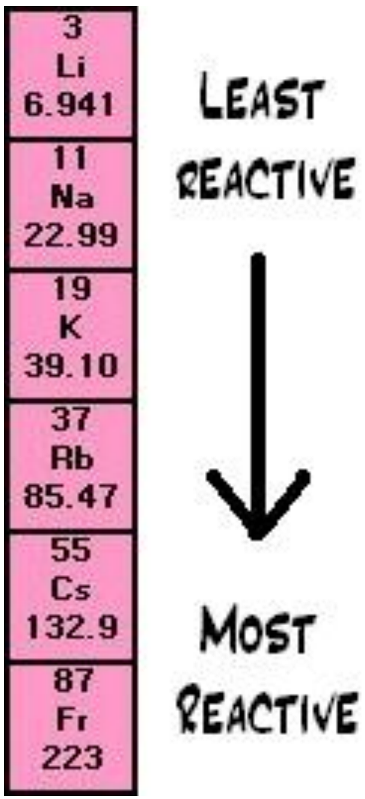
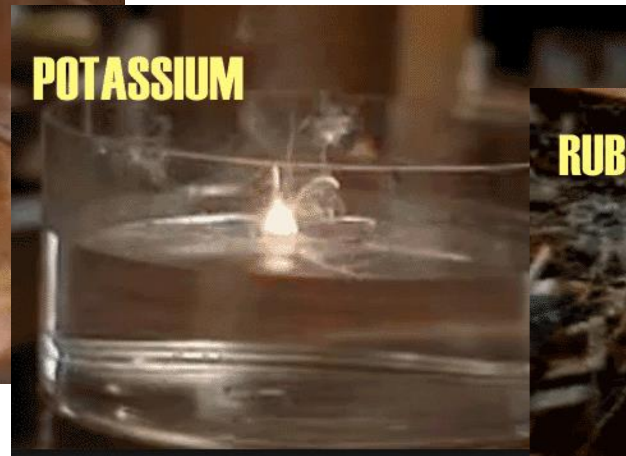
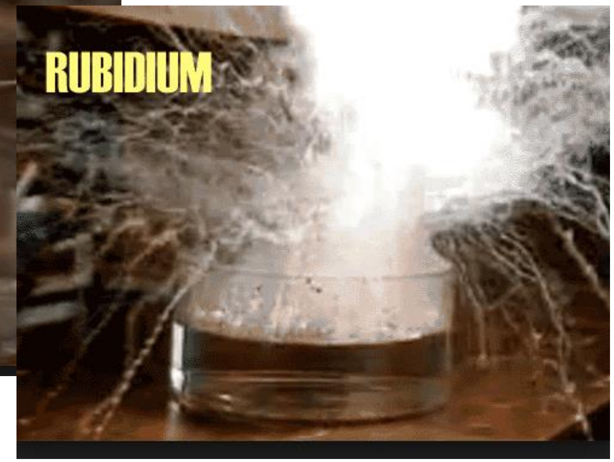
6. The Top Eight Causes of Accidents in Recent Years

Number 1: Accidents with alkali metals



Here you can see that the reactivity level and risks of alkali metals increases in this direction, with Lithium being the least reactive and Caesium having the strongest reaction.





As you can see here, the reactivity level of Caesium is much stronger than that of Lithium.

1.11.21, 11.30h: Approx. 900 mg Na residues remained in a Schlenk flask after reaction. A person wanted to quench these residues in the fume hood. After the person sprayed water into the flask, it exploded shortly afterwards in his hand, which was injured as a result. The explosion also caused a slight fire deflagration, which fortunately went out again immediately and did not spread to other chemicals/solvents. Later, the person testified that he had mistaken the water bottle for the isopropanol bottle. However, it is suspected that water was deliberately used because quenching with isopropanol is too time-consuming.

Fortunately, the person did not suffer any permanent damage to his health.
Not every risk of this kind ends so smoothly.

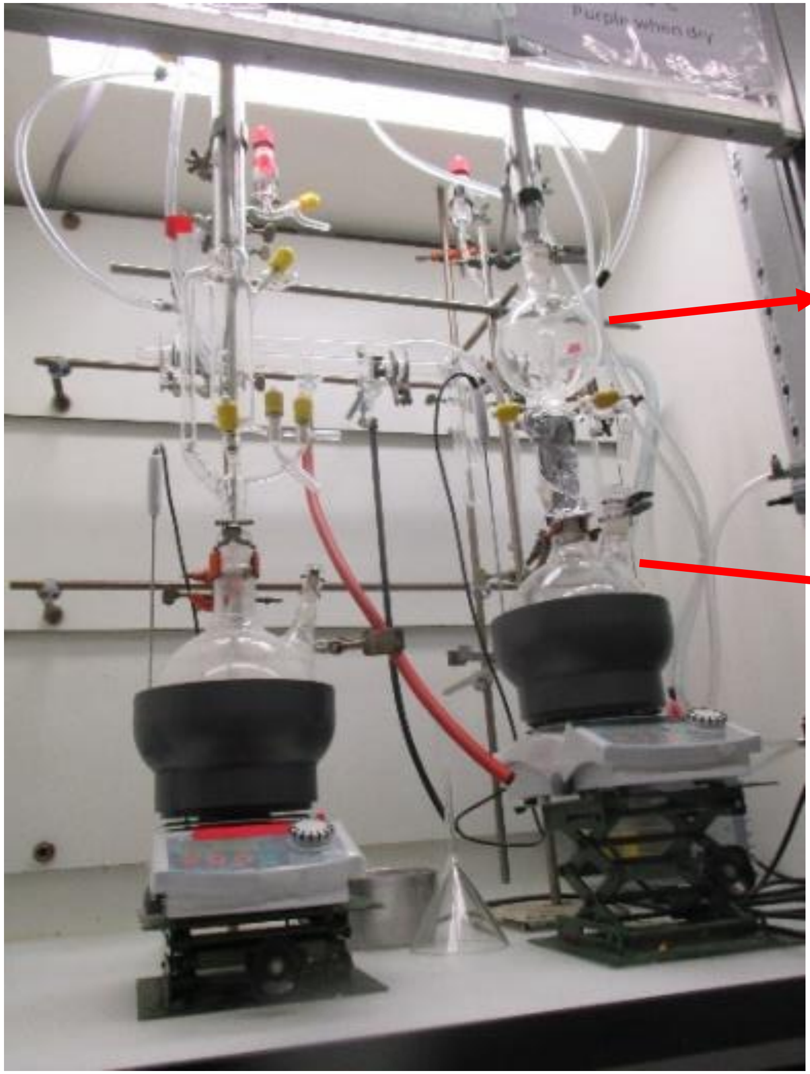
Quenching of sodium residues:

For proper quenching of Na residues, proceed as follows in an empty fume hood: Add toluene to the Na residues, e.g. in a Schlenk flask, under inert gas and stir well, with an ice bath underneath.

Then slowly add isopropanol with a pipette (never directly with the squirt bottle) and check the reaction for heat/bubble formation. This quenching is a slow process that can take several hours. After everything has reacted out, a small sample is drawn from the Schlenk flask. A few drops of water are added to the sample, and if a reaction is observed, further careful quenching with isopropanol is required. The reacted solution is collected as hazardous waste in a waste canister by the SSHE department and disposed of in this way.

19.11.19 ca. 15.15h: In a practicum laboratory a fire suddenly broke out in a fume hood.

Accident object: Distillation apparatus containing alkali metals. The aim of this distillation apparatus was to dry heptane with alkali metal.



reservoir vessel = distilled dry heptane

receiver flask containing alkali metals and heptane

The following concatenations led to the accident:

- The N_2 gas supply hose of a distillation apparatus containing alkali metals in a fume hood was damaged by a student.
- The pressure drop caused a over boiling in the distillation apparatus. The heptane with the alkali metal splashed inside the distillation apparatus up.
- The assistant decided to clean the distillation apparatus after this incident.
- The assistant instructed the student to clean the reservoir vessel, he took care of the receiver flask.
- The student tried to flush out the residue in the reservoir vessel with an acetone squirt bottle. It reacted with smoke formation.
- In another fume hood, where among other things hazardous waste was stored, the student rinsed the reservoir vessel with isopropanol. However, he could not satisfactorily clean the residues contained in the reservoir vessel.
- The student then attempted to rinse the residue with a methylene chloride spray bottle; at this point, deflagration occurred and the fire broke out.

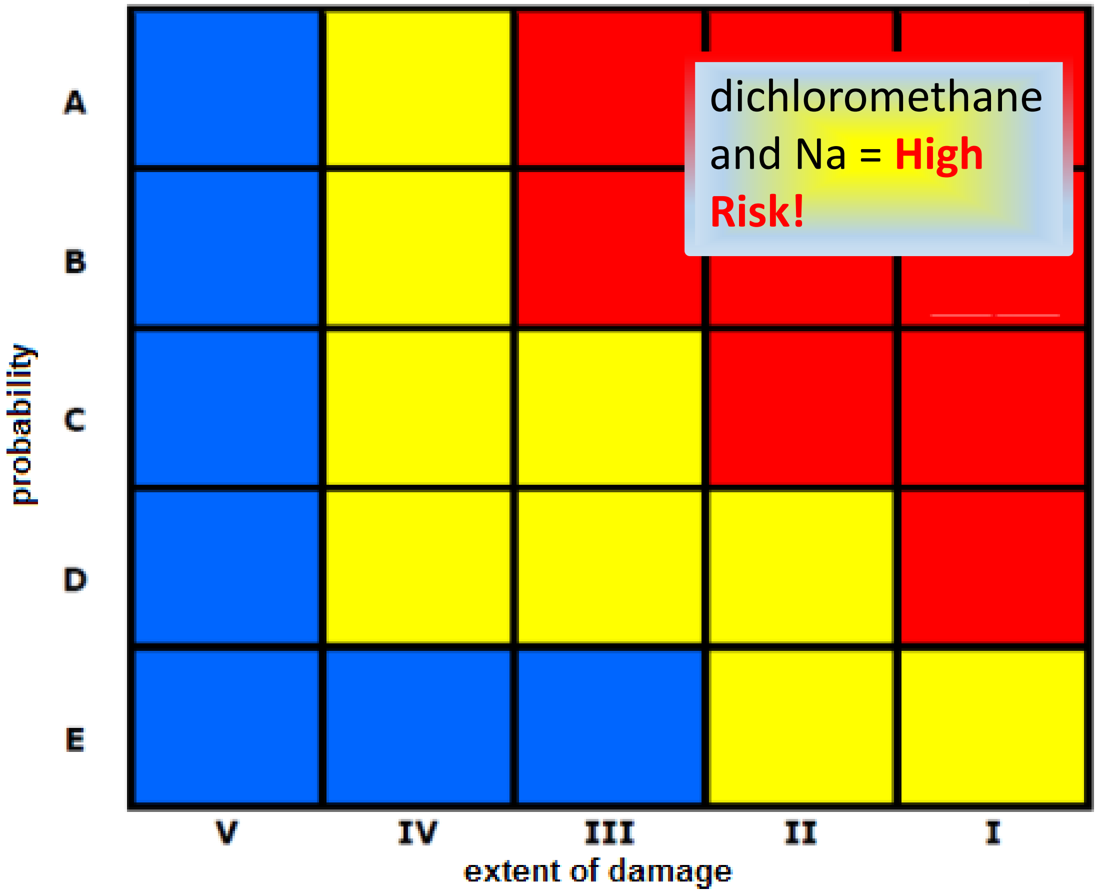
Safety Data Sheet Sodium Metal

→ Section 10 **Stability and Reactivity**

Possibility of dangerous reactions **Risk of explosion** with:

water, alcohols, aluminium halides, ammonium compounds, metal salts, boron compounds, bromine, azides, **halogenated hydrocarbons, organ. Halogenides, chlorine, chlorates, chloroform, hydrogen chloride gas, chromium(VI) oxide, dichloromethane**, ether, dimethylformamide, halogen oxides, ethanol, methanol, alkyl nitrates, nitrites, fluorine, halogens, hydrazines, hydrazine hydrate, hydroxylamine, iodine, halogen-halogen compounds, peroxides, activated carbon, carbon monoxide, copper compounds, Metal oxides, organic nitro compounds, heavy metal salts, perchlorates, phosphorus halides, phosphorus oxides, silicon compounds, silver compounds, selenium, sulphur dioxide, carbon disulphide, hydrogen sulphide, sulphur, acid chlorides, oxygen, hydrochloric acid, nitric acid, mercury compounds, mercury, nitrogen dioxide

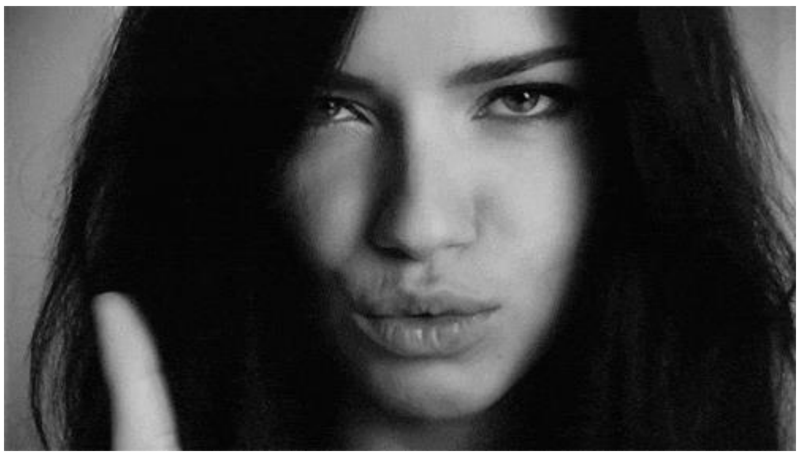
If the persons had taken note of the safety data sheet, they should have recognized immediately...



This is only one example of the many accidents that have occurred with alkali metals.

By the way…

Selfies! Never make and distribute selfies and videos of accident scenes via Social Media!



Mo, 19.1.15, HCI, 18.45h:

Accident description: Two people watched as 500g of rolled Lithium foils in a glove box with a water-free and oxygen-free nitrogen gas atmosphere self-heated and slowly began to melt. The Emergency Desk 888 called the fire brigade and evacuated the building. With the help of dry ice under the steel bottom of the glove box, the Lithium melt was cooled. The fire brigade subsequently removed the cooled solidified molten Lithium with argon gas and transported it out through the windows into the field behind the building.

The solidified molten Lithium in the open field did not react with the air or with direct contact with water. It lay for one week in a barrel in the field. Nevertheless, the molten Lithium carried a high risk! Only as we slowly poured hydrochloric acid into the barrel did the molten Lithium in the water begin to dissolve. With snow and ice, the temperature of the liquid in the barrel was "regulated” at 40 – 50°C. After adding 7L of concentrated hydrochloric acid, the liquid was still strongly basic. With the last half liter of hydrochloric acid, the liquid was acidified. The molten Llithium finally completely dissolved like an effervescent tablet after about 3 hours.

MSDS of Lithium

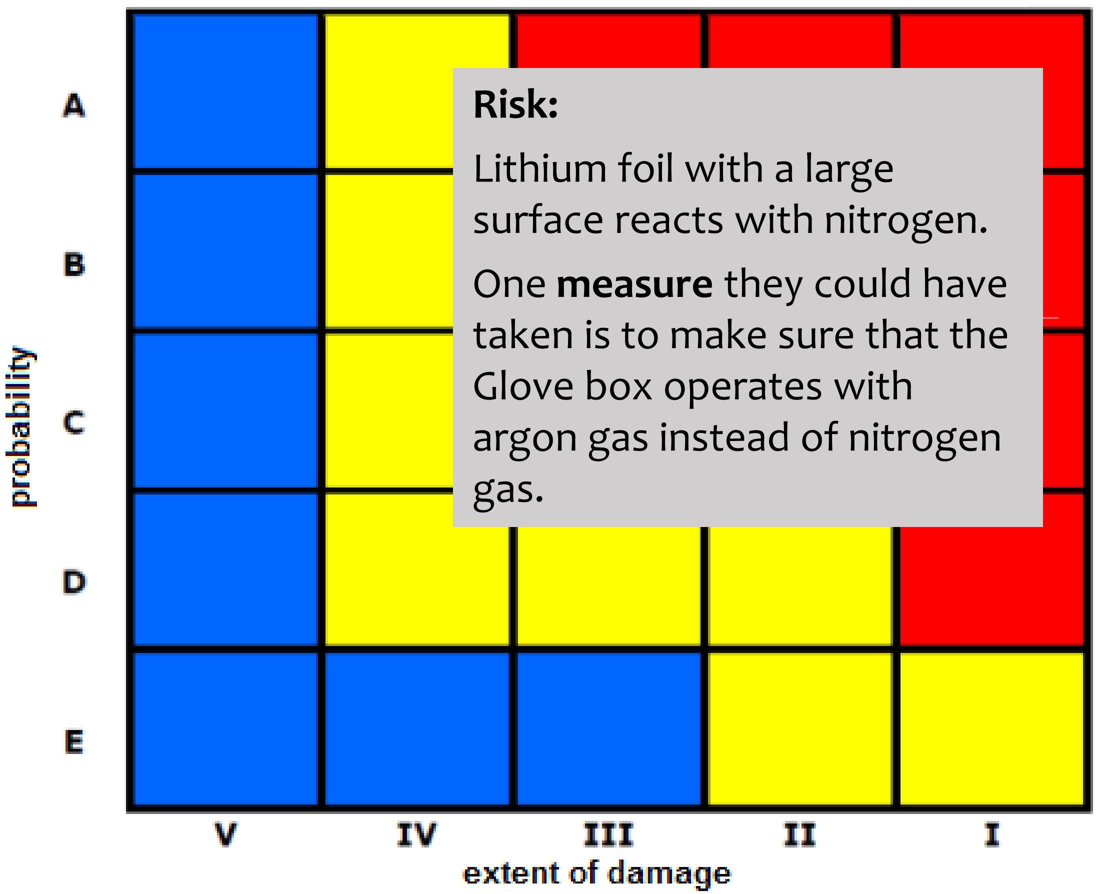
Laboratory personnel acted in accordance with the Material Safety Data Sheet (MSDS) for Lithium.

It is known that Lithium at room temperature reacts slowly with nitrogen (surface-dependent).
$6Li + N_2 \rightarrow Li_3N$

This is not mentioned in the MSDS. Thus, it is generally not unusual that Lithium is processed in glove boxes under oxygen- and water-free nitrogen gas atmospheres.

With an additional risk assessment to the MSDS, the accident could have been prevented.

If they had done a risk assessment before starting the experiment, they would have realized that Lithium foil with a large surface reacts with nitrogen.



Risk:

Lithium foil with a large surface reacts with nitrogen.

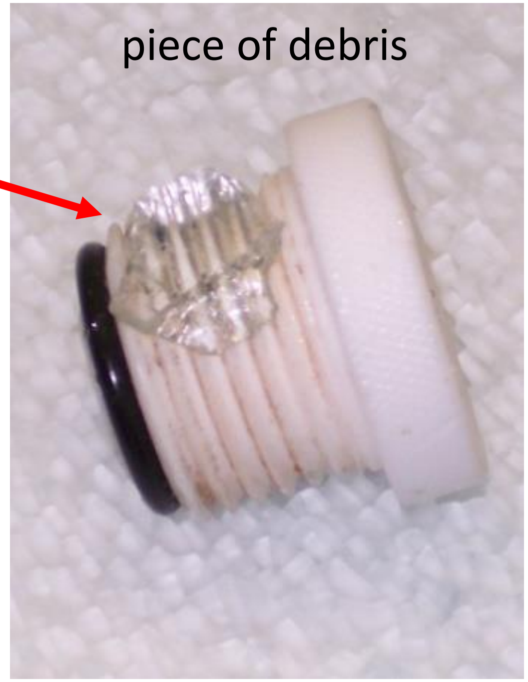
One **measure** they could have taken is to make sure that the Glove box operates with argon gas instead of nitrogen gas.

This is only one example of the many accidents that have occurred with alkali metals.

Number 2: Accidents With Overpressure

Accident description:

…when he heated the apparatus at 150°C, it suddenly exploded....



Manufacturer's information for this glass pressure vessel: *Art.-Nr. Z567248 Aldrich; Heavy-wall borosilicate glass flasks are pressure rated to* ***60 psi (****4.14 bar****)*** *at* ***120°C****.*

CAUTION: *This glassware is not guaranteed against breakage caused by pressure or vacuum. These flasks should never be used if scratched or otherwise damaged.*

The accident was caused by an overpressure explosion involving diisopropylamine. The boiling point of diisopropylamine is 83 - 84°C. In a closed glass vessel we calculated a theoretical pressure of **4.48 bar**.

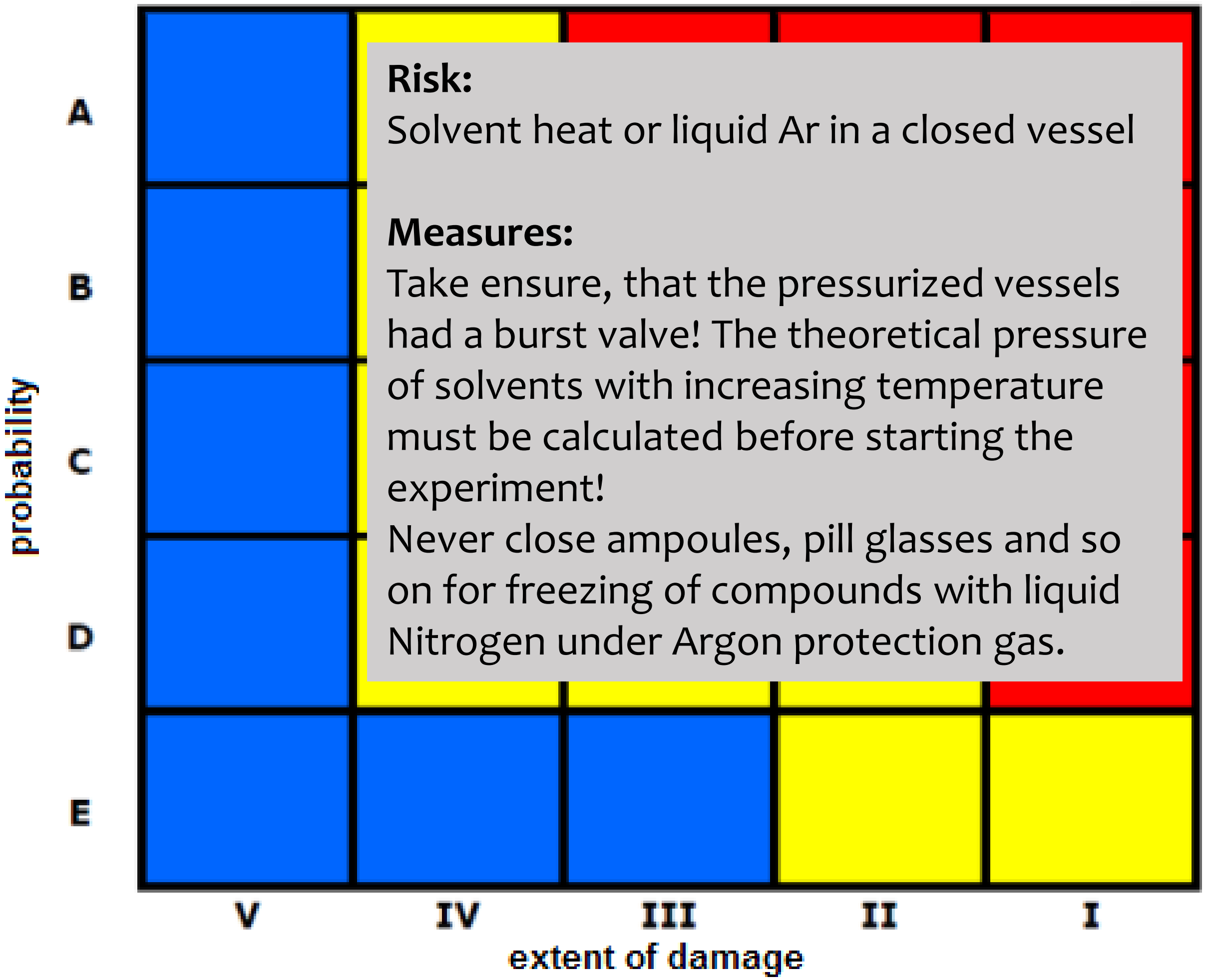
As you can see in the Manufacturer`s information, these glass vessels are only made to withstand a maximum pressure of 4.14 bar. Anything higher than this can cause an explosion.

And this is exactly what happened.

Here is another example of an overpressure accident which often happens in the HCI. A student flushed the solution in the flask with argon and cooled it in liquid nitrogen at the same time. As he closed the tap, there was a short delay followed by an overpressure explosion.

Boiling point liquid Nitrogen: -195.8°C;
Argon turns to liquid at -185.7°C and freezes at -189.2°C

If a risk assessment had been done, they would have realized, that there is a overpressure risk of solvent heat in a closed vessel, that Argon condensate when cooled with liquid nitrogen.



Risk:
Solvent heat or liquid Ar in a closed vessel

Measures:
Take ensure, that the pressurized vessels had a burst valve! The theoretical pressure of solvents with increasing temperature must be calculated before starting the experiment!
Never close ampoules, pill glasses and so on for freezing of compounds with liquid Nitrogen under Argon protection gas.

Number 3: Over Boiling

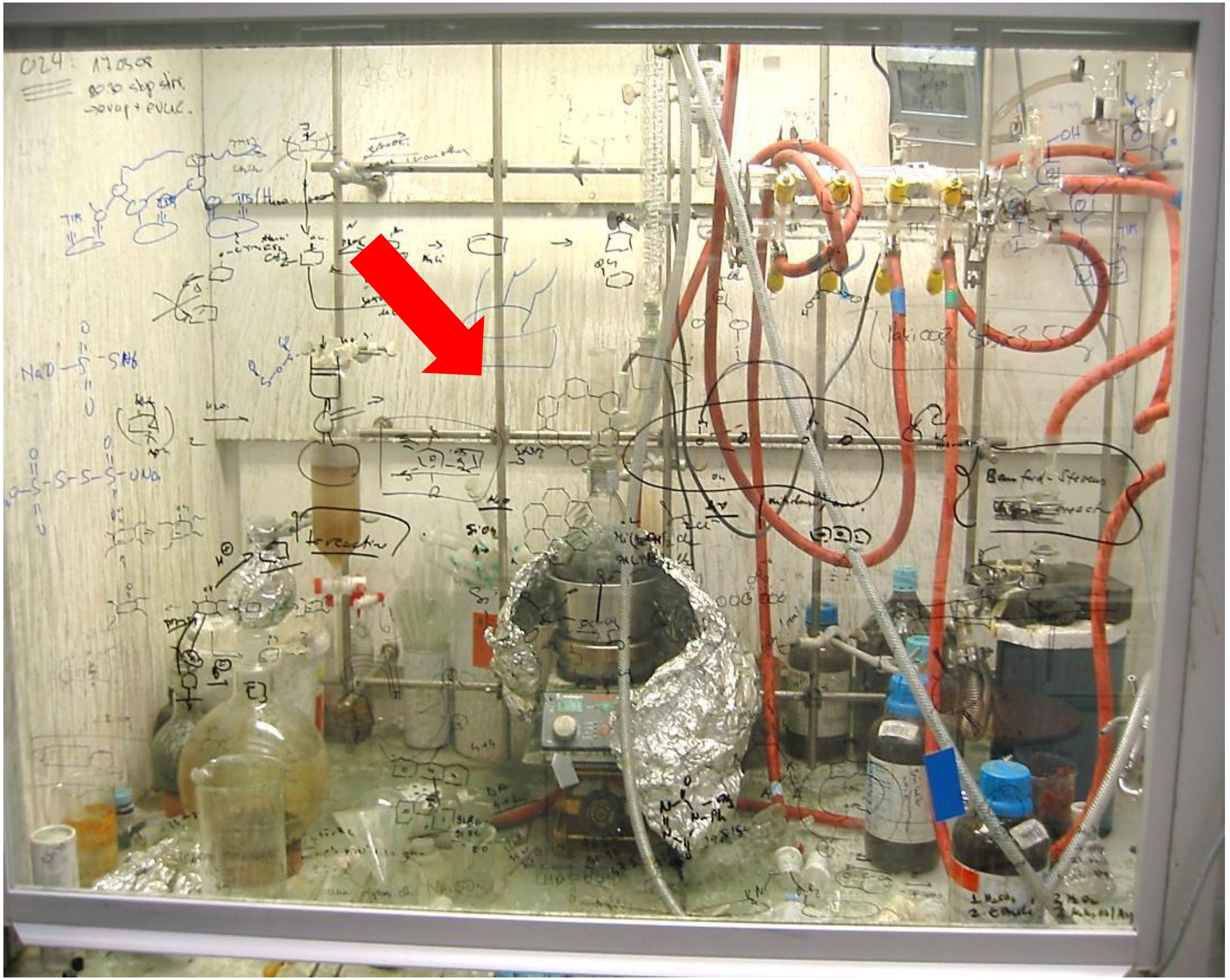
Accident description:

As a student was leaving for her lunch break, smoke and gas started coming out of the flask. She decided to take the flask out of the heating bath and the contents shot out like a fountain.

Her arms and face were burned by the acid.

Another accident description:

..a Student was working and just as he opened the apparatus for adding zinc powder, it started over-boiling and the contents suddenly splashed into his face.



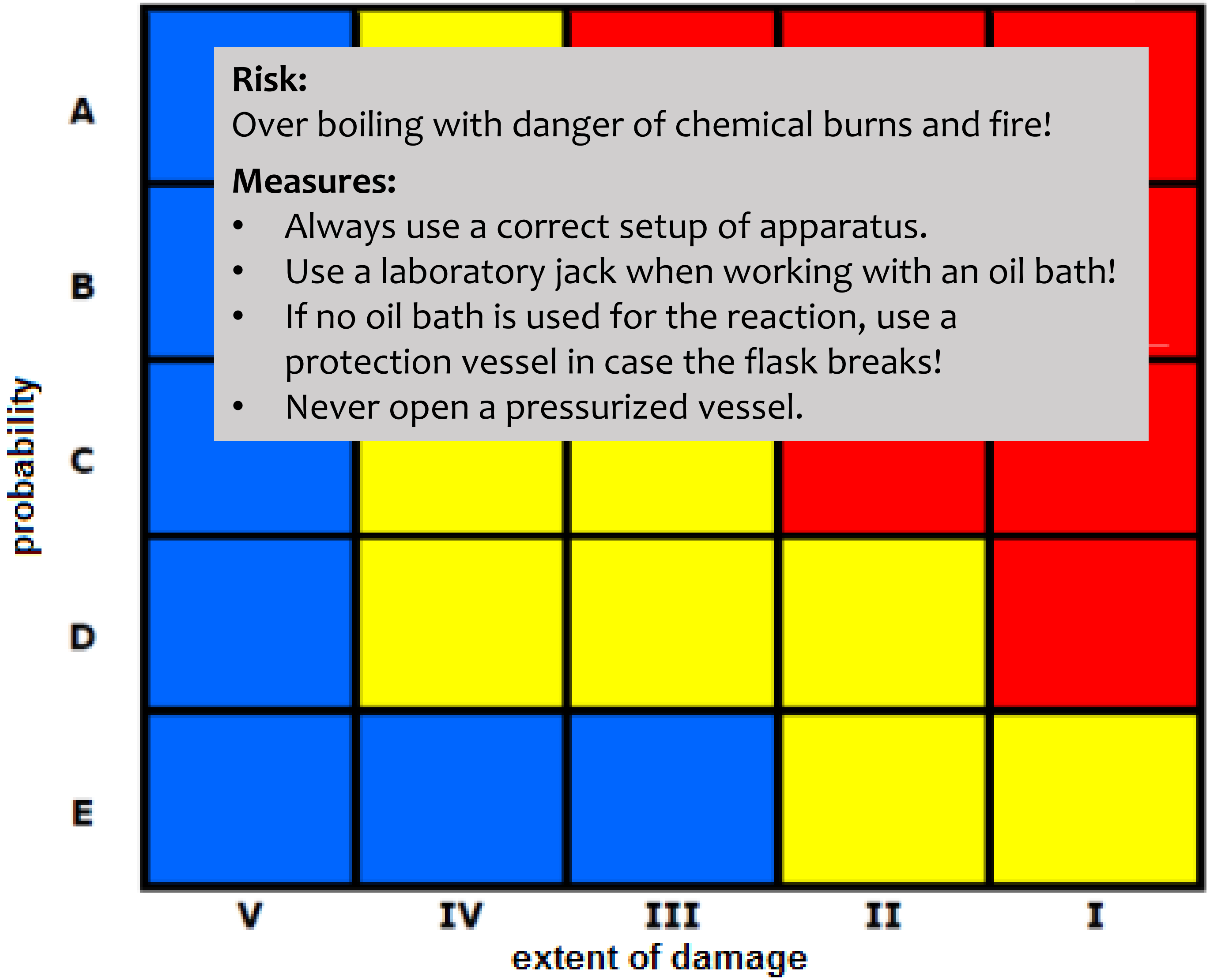
Here we have an overview of the correct way to set up your apparatus, in order to minimize the risk of solvents or acids splashing into your face or on your skin.

WRONG !
Never move a HOT oil bath manually! This can cause severe burns.

CORRECT !
Always use a laboratory jack when working with an oil bath!

CORRECT !
If no oil bath is used for the reaction, use a protection vessel in case the flask breaks!

The obvious risk in this situation is over boiling.

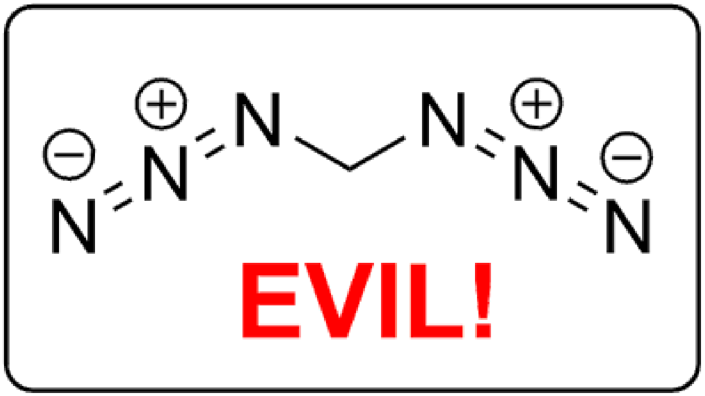


Risk:
Over boiling with danger of chemical burns and fire!

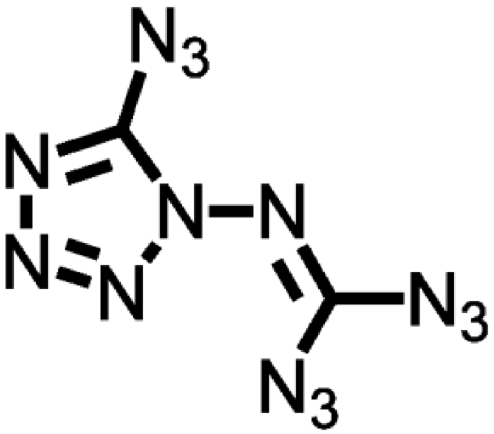
Measures:
- Always use a correct setup of apparatus.
- Use a laboratory jack when working with an oil bath!
- If no oil bath is used for the reaction, use a protection vessel in case the flask breaks!
- Never open a pressurized vessel.

Number 4: Working with azides

Organic azides are potentially-explosive substances that can and will decompose with the slightest input of energy from external sources (heat, light, pressure). Additionally, small molecules containing the azido functionality tend to decompose violently which may result in injury if proper safety precautions are not utilized.



One of the worst azides is **Azidoazide Azide**



- C: 2x
- N: 14x
- O: 0

Unstable!!!

Azidoazide will explode by:

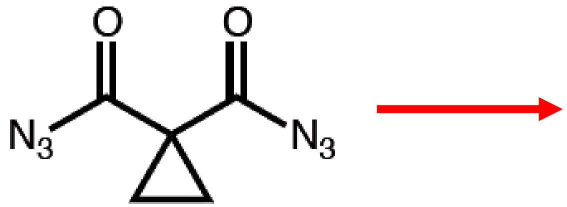
- Touching it
- Dispersing it in solution
- Leaving it undisturbed on a glass plate
- Exposing it to bright light
- and so on

When designing your target azide, keep in mind the following equation. Notice that this equation takes into account all nitrogen atoms in your azide, not just those in the azido group.

$$\frac{N_C + N_O}{N_N} \geq 3$$ = Safe organic azides

N signifies the number of atoms.

Example Acylazid



$$\frac{5\mathrm{C} + 2\mathrm{O}}{6\mathrm{N}} \approx 1$$

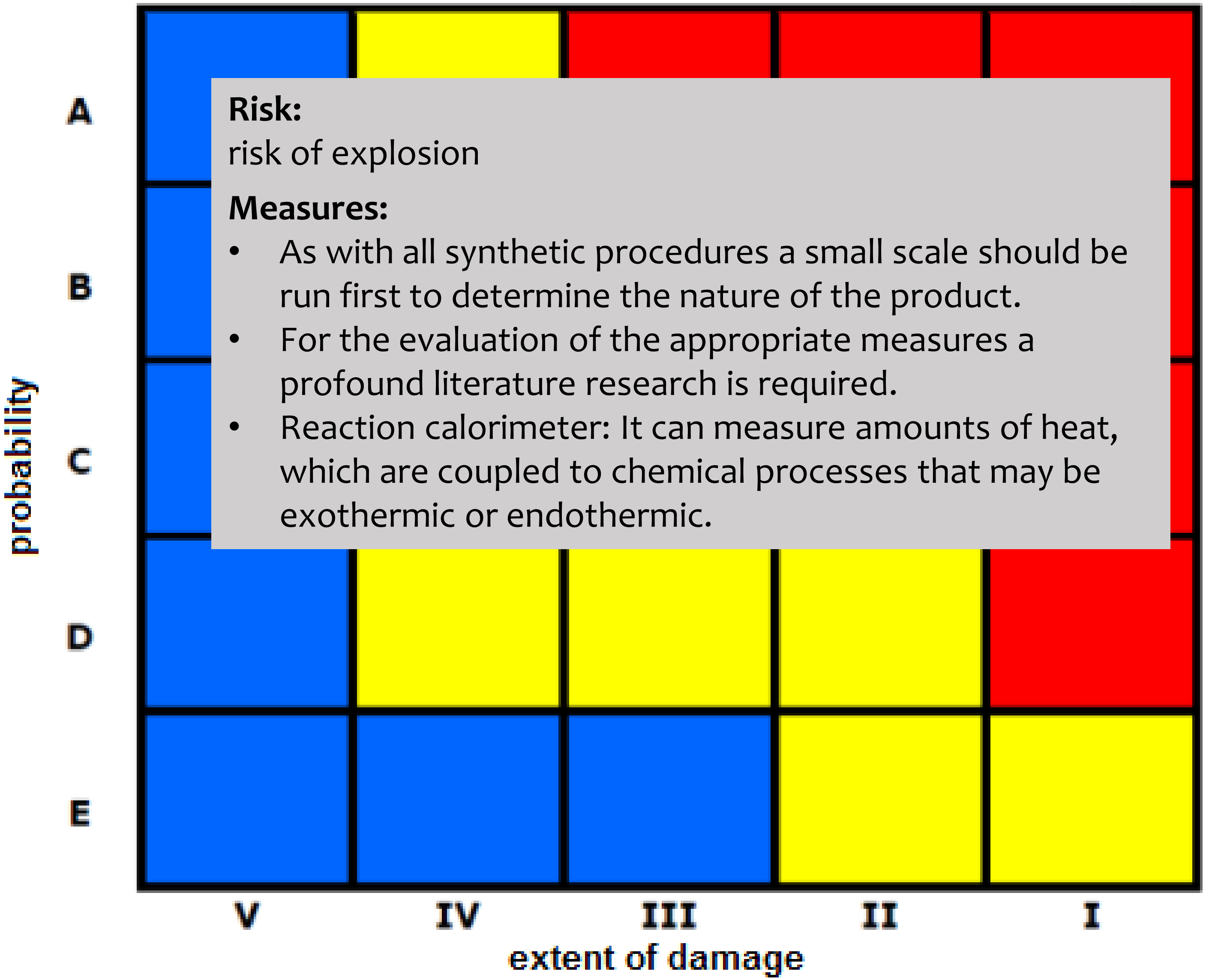
Unstable!

As with all synthetic procedures a small scale (ca. ca. 0.1 – 0.5 gram) should be run first to determine the nature of the product.

Accident description:

A student was attempting **to solve a dried acyl azide** compound in a flask in his fume hood with a solvent filled Pipette when the flask suddenly exploded.

A risk assessment for this situation would look like this:

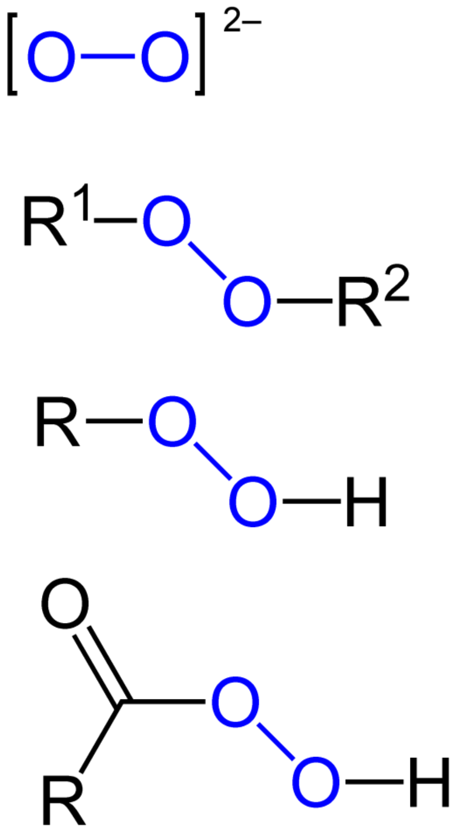


Risk:
risk of explosion

Measures:

- As with all synthetic procedures a small scale should be run first to determine the nature of the product.
- For the evaluation of the appropriate measures a profound literature research is required.
- Reaction calorimeter: It can measure amounts of heat, which are coupled to chemical processes that may be exothermic or endothermic.

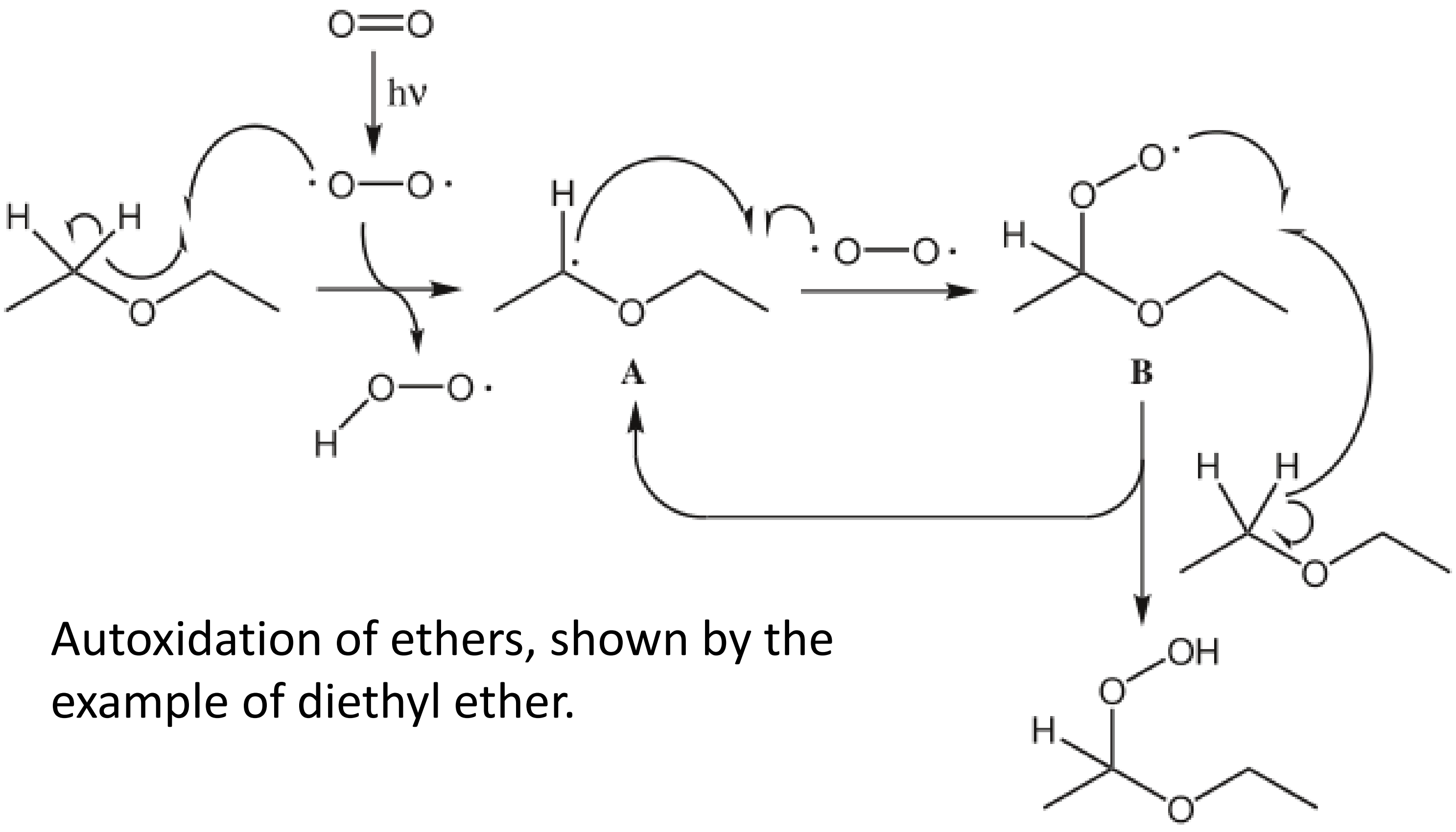
In this context, remember:



Peroxides are labile compounds and can in particularly high concentrations and at elevated temperature show explosive behavior.

Small amounts of peroxides which may arise in storage or reaction vessels can be destroyed with the addition of reducing agents such as iron(II)sulfate.

During storing of ethers, light and atmospheric oxygen can form peroxides. This can for example after a distillation of the ether in the residue accumulate peroxides and explode.

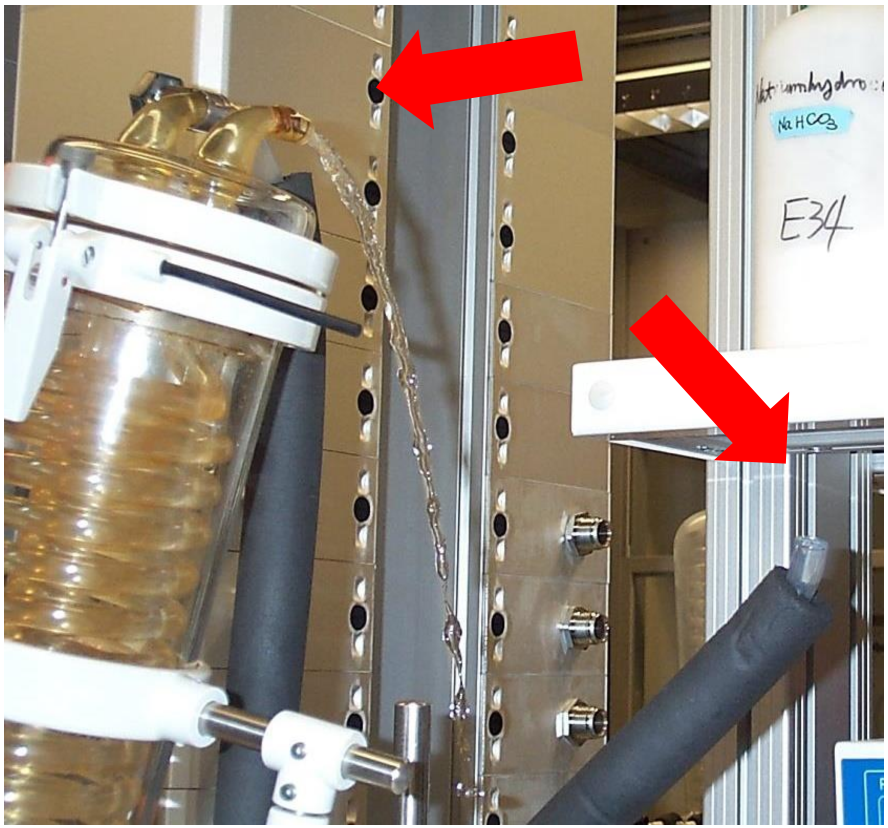


Autoxidation of ethers, shown by the example of diethyl ether.

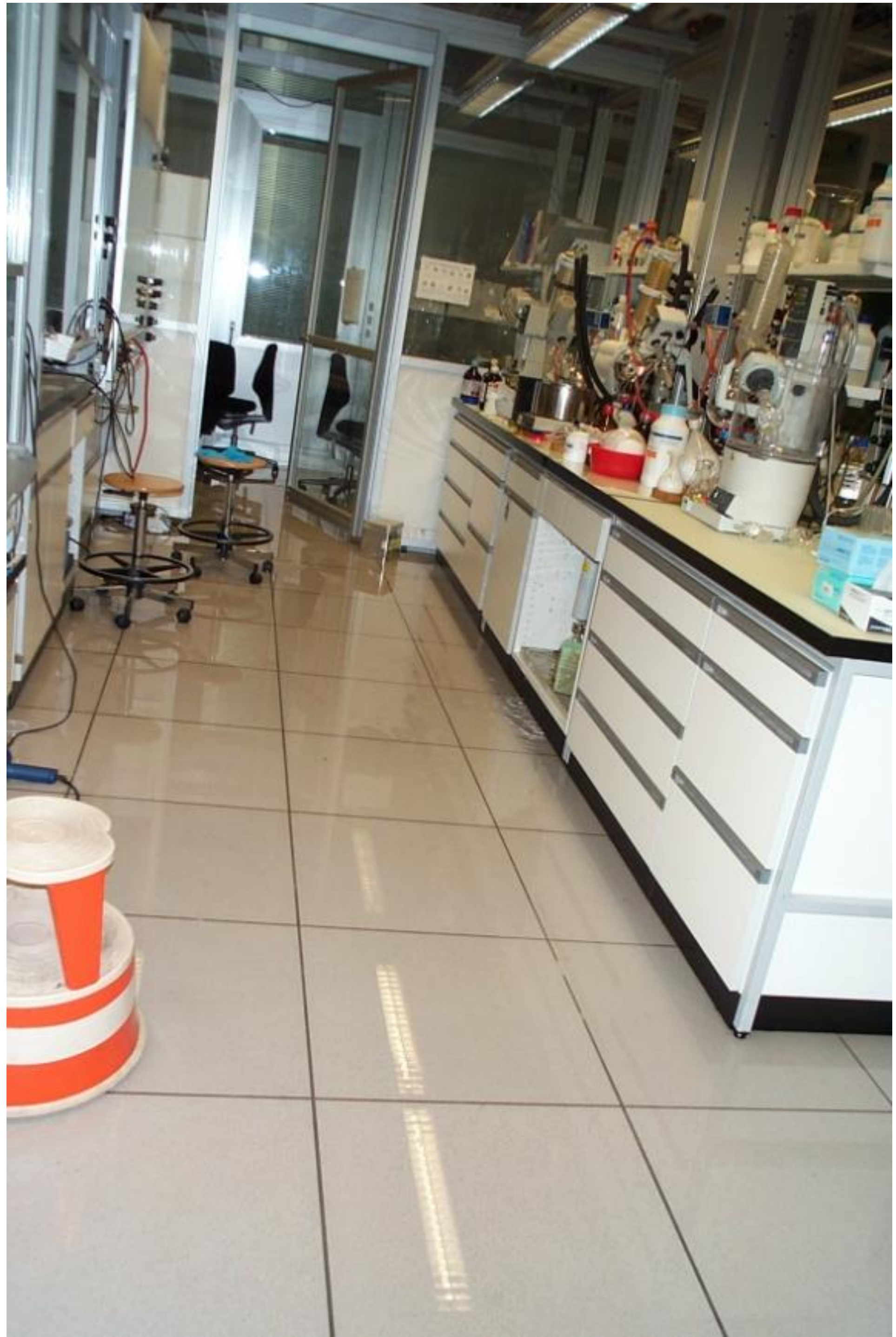
Number 5: Property damage due to water outbreak

Accident description:

The main causes of flooding are coolant hoses that are not secured with clamps. Here you can see the source of the water outbreak....

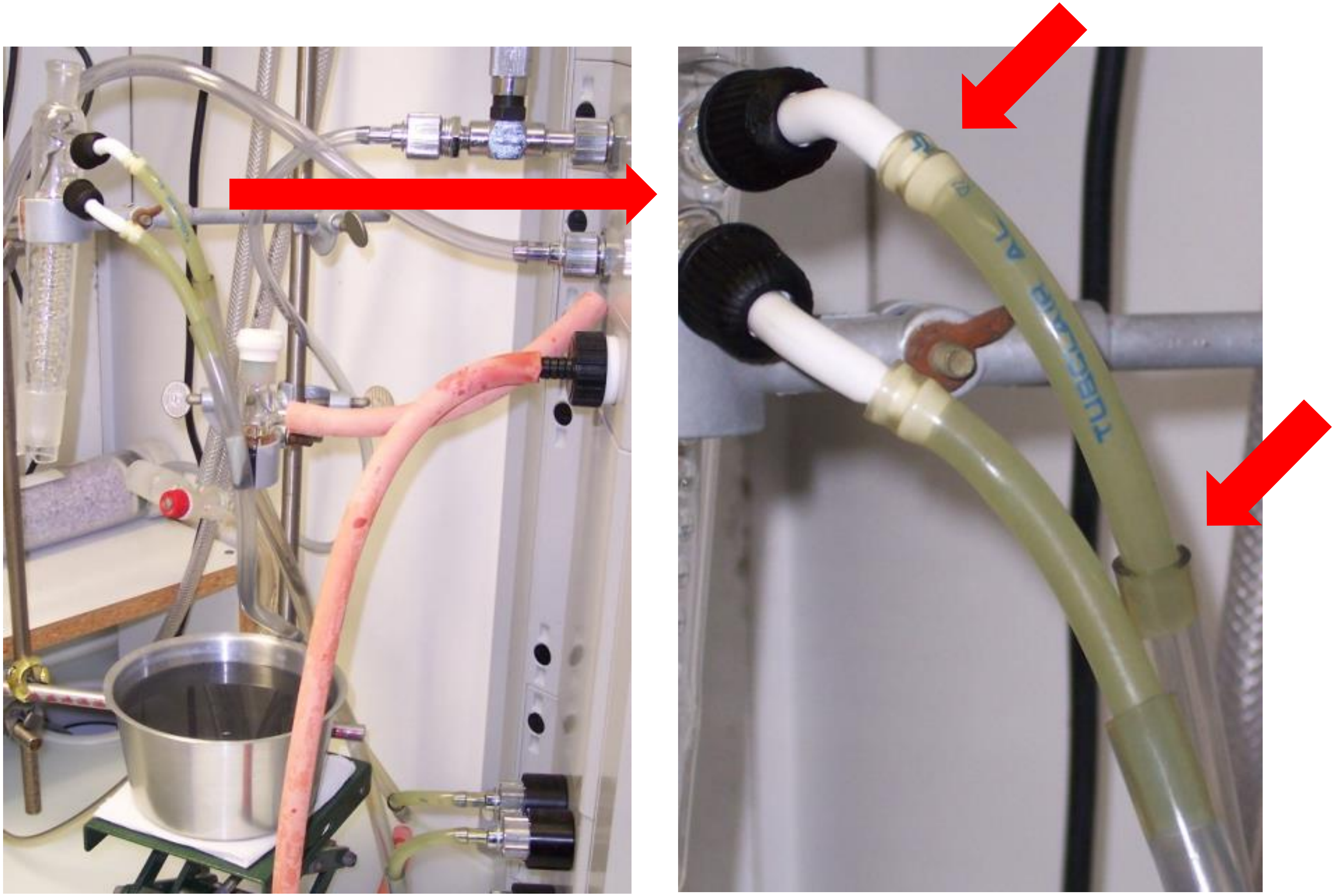


Flooding continues in the laboratory on the lower floors…



…and ends here on the bottom floor.

Here you can see some pictures of how users install cooling water hoses.



6.11.4. Correct tubing for cooling water modules

Allowed	Allowed	Allowed	Forbidden	Forbidden
PVC-tubes	PVC-tubes with mesh	Polyurethane tubes	Silicone tubes	Vacuum or natural rubber tubes
				

Issues of silicone tubes in the cooling water system: The controversial soft silicone tubes are often used for cooling water systems. They are more prone to material fatigue and damage compared to PVC tubes. Also, the sharp edges of the metal hose clips can damage/cut the soft silicone tubes which might cause the tube to suddenly rupture at that point.

6.11.5. Media connectors for cooling water modules

Metal adapters:

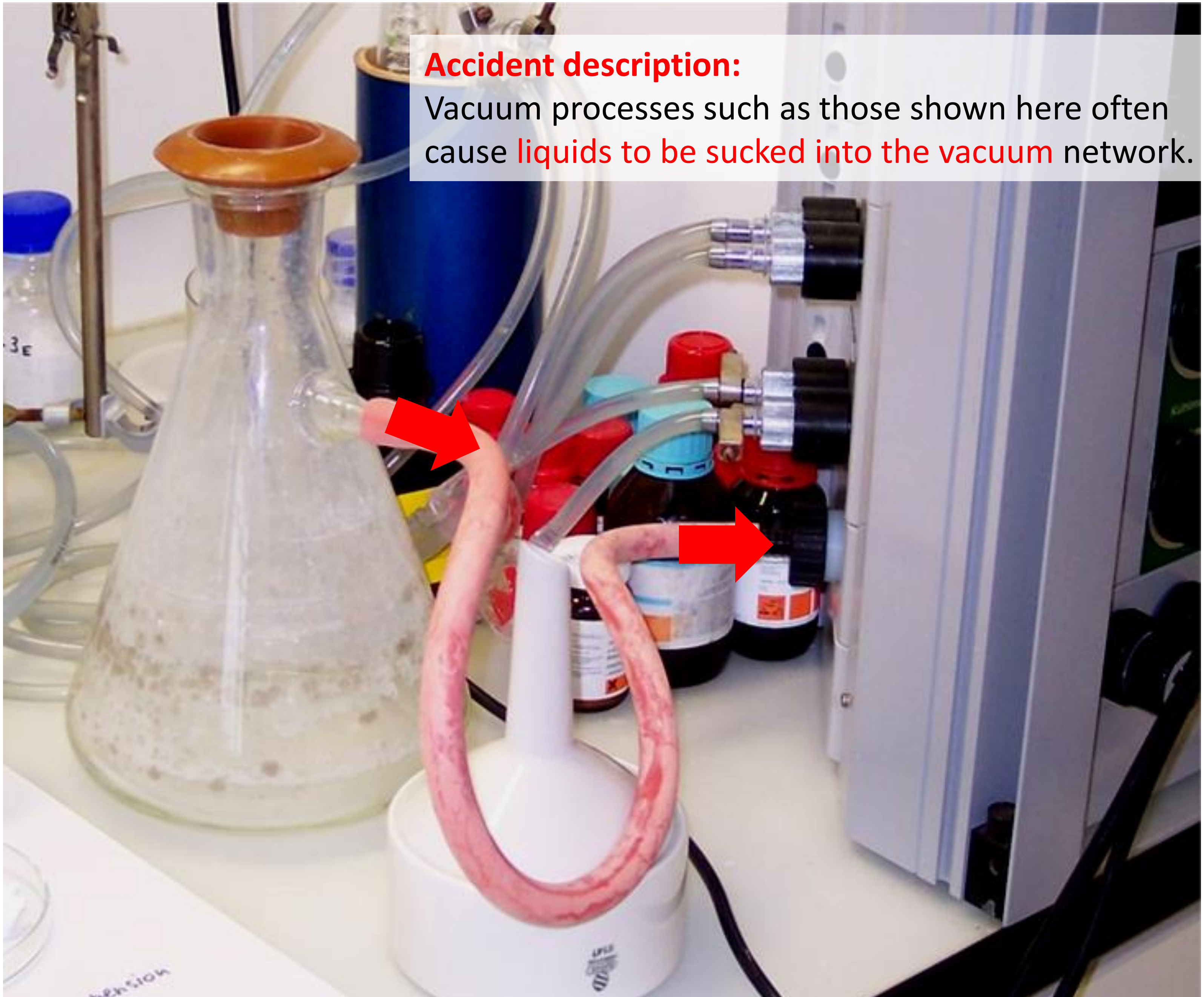
On these, check the O-ring seals on the metal piece regularly and replace them if necessary. The entire sealing depends on these O-rings (see right-hand figure). Adapters with broken O-rings can be brought to the HCI-Shop for repair.

Note: The tension ring keeps the union nut on the metal adapters from falling off. Because of this, you cannot remove it or, as shown on the right, push it back to check the O-ring. The easiest way of checking the O-ring is to shine a torch on the end of the stamp where the O-ring is placed.

Number 6: Property damage due to vacuum

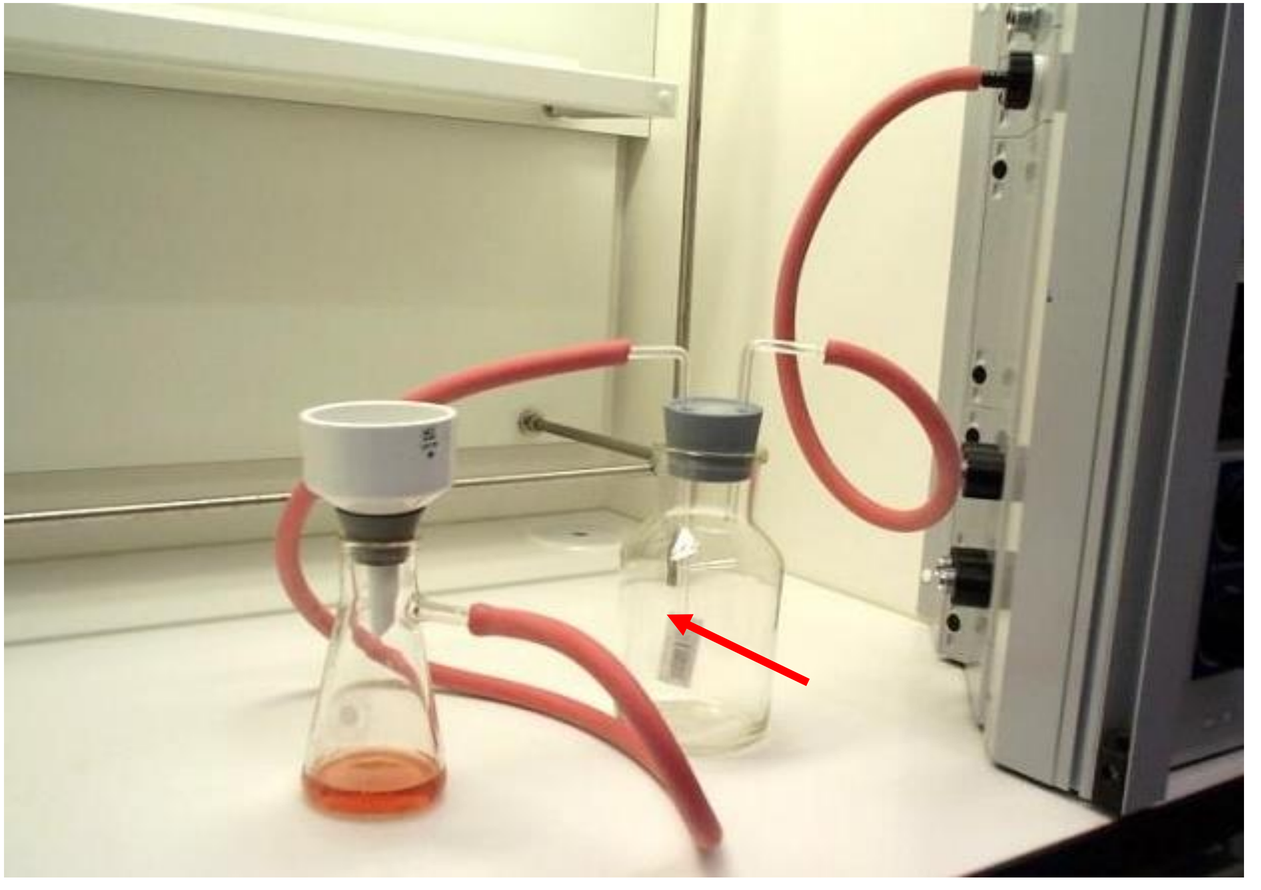
Accident description:

Vacuum processes such as those shown here often cause liquids to be sucked into the vacuum network.



This is the result of sucked liquid. No comment!

It is absolutely forbidden to suck up liquids (even in small amounts) with a vacuum network! A liquid trap must always be between the vacuum using the system and the vacuum module.

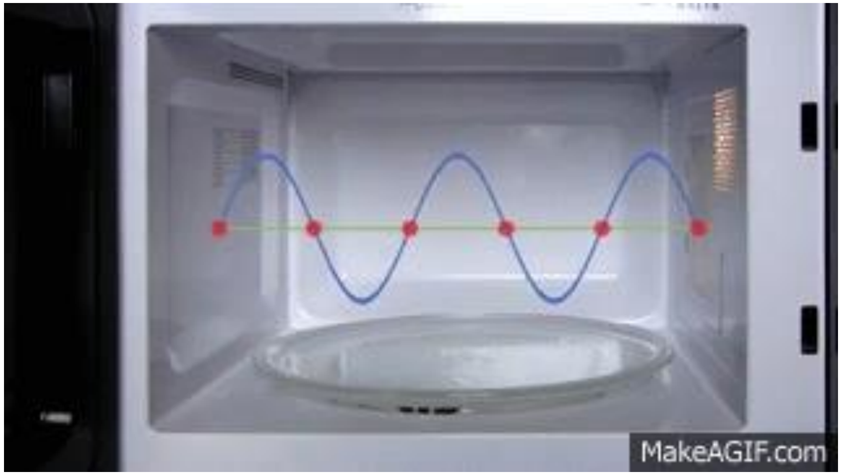


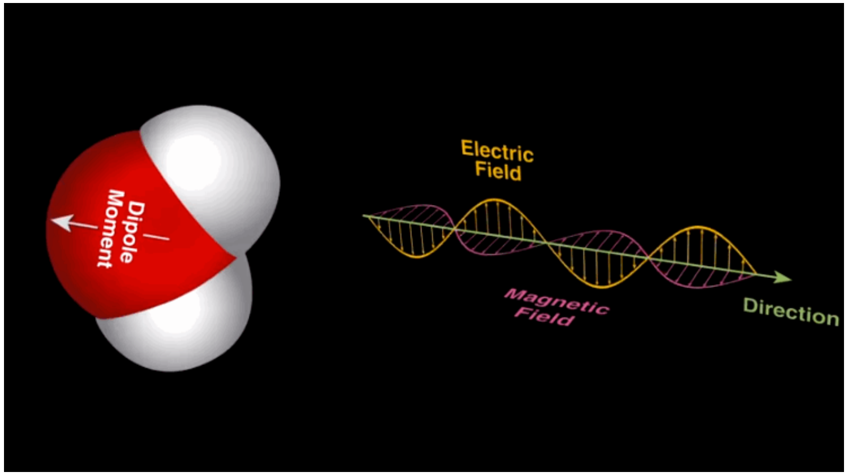
In cases where liquids are accidentally pumped into the vacuum network, notify the safety officer or the assistant immediately.

Number 7: Microwaves

Accident description: When a student returned to the lab after his break, this had happened and the fire brigade was waiting for him. The cause of the accident was poor judgment of the thermal characteristics of the microwave.

Microwaves are a form of electromagnetic radiation with wavelengths ranging from as long as one meter to as short as one millimeter; with frequencies between 300 MHz (0.3 GHz) and 300 GHz.



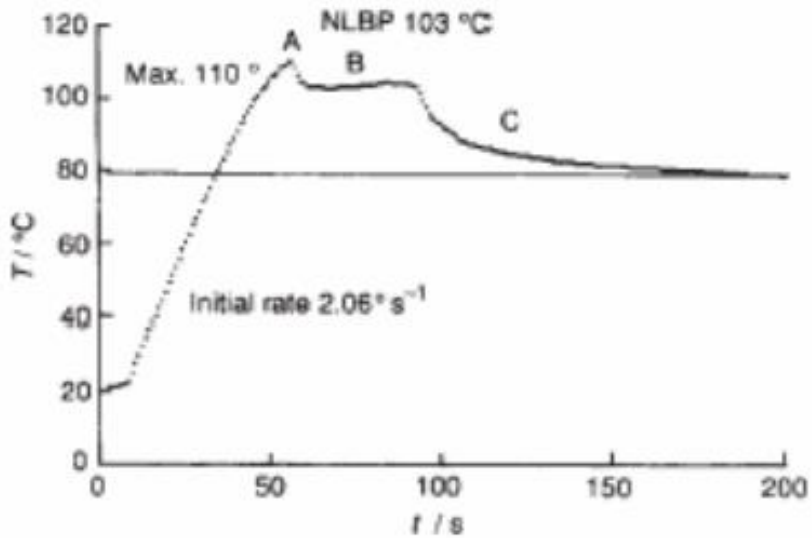


Absorption leads to increased polarization of dipolar molecules. Nonpolar molecules show no absorption.

Field oscillation → rotation of the molecules → heat generation

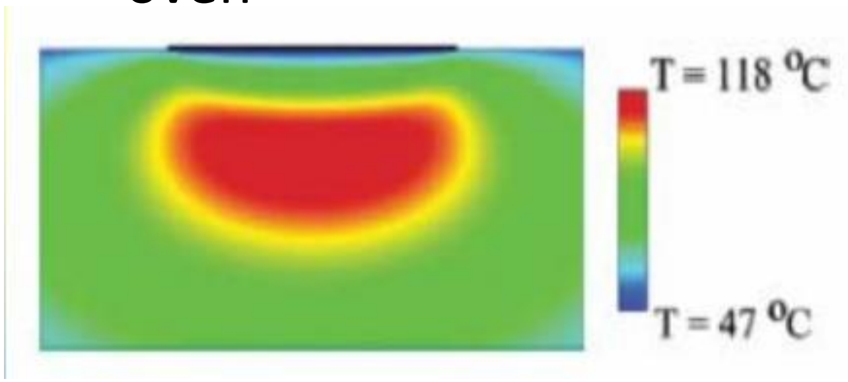
Some examples of microwave effects include:

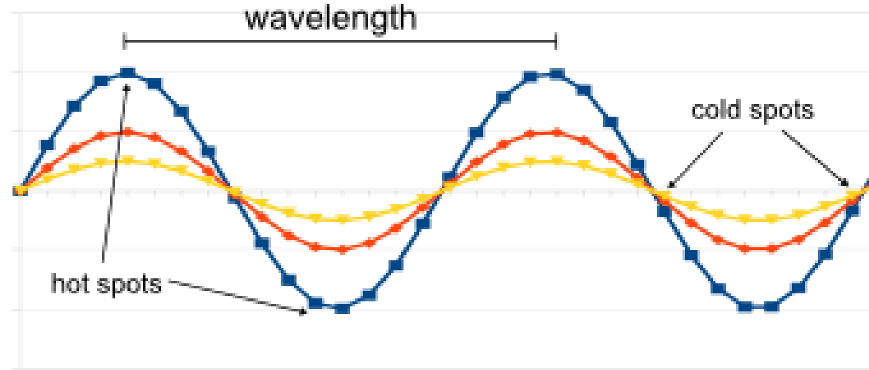
– **Overheating** of solvents e.g. ethanol



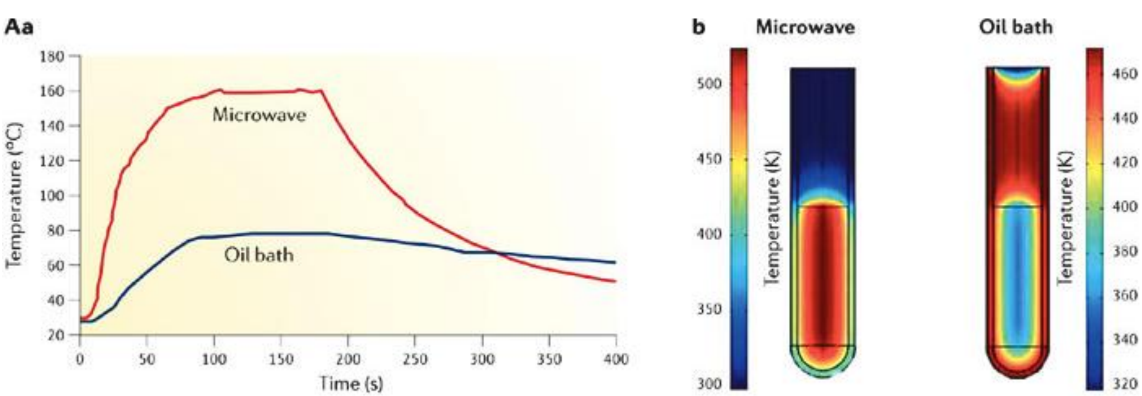
– **Selective heating** of strong microwave absorbing materials, like solvents, catalysts and susceptors. A **susceptor** is a material used for its ability to absorb electromagnetic energy and convert it to heat.

- **Hot spots** in Microwave oven





- **Inverse temperature gradient**



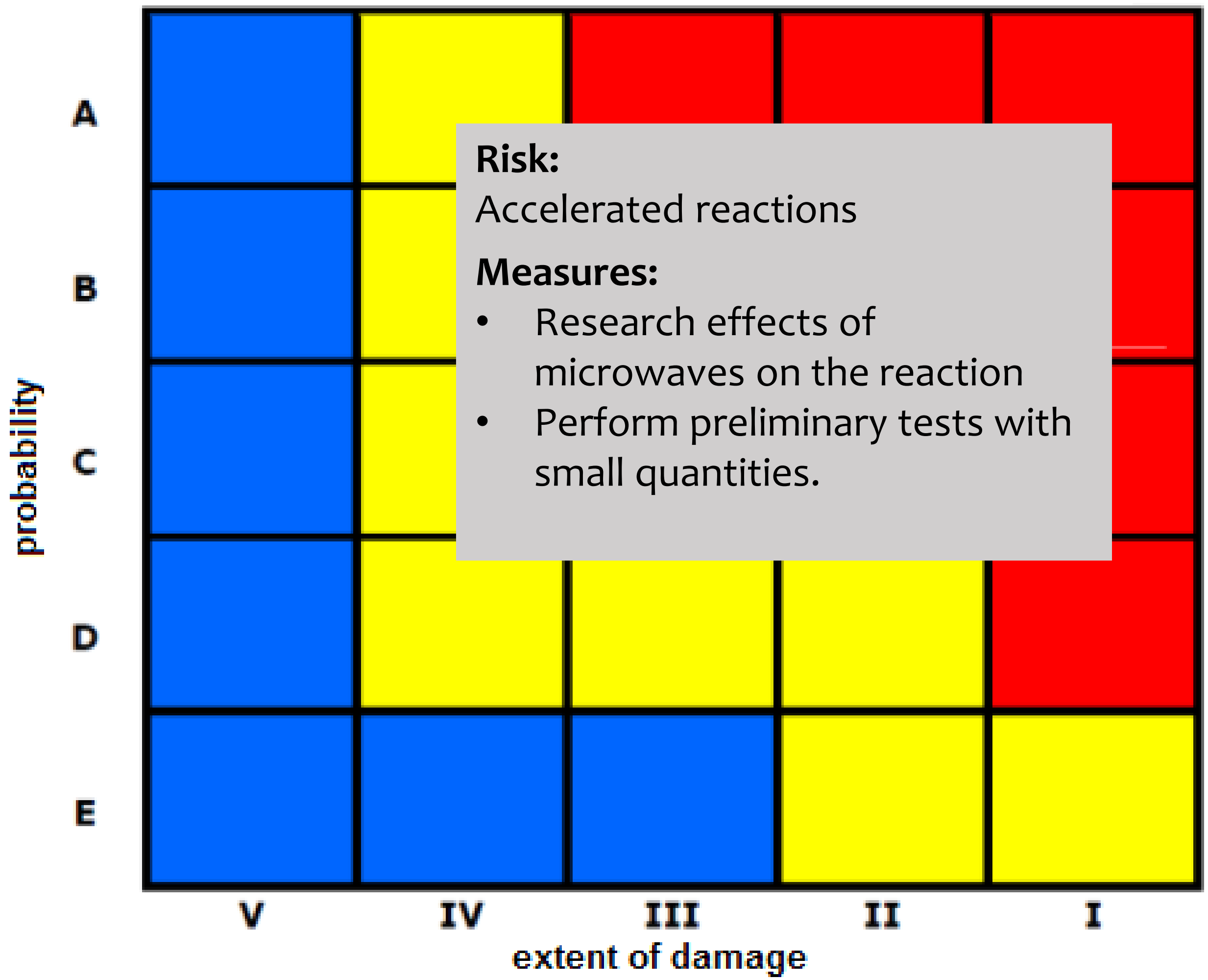
In a normal oven the heat comes from outside, but in a microwave the heat builds on the inside and travels outwards.

Here is a approximate comparison between a conventional oil bath and a microwave. Here you can see that the reaction mechanism is much faster and different as of a conventional oil bath.

Oil bath vs. Microwave

Conventional		Microwave
Solvent: Ethanol		Solvent: Acetic Acid + Ethanol
Heating for several hours under reflux	↔	**10 min**
ca. 80°C		120°C

To bring your risk level down, you must take the following measures.



Risk:
Accelerated reactions

Measures:
- Research effects of microwaves on the reaction
- Perform preliminary tests with small quantities.

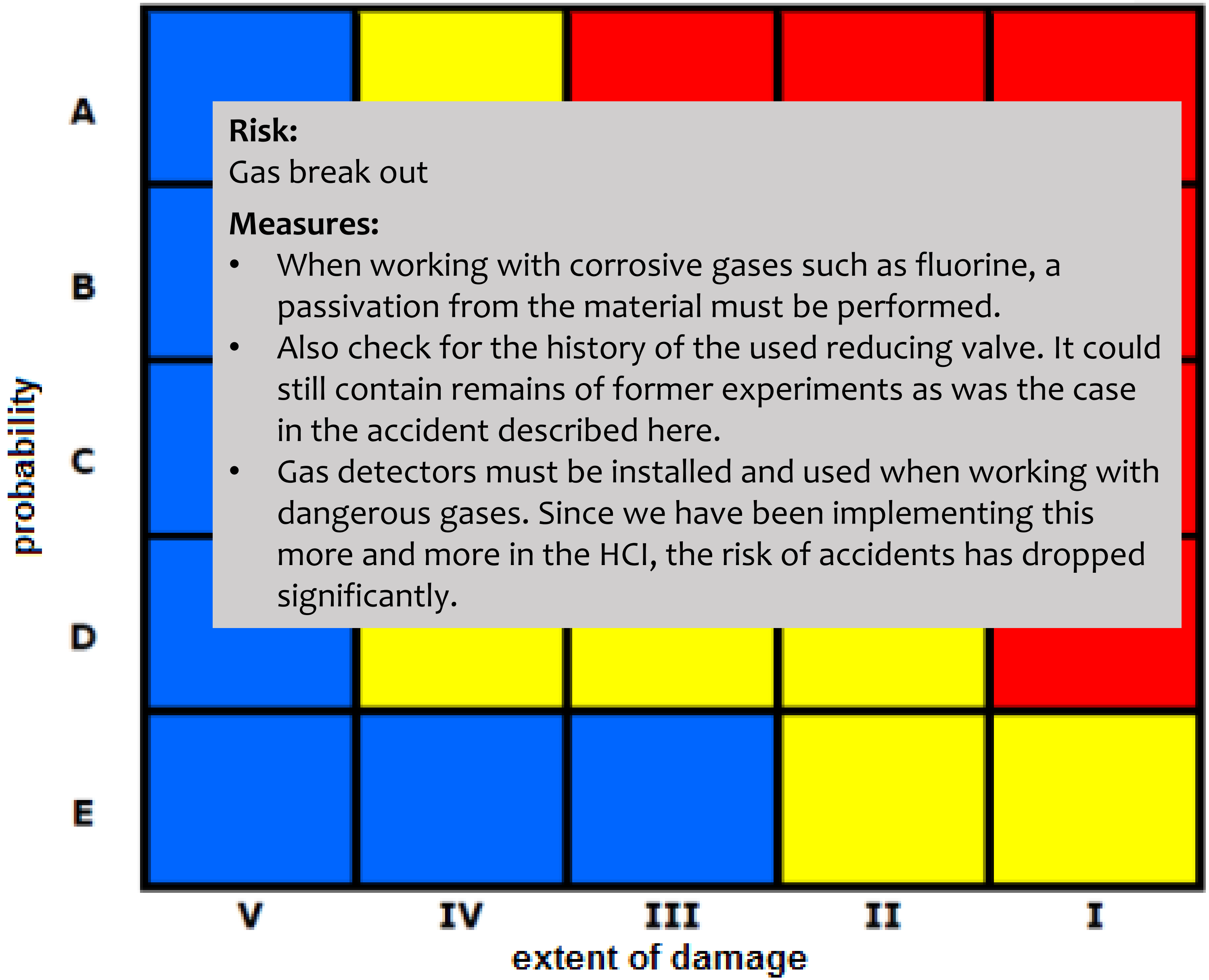
Number 8: Gas breakout

Accident description: A student was working with fluorine gas, when suddenly the reducing valve attached to a 10 L fluorine gas bottle began to glow. This broke and fluorine gas streamed out. The laboratory was immediately evacuated. Through the porthole we watched as the gas bottle burned like a sparkler. Despite the fact that the wrecked fume hood had to be disposed of, it was fortunately able to fully contain the incident.

Elemental fluorine is highly toxic to living organisms. Its effects in humans start at concentrations lower than hydrogen cyanide's 50 ppm and are similar to those of chlorine.

Due to its high reactivity, fluorine must be stored in special containers. The materials shall be so arranged as to form by contact with fluorine, a passivation layer, thus preventing further reaction.

To bring your risk level down in this situation, the following measures must be taken.

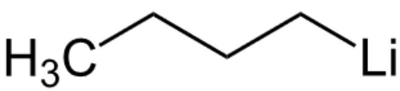


Risk:
Gas break out

Measures:

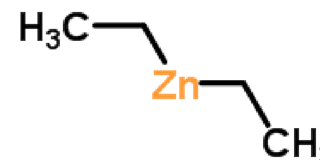
- When working with corrosive gases such as fluorine, a passivation from the material must be performed.
- Also check for the history of the used reducing valve. It could still contain remains of former experiments as was the case in the accident described here.
- Gas detectors must be installed and used when working with dangerous gases. Since we have been implementing this more and more in the HCI, the risk of accidents has dropped significantly.

These were the top eight of the accidents in HCI. But there are many other hazards that can cause accidents…..



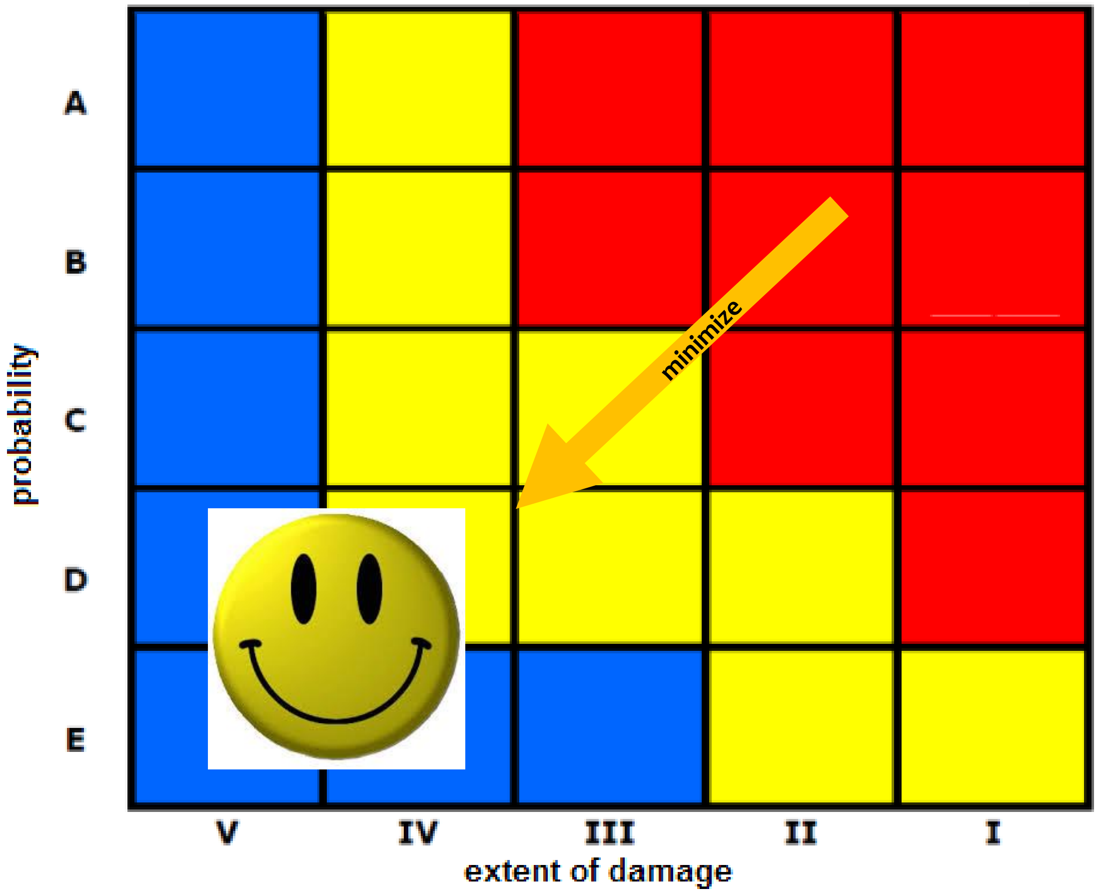
***n*-Butyllithium** (abbreviated ***n*-BuLi**)

Potassium permanganate and glycerin



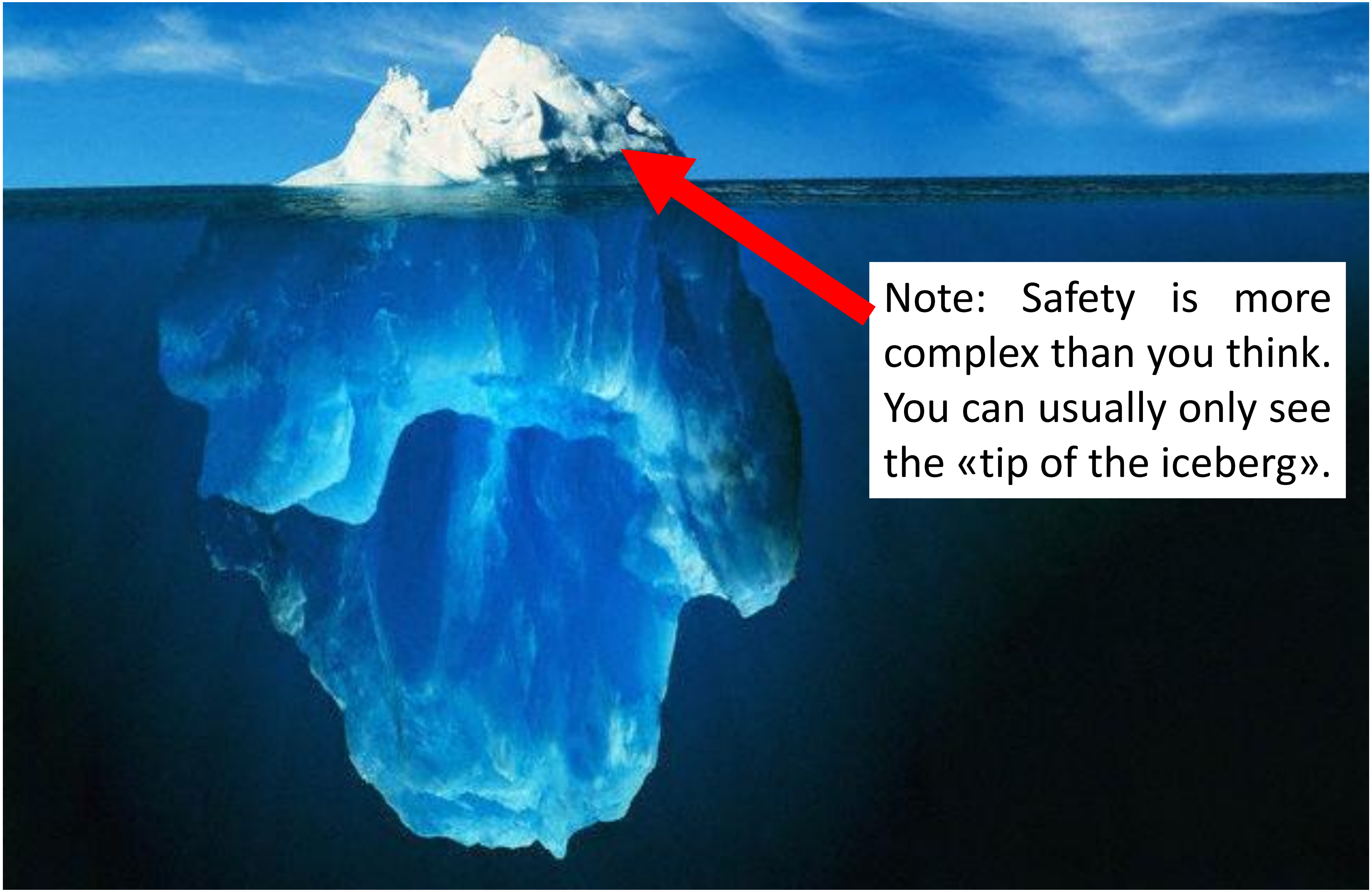
Diethylzinc $(C_2H_5)_2Zn$

If you follow the suggested methods in the previous slides, you can bring your risk level always down.



In conclusion:

We believe that a full risk assessment prior to working with chemicals will help identify the right measures and procedures to minimize risks. With this method, you can improve your safety thinking and your safety behavior. With a risk assessment, you always have the best justification for necessary investment in better safety infrastructure.


Note: Safety is more complex than you think. You can usually only see the «tip of the iceberg».