Guideline on the safety related requirements of the ChemCar-Competition Rev. 9

ChemCar 2021

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Introduction

This guideline lists question complexes, documentations and verifications that are required for the safety consideration of the submitted ChemCar Safety Concepts. Without these documents and verifications a qualified evaluation of the concepts is not possible and thus a security approval cannot be issued.

For clarification, an example of the documentation of the technical data of a ChemCar team in recent years is set at the end of this guideline. This example includes the calculations for estimating the developing reaction heat and the maximum pressure expected (see chapter 7 - 9). Please note that this example provides information only on the form and on the detail of the document but not on the content.

1. Pressure

- Pressure units:
  - Use consistent pressure units – absolute pressure [bar_{abs}] oder relative pressure [bar_g]
- Operating pressure:
  - What is the pressure in normal operation of the ChemCar?
    It is always necessary to document a pressure and give a description why this pressure defines normal operation.
- Maximum pressure expected:
  - What is the maximum pressure reached by reaction if pressure vessel is blocked by malfunction ?
    A worst-case scenario has to be considered. Please discuss what assumptions were made for worst-case.
- Pressure test / manufacturer certificate:
  - Attach the results of the pressure tests performed or hand in a manufacturer certificate. When using a pressure system, a pressure test for the overall system might be necessary even if a manufacturer certificate is available. The requirements and the performance of the pressure test are specified in the ChemCar Safety Rules.

    if not necessary for operation of ChemCar:
    please give a comprehensible explanation why pressure test is not necessary

- Safety valve:
  - All the calculations for the design of the used safety valve (e.g. according to AD-Merkblatt A2) must be provided comprehensibly. Not only the results!

    if not necessary for operation of ChemCar:
    please give a comprehensible explanation why safety valve is not necessary
- Pressure gauge / indicator
  - Ensure, that the ChemCar has a suitable pressure gauge / indicator which has to be included in the process flowchart. It must be possible to read the internal pressure of the ChemCar at any condition (e. g. in case of breakdown of ChemCar)

    if not necessary for operation of ChemCar:
    please give a comprehensible explanation why pressure gauge / indicator is not necessary
- In accordance with the ChemCar Safety Rules, you should pay attention that the pressure content product (pressure * volume) does not exceed 50 [bar * l] as far as possible (scope of pressure equipment directive 2014/68/EU; directive 2009/104/EC "minimum health and safety requirements for the use of work equipment by workers at work"). For the calculation, you have to use the maximum pressure expected (worst-case). If the value exceeds 50 [bar * l], a consultation with the Orga-Team is recommended.

2. Temperature

- Temperature units:
  - Use consistent temperature units – absolute temperature [K] or relative pressure [°C]
- Maximum Temperature:
  - What is the maximum temperature expected during operation of the ChemCar?
    All calculations and their basis must be documented. Please discuss why these are reached during normal operation.
- Thermal hazard potential:
  - Are flash points or ignition points of one or more substances reached?
  - Is there any risk that thermal decomposition of one or more substances occurs? What decomposition products are formed?
  - What secondary reactions can take place?

  - How big is the resulting temperature in this case?

- Adiabatic temperature increase / decrease:
  - Is the reaction exothermic or endothermic?
  - What reaction kinetics does the reaction have?
  - What temperature increase / decrease occurs under adiabatic conditions?
    The complete reaction of maximum quantities of the reactants must be taken into account.

    Note: Calculation of temperature change is always possible. Experiments will be taken as an additional source of information.

  - Results of temperature increase or decrease have to be discussed.
- Hot surfaces:
  - What temperatures can be generated at accessible surfaces?
  - Is it possible that burns due to hot surfaces can occur (guideline: T > 60 °C)?
  - Is a contact protection necessary?
- Cold surfaces:
  - How cold can accessible surfaces get (by reactions or filling processes)?
  - Is it possible to get injuries due to cold surfaces, e. g. frostbites or cold burns (guideline: T < 0 °C)?
  - Is a contact protection necessary?

3. Emissions

- Exhaust emission:
  - Are exhaust gases released before, during or after operation?
    Which exhaust gases are released (e. g. CO_2, CO, O_2…)?
  - Which quantities are released in maximum (document calculations)?
  - What is the maximal released substance concentration in the surrounding area?
  - What are the limits for the released substance (→ toxicity…)?
    Please write down the important limit values and discuss them
  - Is the existing ventilation sufficient to minimize or prevent the danger from released substances?

    If necessary: Please describe retention concept for all gases that must not be released into the surrounding.

N o t e:

According to the rules of ChemCar competition **release of minor amounts of hydrogen** resulting from a side reaction (especially parasitic reaction within an electro chemic battery) are allowed. However, this minor amount has to be calculated and safety issues have to be assessed while creating the safety concept. If the data concerning the formation of hydrogen is incomplete use comprehensible assumptions which have to be presented in detail in the safety concept.

- Noise emission:
  - What is the maximum noise level expected during operation?
  - Is it possible that injuries / impairments occur due to noise exposure (performer and viewers)?

4. Procedure

- Filling / dosing:
  - How is the reactor filled?
  - How are the educts dosed?
  - Is a wrong filling or wrong dosing possible?
  - What consequences can a wrong filling / dosing have?
- Leakage / unintended release:
  This refers to a leakage during operation – competition in the hall.
  - What dangers could be caused by leakage or accidental release?
  - What measures should be taken in case of a leak or an unintentional release (especially liquid leakages)?
  - Is there a retention concept, e. g. collecting basins?
  - What kind of personal protective equipment is necessary in case of unintended release?

    N o t e :

    The handling of unintended release or leakage during work at the ChemCar in preparation room has to be described also.
- Mechanical function:
  - How is the force transmitted?
  - What happens during a mechanical blockage? For example, the blocking of wheels? Is it possible that a hazardous situation can develop?

- Intended mode of operation
  - How is the intended mode of operation definded?
  - How is it planned that the ChemCar – after executing the starting action before the run – will be provided with energy, starts to move, moves on (running) and finally stops?
  - How is the material flow during intended mode of operation?
- Emergency Shutdown
  - Is there an emergency shutdown mechanism?
  - How does this mechanism work? Description of manual function.

5. Documentation

- Basic documents:
  - A detailed functional description of the ChemCar
  - A photo or drawing of ChemCar (even unfinished ChemCar as status quo) – please add date of picture and state of assembly of ChemCar OR show separate part / steps of construction
  - A block flow diagram of the process
  - P&ID of the ChemCar. Pay attention to completeness (piping, inscriptions etc.). Please keep in mind the difference to a block flow diagram
  - Safety Data Sheets of all existing substances (both used substances and produced) – please keep in mind that SDS have to be up to date (ideally not older than 2 years!)
  - H- and P-phrases in written form (not only abbreviations)
  - Summary of all used substances with quantities in a register of hazardous substances
- Operating principle:
  - Description of the relevant system components (turbine, safety-bags etc.) and how they work
- Operating instructions:
  - Operating instructions according to TRGS 555 and GefStoffV § 14 for used reactants, products and potential auxiliaries. In the operating instructions the risks (explosive, oxidizing, toxic etc.), preventable conditions, transport, handling and disposal of the substance must be explained briefly. The minimum required personal protective equipment should be apparent from the operating instructions. An example of an operation instruction

is shown in chapter 9.
► A Safety Data Sheet is no operation instruction but can be used as source of information in preparation of an operation instruction (see. Appendix to TRGS 555)!!!

- Reaction Equation:
  - Document the complete (!) reaction equation, including all side reactions and intermediates
- Calculations:
  - All calculation methods must be documented (maximum temperature, maximum pressure, temperature increase etc.). Not only the results.
    If an Excel-Sheet is used please pay attention to confirmability of the documentation!
- Suitability of the material:
  - Are used materials suitable?
  - Is corrosion or embrittlement of material possible, caused by used or formed substances?
  - Are the used materials suitable for the existing temperature ranges?

Note:
All components of the ChemCar must be considered in this context. For all components that may come into contact with substances / chemicals (educts, intermediate products, products) a material suitability must be proved. This means that it has to be clarified if the utilised materials could interact with the substances / chemicals under operating conditions. In particular, damages or malfunctions of the ChemCar must be taken into consideration, i. e. is a retention of released substances ensured? Is it possible that released substances interact with the retention equipment and affect the retention function significantly?

The proof of the material compatibility (manufacturer specifications, laboratory tests etc.) especially with the chemicals (→ educts, products AND intermediate products) **is an essential part of the safety concept.**
If you hand in lists of material suitability these should be highlighted clearly. It is not necessary to hand in a complete list. The front page and the page with the marked passage are sufficient.

6. Risk assessment

The purpose of a risk assessment is the coverage of the intended use and any faults. The consequences of a disturbance have to be referred to the specific application. A reference to the Safety Data Sheet (general application) is not enough!

In addition to resulting hazards (e. g. explosion risk) caused from the used substances those caused by material properties (glass containers ► splinter protection) or components (fast rotating components ► cover) should be considered also.

Example for a risk assessment (Safety-Analysis Form):

Sequence of Steps	**Potential Hazards**	**Procedure to Control Hazard**	**PPE or Equipment Required**
Emergency shut-down			
	Hazard A (z. B. pressure increase)	Procedure A (z. B. stop educts supply , Opening of the safety valve)	PPE A, B, C (z. B. safety glasses, gloves and gowns)
Start-Up Procedure			
Run Time Procedure			
Shutdown Procedure			
Cleanup / Waste Disposal			

Example for a hazardous substances register:

Chemical Information Page

Fill in as much data below as available. **Be sure to list the units!** If data are not available, leave the field blank.
Material safety Datasheet (MSDS/SDS) for each named hazardous material is mandatory.

Chemical Quantities: List below the chemical names, concentrations, and total quantity of chemical required for the competition.

Chemical Name	Chemical State Solid, Liquid, Gas	Concentration Required	Total Quantity Required for Competition	Specific Personal Protective Equipment / Remarks

Chemical Properties and Hazards for ALL CHEMICALS, including reactants, solvents. intermediates and products.

Chemical Name	Physical State S, L, G	GHS Symbol(s)	H&P- Statements (No. only)		Incompatible Chemicals List chemicals present within the laboratory, and any others that may come in contact.	Flash Point Temp.
			Hazard Statements	*Precautionary Statements*		

General Notes for making the safety concept:

- For preparation of the safety concept (including a risk assessment) it is necessary to answer the questions and remind the hints given at points 1. – 6. of this document. It is a **non-exhaustive enumeration**, what means hazards resulting from your ChemCar in special have to be assessed and discussed by yourself.
- The safety concept that includes the risk assessment has to be done as free text

7. Example: Calculation of the thermal hazard potential

01	**Parameter**									
02	Route	20 m								
03	Time	30 s								
04	**Geometry**									
05	Wheel Diameter	0,2 m								
06	Piston Stroke	0,35 m								
07	Amount Of Rotations	31,83								
08	Cylinder Diameter	0,008 m								
09	Required Volume	0,00056 m^3								
10	**Vehicle Data**									
11	Weight	5 kg								
12	Additional Weight	0,3 kg								
13	Total Weight	6,5 kg								
14	**Dynamic Calculation**									
15	Kinetic Energy	1,44 J								
16	Speed	0,667 m/s								
17	Gravity Constant	9,81 m/s^2								
18	Coefficient Of Friction	0,6								
19	Friction Energy	765,18 J								
20	Efficiency	0,3								
21	Required Power	2555,41 W								
22	Required CO_2-Amount	1,01 mol								
23	Universal Gas Constant	8,314 J/mol/K								
24	Temperture	303,75 K								
25	**Material Value**									
26	Reaction	2 HCl + K_2CO_3 -> 2 KCl + H_2O + CO_2								
27	**Educts**	**Mass [g]**	**Mass Fraction**	**Molar Mass [g/mol]**	**Amount of Substance [mol]**	**Stoichiometry Coefficient**	**Gibbs Enthalpy [kJ/mol]**	**Enthalpy of Formation [kJ/mol]**	**Volume [dm^3]**	
28	Hydrochloric Acid	368,947	0,2	36,461	2024	-2	-93,8	-92,31		
29	Potassium Carbonate	289,637	0,5	138,21	1,048	-1	-1065,4	-1151		
30	Water	1765,424		18	98,079	1	-237,2	-285,83		
31	**Products**	**Mass [g]**	**Mass Fraction**	**Molar Mass [g/mol]**	**Amount of Substance [mol]**	**Stoichiometry Coefficient**	**Gibbs Enthalpy [kJ/mol]**	**Enthalpy of Formation [kJ/mol]**	**Volume [dm^3]**	
32	Carbon Dioxide	44533		44,01	1,012	1	-394,5	-393,5	22,67	
33	Potassium Chloride	150,875		74,551	2,024	2	-406,6	-436		
34	Water	18,214		18	1,012	1	-237,2	-285,8		
35	Molar Ratio	16,8947								
36	**Reaction Value**									
37	Reaction Heat	-872,450 kJ								
38	Gibbs Enthalpy	-191900 J/mol								
39	Excess Factor For Potassium Carbonate	1,036								
40	Reaction Conversion	1,000								
41	Experimentally Determined Volume	0,600 dm^3								
42	**Adiabatic Temperture Increase**									
43	Liquid Phase	3372,981 mol/m^3								
44	Concentration	-215680 J/mol								
45	Reaction Enthalpy	998,00 kg/m^3								
46	Heat Capacity	4184,00 J/kg/K								
47	Temperture Increase	174,22 K								
48	**Generated Pressure**									
49	"Free" Volume in Reactor	0,4211 dm^3								
50	Van-der-Waals Constant	0,3590 $(Pam)^6/mol^2$								
51	a	0,0000427 m3/mol								
52	b	46,89 bar								
53	Pressure by Van-der-Waals	46,89 bar								

$$p \cdot V = R \cdot n \cdot T$$

$$\Delta T_{ad} = \frac{c_0^A \cdot (-\Delta_R H)}{\rho \cdot c_p}$$

$$p = \frac{n \cdot R \cdot T}{V - n \cdot b} - a \cdot \left(\frac{n}{V}\right)^2$$

To calculate the power, which is needed to absolve the required distance in addition of a given weight, this calculation chart is used. The ideal gas law is used to charge the required amount of released gas (here: CO_2) to run a piston engine. The application quantity is given by the stoichiometry of the reaction. The correction is made by experimental data. The heat capacity and the density is assumed as the value of water, because all educts are in liquid form or dissolved in this phase.

8. Example for the design of a safety valve

Resource: AD2000-A2: SAFETY VALVE

01	Opening Pressure		1 bar_g		
02	Item Number			d_0 = 18 mm, α = 0.54	
03	Reference				
04	Resource		A D2000-A2		
05	**Nomination**	**Unit**	**Formula / Symbol**	**Value**	**Remark**
06	**Surroundings Data**				
07	External Pressure	Pa	P_S	1,01E+05	
08	Internal Pressure	Pa	P_0	2,01E+05	1 bar_g
09	Tempreture	K	T	293,15	
10	Passage Surface	m^2	A_0	0,0003	d = 18 mm
11	Effluent Number	-	α	0,54	
12	**Thermodynamic Data**				
13	Substance Notation			28,2 Vol.% NH_3	mixture
14	Molar Mass	kg/mol	M	not necessary	
15	Compressibility	-	Z	0,889	
16	Isentropic Exponent	-	κ	1,4	
17	**Results**				
18	Maximal Mass Flow	kg/s	$\dot{m} = \alpha \cdot A_0 \cdot \psi \cdot \sqrt{2\rho_g P_0}$	2,26E-01	
19	Maximal Mass Flow	kg/h		8126,1807	
20	Maximal Volume Flow	Nm^3/s	$\dot{V}_N = \frac{\dot{m}}{\rho_{gN}}$	1,38E-01	Standard Volume
21	Maximal Volume Flow	Nm^3/h		497,014	
22	Flow Profile	-		critical	
23	**Calculation Part**				
24	Gas Density	kg/m^3	$\rho_g = \frac{P \cdot M}{R \cdot Z \cdot T}$	28,531	
25	Standard Gas Density	kg/m^3	$\rho_{gN} = \frac{101300[Pa] \cdot M}{R \cdot 273{,}15[K]}$	1,635	
26	Pressure Relation In/External	-	$\eta_0 = \frac{P_S}{P_0}$	0,503	
27	Critical Pressure Relation	-	$\eta_{crit} = \left(\frac{2}{\kappa+1}\right)^{\frac{\kappa}{\kappa-1}}$	0,528	
28	Pressure Relation	-	$\eta = \begin{cases} \eta_{crit} > \eta_0 \rightarrow \eta_{crit} \\ \eta_{crit} \leq \eta_0 \rightarrow \eta_0 \end{cases}$	0,528	
29	Effluent Function	-	$\psi = \sqrt{\left(\frac{\kappa}{\kappa-1} \cdot \left(\eta^{\frac{2}{\kappa}} \cdot \left(1 - \eta^{\frac{\kappa-1}{\kappa}}\right)\right)\right)}$	0,484	

9. Example: instruction manual according to TRGS 555/GefStoffV § 14

company	**Draft of the Intruction Manual**	**Date:** **Signature:**

HAZARDOUS SUBSTANCE / OPERATIONS / WORKPLACE

Hydrochlorid Acid, from 10 % to 25 %

HAZARDS FOR HUMEN AND ENVIRONMENT

Attention

Possibly corrosive against metal. (H290)
Causes skin irritation.(H315)
Causes heavy eye irritation. (H319)
Possibly irritation of the air passages. (H335)
- Inhalation, swallow or skin contact can cause health damages. Irritate the air passages, Eyes and Skin. Can cause damage to the gastrointestinal tract. Temporary caused cough, sickness and nasal smell disorder. Possibly damaged lungs, eyes, teethes, kidneys, gastrointestinal and laryngeal attacks.
- Reacts with strong bases under emission of heat. Strong Reaction with sodium and potassium. Intensity and hazardousness of the reaction are influenced by the concentration of the acid. Reacts with amines, silicon oxide and water under emission of heat. Dangerous gases were generated by reaction with potassium manganite, sodium hypochlorite and concentrated sulphuric acid (e.g. chlorine, hydrogen chloride). Dangerous gases were generated by reaction with base medals (Hydrogen). Dangerous Gases were generated by reaction with carbonates (carbon dioxide). Emission of carbon dioxide: Danger of bursting in closed containers! Generating of harmful gases by reaction with nitrogen oxide (Dichloride dimethyl ether).
- WGK: 1 (low hazardous of water)

SAFEGUARDING AND BEHAVIOURAL RULE

- Activate the aspiration and work in its support by emission of damping or haze. Do not leave bundles and barrels open! Avoid splashing and trail by filling and decanting. Hold reactive substances off and add them only safely. Add the water first and afterwards the acid by dissolving and diluting! Control Temperature! Use acid-resistant equipment! Use utensils which protect the skin.
- Do not eat, drink, smoke or sniff. Avoid inhalation of damping and aerosols! Avoid contact with eyes and skin! Clean hands and other contaminate body parts before taking a pause and the end of work. Use skin care products after the work! Rapidly remove product residues from the skin, clean and towel the concerned skin. Do not wear hand or arm decoration. Separately store street and work clothes! Rapidly shift contaminate and soaked work clothes. Use separate cleaning rags and wipes for skin and machines.
- Follow the storage conditions!
- Mind employment conditions!

Supplies at workplace:
- Eye protection: Using frame glasses with side protection by monitoring activity! Basket-shaped glasses by risk of splashing!
- Hand protection: Gloves made of a suitable Material in response of the activity. It is advisable to wear cotton-made undergloves under the protection gloves! Considering the gestation periods of the protection gloves! Using special skin protectant by wearing of the longer term!
- Breath protection: Combination filter E-P2 (yellow/white) or BE-P2 (grey/yellow/white)
- Body protection: Wearing of an synthetic apron by diluting or bottling!

BEHAVIOUR BY EMERGENCY

FIRE SERVICE 112

- Vacating and cordoning off the danger zone; inform the supervisor.
- Wearing eye, hand and by great amounts breath protection to remove leaked or splashed substances. Soaking up with acid binding substances, disposal and residues are washed away with water!
- Dangerous vapors are formed by fire (e.g. hydrogen chloride)! Leaking vapors deposit with spray water; then fast cleaning. Product is not flammable. Danger of Explosion by heating!
- Preventing intrusion in ground, water and canalization!
- Respecting alarm, escape and emergency routes. Alert fire service!

Competent Doctor:
Accident Telephone:

FIRST AID

EMERGENCY CALL 110

By every first aid measure: Mind self-protection, arrange medical treatment. Life saving emergency measures have to performed situational like recovery position, cardiopulmonary resuscitation or shock control. Sterile covering wounds. Resting the body and protecting for heat loss.
After eye contact: Immediately, the eye has to rinsed for minimum 10 minutes by opened eyelid and protected uninvolved eye.
After skin contact: Taking off contaminated clothes, even underwear and shoes, wearing personal protection utilities. Rinsing the skin with much water.
After Inhalation: Take the injured out of the dangerous zone. Fresh air supply by breathing of fresh air or ventilation. Using resuscitation device (self protection). Immediately, even by missing signs of diseases, using a steroid (Dosieraerosol) for inhaling (in spray form). Dosage, kind of use and further treatment according to medical prescription.
After swallow: Directly flush out the mouth. Drink water in small gulps.
First aiders:

PROPER DISPOSAL

10. References

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