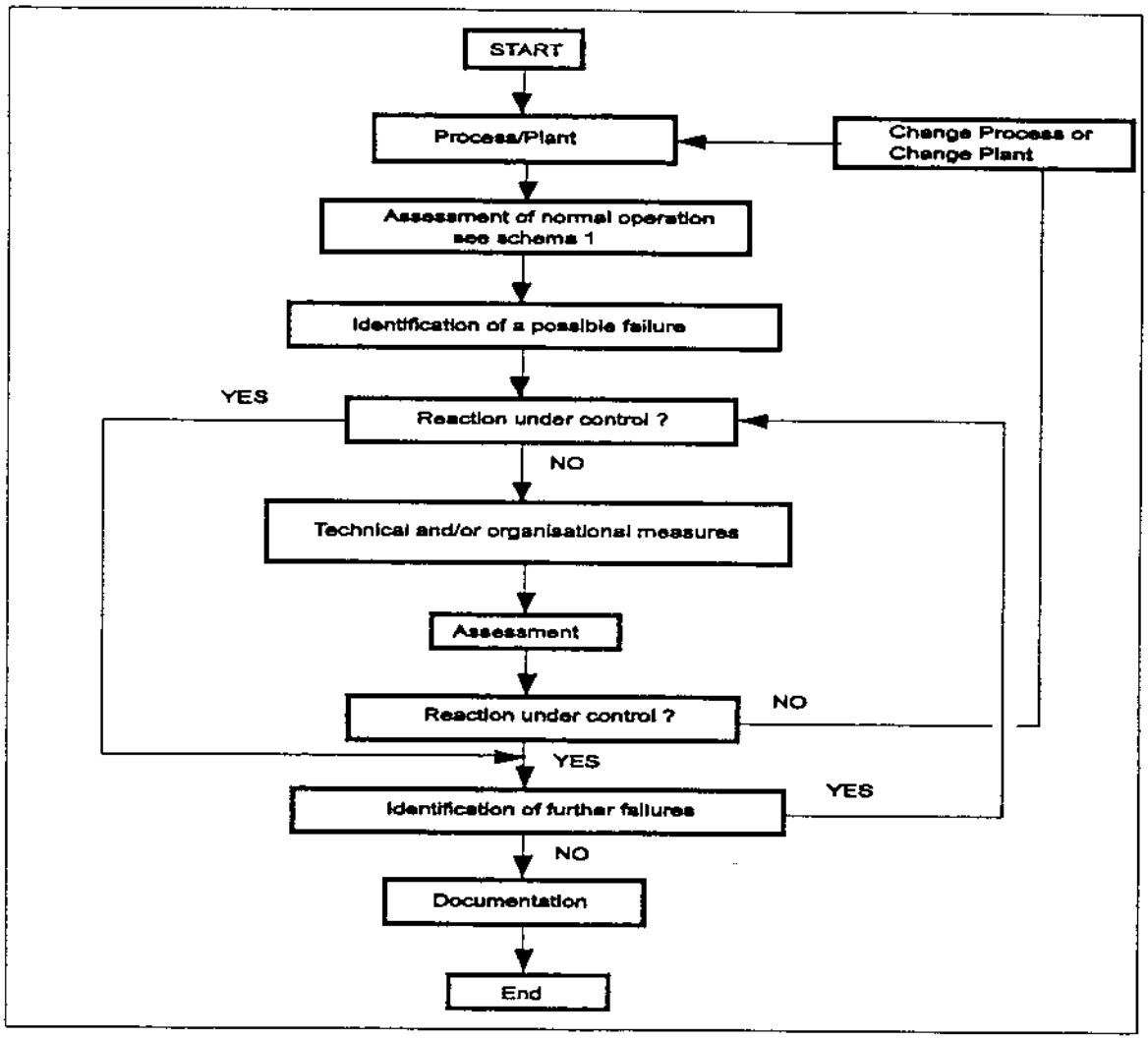
Failure caused by	ΔH_R	dM/dt	$(dQ_R/dt)-(dQ_K/dt)$	T_{exo}	Δn Subst.*
Availability of auxiliary energy, e.g.: - compressed air - nitrogen - electric current - heating medium - cooling medium - ventilation					
Heating/cooling medium (temperature), e.g.: - temperature exceeds/falls below the temperature defined for safe process operation					
Process control equipment, e.g.: - failure					
Material flows, e.g.: - failure of pumps/valves - incorrect operation of valves - blocking of lines/valves/fittings (in particular venting pipes) - backflow from other parts of the plant					
Filling level, e.g.: - overfilling - leakage from a dump valve - flooding of condensers (heat exchangers)					
Agitation, e.g.: - failure - increased viscosity - mechanical introduction of heat					
Integrity of components: - corrosion (in particular with resulting material overflow from/to heat transfer systems) - mechanical damage					

*Δn Subst: Formation of new, unwanted products or by-products which lead to an increase in the reaction enthalpy or gas formation or reduction of the limit temperature T_{exo}.

In addition to the effects due to deviations in the chemical process or the technical operation of the plant, deviations in the superimposed atmosphere should be checked (e.g. formation of explosive mixtures, generation of oxidising gases such as chlorine or NO_x, loss of stability of gases capable of decomposition).

It is advisable to perform a structured safety assessment for a reaction with a given process in a given plant, for example in accordance with schema 2.

Schema 2: Safety assessment procedure



The result of the safety assessment needs to be documented with an assessment of normal operation and the failure modes considered and the measures adopted (see section D), using tables 1 and 2 for identification of possible failures.

D. Selection and extent of measures to be adopted

The hazard potential of an exothermic reaction should be determined by reference to the key parameters of the intended reaction, along with side and secondary reactions (especially ΔH_R and dM/dt). It is necessary to consider the effects of possible failures in the system, i.e. temperature increase $\Delta T_{failure}$ in a system as a result of energy release, and increased gas production $\Delta(dM/dt)_{failure}$ which can produce a build-up of pressure.

In particular, for the temperature and the production of gas (which correlates with pressure build-up)

$$T_{process} + \Delta T_{failure} < T_{max.. design}$$

and

$$(dM/dt)_{process} + \Delta(dM/dt)_{failure} < (dM/dt)_{max. design}$$

i.e. if the design limits of the process engineering plant are not exceeded even under failure conditions, then the chemical reaction in this process using this equipment can be regarded as adequately controlled, even under the failure conditions considered.

Otherwise, that is if the consideration of the failures show that these inequalities are not satisfied, then additional measures and their extent should be defined in such a way that a serious hazard can be reliably excluded[3].

Where additional measures are concerned, a distinction can be made between preventive measures to prevent an uncontrolled reaction, and design measures to prevent inadmissible effects when an uncontrolled reaction occurs. Depending on the circumstances of the individual case the following may be considered either as alternatives or in combination:

- <u>preventive measures:</u>
  - organisational measures
  - concepts involving control engineering techniques
  - reaction stoppers
  - emergency cooling
- <u>design measures:</u>
  - pressure-resistant construction
  - pressure relief

As a matter of principle, preventive measures should be given preference; the order given does not represent a rank order.

The reasoning for the selection of measures must be documented.

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3 Technical standards specify numerous boundary conditions for the protective measures to be conceived and also describe solutions which are considered to be adequately safe. The following German standards in particular are of interest:
- DruckbehV with TRB 403, TRB 404, AD-Merkblatt A6
- BImSchG together with StörfallV
- GefahrstoffV with TRGS 300, ArbeitsstättenV, UVVen

If significant damage can be expected, then, in order to reduce the probability of a feared event[4], the following procedure should be adopted:

a) If the event can only result from several independent failures, then it is necessary to determine for the individual case whether additional measures need to be adopted. However it is necessary to establish whether the failures or malfunctions leading to the event are really independent of one another, and to what extent it is reasonable to assume no simultaneous occurrence.

For example, if a failure or malfunction does not initially affect the process it may not be remedied straight away; it is possible then that a second failure occurs before the first failure has been remedied. The same applies to undetected failures. Such failures should be treated in the same way as dependent or common cause failures.

If the failure analysis leads to the result that the simultaneous occurrence of the failures or malfunctions required to cause the feared event can be excluded because of its improbability, then no additional safety measures need to be adopted.

If the special combination of failures required to cause a feared event cannot be excluded with adequate certainty, then, as a rule, one additional preventive measure to make each failure mode discontinuous is sufficient.

b) However, if the event is produced by a single failure, then each corresponding failure path needs to be interrupted with a high-availability safety device. This is achieved for example by deployment of redundant measures ("single failure tolerance principle" /13/) or single "fail-safe" measures. As a rule, organisational measures alone are no longer sufficient in this case.

If design measures are adopted to prevent inadmissible effects of an uncontrolled reaction, then pressure-resistant designs or pressure relief equipment are deemed to offer the required high availability. A design measure, in particular pressure relief equipment, may be appropriate and indeed required if (because of the complexity of the causal chains concerned) a completely reliable analysis of all possible deviations and their causes and effects is not possible.

A pressure-resistant design is usually not justifiable from the point of view of the technical equipment required, because of the strength necessary to resist extreme pressures. Equally, safe relief through pressure relief equipment can in certain cases be technically difficult and very elaborate, for example if collecting systems become necessary. A separate document deals with the conditions and the method for hazard-free discharge using pressure relief systems.

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4 The term "event" in this guide should be interpreted as the "excess over the design limits" of the process engineering plant.

E. Definitions

Adiabatic temperature increase
The adiabatic temperature increase ("ΔT_{adiab}") is here the temperature increase in a process engineering reaction system, if the process takes place without heat or mass interchange with its environment (e.g. following complete failure of cooling in a closed reaction vessel).

Autocatalysis
During autocatalysis, a reaction product formed during reaction acts as a catalyst, with the progress of reaction being accelerated even at constant temperature. One example is the acid-catalysed saponification of various esters and related compounds. Experimentally, autocatalytic reactions can be identified without significant effort, using differential thermal analysis methods.

Calorimetry
Calorimetry is a measuring technique during which measurements of temperature (among other values) allow the evaluation of the rate of heat production and the total heat produced during chemical or physical events. Reaction calorimeters with reaction volumes ranging from 0.1 to 2 litres in which the process can be performed under conditions close to those encountered in practice have proved useful.

Deflagration
Deflagration represents the progressive reaction of a substance after a locally triggered reaction start. The reaction spreads with a speed less than the speed of sound. During deflagration, large quantities of hot gases are released, and some of these may be combustible. The rate of deflagration increases with the temperature and, as a rule, with the pressure.

Differential thermal analysis
Differential thermal analysis ("DTA") is a measuring method which makes it possible to study the heat transfer produced during physical and chemical reactions with small quantities of samples (as a rule a few milligrammes). This analysis is therefore used for investigating the thermal stability of substances and in many cases can be used to assess the thermal potential of chemical reactions.

Heat removal capacity
The heat removal power dQ_K/dt describes the total heat removed from the system in a given unit of time. This can be made up of the cooling power, the evaporation rate, and other factors.

Limit temperature
The limit temperature ("T_{exo}") is the maximum permitted temperature at which a substance or reaction mixture can just be handled without risk. It should be defined according to the process parameters and the measuring methods used for determination of the characteristics of the substances. For example, in a continuous process, where substances are only exposed to a high temperature relatively briefly, the limit temperature can be set at a higher level then in a batch process, where substances may be exposed to high temperatures for a prolonged period of time.

Pressure relief
The principle of pressure relief of vessels consists of limiting the pressure through removal of gaseous or multi-phase material flow in the case of an explosion or a runaway reaction by allowing certain predetermined openings to be opened in such a way that the pressure in the vessel does not exceed a predetermined permitted value.

Pressure resistant design
A pressure resistant design is a design where, in the case of an explosion or a runaway reaction, the pressure does not exceed the design pressure of the vessel or the unit. If there is a possibility of condensed material decomposing, then, because of the high pressures involved, a pressure-resistant design usually involves considerable expense.

Reaction stopper
A reaction stopper is the name for a system whereby an inhibiting substance can be introduced rapidly and effectively to the reaction vessel from a reservoir via a pipe which is protected with appropriate isolation valves, irrespective of other steps which may be necessary. The reaction stopper can be initiated manually or automatically, if certain process parameters are exceeded.

Rate of heat production/reaction power
The rate of heat reduction dQ_R/dt is the quantity of heat liberated per unit of time. This is proportional to the speed of the reaction, which is in turn a function of the concentrations and the temperature.

Reaction enthalpy
The reaction enthalpy ΔH_R of a reaction is the quantity of heat (as determined by the reaction equation) either taken up by the system at constant pressure (for an endothermic reaction) or delivered by the system at constant pressure (for an exothermic reaction). The reaction enthalpy ΔH_R depends both on the chemical nature of the individual reactants and their physical state.

Single failure tolerance principle
Here: A process or a plant complies with the single failure tolerance principle, if it is designed or equipped in such a way that any single failure - even in a protective system - does not cause a feared event.

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DIN/VDE 2180 Sicherung von Anlagen der Verfahrenstechnik mit Mitteln der Meß-, Steuerungs- und Regelungstechnik, 1984, Beuth Verlag, Berlin;
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NAMUR NE 31 "Anlagensicherung mit Mitteln der Prozeßleittechnik", 1992

G. Appendix

1. List of compounds and substances

2. Examples

   2.1 Methods and equipment

   2.2 Hazard potential

   2.3 Normal operation

   2.4 Deviations (failures)

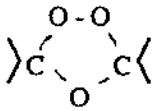
   2.5 Various cases with measures proposed

1. List of compounds and substances[5]

1.1 Classes of unstable compounds

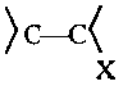
Frequently used classes of compounds where experience has shown that they have a high thermo-dynamic instability which is associated with the liberation of large amounts of energy.

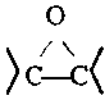
1.1.1 Typical functional groups in unstable compounds

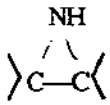
$-NO_x$	Nitro and nitroso compounds
$-ONO_x$	Esters of nitric and nitrous acid
$\rangle N-X$	Halogenated nitrogen compounds (X = halogen)
$-N\equiv N^+$	Diazonium salts, also triazene, tetrazene
-N=N-	Azo compounds
-O-O-	Peroxides, per-acids Numerous unsaturated hydrocarbons, aldehydes, ketones, ethers and some cyclic hydrocarbons (e.g. Dekalin) tend to form peroxides in the presence of air
	Ozonides
-C≡C-	Acetylene, acetylides
$-N_3$	Hydrogen nitrides, azides
-HN-NH-	Hydrazides
$-ClO_4$	Perchloric acids, perchlorates
	Fulminates, also oximates, salts of aci-nitrogen compounds

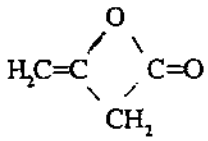
5 This list does not claim to be complete.

1.1.2 Polymerisable compounds


Substituted olefins (X = e.g. -F; -Cl; -CN; -COOR; -CH=CHR; -C_6H_5)


Epoxides


Aziridines


Diketene

Catalytic effects produced by acids, bases, radical-producing compounds, metals and metal salts must be allowed for.

1.2 Oxidising agents

Frequently used oxidising agents which may liberate significant quantities of energy with combustible/reducing substances:

$HClO_4$ (conc.)/perchlorates
HNO_3 (conc.)/nitrates
CrO_3/chromates
$KMnO_4$
Chlorates
Nitrating acids
Alkyl nitrites
H_2O_2
organic and inorganic peroxides
SO_3/oleum
Oxygen/ozone
Chlorine

1.3 Reducing agents

Frequently used reducing agents which can lead to significant liberation of energy with oxidising substances:

metals (e.g. sodium, zinc)
organo-metallic compounds
hydrides (e.g. $LiAlH_4$, $NaBH_4$)
silanes
hydrogen

2. Examples

The procedure proposed in the guide will now be illustrated by reference to some examples of semi-batch reactions.

To simplify the description and illustrate the most important steps for the assessment of a reaction and for deciding on nature and extent of the measures required, three 'didactic' examples ("cases 1 - 3") have been selected which are characterised by the following limits:

1. Only one homogeneous single step reaction is performed. No side reactions should take place. For the processes under consideration, the reaction mechanisms remain unchanged. Interactions of the chemical substances and reaction mixtures with the material in the equipment are excluded.

2. Relevant material properties and process and plant-specific parameters are completely known for the examples and the solutions proposed, and have been abstracted and detailed only as far as necessary. Any calculations necessary are based on the literature detailed in the guides.

3. Only a certain section (always the same) in the spectrum of possible failures is considered.

4. The failures considered may be regarded as independent from another and are not based on "common mode" failure. In addition, the measures adopted should be effective independently of one another.

5. The proposed technical and organisational methods are exclusively of the "preventive" kind and represent just one choice among the various possible problem solutions. The solutions given as examples therefore do not exclude the possibility of "design" measures such as pressure-resistant design or pressure relief (perhaps with a collecting system); to decide on these, as a rule, further investigations and information beyond that provided here would be necessary.

6. It is presupposed that the measures are practicable for the various examples and are also effectively applied.

It follows that the examples and solutions are not directly applicable to individual practical cases without further modification, since in practice the circumstances may be much more complex. In particular, the consideration of the failures must not be confined to the failures selected for the examples, and it is further necessary to determine and consider possible interrelationships between failures.

2.1 Equipment and apparatus

In a reaction vessel which cannot be isolated from its breathing system and which is heated via its mantle using an open water circuit (also used for cooling), an exothermic reaction of the type

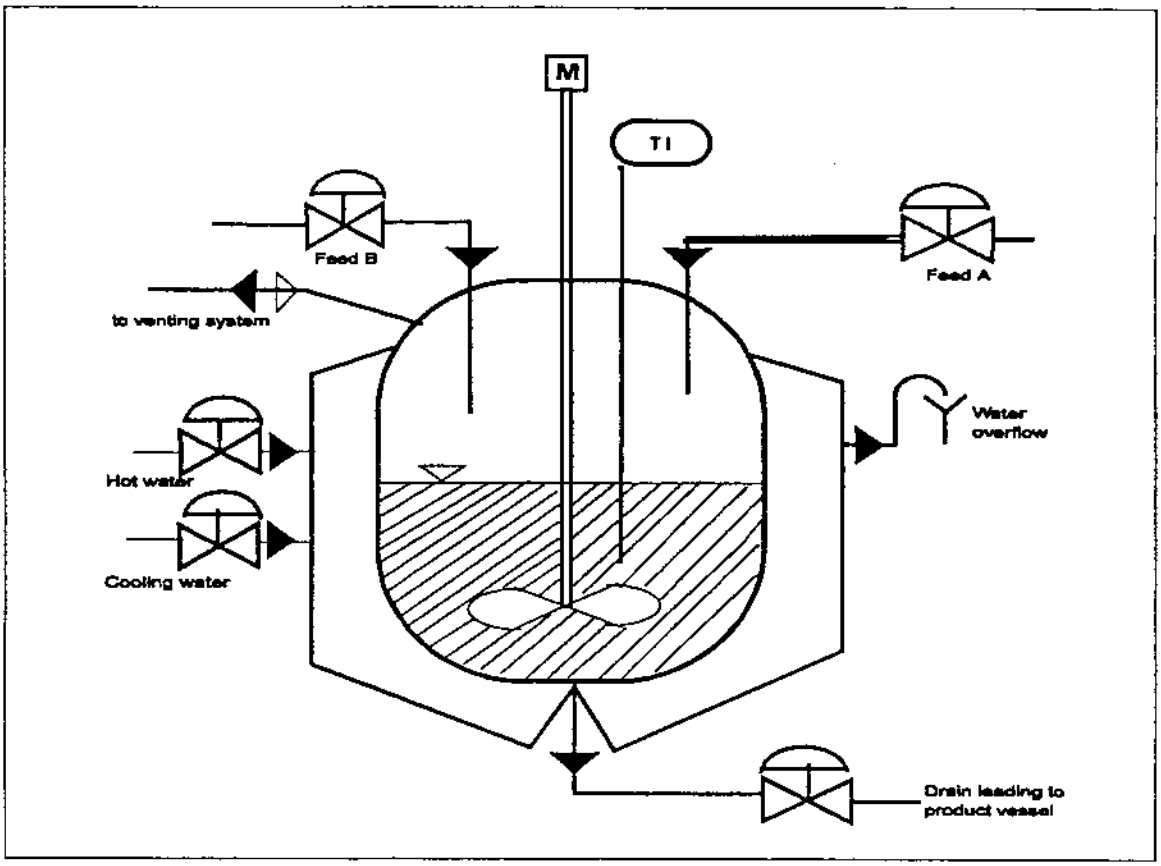
$$A + B \rightarrow C \qquad \text{(cases 1 and 3)}$$

and

$$A + B \xrightarrow{D} C \qquad \text{(case 2)}$$

is to be performed. In cases 1 and 3 it is intended to have compound B already in the reactor at ambient temperature to start with. In case 2, B is present in the reactor vessel dissolved in an inert solvent D. Afterwards, the vessel is heated approximately to nominal temperature (T_{nom} = 80°C). Compound A, which is supplied cold (at ambient temperature) using a metering system is then supposed to be admixed over a predetermined period at a constant rate. The heat liberated during the reaction is removed using the water for heating/cooling (see Fig. 1).

Fig. 1: Reaction vessel



2.2 Hazard potential

In all cases the reaction is an exothermic reaction and the reaction enthalpy ΔH_R is known, so the adiabatic temperature rise can be defined in each case as $\Delta T_{adiab} > 50°K$.
Below 60°C the reaction starts to "go to sleep", so that an undesirable accumulation of reactants is to be anticipated. If the reaction is then started, a higher reaction power must be anticipated.

By DTA and caloric measurements it has been determined that above the limit temperature T_{exo} the end product decomposes strongly exothermicly in an uncontrolled reaction

$$C \rightarrow \text{decomposition products.}$$

This produces significant amounts of gases which would lead to the design limits of the vessel being exceeded:

$$(dM/dt)_{decomposition} > (dM/dt)_{max.\ design}$$

The temperatures T_{exo} in each case for cases 1 - 3 were determined in accordance with the experimental results. They are distinctly above 100°C. Because of the relation between T_{exo} and the production of gas, the design limit with regard to temperature ($T_{max.\ design}$) must be set as T_{exo} (unless for example the materials used make it necessary to prescribe a lower maximum temperature, not a possibility considered here).

2.3 Normal operation

The investigations of the starting components A and B show exothermic behaviour and gas development only at temperatures above 300°C. In terms of energy release, these are of the order of 300 J/g, so that explosive properties or deflagration need not be anticipated.
Investigations of samples of reaction mixtures at different phases of reaction confirm the reaction enthalpy of the required process and show no need to reduce T_{exo}.

Substances A and B and the reaction mixtures have a negligible vapour pressure below T_{exo}. The solvent D used in case 2 is chemically inert over a wide temperature range for the reaction concerned, has a high boiling point T_s (> 180°C) and is thermally stable at temperatures up to and over 200°C.

Consequently, significant gas production need only be anticipated in conjunction with the decomposition reaction of substance C; for normal operation, all possible vapour/gas volumes produced can be controlled using the equipment provided.

For process reasons, and here especially because of the relatively high adiabatic temperature rise ΔT_{adiab} (> 50°K), heat removal capacity and reaction power must be matched to suit one another. The cooling power has therefore been chosen in such a way that the heat of reaction liberated at the proposed metering rate is removed at the set point temperature.

Normal operation may therefore be regarded as safe.

2.4 Deviations (failures)

Three examples have been used to which the above conditions apply equally, although they differ with regard to certain reaction and processing data. The following failures may change the temperature level towards T_{exo}:

I. Deviations in reaction conditions (see table 1)

- *a) reaction temperature too high*
- *b) delayed reaction start (because of too low a temperature, leading to accumulation with subsequent increased reaction power)*
- *c) only half the quantity of component D is used*

II. Deviations in the operation of the installation (see table 2)

- *a) stirrer failure (leading to accumulation with subsequent increase in reaction power)*
- *b) failure of the cooling system at the beginning of the reaction (e.g. failure of the thermal transfer fluid pump)*

2.5 Various cases with measures proposed

2.5.1 Case 1

Reaction $A_1 + B_1 \rightarrow C_1$

Important data and information for assessment

Substance/Reaction	Data and information
A_1	Pure substance; thermally stable up to above T_{exo}
B_1	Pure substance; thermally stable up to above T_{exo}
C_1	$T_{exo} = 180°C$; $(dM/dt)_{decomposition} > (dM/dt)_{max.\ design}$
$A_1 + B_1 \rightarrow C_1$	Spontaneous reaction at 80°C; $T_{exo} = 180°C$; $\Delta T_{adiab} = 75°K$

Assessment of failures:

I a) The maximum possible heating temperature is 95°C, because of the open water circuit. Consequently T_{exo} cannot be reached through external heating.

I b) Reactive power cannot be removed completely by the cooling system so that the temperature increases above the set point. The maximum temperature which can be reached is $T_{process} + \Delta T_{adiab}$. With $T_{process} < 80°C$ it remains below T_{exo} (even if the heat removal capacity = 0!)

I c) This failure is not possible, since solvent D is not required.

II a) As under I b), but with $T_{process} < 80°C$. Here again the system remains below T_{exo}.

II b) As under II a).

Each failure on its own satisfies the inequalities

$$T_{process} + \Delta T_{failure} < T_{max.\ design}$$

and

$$(dM/dt)_{process} + \Delta(dM/dt)_{failure} < (dM/dt)_{max.\ design}$$

Even the most unfavourable combination, the combination of several failures, and especially I a) with II a) or II b), with a maximum temperature of 170°C ($< T_{exo}$), does not lead to the design limits being exceeded.

Measures proposed:

With regard to the failures considered, no additional measures pursuant to section D are required.

2.5.2 Case 2

The reaction $A_2 + B_2 \xrightarrow{D} C_2$

is to be performed in solvent D. The component B_2 is supposed to have been dissolved in solvent D in the prescribed quantity.

Important data and information for assessment:

Substance/Reaction	Data and information
A_2	Pure substance; thermally stable up to above T_{exo}
B_2	Solution in D; thermally stable up to above T_{exo}
C_2	$T_{exo} = 180°C$; $(dM/dt)_{decomposition} > (dM/dt)_{max.\ design}$
D	chemically inert; $T_s > 180°C$; thermally stable up to over 200°C
$A_2 + B_2 \xrightarrow{D} C_2$	Spontaneous reaction at 80°C; $T_{exo} = 180°C$; $\Delta T_{adiab} = 75°K$ $(dQ_R/dt)_{normal\ operation} = 95$ KW; product of heat transfer coefficient and heat transfer area k x F = 4.5 KW/°K

Assessment of failures:

I a) The maximum possible heating temperature is 95°C, because of the open water circuit. Consequently T_{exo} cannot be reached through external heating.

I b) Reactive power cannot be removed completely by the cooling system so the temperature will increase above the set point. The maximum temperature which can be reached is $T_{process} + \Delta T_{adiab}$. With $T_{process} < 80°C$ it remains below T_{exo} (even if the heat removal capacity = 0!)

I c) If only half the solvent quantity D is used, T_{exo} remains unchanged at 180°C, but the adiabatic temperature increase rises because of the reduced quantity of D, and therefore the changed total heat capacity of the reaction mixture, to $\Delta T_{adiab} = 112°K$. At the same time, the reaction power increases. However, through reactor cooling it can still be reliably removed ($\Delta T_{failure}$ = approx. 17°K).
Even with this failure, the system still remains below T_{exo}.

II a) As under I a), but with $T_{process} < 80°C$. Here again the system remains below T_{exo}.

II b) As under II a).

Each failure on its own satisfies the inequalities

$$T_{process} + \Delta T_{failure} < T_{max.\ design}$$

and

$$(dM/dt)_{process} + \Delta(dM/dt)_{failure} < (dM/dt)_{max.\ design}$$

But if one now considers combinations of two failures, namely:

α) insufficient solvent quantity D and simultaneous failure of stirrer [failures I c) and II a)], T_{exo} may be exceeded:
(80 + 112)°C = 192°C > (T_{exo} = 180°C). Assumption: heat removal power = 0

or

ß) solvent quantity D too small and cooling failure at the same time at the beginning of the reaction [failures I c) + II b)], T_{exo} may also be exceeded:
(80 + 112)°C = 192°C > (T_{exo} = 180°C). Assumption: heat removal power = 0

Consequence:

The above inequalities are no longer satisfied. Additional measures are required. To trigger an event (excess over design limits), at least two failures are necessary. Consequently the chain of events detailed under II a) and II b) must be interrupted by one measure in each case. These measures must be effective independently of one another. The same applies in respect of the measures concerning the failure mode which leads to a reduction in the solvent quantity D.

Measures proposed (see fig. 2):

α) Incorrect starting concentration and stirrer failure:

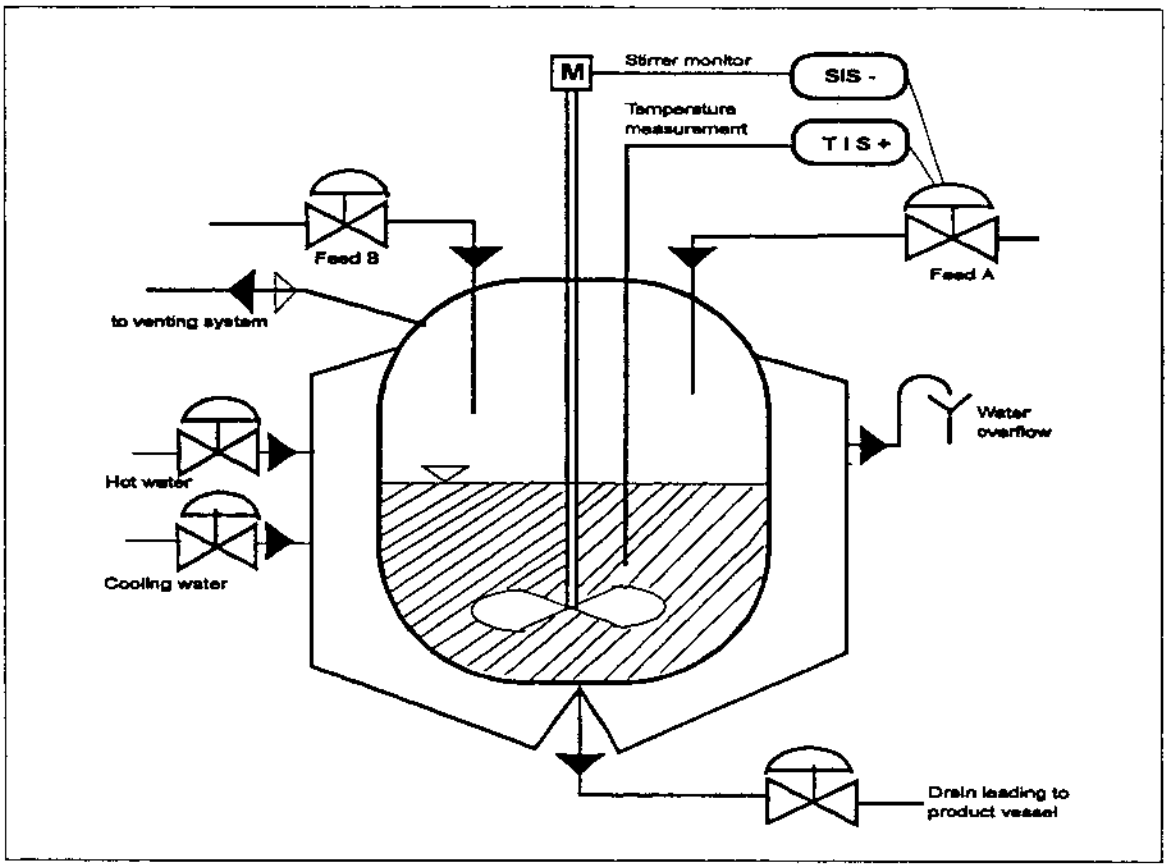
1. Simple interlock of the inlet valve for component A_2 with the stirrer function SIS- (valve closes when the stirrer is stationary), and
2. ensuring that the correct quantity D is added by using a suitable organisational measure (safety operating instruction).

ß) Incorrect starting concentration and loss of cooling:

1. Simple interlock of the inlet valve for component A_2 with the temperature controller in the reactor TIS+ (valve closes when a maximum temperature, for example 100°C is reached), and
2. ensuring that the correct quantity D is added by using a suitable organisational measure (safety operating instruction).

These measures do not change the parameters for normal operation so that it is not necessary to perform an iterative assessment of normal operation (see schema 2 with schema 1).
No further measures are required with regard to the failures considered.

Fig. 2: Equipment of reaction vessel (schematic), case 2



2.5.3 Case 3

Reaction $A_3 + B_3 \rightarrow C_3$

Important data and information for assessment:

Substance/Reaction	Data and information
A_3	Pure substance; thermally stable up to above T_{exo}
B_3	Pure substance; thermally stable up to above T_{exo}
C_3	$T_{exo} = 120°C$; $(dM/dt)_{decomposition} > (dM/dt)_{max.\ design}$
$A_3 + B_3 \rightarrow C_3$	Spontaneous reaction at 80°C; $T_{exo} = 120°C$; $\Delta T_{adiab} = 225°K$

Assessment of failures:

I a) The maximum possible heating temperature is 95°C, because of the open water circuit. Consequently T_{exo} cannot be reached through external heating.

I b) Reactive power cannot be removed completely by the cooling system, so the temperature will increase above the set point. The maximum temperature can now exceed T_{exo} with $T_{process} + \Delta T_{adiab}$ (including for $T_{process} > 80°C$). With cooling available, 160°C would be reached.

I c) This failure is not possible, since solvent D is not required.

II a) As under I b), but with $T_{process} < 80°C$. Here again the system may exceed T_{exo}.

II b) As under II a).

Each of the failures I b), II a) and II b) on its own no longer satisfies the inequalities referred to; **we now have**

$$T_{process} + \Delta T_{failure} > T_{max.\ design}$$

and

$$(dM/dt)_{process} + \Delta(dM/dt)_{failure} > (dM/dt)_{max.\ design}$$

Consequence:

Additional measures are required. In three cases even a simple failure triggers the feared event (exceeding the design limits). The corresponding three chains of events must therefore be interrupted by a *high availability safety device*. The measures proposed (see below) also interrupt the chains of events of possible failure combinations.

Measures proposed (see fig. 3):

I a) Redundant temperature measurement with feed valve (metering of component A_3) when the vessel temperature falls below the minimum temperature, TIS–

II a) Redundant temperature measurement with feed valve (metering of component A_3) when the vessel temperature exceeds the maximum temperature, TIS+

In order to satisfy the redundancy requirement relating to I a), the measurement is also used with the circuit for case II a) with S- being added. In the same way, in order to satisfy the redundancy requirement for II a) the measurement using the circuit for I a) is also used and supplemented with S+.

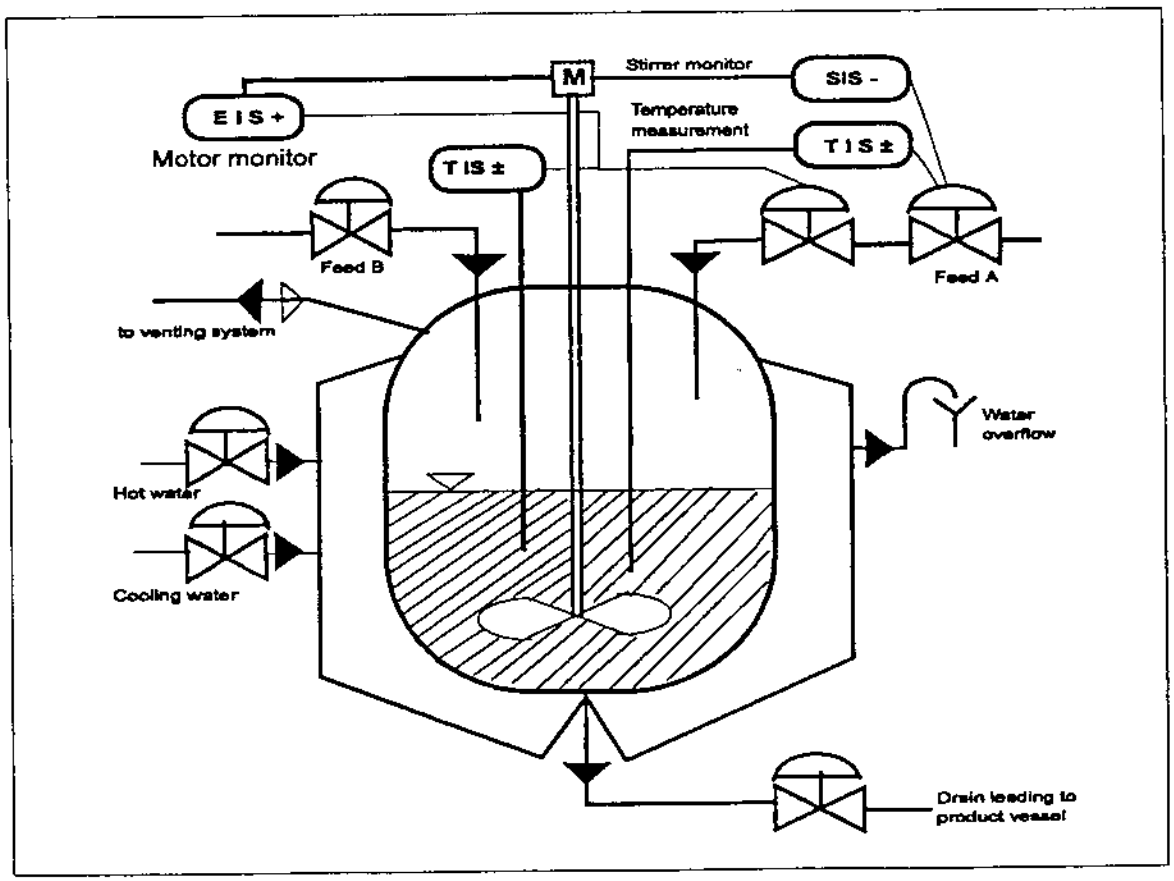
II b) Speed control of the stirrer, SIS-, and monitoring of the stirrer motor, EIS- (redundancy through diversity)

The above measures do not change the parameters for normal operation, so that iterative assessment of normal operation (see schema 2 with schema 1) is not required.

Notes:

In case 3 the unusual feature is the relatively high reaction enthalpy which goes along with a low limit temperature T_{exo}. An alternative safety solution here would be controlling these two parameters, for example by process and plant engineering changes ensuring fully continuous operation (flow reactor with pump, with the assistance of solvents). In that way (because of the short residence times and the dilution effect) the limit temperature T_{exo} could be raised and (because of the dilution effect) the adiabatic temperature increase ΔT_{adiab} would be reduced. However, such a change in the process and the installation makes it necessary to perform an iterative safety-technical assessment of the reaction in every case; other measures may become necessary.

Fig. 3: Equipment of the reaction vessel (schematic), case 3



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