Expert Commission
for Safety in the
Swiss Chemical Industry

# Thermal Safety Tutorial

# 1 Introduction

Version 2.0 2011

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This Thermal Safety Tutorial is the second version of a computer assisted learning tool that was originally issued in 1997. It is designed to provide guidance for the assessment of the thermal risks of a chemical process.
The Expert Commission for Safety in the Swiss Chemical Industry (ESCIS) developed this Tutorial because most reactions in the chemical industry are exothermic. Table 1 shows a number of severe accidents that occurred between 1976 and 2007.

*Table 1-1 Accidents caused by runaway reactions*

| **Year** | **Location** | **Accident** | **Effect** |
|---|---|---|---|
| 1976 | Seveso (I) | Heat accumulation during production of Trichlorophenol | Release of highly toxic dioxins, major environmental damage, 200 injured |
| 1984 | Bhopal (IND) | Exothermic reaction of Methylisocyanate with water | Release of 25-40 t of Methylisocyanate<br>>5000 fatalities, >100000 injured |
| 1992 | Castleford (UK) | Exothermic decomposition of residues containing nitrocompounds in still base | 5 fatalities, >150 injured, severe damage to buildings |
| 1993 | Griessheim (D) | *Runaway reaction* [1] after *reactant accumulation* | Release of several tons of ortho-Nitroanisole, dispersion over residential area |
| 1997 | Columbus (USA) | Violent explosion after *runaway* during production of a Phenol Formaldehyde resin | 1 fatality, 7 injured, evacuation of residents for several hours |
| 1998 | Paterson (USA) | *Runaway* of a batch reaction | 9 injured, neighbors evacuated, severe damage to buildings |
| 1999 | Wuppertal-Elberfeld (D) | *Runaway* caused by loading the wrong reactant | >90 injured, severe damage to plant |
| 2001 | Schweizerhalle (CH) | Explosion after exothermic decomposition of Lithium stored in Tetrahydrofuran | Explosion and fire, severe damage to building |
| 2001 | Schweizerhalle (CH) | Deflagration of an organic Nitro compound in a tube reactor | Explosion, severe damage to building |
| 2005 | Grenzach (D) | Exothermic reaction of organic deposits in ventilation ducts with nitrous gases | Self-ignition and fire, spreading over the entire ventilations system, severe damage to building |
| 2007 | Waldenburg (CH) | Unintended reaction between Sulfuric acid and Potassiumcyanide | 33 injured, 80 evacuated |

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[1] Terms defined in the Glossary are printed in *italics*, see chapter 8.4.

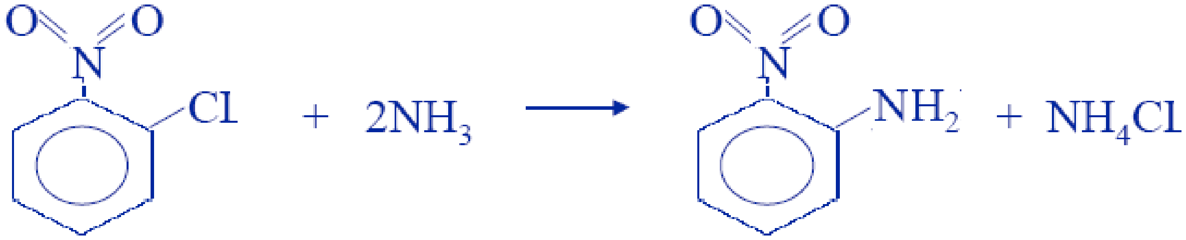
Such accidents can be prevented if the hazards associated with the substances and the chemical reactions involved are systematically identified and assessed based on safety data and if the appropriate technical and *organizational measures* (Definitions see Glossary, chap. 8.4) are put in place and are properly maintained.

The assessment of the thermal risks associated with a chemical process requires the evaluation of both the severity and the probability of possible incidents resulting from the uncontrolled release of chemical energy. To evaluate the risks, the general chemical properties, in particular the stoichiometry, the reactivity with other substances and construction materials must be understood. Furthermore knowledge of the thermodynamics and kinetics of the main reaction and relevant secondary reactions is required. This information must then be evaluated in a systematic way.
This Tutorial will make its user familiar with the relevant facts and the concepts to control the thermal risks associated with the synthesis (intended) reaction and to avoid secondary (unintended) reactions. Improved screening methods will be introduced to determine the required safety parameters.
The tutorial will therefore provide a convenient and efficient method to assist the fine chemical and pharmaceutical industries in the assessment of the thermal process safety hazards associated with the handling and processing reactive chemicals.

## 1.1 Incident Case Studies

Case studies give insight in the reality, which often is more complex than theoretical considerations in class room exercises. Learning lessons from such incidents is one of the best methods to continuously improve safety in the process industry.
The following typical cases based on actual real industrial incidents will pin-point important causes and illustrate possible consequences.

### 1.1.1 Runaway of an Amination Reaction



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

**Causes:**
Aminations are highly exothermic reactions that are normally run as a “batch process” where all the reactants are added before the reaction is initiated. As a result, the entire energy potential inherent to both the synthesis reaction and any secondary reactions is contained in the vessel at the beginning of the process. Once the mass is heated to the temperature, at

which the wanted reaction runs at a reasonable rate, the only possibility to control the reaction is to control the temperature by heat removal through the jacket.
If the *heat production* exceeds the heat removal capacity of the reactor, e.g. due to a cooling failure or due to wrong loading of the reactor, a *runaway reaction* may occur, which results in a rapid temperature and pressure increase in the vessel and in the worst case, a mechanical failure of the autoclave.

### 1.1.2 Runaway of a Polytropic Reaction

The following explosion and fire occurred during the synthesis of a specialty chemical in an 8 $m^3$ vessel.
The product was manufactured by the mixing the two reactants at 40 °C. The reaction was started by heating to 90 °C. Then the heating had to be switched off as the heat of reaction produced a further increase in temperature. By manually controlling the cooling water, the increase in temperature had to be stopped between 150 and 160 °C. Then the reaction had to be completed at this temperature.
On the day of the incident the following process deviations occurred:
Heating was started faster than usual. Then the cooling capacity of the reactor was not sufficient to keep the temperature below 160 °C. The reaction mixture started to boil, and at 180-190 °C the pressure inside exceeded the set pressure of the rupture disks. These were, however, not sufficiently large to relieve the pressure. As a result the glass line to the condenser and the condensate return line shattered and finally the manhole hatch was blown off. The expanding vapors and decomposition gases propelled the reaction mixture through the roof, and ignition occurred.
The operators, which were still near the vessel were severely injured.

**Causes:**
This highly exothermic reaction was run as a “batch process” where all the reactants are added before the reaction is initiated. As a result, the entire energy potential inherent to both the synthesis reaction and any secondary reactions was contained in the vessel at the beginning of the process. Once the mass was heated to the temperature, at which the wanted reaction runs at a reasonable rate, the only possibility to control the reaction is to control the temperature by heat removal through the jacket.
After heating initially too fast, cooling through the jacket was obviously not sufficient, a *runaway* occurred, which resulted in a rapid temperature and pressure increase in the vessel. Because the emergency pressure relief systems were not designed appropriately the manhole hatch was blown off.

### 1.1.3 Runaway of a Sulfonation Reaction

To manufacture 2-Chloro-5-nitrobenzenesulfonic acid, 1-Chloro-4-nitrobenzene was melted by heating to about 100 °C. It was then transferred within 20 minutes into a vessel containing 20 % Oleum at a temperature of 50 °C. With the reactor closed and the double-wall jacket empty, the temperature was allowed to increase within one hour to 120-125 °C. The reaction mixture was then held at this temperature for several hours allowing the reaction to run to completion under 2 bar pressure.
As temperature monitoring was not foreseen in this phase nobody noticed that the temperature steadily increased during the next two hours. Shortly after 138 °C was reached, a violent explosion occurred. The force of the explosion caused the reactor to shift from its platform and the cover to be blown through the roof of the building into the surrounding plant area.

**Causes:**
In the planned course of the reaction, i.e. heating to 125 °C and holding for a period of

several hours, the desired product is obtained in good yield with a minimum of by-products present. This proves that at this temperature the desired reaction is dominant and the *reaction rates* of any decomposition reactions are relatively small. This strongly suggests that the initial driving force of this incident was the accumulated heat of reaction of the intended reaction.
Because a steam heated jacket provides practically no heat exchange between the reaction mass and the jacket at 125 °C and normal pressure, the temperature of the reaction mixture slowly increased. This was not notified, because temperature monitoring was not foreseen. At 138 °C the decomposition reaction, which followed an *autocatalytic* mechanism, i.e. the *reaction rate* increased even at constant temperature, became dominant and provided the main part of the destructive force.

### 1.1.4 Runaway of a Polymerization Reaction

A polymer was produced through simultaneous addition of Acrylic acid and a Sodium persulfate solution over a two-hour period to a solution of Sodium thiosulfate. This solution was held under reflux conditions at 100-105 °C during the entire addition. When the incident occurred, the temperature rose very rapidly to 130 °C within 90 minutes after the start of the additions. Due to this rapid increase in temperature and pressure the reaction mixture was released through the gaskets of the vessel into the plant even though both the bursting disc and safety valve had already been activated.

**Causes:**
The investigation showed that at the time of the incident 80 % of the acrylic acid but only 10 % of the required Sodium persulfate solution had been added. It was found that under these conditions only a small additional amount of Persulfate can initiate a spontaneous polymerization.
The Persulfate (catalyst) was not added in accordance with the procedure due to either the discontinuous running of the dosing pump or intermittent blockage of the inlet.
Thus a high amount of unreacted monomer (Acrylic acid) was present in the reactor. The *runaway* occurred when the addition of Persulfate was continued and initiated the spontaneous polymerization.
In such a case, the safety of the process obviously depends on the *exact* adherence to the dosing profile of both components. The *reaction rate* is strongly dependent on the amount of catalyst present.
Such a process can be performed safely only if the concentration dependence of the *reaction rate* is accurately known, if reactant quality can be assured and if the process control is performed and checked meticulously.

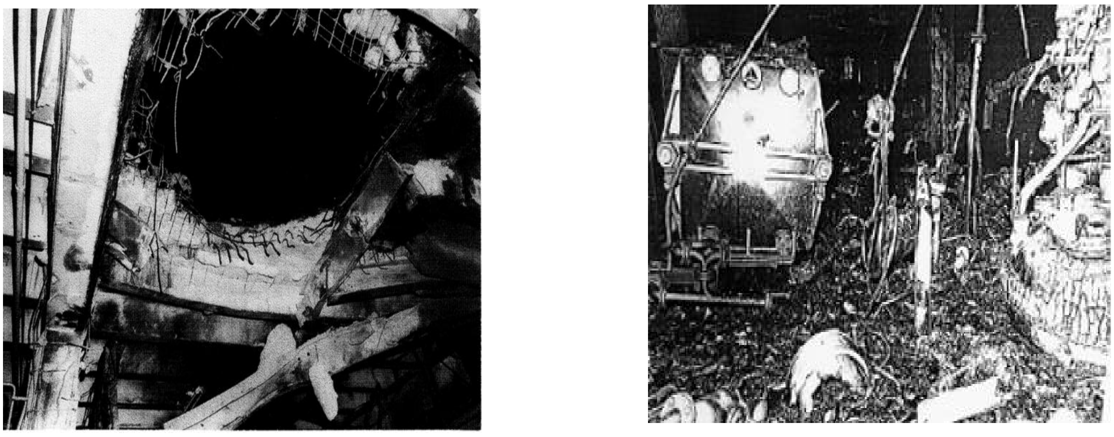


*Fig. 1-1 View of the site after a thermal explosion of a reaction vessel*

### 1.1.5 Abnormal Process of a Sulfonation Reaction

In the sulfonation of a nitroaromatic compound, a certain amount of reacted sulfonation mass from the previous operation was always added at the start. This “heel” was heated to 85 °C using a jacket vapor temperature of 150 °C. The melted aromatic compound and Oleum were then added simultaneously. Making use of the heat of reaction to the temperature was raised to 110 °C where the cooling was automatically switched on.
On the day of the incident, at a temperature somewhat in excess of 100 °C a rapid increase in pressure occurred. The reactor cover ruptured and the reaction mass was discharged like a lava stream causing considerable material damage.

**Causes:**
The investigation established the following case history and revealed the underlying reasons of the incident.
About one year before the incident the reactor vessel had been fitted with an additional cooling coil inside the tank for a different process. Related to this somewhat unusual arrangement, a space-saving turbine agitator was installed with a high base clearance compared with that of the standard agitator.
Later, corrosion was found in the internal cooling coil. Since the process that made the auxiliary cooling necessary was no longer being run, the internal cooling coil was removed. Approximately six months later, the agitator was moved to its topmost position during a maintenance check and was not returned to its original position.
As a result of this modification in agitator position, it was not immersed in the reaction mass at the beginning of the sulfonation reaction.
When the two reactants were added to the reactor, the melted aromatic compound remained on the surface of the unstirred mass whereas the heavier, cold Oleum formed a lower layer. The temperature sensor was located in the lower half of the reactor. It correctly reported the low temperature at this location which caused the control system to switch on full steam heating on the jacket. Both reactant layers were heated. With increasing volume, immersion of the agitator gradually increased. When the interface between the two layers reached the stirrer, rapid mixing of accumulated reactants occurred and a rapid exothermic reaction began. When the temperature reached 170-200 °C, a highly exothermic decomposition was initiated and contributed to the self-heating process.
This case points out the risks associated with modifications of existing plants. Although in retrospect the incident followed a logical course, the sequence of events could hardly have been predicted by a risk analysis. At the time of the introduction of the process, a risk analysis had been completed and the associated risk had been considered as acceptable. However, no management of change procedure (MOC) had been in place and as a result no one had systematically analyzed the consequences of the changes made in the plant. Long-term control over changes in procedures or reactor design is *very* demanding and the safety design of the system with clearly documented critical limits is essential.

### 1.1.6 Storage at elevated Temperatures under Heat Accumulation Conditions

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

**Causes:**
In contrast to the cases discussed previously, the primary driving force of this explosion was not a synthesis reaction but a decomposition reaction. The material degraded due to the fact that a slow decomposition reaction took place under storage conditions. The value for the decomposition determined in the laboratory indicated a slow *reaction rate*, but the laboratory testing was done without taking into consideration self-heating which occurred in the unstirred vessel virtually. Typical of this heat accumulation incident is the relatively long time over which, starting from slow initial rates, a thermal explosion gradually developed. A correct interpretation of the available information could have *predicted* this incident, and it could have been detected at an early stage if a temperature alarm had been installed.

### 1.1.7 Thermal Runaway of a Phenolation Reaction

During the synthesis of Sodium phenolate in an 8 $m^3$ reactor, an overpressure occurred inside the reactor. This pressure was initially released by the safety valve and later on by the rupture of the manhole lid, with consequent release of product.
No employees were affected, but roofing, pipe rack supports, mechanical, electrical and instrumentation installations of the reactors nearby were damaged.

**Causes:**
Calorimetric studies showed that an accumulation of caustic soda can occur when the dosage is too fast or at too low temperature. In addition, a too fast dosage leads to a nonhomogeneous reaction mass.
Thus un-reacted caustic soda was accumulated in the reactor due to either of these factors. Suddenly the *reaction rate* increased - possibly due to phase transition effect, as the reaction mixture consists of an organic and an inorganic phase. The increased *heat production* exceeded the heat removal capacity of the reactor and a thermal *runaway* occurred.

### 1.1.8 Decomposition of a freshly milled Product in a Container

A 1400 L container holding freshly milled product in a high storage rack attracted attention by severe smoke development. Its cover had been blown off and its content had flowed out of the container like a lava stream. The ongoing reaction could only be stopped by *flooding* the container with water.

**Causes:**
On the basis of the product data, it was assumed that the product had been heated up slightly during milling and that accelerated self-heating had occurred under the *heat accumulation conditions* prevailing in the container.
Comments:
This incident is representative of a series of similar incidents caused by the discharge of warm or hot material into unstirred bulk containers after milling or drying operations. A typical feature is that no noticeable problems arise during the process in the production area and the thermal decomposition was not observed until hours after discharging.
The critical temperature in unstirred bulk containers can be considerably lower than discharge temperatures for milling and drying operations. This case also shows clearly that the temperature is not the only parameter to be considered when assessing thermal risks: The powder was not dangerous during the process but caused a smoldering fire in the container. Thus the term "first exothermicity", which is supposed to be the limit between safe and unsafe conditions, can be misleading. Its use should be limited to qualitative reporting of the result of a specified experiment and to compare safety assessment procedures.

### 1.1.9 Self-heating of a Product in a heated Conveyor Line

After removing the solvent in a thin-film evaporator, the distillation residue was transferred with a screw pump to a control valve. To keep the residue liquid, the entire system had to be heated to above 250 °C. One day the product line between the screw pump and the control valve burst. The heating medium (Diphyl, 7 bar, 290 °C) was released into the work room.

**Causes:**
The cause of this was blockage of the control valve. The product flow stopped, the motionless product heated up, initially owing to the entrainment of mechanical energy from the screw pump but soon as a result of heat from an incipient decomposition. Owing to the temperature rise and the decomposition gases formed, the pressure rose until the line burst. In this example, the primary cause was not the decomposition of reaction mass but rather the impairment of the material flow and the input of mechanical energy by the pump.

### 1.1.10 Mis-identification of Chemicals

For the production of an agrochemical, a reaction involving 600 kg Chloronitrotoluene, 1050 kg Dimethyl sulfoxide and 500 kg Potassium carbonate was carried out. Two operators and the plant manager checked the correct loading of the reactor and then left the production room.
Shortly after that, the reactor exploded. The pressure wave destroyed part of the light roof and combustible materials, which were released caused a fire in the production room. It took several hours to put the fire out. Eleven employees were injured, two of them suffered perforated eardrums. In total, 102 persons, most of them from the neighbouring residential area, required ambulant treatment.

**Causes:**
The cause for this violent exothermic reaction was the mis-identification of raw materials. Instead of Potassium carbonate, labelled "Potash", Potassium hydroxide ("caustic potash"), which was supplied in similar bags labelled with "Potassium hydroxide" was filled into the reactor. Potassium hydroxide undergoes a violent reaction with Chloronitrotoluene.

### 1.1.11 Analysis of the Case Studies

- Chemical reactions may involve high energy potentials which may lead to devastating effects

- Conducting chemical processes safely requires due consideration of
  - characteristics of involved substances, as described by safety data
  - the kinetics of the involved reactions (*heat production*)
  - plant design and construction (heat removal)
  - operating procedures and *Process Control System* (*PCS*) (monitoring and control)

- Before carrying out a new chemical process, a systematic and comprehensive risk analysis must be carried out to define appropriate safety concepts. A regular update of this analysis and the concept is necessary.
  In the following sections such a risk analysis method will be demonstrated and measures to reduce the risk of thermal hazards will be discussed.

## 1.2 Heat Balance

The *heat balance* is a central element for the understanding of the basic concepts in thermal safety analysis.
The *heat balance* deals with the change of the thermal energy contained (or in other words accumulated) in a reactor.
This change is equal to the difference between the energy generated inside the reactor (*heat production*) and the energy dissipated to the cooling system or the environment (heat removal):
If in a given period of time more heat is produced than removed in a system, the difference remains in the system and leads to an increase in temperature. On the other hand, if heat removal prevails, the temperature will decrease.
Thus the *heat balance* is the key to understand temperature changes in a system.
Therefore, the tutorial is structured according to the terms of a *heat balance*:

- ***Heat production*** is discussed in chapter 2.
- Chapter 3 contains information on **heat removal**.
- Scenarios where the ***heat balance*** is not in equilibrium are treated in chapter 4 and chapter 5.
- Finally an overview on ***risk reducing measures*** is given in chapter 6.
- Chapter 7 is a compendium of **experimental methods** for the study of thermal characteristics of reactions and substances.