

# SAFETY & HAZARDOUS MATERIALS DISPOSAL MANUAL-PDEU



**Pandit Deendayal Energy University**

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## OVERVIEW

The Pandit Deendayal Energy University has multiple laboratories and workshops across its campus. To protect people, property, and the environment, many laboratories and workshops which utilize or manufacture hazardous compounds that must be appropriately disposed of. The material in this guidebook will assist you in achieving that aim.

### Purpose

This manual's procedures and rules are written for three reasons:

- (i) To protect our people from health risks and accidents.
- (ii) To be able to respond appropriately in the case of emergencies.
- (iii) To reduce the environmental impact and dangers involved with our work.

This document is a resource for all faculty, students, and researchers that generate or utilize hazardous materials and chemicals in the course of their work, studies, or in research. The procedures for handling and disposal of unused, leftover, undesired, or trash hazardous materials are addressed in this manual.

This guideline specifies the safety parameters, Chemical handling, labeling and waste management standards for hazardous materials transportation and disposal.

## 2. PROTECTION OF PEOPLE & SAFETY PRECAUTIONS

### Personal Protection Equipment (PPE's)

#### 1. Face shield



Face protection from objects and spillage of chemicals, hot water flash a **face shield** is a device used to protect wearer's entire face (or part of it) from chemical splashes (in industry), or potentially infectious fluid (in medical). Face shield, commonly intended to shield the wearer's face, or portions thereof, in addition to the eyes, from certain hazards, depending on face shield type. Face shields shall be used only in conjunction with spectacles and/or goggles.

#### 2. Safety goggles



**Goggles** or **safety glasses** are forms of protective eyewear that usually enclose or protect the area surrounding the eye in order to prevent particulates, water or chemicals from striking the eyes and for the protection from energy beams (lasers) which can lead to eye injuries. They are used in chemistry laboratories while working with larger quantities of strongly corroding acids or caustic solutions, you should use closed eye goggles and carry a face shield.

You should **not wear contact lenses** when handling chemicals, since they can strengthen the effect of chemicals penetrating between lens and eyes and, in some cases, certain chemicals make the removal of the lenses difficult!

When operating lasers, special laser eye protectors will be provided to protect for the specific range of wavelengths of the laser.

### 3. Safety gloves



**Chemical resistant gloves** protect your hands from solvents. When these chemicals touch your skin, they can irritate or burn the skin or cause an allergic reaction. They may also pass right through the skin and cause harm to other parts of your body, just as if you inhaled them.

### 4. Lab coat



A **laboratory coat** or equivalent protective clothing is required for work with hazardous chemicals. When properly used, lab coats...

- (a) Provide protection of skin and personal clothing from incidental contact and small splashes.
- (b) Prevent the spread of contamination outside the lab (provided they are not worn outside the lab).
- (c) Provide a removable barrier in the event of an incident involving a spill or splash of hazardous substances.

### 5. Safety shoes





**Safety shoes** or steel toe boot (also known as a safety boot, steel capped boot or safety shoe) is a durable boot or shoe that has a protective reinforcement on the toe which protects the foot from falling objects or spillage of chemicals.

## 6. Safety Mask



A **respirator** is a device designed to protect the wearer from inhaling particulate matter, including airborne microorganisms, fumes, vapors, i.e. gases. Respirators range from relatively inexpensive single-use, disposable face masks to more robust.

## FIRSTAID

Each laboratory is equipped with a first-aid kit. Before you begin working, familiarize yourself with the location.

### Few Rescuing Tips:

The person should be removed from the source of danger and life saving steps should be taken as soon as possible.

*Consider the cardinal rule in each circumstance to be*

*Self-preservation!*

Electrical accidents

Turn off power source (turn off, unplug and remove fuse at main junction box). If this is not immediately possible, separate victim from charged area by using a non-conductive material (such as a wooden slat) or pull away victim from the site by grabbing the clothes. You should insulate yourself by standing on a grounded base (such as a dry board, thick newspaper) making sure to touch nothing (wall, other person etc.)

Accidents with gas

Rescue on with the use of respiratory

Or poisonous steam

Protection. Move victim immediately to fresh air

Accidents with fire

Stop burning victim and extinguish fire (emergency shower, dousing blanket, and towels, especially synthetic materials, never with the hand!)

Caustic burns

Immediately remove contaminated clothing.

## **Observe the following:**

- Examine breathing and pulse
- Do not leave victim to cool (cover with blanket).
- Clear obstacles blocking air passage.
- Free victim of restraining clothes.
- Contact medical facilities for further treatment.

### **● In Case of Unconsciousness**

The unconscious person must be positioned onto his side as soon as possible to avoid suffocation from foreign bodies or the tongue rolling to the back of the mouth. Check to see if the breathing path is clear. Foreign bodies must be removed immediately!!

### **● In Case of Respiratory Arrest**

With respiratory arrest (no audible or visible air flow from nose or mouth perceived; no lifting and lowering of thorax), artificial respiration should be immediately administered:

Lay victim on his back (possibly sideways), while placing one hand on the forehead and the other hand under the chin, gently tipping the head backwards. With the mouth opened wide, blow into the nose (one can place a handkerchief or the like in between). If the nose is clogged, blow into the victim's slightly opened mouth.

While taking a deep breath, keep an eye on the victim's releasing air, thorax's movement & breathing sound. Before blowing in again, always wait for the victim to exhale! Perform the first two artificial respiration breaths rapidly yet deeply, and then repeat the process 12 to 15 times each minute (once every 4 to 5 seconds, waiting for air to be evacuated between each breath!). Only stop artificial respiration when the victim is able to breathe on his or her own again, or when the medics arrive!

### **● In Case of Cardiac/Circulatory Arrest:**

If the following three symptoms are all present, begin immediately with CPR:

- unconsciousness
- respiratory arrest
- no pulse (carotid artery)

Preferably, two people should perform the CPR together (one person to perform artificial respiration, the other to give heart massage).

- **In Case of Bleeding Wounds:**

Firstly try to stop bleeding, apply direct pressure on the cut/wound with a clean cloth, tissue or with piece of gauze until bleeding stops. Do not apply a tourniquet unless the bleeding is severe and not stopped with direct pressure. For cleaning of cut/wound: clean with soap and warm water. Try to rinse soap out of wound to prevent irritation. Do not use hydrogen peroxide or iodine, which can damage tissue. Apply antibiotic cream to reduce risk of infection and cover with a sterile bandage.

If there is major cut or any of following symptoms, immediately seeks medics!

- Wound is deep or wound has dirt/chemical stuck and won't come out.
- Wound shows signs of infection such as redness, tenderness or thick discharge.
- Call doctor immediately if victim feels fever or the affected area feels numb by victim.
- If the person has a punctured wound.

- **In case of Eye Injury:**

If chemicals come in contact with the eyes, they must be rinsed at least 10 to 15 minutes with the help of an eye bath or calmly flowing lukewarm water jet. A second person should keep the eyes of the victim open. If wearing contact lenses, immediately remove them.

If foreign bodies (e.g., glass fragments) get into the eyes, the victim must be prevented from rubbing them and, if required, the eyes must be flushed as indicated above.

- Tweezers should only be used to remove loosely sitting foreign bodies, such as with the corner of a clean cloth. Never attempt to remove foreign bodies that have been stuck!
- Transport the person in a lying down position to the eye clinic.

- **In case of Burns:**

In case of a lab fire or explosion, ensure safety first and call emergency immediately for help. Evacuate the building safely and pull the fire alarm or alert nearby people, if possible.

After extinguishing fire, immediately remove clothing that does not stick to the skin. Cool burned area of skin with cold water until pain is relieved (20 to 30 minutes). Then afterwards, seek further medical treatment!

In case of caustic burns, immediately take off contaminated clothes; do not use anymore. Rinse affected area with large quantities of water. Remove organic substances with soap and water, never with solvents (alcohol etc.).

- **In case of Poisoning:**

A sample of the poison (substance, gas sample, vomit, etc.) must be taken along in the case of poisoning for proper medical care!

**-Standard poisons** (metal salts, organic substances, insecticide, etc.) and **water-insoluble solvents** (benzene, toluene, petroleum, ether, etc.). Induce vomiting as soon as possible, either with mechanical irritation of the throat wall or by the ingestion of lukewarm salt water (approx. 3 heaping teaspoons of salt per glass). Repeat until vomiting is cleared. Subsequently, seek medical treatment.

**-Corrosive liquids** (acids, caustic solutions, etc.)

Immediately drink as much water as possible, do not induce vomiting, and seek medical assistance.

In case of gas poisoning, After rescuing victim from danger zone, move him/her to fresh air, calm victim and observe breathing, resuscitating if necessary Deliver to hospital with ambulance.

### **Important:**

- **Do not give anything to drink to unconscious persons; they could suffocate!**
- **Never attempt to neutralize ingested chemical with another!**

### **3. LABORATORY CHEMICAL MANAGEMENT**

Laboratory chemical management is important for the several reasons. Here are some common causes responsible for causing accidents.

- (1) The hood doors were opened beyond their design parameters.
- (2) storing too many chemicals, or incompatible chemicals, in inappropriate locations, particularly in hoods, by packing hoods with solid equipment, equipment too large for the hood, too much equipment for the size of the hood, by placing numerous things that do not belong in a hood
- (3) Keeping flammable storage cabinets ventilated
- (4) Obstructing easy laboratory exit access by allowing equipment and ancillary materials to be routinely placed in exit aisles, adding equipment or casework that creates longer dead ends (aisles with only one effective exit), or installing oversized equipment in too small a space, resulting in undersized and/or convoluted laboratory exit paths
- (5) Having only one exit from a laboratory
- (6) Overusing power strips, extension cords, and similar flexible cords for typical continuous activities
- (7) Failing to comply with the NFPA 55 Compressed Gases and Cryogenic Fluids Code and NFPA 45 compressed gas storage requirements by storing too many gases in a laboratory, failing to properly separate incompatible gases, and/or piping the gases with no pressure relief protection for downstream components.
- (8) Failing to provide an appropriate independent failsafe over temperature protection for hot equipment, as required by NFPA 45 11.3.3.4, with a manual reset.
- (9) Constructing pilot plants and other larger equipment that uses huge amounts of flammable materials in a laboratory space without first determining whether the area requires a higher electrical classification.

To prevent accident and before entering the laboratory, people should be aware of the following points.

## ❖ A Guide to Chemical Hazard Symbol

-These four characteristics are **Ignitability**, **Corrosivity**, **Reactivity**, and **Toxicity**.

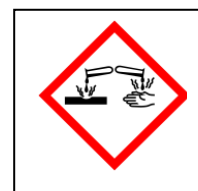
### Ignitability

- Liquids with a flash point less than 140°F
- Solids capable of spontaneous combustion under normal Temperature and pressure
- Oxidizing materials
- Ignitable compressed gases
- Examples include ethanol, sodium nitrate, hydrogen gas, xylene and acetone



### Corrosivity

- Aqueous solutions with a pH less than or equal to 2 or greater than or equal to 12.5
- This does not apply to solid or non-aqueous materials.
- Examples include hydrochloric acid, nitric acid, and Sodium hydroxide.



### Reactivity

- Materials that react violently or generate toxic fumes when Mixed with water
- Cyanide or sulphide bearing wastes which evolve toxic fumes When mixed with acids or bases
- Materials that are normally unstable or explosive
- Examples include sodium metal, reactive sulphides, potassium cyanide and picric acid.



### Toxicity

- Toxicity characteristic refers to wastes that, if Inappropriately handled of, and have the potential to disturb groundwater.
- Due to their potential to spill out inland c certain dangerous Compounds are classified as hazardous waste. The list now contains 40 toxins, including heavy metals, pesticide, and chemical compounds



The **Toxicity** characteristic applies to wastes that have the potential to contaminate groundwater if improperly disposed of. These materials are regulated as hazardous waste due to their potential to leach out specific toxic substances in a landfill. There are currently 40 contaminants on the list that include certain heavy metals, pesticides and organic compounds.

<b>EPA HW No.</b>	<b>Contaminant</b>	<b>Level (mg/L)</b>
D004	Arsenic	5.0
D005	Barium	100.0
D006	Cadmium	1.0
D007	Chromium	5.0
D008	Lead	5.0
D009	Mercury	0.2
D010	Selenium	1.0
D011	Silver	5.0
D012	Endrin	0.02
D013	Lindane	0.4
D014	Methoxychlor	10.0
D015	Toxaphene	0.5
D016	2,4-D	10.0
D017	2,4,5-TP Silvex	1.0
D018	Benzene	0.5
D019	Carbon tetrachloride	0.5
D020	Chlordane	0.03
D021	Chlorobenzene	100.0
D022	Chloroform	6.0
D023	o-Cresol	200.0

<b>EPA HW No.</b>	<b>Contaminant</b>	<b>Level (mg/L)</b>
D024	m-Cresol	200.0
D026	Cresol	200.0
D027	1,4-Dichlorobenzene	7.5
D028	1,2-Dichloroethane	0.5
D029	1,1-Dichloroethylene	0.7
D030	2,4-Dinitrotoluene	0.13
D031	Heptachlor	0.008
D025	p-Cresol	200.0
D032	Hexachlorobenzene	0.13
D033	Hexachlorobutadiene	0.5
D034	Hexachloroethane	3.0
D035	Methyl ethyl ketone	200.0
D036	Nitrobenzene	2.0
D037	Pentachlorophenol	100.0
D038	Pyridine	5.0
D039	Tetrachloroethylene	0.7
D040	Trichloroethylene	0.5
D041	2,4,5-Trichlorophenol	400.0
D042	2,4,6-Trichlorophenol	2.0
D043	Vinyl chloride	0.2



## LABORATORY PRACTICES

- **General Ethics:**

- Never work alone in the laboratory.
- Smoking is prohibited in the chemistry laboratory due to the risk of fire and oral toxicity.
- Food and beverages are not allowed to be stored or consumed in the lab. Food that is utilised in the laboratory for research should be labelled with the following information:



- Visitors are only allowed into the laboratory with the lab supervisor's prior authorization with their own protection, provide them with visitor safety glasses at all times.
- In the evenings, close the windows and vents, cut off certain sources (water, gas, electricity, etc.), store the stools, turn off scales, clean, and cover.

- **Consider Following Essential Things.**

### **FOR CHEMICAL:**

- Important information about handling chemicals can be found in the MSDS. A comprehensive file of MSDSs must be kept in the laboratory or be readily accessible online to all students.
- Trained laboratory personnel should always read and heed the label and the MSDS before using a chemical for the first time.
- Laboratory personnel should be familiar with the types of PPE that must be worn when handling the chemical. Ensure that the ventilation will be adequate to handle the chemicals in the laboratory. One should be familiar with appropriate actions to be taken in the event of a chemical spill, fire, or explosion
- Markeachchemicalbottlewithal**label**thatindicatesatleastthefollowing information:
  - name of the substance
  - molecular formula
  - date of filling
  - name of the responsible person

Write only with water-resistant, black felt-tip pens or ballpoint pens, as other pens become illegible after a short time. At the chemical counter, labels are available for indicating the poison class.

- The purchase of poisons of class 1 and 2 for private purposes as well as any procurement of chemicals for a third party is forbidden.
- One needs to submit a **poison form** signed by the lab supervisor to purchase

poisons of classes 1 and 2.

- Store only the smallest possible amount of chemicals in the laboratory.
- **Inform yourself** carefully before you begin an experiment, about the physical properties, the toxic and the (possibly dangerous) reaction properties of the appropriate chemicals.
- Chemical solutions should **never be pipette with the mouth**. Always use pipetting aids (danger of oral poisoning!).
- For experiments, only use undamaged, **clean containers**. Never use container that contain left over chemicals.
- **Food containers** should **not** be used for the storage of chemicals.
- Use the smallest possible quantities for experiments.
- Place chemical containers, bottles, and devices **always as far back** as possible on the work surface (danger of falling off when knocked against).

When heating material in an open container, point the opening away from people.

Use **boiling stones** when heating substances and make sure that the stones are added when the solution is far below the boiling point. Otherwise the liquid could suddenly cook over and spray all over (boiling retardation).

Always immediately remove spilled chemicals, water puddles from the ground (danger of injuries).

Use caution when **diluting concentrated acids** with water preparing solutions consisting of **solid alkali hydroxides** (e.g., KOH, NaOH). Always add acid or base into water while stirring, never in reverse (heat development!)

## FOR SOLVENTS

- Reduce the **stored supplies** to a minimum (fire risk). At the workbench and in the fume hood, use bottles that contain a maximum amount of 500ml.
- Solvents of the **ether group** ( $R_1-O-R_2$ , e.g.,  $CH_3-O-CH_3$ ) and many hydrocarbons (e.g. butene  $C_4H_8$ ) form highly explosive peroxides after long standing. Before each handling, control the peroxide content with the Mercloquant peroxide test! If it is higher than 0.01% (= 100 ppm, indicated as  $H_2O_2$ ), the peroxides must be eliminated. Control periodically every 3 months. Do not open bottle if you observe unusual viscosity or crystallization! Inform the lab supervisor.
- When distilling peroxide-forming compounds, leave a small amount in the flask never evaporate everything! Store distillates protected from light and if possible, with an inhibitor.

## HANDLING OF GLASS

- Be careful when working with glass and glass equipment, in particular when e.g., introducing glass tubes into rubber hoses. **Protect your hands** (use gloves). Puncture wounds due to broken off glass tubes are dangerous!
- **Thin-walled glass containers**, especially measuring and Erlenmeyer flasks should **not be evacuated**. Vacuum desiccators should be covered with parafilm. They should not be transported in an evacuated condition.
- **Thick-walled vacuum flasks** should not be heated (suitable for evacuation).
- When transporting **large glass flasks**, never hold by the neck and not at all by the plug. Always **hold at the base** (danger of breaking). They may only be stored at the lower shelf.
- Never fill glass containers over 90 percent of filling capacity. To avoid the occurrence of stuck glass plugs, it is advisable to use **screw-on caps** if possible
- Do not force open **jammed glass plugs**. Rather, loosen by tapping it lightly with a wooden stick or slightly warming the outside (at the same time, if possible, cooling the inside).
- Dispose **glass waste**, after cleaning with the appropriate solvent, into their particular intended container. Never dispose of the in the normal waste container (danger of injury to cleaning staff!).

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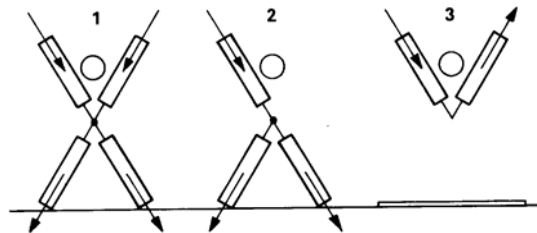
## 4. WORKING WITH ELECTRICITY

In this chapter you receive instructions in handling low-voltage electricity (50 - 1000 volt) and also correct conduct when working with high voltage electricity (over 1000 volt). Weak current (< 50 volt, < 2 A), that is used, for example, for surveys is considered harmless. With small voltages (< 50 volt) the fire risk, above all, should be considered. In most cases, they are not considered lethal to humans.

First some general remarks about electricity:

Normally, with the isolation of electrical devices, the human body is prevented from coming directly into contact with the flow of electricity. However, incorrect isolation or inappropriate handling of electrical installations can lead to an electrical circuit, which can be closed by the human body. There are three frequent ways of current to flow (see below).

1 Hands - Feet (resistance approx. 550 Ohm) 2



Hand - Feet (resistance approx. 750 Ohm)

3 Hand - Hand with isolated ground (resistance approx. 1000 Ohm)

Fig. 4.1: The three most frequent flow of current through humans. From: SBA Nr. 135, SUVA

The resistance of the body depends on the electrical path, the humidity of the skin and the articles of clothing, floors, and footwear among other things. The values given above are, therefore, only estimations. In Switzerland, for the calculation of electrical shock, a body resistance of 1000 ohms is calculated.

The human body can be damaged directly, on one hand, by flowing current. In particular, if the heart lies in the conducting path (1 and 3, see also table 4.1). On the other hand, smaller currents can also frequently lead to indirect damages, as when a person frightened by an electrical impact, falls off a chair or stool.

With current flow over the body by an electric circuit it applies that the current,  $I$ , becomes stronger, the larger the voltage,  $U$ , and the smaller the resistance,  $R$ , that is,  
 $U=IR$  [ampere]

Decisive for the effect of the current on the body is the current intensity,  $I$ , and the impact time. For example a potential of 220 V and a flow from the hands to the feet (resistance about 550 ohms) creates a current of:

$$I = \frac{220V}{550 \text{ ohm}} \\ = 0.4 \text{ ampere}$$

Since electric current stimulates muscles it has flowed through to contract, it usually causes strong muscle cramping if the current flow is not interrupted. This becomes a problem, in particular, with the respiratory muscles that are stilled. With the heart muscle, whose function is based on electro-chemical procedures, external acting current can lead to heart ventricular fibrillations (irregular, cramp-like contractions of individual muscle fibers), whereby blood transport is practically interrupted and the victim is in a state of mortal danger. Already a current of 400 mill amperes (see above) can release such heart ventricular fibrillations. If the current flow manages to break through before the lapse of a heart period (approx. 0.8 seconds) high current can then be withstood without larger damage.

In the following table the possible effects of electric shock are represented according to current amperage and reaction time (threshold values):

Current	Effects of current
0,05 mA	tingle, perceptible with tongue 1 mA tingle, perceptible with finger
1 to 15 mA	increased tingle, finally start of muscle cramps
15 to 20 mA	“let go” range (hand cannot be removed from grasped conductor anymore)
20 to 50 mA	increasing muscle cramps, difficulty in breathing, respiratory arrest and in 3 to 4 minutes asphyxiation (in case current flow is not interrupted)
50 mA	ventricular fibrillation after a few seconds possible; death (flicker threshold) over 50 mA ventricular fibrillation in (fractions of) seconds; death
Over 3	A severe burns; death

Table 4.1: Possible effects of electric shock. From: SBA Nr. 135, SUVA

In addition, the current flow has thermal effects. With small entry surfaces (e.g., small wires) already currents of 220 V can lead to burns, which can reach deep in the skin and develop into focal infections. Large burn wounds are even life threatening due to the associated ample loss of liquid. Particularly during longer action of direct current, comes the danger of blood decomposition.

These examples show that in handling relatively deep voltages and current, certain caution is necessary. The following instructions should, therefore, be followed when handling technical devices!

---

## 4.1 General Conduct

- Immediately report any **defects on the cable, plug or apparatus pairs** to a supervisor. You should not try, under any circumstances, to repaired effect provisionally (insulating tape, etc.).
- Only **expert personnel** (operations electricians, house servicemen) **installations** in the house net.
- Electrical equipment may not be placed within range of **splash in water**.
- **Never by pass or change protective devices** (fuses, safety switch, etc).
- Apparatus that cannot be grounded for instrumentation reasons must be secured by enough isolating transformers or circuit breakers.
- Use plastics or ceramics for **insulation**; cardboard and wood are principally unsuitable for this purpose.
- **Disconnect** electrical devices **from the electrical source** before any manipulation.
- For high voltage systems, do not use banana plugs and extension cords with reciprocal plugs. Blank wires and crosspieces, which impair the effectiveness of protective grounding, are dangerous!
- Make certain when laying out extension cords that nobody can stumble over them (if necessary, tape to affix). For permanent installations, the extensioncordmaynotbelongerthan5meters.Extensioncordrollsmust is completely unrolled before operations, in particular if high performance devices are connected. (Rolled-up cables are fire risks because of increased resistance).
- When using altered devices and plugs (esp. untested ones), it should be clarified whether suitable security is available (in the ideal case, FI-switch).Speak with responsible personnel to clear any uncertainties.
- Always get expert help if you are in doubt about whether the equipment to be used improperly installed and functional.

---

## 4.2 Working with High Voltage

This section deals particularly with the use of high voltage for experimental purposes as for example, in the high voltage laboratory. It should not be forgotten, however, that **many devices, which must deliver high performance of any kind, must also be operated with high voltage.** This applies e.g., to all lasers of the class 4, to NMR devices, and to electron microscopes. **The following applies to all these devices:**

- Before each manipulation** for which the housing must be opened, the equipment should be **removed** absolutely from the **current supply**.
- In case the fuse is to be unscrewed; a **warning card** should be attached to the fuse box so that no one inadvertently screws in the fuse too early!

Areas where one works with high voltage and devices that are operated with high voltage are marked by this danger warning:



### 4.2.1 General Facts

Consider for allow-voltage circuits (220V)

Inform yourself before you begin with setting up an experiment, about **Proper behavior in case of accidents** with electricity (see Chapter 2).

Inform yourself before the execution of **experiments with gases** properties and potential dangers Also bear in mind that during the experiment that other (possibly toxic) compounds could develop.

Regard each experimental test setup, which **is not visibly** grounded (grounding bar), as standing under tension. Simply getting close can be lethal!

Use the red **emergency switches only in case of an accident** (immediately disconnects the whole laboratory supply and sets off an alarm by the technical staff, so that rapid assistance is ensured).

### 4.2.2 Experimental Setup

High voltage outlet parts may be found **only within** the enclosed **experimental field**.

They are to be secured and constructed in such a way that no danger can exist outside of the experimental field.

The **entrance** to the experimental field is to be secured with fences and blocking door.

- 
- The supports of the grounding rod(s) and all stopper grids and doors must be within the **safety area**.
  - Before the first running of the testing equipment**, the function of safety must be examined beforehand.
  - when making **big changes** to the testing equipment, reexamine the security inside and outside of the experimental field.

### 4.2.3 Operation

- do not use the safety switch for routine switching off of the testing equipment
- before entering** the experimental field, make sure that:
  - 4.2.3.1.1 All sources of **high voltage** are switched off.
  - 4.2.3.1.2 The high voltage circuit has reliable contacts and stays **grounded** with the grounding rod.
  - 4.2.3.1.3 All **condensers** in the experimental field are unloaded and grounded, especially with direct and alternating current experiments.
- Check **before switching on** the high voltage testing equipment if:
  - **All persons have left the experimental field.**
  - **The grounding bar has been removed and hung up at its intended place.**
  - **The entrance to the experimental field has been closed off with the blocking door.**
- if there is **any uncertainty whatsoever**, seek expert advice (specialized group: high voltage technology).

### 4.2.4 Disposal Considerations

- Take heed when performing experiments with gas for proper elimination of **waste products**. Pay special attention when dismantling the apparatus that no gases escape into the lab atmosphere.



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### 4.3 WORKING WITH RADIOACTIVE MATERIALS

Radioactive materials are understood as substances, which send ionizing radiation through spontaneous decay of their atomic nuclei. This radiation is again in the position to produce by splitting off from electrons or by fragmentation of atoms or molecules ions the radioactive materials you come in contact with at ETHZ comes the form of “**open**” or “**sealed**” **sources**.

“**Open**” is understood as sources, which contain materials that can escape and thus, cause contamination. Typical isotopes are hydrogen-3 (tritium), carbon-14, phosphorus-32 or sulfur-35. They are used for example, as markers in biochemistry. With all open sources, the danger of incorporation exists, e.g., by inhalation of contaminated air.

Sources are “**sealed**” if, by their design, escape of radioactive materials under normal working conditions is impossible. They are used particularly in the measurement and control engineering and in medicine (for example, cobalt-60, and strontium-90). X-ray machines are another type of sealed sources. They are used, in particular, for structural analysis and material testing. With sealed sources, the major danger is of external irradiation in case the equipment is not sufficiently shielded or used inappropriately.

Except for sealed sources such as x-ray units, which intentionally produce ionizing radiation, **devices that are operated with high voltage, such as electron microscopes, can form (unintended) ionizing radiation**. The radiation can come from particles of high energy that are stopped, for example, in the interior of the equipment. Normally this radiation is shielded by the equipment lining. Nevertheless, a certain caution is required in handling such devices with regards to their radioactive emissions. For example, linings should not be removed or flanges themselves must be replaced.

The average annual radiation dose from natural sources in Switzerland amounts to about 3.5 mSv (the unit, “Sievert” stands for the equivalence dose, i.e. the absorbed dose multiplied by the valuation factor of the particular type of radioactivity; determinant for damages), whereby, radon has the largest presence in dwellings. The average emission from artificial sources amounts to about 1.4 mSv, whereby medical applications should be noted.

The **effects of ionizing radiation** on the body are dependent on the dose and above all, the effective period. For example, a whole-body dose of 5 sV is deadly when accumulated within a few seconds but when slowly applied over week’s shows no tangible, clinical effect.

With acute surface irradiation starting from short time doses of approximately 0.5 sV and above, non-stochastic radiation damage (i.e. for each person irradiated with this dose, dose-dependent) is to be expected. Purely external radiation results, thereby, to damage of the skin and possibly the underlying tissue. After a latency of days or weeks, follow inflammation reactions and necroses. Acute whole-body irradiation from 0.5 to 1 sV upwards results in the so-called, “radiation sickness” (nausea, later skin damage, hair loss, typical chromosomal mutations, etc.).

---

After incorporation, in principle, the same acute damage is to be expected, whereby individual substances are often accumulated in certain tissues (e.g., iodine-125 in the thyroid). The biological half-life varies, therefore, between a few hours and several decades.

With the chronic load of the body with ionizing radiation, the cancer risk and the danger of genetic damage are to be considered primarily. It is crucial here that for these damages no threshold dose is known!

Preventative measures are, therefore, necessary when working with radioactive materials, which are described in the following. In addition, you will find instructions for the correct behavior in accidents and for waste disposal.

## 5.1 General Conduct

### 5.1.1 General Principles

- do not work with radioactive materials **without proper training** from an experienced person.
- never work alone**, if possible, in an isotope laboratory.
- Work in such a way that **any contamination** of hood, walls, floor, worktools etc., **does not happen**.
- Should a **contamination** occur, **promptly report** incident to the institute radiation safety officer.
- Food and drinks** may not be stored or consumed in the laboratory.
- Smoking** is generally forbidden in the laboratory.
- Do not blow your nose in the lab**. Otherwise, radioactive substances reach your face or nose through possibly contaminated gloves.
- Do not use cosmetics** (esp. moisturizing creams) in the lab. The liposomes they contain could transport radioactive substances into the skin.
- With the use of radioactive materials that cannot be burned, plan ahead in to keep the quantity of the **produced waste** to a **minimum**. However, waste avoidance should not be done at expense of work safety (e.g., continuing to work with contaminated gloves to avoid producing waste).
- Nothing** may be **brought out** of the **secure zone** without first being **checked**  
For radioactivity.

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### 5.1.2 Work Clothing

- When working in the isotope lab, always wear gloves and a special **labcoat**.
- Wear **gloves** when working with open sources Working Place.
- at the working place the following should be within **easy reach**:
  - sufficient quantity of gloves (see above)
  - Kleenex
  - waste container
  - Contamination monitor (except for work with  $^3\text{H}$ ).
- In principle, work with open sources should be done under the hood.
- Work on a clearly defined place, with absorbent material (e.g., Benchcote) lid over tanks made from high-grade steel or PVC.
- always immediately mark all containers, particularly those with radioactive contents:
  - type of nuclide
  - activity
  - Name of responsible persons.

This applies particularly to containers that are stored in generally accessible refrigerators and freezers. Use water-resistant felt-tip or ballpoint pens for writing.

- The **house vacuum** may not be used .Use the water-jet pump with a vacuum controller.
- Avoid**, if possible, the use of **syringes and cannulas** (danger of injury) contamination.
- Wash off** instruments only outside of the hood. Only use basins where waste water is monitored before entering the canalization.
- Do **not** bring **office materials** into a laboratory, which works with open sources.
- With work that lasts longer than 24 hours, assign should be placed on the hood.

## 5.2 Properties of Important Isotopes

### Explanations:

- Unit Becquerel (Bq): measurement of activity, i.e. the number of radioactive decay per time unit. Still often use the historical unit curie ( $1\text{Ci}=3.7\cdot 10^{10}\text{Bq}$ ).
- The contamination dose refers to the amount of energy taken up by bare skin.
- The subsequent dose, E50, designates the average dose that one receives after the incorporation of a certain activity before the substance decays or is discharged.

### 5.2.1 Iodine-125

<b>Type of the radiation</b>	$\gamma$ - radiation
<b>Decay</b>	$\text{I-125} \rightarrow \text{Te-125} + \text{photon} + \text{energy (max. 0.000035 MeV)}$
<b>Range in air</b>	practically unlimited
<b>Range in water or Plexiglas</b>	practically unlimited
<b>Range in lead</b>	0.01 cm lead reduces radiation to 10% of the initial value
<b>Radioactive half-life</b>	59.6 days
<b>Direct dose</b>	9.25 MBq, 1 cm distance $\rightarrow$ 50 $\mu\text{Sv/h}$
<b>Contamination dose</b>	9.25 MBq, 100 $\text{cm}^2 \rightarrow$ 0.15 mSv/min
<b>Subsequent dose E50</b>	9.25 MBq, incorporated $\rightarrow$ 157 mSv
<b>Characteristics</b>	Accumulates in thyroid, long biological half-life (40 days). Use special caution in handling! Give iodide tablet immediately upon incorporation.

### 5.2.2 Carbon-14

<b>Type of the radiation</b>	$\beta$ -radiation
<b>Decay</b>	$\text{C-14} \rightarrow \text{N-14} + \text{electron} + \text{antineutrino} + \text{energy (max. 0.157 MeV)}$
<b>Range in air</b>	centimeter range
<b>Range in water or Plexiglas</b>	millimeter range
<b>Radioactive half-life</b>	5730 years
<b>Direct dose</b>	9.25 MBq, no Plexiglas, 10 cm distance $\rightarrow$ 31 $\mu\text{Sv/min}$
	9.25 MBq, Plexiglas $\rightarrow$ < 0.1 $\mu\text{Sv/h}$
<b>Contamination dose</b>	9.25 MBq, 100 $\text{cm}^2 \rightarrow$ 0.5 mSv/min
<b>Subsequent dose E50</b>	9.25 MBq, incorporated $\rightarrow$ 5.2 mSv
<b>Characteristics</b>	Biological properties similar to sulfur-35

### 5.2.3 Phosphorus-32

<b>Type of the radiation</b>	$\beta$ –radiation
<b>Decay</b>	P-32 $\rightarrow$ S-32 + electron + antineutrino + energy (max. 1.7 MeV)
<b>Range in air</b>	meter range
<b>Range in water or Plexiglas</b>	1 to 10 mm
<b>Radioactive half-life</b>	14,29 days
<b>Direct dose</b>	9.25 MBq, Plexiglas, 1 cm distance $\rightarrow$ 0.8 $\mu$ Sv/min 9.25 MBq, Plexiglas, 50 cm distance $\rightarrow$ 0.0003 $\mu$ Sv/min
<b>Contamination dose</b>	9.25 MBq, 100 cm <sup>2</sup> $\rightarrow$ 2.5 mSv/min
<b>Subsequent dose E50</b>	9.25 MBq, incorporated $\rightarrow$ 23 mSv

### 5.2.4 Sulfur-35

<b>Type of the radiation</b>	$\beta$ –radiation
<b>Decay</b>	S-35 $\rightarrow$ Cl-35 + electron + antineutrino + energy (max. 0.167 MeV)
<b>Range in air</b>	centimeter range
<b>Range in water or Plexiglas</b>	millimeter range
<b>Radioactive half-life</b>	87.4 days
<b>Direct dose</b>	9.25 MBq, no Plexiglas, 10 cm distance $\rightarrow$ 31 $\mu$ Sv/min 9.25 MBq, Plexiglas $\rightarrow$ < 0.1 $\mu$ Sv/h
<b>Contamination dose</b>	9.25 MBq, 100 cm <sup>2</sup> $\rightarrow$ 0.5 mSv/min
<b>Subsequent dose E50</b>	9.25 MBq, incorporated $\rightarrow$ 2.6 mSv
<b>Characteristics</b>	Due to minimal radiation energy, emitted radiation is mostly blocked by rubber gloves. Instead contamination and incorporation are dangerous. With accumulated incorporation, higher doses with long t <sub>1/2</sub> . Sulfur compounds (esp. TRAN35-S) are often volatile!

### 5.2.5 Tritium(Hydrogen-3)

<b>Type of the radiation</b>	$\beta$ –radiation
<b>Decay</b>	H-3 $\rightarrow$ He-3 + electron + antineutrino + energy (max. 0.000018 MeV)
<b>Range in air</b>	millimeter range
<b>Range in water or Plexiglas</b>	micrometer range
<b>Radioactive half-life</b>	12,4 years
<b>Direct dose</b>	9.25 MBq, no Plexiglas, 10 cm distance $\rightarrow$ < 0.1 $\mu$ Sv/h
<b>Contamination dose</b>	9.25 MBq, 100 cm <sup>2</sup> $\rightarrow$ < 0.1 $\mu$ Sv/h
<b>Subsequent dose E50</b>	9.25 MBq, incorporated $\rightarrow$ 37 mSv
<b>Characteristics</b>	Tritium-radiation is not detectable with conventional monitors. Damaging upon incorporation (detected though urine test).

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### 5.3 Behavior in Case of Accidents

**Stay calm. Do not move around** (further contamination), **do not** leave secure zone **for any reason.** (Exception: fire: leave lab, close door, stay in front of the room!)

**First aid:**

- **Contamination of intact skin:**

A quick reaction is important! Using caution, immediately remove contaminated gloves (dispose) and lab coat, as well as contaminated clothes (plastic bag). Wipe off contamination with a tissue and wash thoroughly with soap and water. If necessary, the upper layer of hard skin may be scraped off using proper instruments (do not create open wounds!). Take care that a further secondary skin surface is not contaminated! See physician for further treatment.

- **Contamination of wounds:**

Also here, a quick reaction is important. If possible, induce self-cleaning of the wound through forced bleeding (pressure or tying of rubber hose). Take care that a further secondary skin surface is not contaminated! See physician for further treatment.

- **Incorporation:**

If available in lab, immediately administer specific antidote (decorporation agent) to reduce the effect on the intended organ (i.e. potassium iodide with iodine-125). Find out the name, approximate amount of isotope, method and time point of incorporation. See physician for further treatment.

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## 5.4 Disposal Considerations

( $t_{1/2}$  = half-life)

### 1. Solid Waste

**Radioactive symbol must be made unrecognizable.**

Description	Remarks	Disposal
$t_{1/2} < 60$ days	including sulfur- 35 ( $t_{1/2}$ 87,5 days) collect separately, label clearly and permanently: nuclide, date of filling, responsible persons	collection container, decay facility
Type 1	Ra-226, Ra-228	collection container
Type 2	all $\alpha$ -emitter except for Ra-226, Ra-228	collection container
Type 3	H-3 and C-14	collection container
Type 4	nuclide with $t_{1/2} > 60$ days except for $\alpha$ -emitter and H-3, C-14	collection container
Type 5	neutron sources	collection container

### 2. Liquid wastes

**Never pour into drain!**

**Dilution of active waste, in order to release to the outside, is highly forbidden and subject to fines!**

Separate according to isotope in labeled PVC-bottles in the hood or collect in 10-liter- canisters.

**C-14 waste:** add 0.05% sodium azide (possible formation of  $^{14}\text{CO}_2$ )

Dispose through specialized personnel.

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## 6. WORKING WITH STRONG MAGNETIC FIELDS

Strong magnetic fields are used, for example, in NMR tests (= Nuclear Magnetic Resonance), in order to identify materials or examine chemical structures. It takes advantage of the reciprocal effect of magnetic atomic nuclei with external magnetic fields. Magnetic fields also develop in radiographic electron microscopes. The lenses of these microscopes have electromagnetic coils that are supplied with high voltage. Between the coils a magnetic field forms. Since this magnetic field is sufficiently shielded under normal conditions to prevent being a threat to people, **this chapter concentrates only on NMR work.**

NMR devices produce, on the one hand, a very strong homogeneous magnetic field and, on the other hand, a high frequency magnetic alternating radio wave. In work with NMR, the safety boundaries of the homogeneous magnetic field are relevant since the radio field is well shielded. Bear in mind that the pulling power of the coils decrease according to the ratio,  $1/r^2$ , i.e. the closer one approaches with the magnet towards a metallic object, the stronger is the attraction. Thus, particularly, if a heavy object like a compressed gas bottle is placed in motion towards a magnet, it can be hardly brought to the stop. Therefore, some warnings must be obeyed in order to avoid, on one hand, injuries and, on the other hand, expensive damage to the equipment.

Health effects of longer exposure to strong magnetic fields on the human body are controversially discussed. A clear working mechanism could not be proven so far.

For questions concerning behavior in case of accidents, refer to Chapter 2.

### 6.1 General Conduct

- Wearers of **cardiac pacemakers** (especially older models) are endangered. The function of the pacesetter can be impaired or even interrupted. Consult a physician before work with NMR.

#### Safety margins:

- devices with frequencies up to 500MHz: 5 meters
- devices with frequencies from 500 -800MHz: 8 meters

These distances apply both in horizontal **and in vertical direction**, thus, also rooms that are over or under a room with NMR equipment. This **warning sign** marks all areas concerned:





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Wearers of **metallic prostheses** or persons, which have not had metals or **plates** removed after an operation must, before working on NMR equipment, confirm whether the metal parts react magnetically. If it is, the **safe distance from the NMR is 5meters**.

- Before entering the NMR laboratory **remove all metallic objects** (key, ~~air~~ tools etc.) from bags and put down all jewelry that could react magnetically.
- Do **not** bring **credit cards, copy cards, floppy disks, etc** to the laboratory. The magnetic strips will be deleted and thus, cardsordisks will be rendered useless.
- Compressed gas bottles may not be brought** into the NMR laboratory. Exists the danger of damage to the equipment and the bottle that can lead, depending upon the gas, to injuries, fires or explosions.
  - Only authorized persons may do **manipulations** of any kind to the equipment.
- Never look into the sample in let pipe. There is danger of injury in case someone ejects ~~sample~~ at the same time.
- With experiments, do not exceed temperature gradients over **the boiling the freezing point of the sample**. Dangerous pressure scan develop which can cause the sample tube to burst.
- The interior of NMR machines contains liquid inert gas. If the super conduction ~~it~~ the equipment for any reason is waived, the gas escapes through the release valve upward into the laboratory atmosphere (so-called "**Quench**"; loud hissing, visible gas fog over the equipment). The gas is usually harmless; however, it displaces the breathing air in the area, creating the danger of suffocation. In addition, there exists with all liquid gases, due to their low temperature, the danger of burn-like injuries upon skin contact.
  - Immediately leave the room, close the door.
  - Upon prolonged skin or eye contact immediately wash thoroughly with cold water. Treat like a burn (refer to Chapter2).
  - Inform responsible persons.
  - Enter room only after the unknown gas has been cleared from the room.

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## 7. HANDLING OF COMPRESSED GAS BOTTLES AND GAS

The following incident shows that anything can happen with the inappropriate treatment of compressed gas bottles:

Six carbon dioxide bottles, components of a fire extinguishing system, had been removed from their fixed location on the walls so that painters could paint the wall unhindered. As the cylinders were being reinstalled, they noticed that one of them was leaking. One of the painters took it over his shoulder and tried to drag it over the floor. At this moment the cylinder valve shot out, and the cylinder became a jet-driven, 100-kilo iron projectile. The painter held the cylinder to the ground, but he could not hold on to it for long. The cylinder raced across the ground, struck another cylinder and bent its valve. Then it turned and after approximately 6 meters, struck the ladder of a painter who then fell down. After spinning several times, the cylinder shot against a wall. Again it turned, crossed the area and pursued an electrician. After approximately 12 meters it struck the wall again and broke off four bricks. After renewed turning, it again pursued the electrician through an open door. The electrician brought himself to safety by escaping through a side door, at that time the cylinder shot a further 20 meters straight ahead. Finally it fell into a pit, where the remaining gas could leak out without causing further damage.

This incident, from a distance, seems extremely amusing for those not present but surely not for those that were. It shows clearly the dangers of gas bottles with compressed contents. After shooting off the valve, a gas bottle can go on a free flight of about 800 meters or pierce concrete walls of approximately 20 cm thickness. Heeding the following general instructions regarding the handling of compressed gas bottles protects you quite reliably from such incidents.

Gas cylinders are themselves not only a danger physically but also their actual contents, the gases, can be flammable, explosive or toxic. At the end, the frequently used gases, their possible dangers, and the necessary safety precautions will be described. For questions regarding waste disposal see Chapter 3.5.

### 7.1 General Facts

Compressed gas bottles contain gases in compressed or liquefied condition (see Table 7.1). The filling pressure of compressed gases amounts to normally 200 bar. With liquefied gases, the filling pressure corresponds to the steam pressure of the respective connection. As temperature rises, the pressure in the compressed gas bottles rises strongly in accordance with the steam pressure equation:

$$\frac{dP}{dT} = \frac{L}{T} (V_1 - V_2)$$

$p$  = steam pressure [bar]  $T$   
= temperature [K]

$L$  = heat of transformation (e.g., evaporation enthalpy)  $V_1$  =  
volume in steam form or liquid condition

$V_2$  = volume in liquid or solid condition

### 7.1.1 Reception of Gas Cylinders

Upon receipt of the gas cylinders, check if the indicated names of the gases correspond with the color code of the bottle:

Name	Color code		Physical state	Pressure
	new	Old		
acetylene (dissolved)	oxide red	Orange	gas	15 bar
Ammonia	zinc yellow	Violet	Liquid	8 - 10 bar
Argon	emerald green	brown / green	com gas	200 bar
Butane	fire red	Gray	Liquid	5 - 10 bar
Chlorine	yellow	Yellow	Liquid	6 - 8 bar
hydrochloric acid	yellow	yellow / red	Liquid	60 - 80 bar
Ethylene	fire red	Gray	Liquid	20 - 30 bar
forming gas (N <sub>2</sub> /H <sub>2</sub> )	fire red	red / green	com gas	200 bar
Helium	olive brown	yellow / green	com gas	200 bar
carbon dioxide	dusty gray	Black	Liquid	60 bar
carbon monoxide	zinc yellow	Gray	com gas	200 bar
Air	yellow green	Brown	com gas	200 bar
Methane	fire red	red / brown	com gas	175 - 200 bar
Propane	fire red	Gray	Liquid	10 - 15 bar
Oxygen	pure white	Blue	com gas	200 bar
sulfur dioxide	zinc yellow	Gray	Liquid	5 - 10 bar
sulfur hexafluoride	yellow green	Gray	Liquid	17 bar
hydrogen sulfide	zinc yellow	Gray	Liquid	5 - 15 bar
Nitrogen	deep black	Green	com gas	200 bar
nitrogen dioxide	zinc yellow	Gray	Liquid	10 bar
Hydrogen	fire red	Red	com gas	180 - 300 bar

Table 7.1: Name, color code, condition, and cylinder pressure of selected gases

**If there is a discrepancy, the bottle should be returned to the supplier immediately.** Do not withdraw a sample from the cylinder to check its actual contents.

### 7.1.2 Transport

- Transport compressed gas bottles only with the **valve protection cap** in place.
- Always **use a cart when moving bottles**, especially if the regulator is already installed and the valve protective cap cannot be put in place. Secure the gas bottle with a fireproof chain during transport.
- never attempt** to roll, tow along, or drag over the ground a gas bottle. Avoid dropping and striking gas bottles against each other.

---

### 7.1.3 Storage

- Compressed gas bottles may be stored, over long periods of time, only in well ventilated, fire proof areas.
- The storage installations of combustible gases must be explosion-proof, and area should be clear of any sources of heat or ignition. **The laboratory is not a suitable place for the storage of gas bottles!**
- Fittings must be in place, which **prevent the gas bottles from falling over**. It is advisable to separate the bottles according to their type (flammable, corrosive, nonflammable).
- Empty and full bottles must be stored separately. Empty bottles should be marked (e.g., tape with label).

### 7.1.4 Valves and Fittings

Only knowledgeable personnel should handle the valves in any way. The gas bottles have distinct threaded connections according to the type of gas it contains. The basic differences (numbers refer to pg.38):

- Left thread (1) (this means turn counter clockwise to open) for combustible gas
  - Right thread (1) for non-combustible gas
  - Screw valve (1) (can only be opened with special wrench) for corrosive gas (chlorine, hydrofluoric acid, etc.)
  - Inner thread (this means pressure reduction valve would be screwed into the threaded pipe (2))for compressed air, acetylene
  - Outer thread (this means pressure reduction valve would be screwed, as above in (2), with a connecting nut over the threaded pipe) for oxygen, nitrogen, hydrogen, etc.
- 
- The use of **adaptor valve** is allowed only in rare cases because of the risk of dangerous mix-ups. In each case, it is necessary to meet extra security measures(training of personnel ,supervision, etc.).
  - for the corresponding gas, use only **certified pressure regulators**. To apply **especially for compressed oxygen**. Only absolutely oil-free and fat- free fittings with flame-resistant seals issued by the Swiss Association for Welding Technique (Schweizerischen Verband für Schweißtechnik-SVS) (refer to Chapter 7.2.5).

---

### 7.1.5 At the Place of Use

- If the cylinder is only needed for a short time at a specific place; it can be used in a lying position (except for liquid gas). Standing cylinders must at least be secured with a fire-resistant chain. If the cylinder will be used regularly or for a longer period of time, it should be secured with permanently mounted clips, clamps, chains, or similar.
- No part of a pressurized gas cylinder** may be set at temperatures **over liquid and over 60°C for compressed gases**. The location is to be selected accordingly (not in the proximity of heaters, hot liquefying baths, etc.).

Remember that **some gases react with certain materials violently** (refer to Chapter 7.2).

When using **corrosive gases** (chlorine, hydrogen fluoride, etc.) the valve must be used frequently in order to avoid blockage. The pressure-regulator should not be left on the bottle unless it is often used. Close the valve after every use and rinse the pressure reduction valve with dry air or nitrogen.

Further precautionary measures are described in **Chapter 3.2 - Chemical Reactions under Increased Pressure**.

### 7.1.6 Placing into Operation

#### Liquefied gases

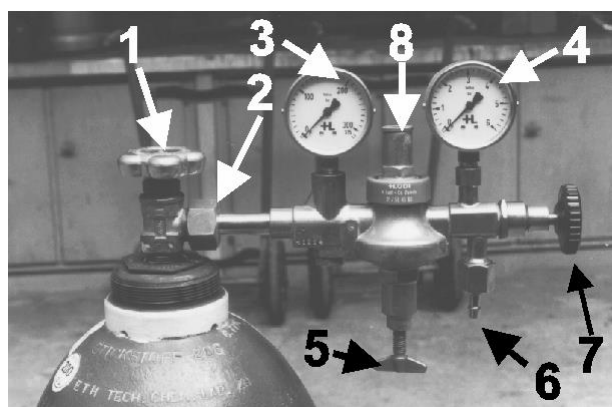
Liquefied gases are taken at a pressure so that the vapor pressure corresponds to the room temperature.

When one takes a large amount of gas, the contents **cool off strongly** due to the necessary heat of evaporation (see equation, pg. 49). In this case, the bottle can be warmed in a water bath (not over 40°C!), so that the casing does not incur any damage due to the low temperature. Do not use any heating tapes, infrared emitters, or similar. The pressure-reduction valve may not be heated. What comes out of the bottle may be warmed by a special heating device that prevents the freezing of the reduction valve. Otherwise, withdrawal is similar to compressed gases (see below).

Generally, skin contact should be avoided when handling liquid gasses since the cold gases cause “burns”. Preferably, work with gloves.

## Compressed gases

The gas is taken from the compressed gas bottle by means of the pressure-regulator (see below):



- 1 cylinder valve
- 2 junction coupling ring
- 3 contents manometer
- 4 operating pressure manometer
- 5 pressure regulator
- 6 hose connection plug
- 7 locking screw
- 8 pressure-relief valve

Abb. 7.1: Standard pressure reduction valve

### Withdrawal of gas (not on the first withdrawal)

1. Check whether the locking screw (7) is closed; otherwise, close.
2. Open cylinder valve (1) slowly and without jerking (only with the hand!). Afterwards, examine whether the bolt connection (2) between the cylinder valve and the pressure-relief valve is not leaky (for example, with soapy water, never with open flame). Leakages are to be repaired immediately.
3. Examine the working pressure on the operating pressure manometer (4). Do not exceed maximum pressure (usually marked red).
4. Open locking screw (7) slowly. The gas will now flow out.

#### 7.1.7 Placing Out of Operation

1. Close cylinder valve (1).
2. Close locking screw (7).
3. With corrosive gases, the pressure-reduction valve should also be unscrewed and flushed with dry nitrogen.  
With toxic gases, flush whole system, if possible.

- Gasbottles should never be completely emptied. They should always have **excess pressure of at least 2 bars** left over. Empty bottles must be clearly marked as such. Return the gas bottles **before the expiration date** to the distributor.

## 7.2 Characteristics of Selected Gases

### Explanation:

Density:	at 0°C and 1013mbar
Vapor pressure:	at 20°C
R-and S-Phrases:	refer to Chapter 4.3, pg. 21 to23
Poison class:	for explanations, refer to Chapter 3.4.1, pg. 23 MAK-
Value:	<b>Maximal Arbeitsplatzkonzentration</b> in ml/m <sup>3</sup> =ppm (Maximum workplace concentration) At this concentration, the material does not cause damage at daily working times of 8 to 9 hours and up to 45 hours per week and also not over a longer period of time.

## 7.2.1. Acetylene

<b>1. Chemical characteristics</b> Formula: CH=CH Form: dissolved under pressure in acetone, chemically unstable Appearance, Odor: colorless, odorless (badly smelling impurities)
<b>2. Physical Data and Safety Indications</b> Change of state: Melting point: -82°C Boiling point: -83.8 °C Density: 1.11 kg/m <sup>3</sup> Vapor pressure: - Flash point: - 81.8 °C Flammable temperature: ca. 300°C Explosive limit: 1.5 - 82 vol.%
<b>3. Hazardous Reactions and Decomposition Products</b> Decomposition upon explosion possible already with slight overpressure at normal temperature or by normal pressure starting at approx. 160°C. Decomposition into the elements when heated under exclusion of air. Develops explosive heavy metal acetylides upon contact with heavy metals, esp. copper and silver. Acetylene-halogen mixtures explode very easily, spontaneous combustion in chlorine gas atmospheres. Acetylene-air mixtures at a far distance is combustible, already the sparks of a hammer blow is sufficient for ignition.
<b>4. Regulations</b> Risk warning: flammable R-Phrases: 11-14-34 S-Phrases: 9-16-26
<b>5. Protective Measures, Handling</b> <b>- Personal protective equipment:</b> none <b>- Handling precautions:</b> none <b>- Fire and Explosion Protection:</b> No part of equipment should consist of copper or silver. Do not place overpressure on gas. Never warm bottle. Do not allow gas to escape into lab atmosphere; do not allow coming into contact with halogens. Electrical installations should be explosion resistant (Ex.Schutz).
<b>6. Measures in Case of Accident or Fire</b> <b>- After warming of bottle, flame rebound</b> Close valve; inform responsible persons. When cylinder feels warm, bring immediately outside (if the bottle can still be touched with bare hands). From a safe distance, cool with water spray (jet spray) outside or directly in the lab. Alert and fire dept. and block off area. <b>If cylinder valve cannot be closed,</b> extinguish resulting flame only during the first minute with carbon dioxide or powder type fire extinguisher. Immediately eliminate all ignition sources. Open windows and doors. Inform responsible persons. Transport outside as above; otherwise, start with Cooling. Alert and fire dept.
<b>7. Toxicological Information</b> Poison class: - MAK-value: 1000 ppm
<b>8. Ecological Information</b> None

## 7.2.2. Ammonia

<b>1. Chemical characteristics</b> Formula: NH <sub>3</sub> Form: gas, liquid Appearance, Odor: colorless, extremely pungent
<b>2. Physical Data and Safety Indications</b> Change of state: Melting point: -77.7°C Boiling point: -33.3°C Density: 0.73 kg/m <sup>3</sup> Vapor pressure: 7.71 bar Flash point: - Flammable temperature: 630°C Explosive limit: 15 - 28 Vol.%
<b>3. Hazardous Reactions and Decomposition Products</b> Ammonia is inflammable, forming a combustible mixture with air and oxygen. The auto ignition temperature is strongly reduced by different catalysts like platinum. Reacts with ammonia and chlorine exothermically under flaming.
<b>4. Regulations</b> Risk warning: toxic, corrosive R-Phrases: 10-23 S-Phrases: 7/9-16-38
<b>5. Protective Measures, Handling</b> <b>- Personal protective equipment:</b> K-filter on gas masks (green). Wear gloves and glasses. <b>- Handling precautions:</b> Corrosive on skin, eyes, and mucous membranes. All skin contact with liquid gas lead to freezing by "burning wounds". Avoid skin contact. <b>- Fire and Explosion Protection:</b> No part of equipment should contain copper or brass. Do not allow gas to be released into lab atmosphere. Do not bring into contact with chlorine.
<b>6. Measures in Case of Accident or Fire</b> <b>- After gas release:</b> Dampen vapors with water jet spray. Neutralize resulting ammonia-water with diluted sulfuric acid. Do <b>not</b> give water to released <b>liquid</b> NH <sub>3</sub> , CO <sub>2</sub> -foam. <b>- First aid:</b> Rescue only with respiratory protection. Bring victim immediately to fresh air. Contact a physician. In case of skin and eye contact, rinse well with cold water. Treat like a burn. Also refer to Chapter 2.
<b>7. Toxicological Information</b> Poison class: 2 MAK-value: 25 ppm
<b>8. Ecological Information</b> Poisonous to fish. (harmful concentration 1.25 mg/L)



### 7.2.3. Carbon Monoxide

<b>1. Chemical characteristics</b> Formula: CO Form: Gas Color, Odor: colorless, odorless
<b>2. Physical Data and Safety Indications</b> Change of state: Melting point: -205°C Boiling point: -191.5°C Density: 1.17 kg/m <sup>3</sup> Vapor pressure: - Flash point: 630°C Flammable temperature: 630°C Explosive limit: 12.5 – 74.2 vol.%
<b>3. Hazardous Reactions and Decomposition Products</b> None.
<b>4. Regulations</b> Risk warning: flammable, corrosive R-Phrases: 12-23 S-Phrases: 7-16
<b>5. Protective Measures, Handling</b> <b>- Personal protective equipment:</b> With long exposure, respiratory protection recommended; wear gloves and glasses. <b>- Handling precautions:</b> none <b>- Fire and Explosion Protection:</b> Electrical installations should be explosion resistant (Ex.Schutz).
<b>6. Measures in Case of Accident or Fire</b> <b>- After gas release:</b> Vacate danger zone as soon as possible. Enter zone only with full respiratory protection and safety rope. <b>- First aid:</b> Rescue only with full respiratory protection. Bring victim immediately to fresh air, artificially resuscitate with oxygen. Contact a physician. Refer also to Chapter 2.
<b>7. Toxicological Information</b> Poison class: 3 MAK-value: 30 ppm Very dangerous! Displaces oxygen from the hemoglobin bond, being 300 times higher in affinity. Leads to asphyxiation. 0.1 % in the air is already harmful, 1% toxic. Especially Dangerous due to odorless properties. First signs: headache, dizziness, tingling skin, then loss of consciousness, collapse and very weak pulse.
<b>8. Ecological Information</b> Considered poisonous to environment.

## 7.2.4. Natural Gas

For example. methane, similar to ethane, butane, propane, etc. Data in () in each case for ethane, butane, propane

<b>1. Chemical characteristics</b> Formula: CH <sub>4</sub> Form: gas, (liquid) Color, Odor: colorless, odorless (provided with odor)
<b>2. Physical Data and Safety Indications</b> Change of state: Melting point: -182°C Boiling point: -162°C Density: 0.84 kg/m <sup>3</sup> Vapor pressure: - Flash point: - Flammable temperature: 595°C Explosive limits: 5 - 15 vol.%, especially dangerous 9.4 vol.%
<b>3. Hazardous Reactions and Decomposition Products</b> Highly flammable. Forms with air a combustible mixture. Methane is lighter than air. (Propane, butane and other liquid natural gas are, however, heavier than air; therefore, they go to the ground, penetrating cellars, drains, etc.). Strong reaction with chlorine and fluoride.
<b>4. Regulations</b> Risk warning: flammable R-Phrases: 12 S-Phrases: 9-16-33
<b>5. Protective Measures, Handling</b> <b>- Personal protective equipment:</b> none <b>- Handling precautions:</b> All skin contact with liquid gas lead to freezing by "burning wounds". Avoid skin contact. <b>- Fire and Explosion Protection:</b> Avoid open sources of ignition within the range of natural gas. Do not allow methane to come in contact with chlorine or fluoride. Avoid working in areas with drains or the like if working with natural gas that is heavier than air. Electrical installations should be explosion resistant (Ex.Schutz).
<b>6. Measures in Case of Accident or Fire</b> <b>- After light gas leak:</b> Immediately remove open ignition sources. Close cylinder valve. Open window (allows circulation). Leave room, close door. Methane is a non-toxic stifling gas that causes loss of oxygen, resulting in respiratory collapse. Inform responsible persons. <b>In case the valve cannot be closed</b> , place bottle, if possible, in hood. Open window (allows air circulation). Leave room, close door. Inform responsible persons. Call Abt. S+U (Tel. 888). <b>- After heavy gas leak:</b> Consider self-protection! Immediately remove open ignition sources. If possible, close cylinder valve and open window. Leave room, close door. Inform responsible persons. Call Abt. S+U (Tel. 888) and possibly. fire dept. <b>First aid:</b> Think of self-protection when giving aid. Bring victim to fresh air, allow breathing deeply. If victim loses consciousness, contact a physician. In case of skin contact, run affected part under cold, running water. Treat like a burn. Also refer to Chapter 2.
<b>7. Toxicological Information</b> Poison class: 5, non-toxic stifling gas MAK-value: 10,000 ppm
<b>8. Ecological Information</b> none

## 7.2.5. Oxygen

<b>1. Chemical characteristics</b> Formula: O <sub>2</sub> Form: Gas Color, Odor: colorless, odorless
<b>2. Physical Data and Safety Indications</b> Change of state: Melting point: -218°C Boiling point: -182.97°C Density: 1.35 kg/m <sup>3</sup> Vapor pressure: - Flash point: - Flammable temperature: - Explosive limit: -
<b>3. Hazardous Reactions and Decomposition Products</b> Oxidations with oxygen are frequently strongly exothermic, sometimes uncontrollable (e.g., detonating gas reactions). Self-inflammable materials (e.g., alkyl metals, metal or nonmetal hydrides, some metallic powders etc.) immediately catch fire upon contact with oxygen (rd 21 - 23 vol %). Higher oxygen contents increase the inflammation risk substantially. Pure oxygen ignites organic materials (oil, fat, etc.) at room temperature, whereby some metal parts burn down. With concentrated oxygen, there is the danger of explosion.
<b>4. Regulations</b> Risk warning: oxidizing R-Phrases: 8 S-Phrases: 17-21
<b>5. Protective Measures, Handling</b> <b>- Personal protective equipment:</b> none <b>- Handling precautions:</b> Breathing air with 75% oxygen leads to feeling unwell after a while, difficulty in breathing, pulmonary edema formation possible. <b>- Fire and Explosion Protection:</b> Use only absolutely oil- and grease-free fittings with flame-resistant seals. Use these fittings exclusively for oxygen. Never use oxygen for blowing off clothes etc. Avoid contact with flammable materials.
<b>6. Measures in Case of Accident or Fire</b> <b>- After heavy gas leak:</b> Immediately remove all ignition sources, self-igniting materials, etc. Air thoroughly. <b>- Flame rebound or like</b> Immediately close cylinder valve if safe to do so. Cool bottle with water jet spray from a safe distance. If not possible, leave room immediately. (Bottle burns out completely, danger of explosion upon contact with slightly- or self-igniting materials). Inform fire dept. Evacuate area.
<b>7. Toxicological Information</b> Poison class: - MAK-value: -
<b>8. Ecological Information</b> none

## 7.2.6. SulfurHexafluoride

<b>1. Chemical characteristics</b> Formula: SF <sub>6</sub> Form: gas, liquid Color, Odor: colorless, odorless
<b>2. Physical Data and Safety Indications</b> Change of state: Melting point: -51°C Boiling point: -63.8°C Density: 6.27 kg/m <sup>3</sup> Vapor pressure: 21.08 bar Flash point: - Flammable temperature: - Explosive limit: -
<b>3. Hazardous Reactions and Decomposition Products</b> NH <sub>3</sub> Si <sub>2</sub> explodes violently upon contact with SF <sub>6</sub> . Thermal load or the use of high-voltage equipment can lead to formation of S <sub>2</sub> F <sub>10</sub> , which was used in the past as a war weapon. S <sub>2</sub> F <sub>10</sub> leads to strong acute irritation of breathing passage leading up to pulmonary edema.
<b>4. Regulations</b> Risk warning: - R-Phrases:- S-Phrases:-
<b>5. Protective Measures, Handling</b> <b>- Personal protective equipment:</b> none <b>- Handling precautions:</b> All skin contact with liquid gas lead to freezing by "burning wounds". Avoid skin contact. <b>- Fire and Explosion Protection:</b> Do not bring in contact with H <sub>6</sub> Si <sub>2</sub> .
<b>6. Measures in Case of Accident or Fire</b> <b>- After gas leak:</b> Close valve if possible. Otherwise, place bottle in hood, Open window. Leave room (stifling gas), close door. Inform responsible persons <b>- After gas leak, during or after the bottle of gas is warmed or high voltage given:</b> Leave room immediately (formation of S <sub>2</sub> F <sub>10</sub> ), close door. Evacuate area, <b>Upon contact with H<sub>6</sub>Si<sub>2</sub>:</b> Immediately interrupt reaction, if possible Otherwise leave room (danger of explosion), and evacuate area. And fire dept. Rescue only with respiratory protection. After inhalation of SF <sub>6</sub> , bring victim to fresh air, allow breathing deeply, if necessary apply artificial respiration and contact physician. After inhalation of S <sub>2</sub> F <sub>10</sub> , bring victim immediately to fresh air. Bring in for immediate treatment to emergency station Monitor afterwards! Upon skin contact, place affected skin under cold, running water. Treat like a burn. Also refer to Chapter 2.
<b>7. Toxicological Information</b> Poison class: - MAK-value: -, non-toxic stifling gas MAK-value for S <sub>2</sub> F <sub>10</sub> : 0.01 ppm
<b>8. Ecological Information</b> none

## 7.2.7. Hydrogen Sulfide

<b>1. Chemical characteristics</b> Formula: H <sub>2</sub> S Form: gas, liquid Color, Odor: colorless, smells like rotten eggs
<b>2. Physical Data and Safety Indications</b> Change of state: Melting point: -86°C Boiling point: -60°C Density: 1,45 kg/m <sup>3</sup> Vapor pressure: 18 bar Flash point: - Flammable temperature: 220 - 270°C Explosive limit: 4.3 – 45.5 Vol.%
<b>3. Hazardous Reactions and Decomposition Products</b> Reacts with all oxidizing agents violently under ignition or explosion. As with most metallic oxides, it reacts under ignition with nitric acid or oxygen. Violent reactions with halogens (except iodine). Caution with unintentional formation of hydrogen sulfide (e.g., by reaction of sulfide and acid). Forms sulfur dioxide when burned.
<b>4. Regulations</b> Risk warning: highly flammable, very toxic R-Phrases: 13-26 S-Phrases: 7/9-25-45
<b>5. Protective Measures, Handling</b> <b>- Personal protective equipment:</b> B-Filter with the use of gas masks (gray). Respiratory protection recommended by longer exposure (Perception threshold!). Wear eye protection, gloves. <b>- Handling precautions:</b> Avoid contact with skin and eyes (skin protection). Do not inhale. All skin contact with liquid gas lead to freezing by "burning wounds". <b>- Fire and Explosion Protection:</b> Do not bring in contact with oxidizing agents, metal oxides, nitric acid and oxygen. Avoid contact with halogens. Electrical installations should be explosion resistant (Ex.Schutz).
<b>6. Measures in Case of Accident or Fire</b> <b>- After gas leak:</b> Leave room immediately! Evacuate area, alert Fire dept. <b>- With violent reaction process:</b> If possible, immediately interrupt reaction. (Fire extinguisher: carbon dioxide, water vapor). Otherwise, leave room immediately, evacuate area (danger of explosion). Inform fire dept <b>- First aid:</b> Rescue only with full respiratory protection and safety rope. Bring victim immediately to fresh air. If necessary, give artificial respiration with oxygen. Contact a physician. Upon skin contact, run cold water over affected part. Treat like burn. Also refer to Chapter 2.
<b>7. Toxicological Information</b> Poison class: 2 MAK-value: 10 ppm Odors starting at 150 ppm no longer perceptible!
<b>8. Ecological Information</b> Hazardous to waters.

## 7.2.8. Nitrogen

An example of extremely cold gas.

<b>1. Chemical characteristics</b> Formula: N <sub>2</sub> Form: Gas, liquid Color, Odor: colorless, odorless
<b>2. Physical Data and Safety Indications</b> Change of state: Melting point: -210°C Boiling point: -195.8°C Density: 1.185 kg/m <sup>3</sup> Vapor pressure: - Flash point: - Flammable temperature: - Explosive limit: -
<b>3. Hazardous Reactions and Decomposition Products</b> With open use, oxygen is condensed by the surrounding air through heat exchange, whereby gradually an enrichment of strongly oxidizing liquid oxygen takes place. The same happens in the bottle after longer standing.
<b>4. Regulations</b> Risk warning: - R-Phrases:- S-Phrases:-
<b>5. Protective Measures, Handling</b> <b>- Personal protective equipment:</b> Respiratory protection recommended for long exposure. Wear gloves, glasses. <b>- Handling precautions:</b> Nitrogen hinders up to 88 % of breathing through oxygenation. All skin contact with liquid gas lead to freezing by "burning wounds". Avoid skin contact. <b>- Fire and Explosion Protection:</b> With open use or other danger of contact with easily flammable material, only use freshly obtained nitrogen. Use caution when using small containers. (Expansion around factor 500 to 1000 with evaporation).
<b>6. Measures in Case of Accident or Fire</b> <b>- by gas escape:</b> Avoid skin contact. If possible, close valve. Otherwise, place bottle in hood, Open window. Leave room (stifling gas), close door. Alert Abt. S+U (Tel. 888). <b>- First aid:</b> Rescue only with respiratory protection. Bring victim immediately to fresh air. If necessary, give artificial respiration and contact a physician. Upon skin contact, run cold water on affected part. Treat Like burn. Also refer to Chapter 2.
<b>7. Toxicological Information</b> Poison class: - MAK-value: -
<b>8. Ecological Information</b> none

## 7.2.9. Nitrogen Dioxide

(Applies generally to nitrogen oxide)

<b>1. Chemical characteristics</b> Formula: NO <sub>2</sub> Form: Gas, liquid Color, Odor: colorless, odorless
<b>2. Physical Data and Safety Indications</b> Change of state: Melting point: -11.3°C Boiling point: 21°C Density: 1.95 kg/m <sup>3</sup> Vapor pressure: - Flash point: - Flammable temperature: - Explosive limit: -
<b>3. Hazardous Reactions and Decomposition Products</b> Reacts with organic materials (oil, fat, etc.) already at room temp. Under ignition or explosion. , Strongly corrosive upon contact with hydrogen compounds or water formation of nitric acid.
<b>4. Regulations</b> Risk warning: oxidizing, irritant, toxic R-Phrases: 26-37 S-Phrases: 7/9-26-45
<b>5. Protective Measures, Handling</b> <b>- Personal protective equipment:</b> NO-Filter in gas mask (blue). Respiratory protection recommended for longer exposure. Wear gloves, glasses. <b>- Handling precautions:</b> Irritates eyes and mucous membranes. All skin contact with liquid gas lead to freezing by "burning wounds". Avoid skin contact. <b>- Fire and Explosion Protection:</b> Use only absolutely oil- and fat-free fittings with fire-resistant seals.
<b>6. Measures in Case of Accident or Fire</b> <b>- After gas leak:</b> Leave room immediately (danger of poisoning, explosion!). evacuate area, inform fire dept. (Tel 0-118) and Abt. S + U (Tel. 888). <b>- After backfire or similar:</b> If possible, immediately close cylinder valve. Fire extinguisher: use Fire Class C. Otherwise, leave room, and evacuate area. Inform fire dept <b>- First aid:</b> Rescue only with full respiratory protection and safety rope. Bring victim immediately to fresh air, keep absolutely still. If necessary give artificial respiration. Treat further through physician. (danger of pulmonary edema) Upon skin contact, rinse affected area with cold water. Treat like burn. Also refer to Chapter2.
<b>7. Toxicological Information</b> Poison class: 2 MAK-value: 3 ppm Poisoning symptoms can appears only after several hours!
<b>8. Ecological Information</b> none

## 7.2.10. Hydrogen

<b>1. Chemical characteristics</b> Formula: H <sub>2</sub> Form: Gas Color, Odor: colorless, odorless
<b>2. Physical Data and Safety Indications</b> Change of state: Melting point: -259°C Boiling point: -253°C Density: 0.085 kg/m <sup>3</sup> Vapor pressure: - Flash point: -240°C Flammable temperature: 560°C Explosive limit: 4.0 – 75.6 Vol.%.
<b>3. Hazardous Reactions and Decomposition Products</b> Presence from far distance of hydrogen air (or oxygen) mixtures is combustible (detonating gas reaction!). Burns with very hot flame (up to 3000°C). Very violent reaction leading up to explosion with oxygen compounds, metal and nonmetallic oxides. Sunlight already induces combustion of formed chlorine from chlorine-hydrogen gas mixture. Possible spontaneous combustion upon discharge under high pressure.
<b>4. Regulations</b> Risk warning: flammable R-Phrases: 12 S-Phrases: 7/9
<b>5. Protective Measures, Handling</b> - <b>Personal protective equipment:</b> none - <b>Handling precautions:</b> none - <b>Fire and Explosion Protection:</b> Avoid all ignition sources (also hot surfaces) in the area. Prevent formation of oxyhydrogen mixtures und discharge into lab atmosphere. Do not bring in contact with oxygen compounds, metal- or nonmetal oxides. Do not try to detect leaks with flame. Electrical installations should be explosion resistant (Ex.Schutz).
<b>6. Measures in Case of Accident or Fire</b> - <b>by gasescape:</b> Spontaneous combustion highly possible. (Be careful: almost invisible flame, approach only with wind coming from behind). If possible, close cylinder valve. If valve cannot be closed, aerate and from a safe distance keep area cool with water jet spray. Inform fire dept. Evacuate area. - <b>Firstaid:</b> Bring victims to fresh air, allow to breathe deeply. If necessary apply artificial respiration, contact physician. Also refer to Chapter 2.
<b>7. Toxicological Information</b> Poison class: -, non-toxic stifling gas MAK-value: -
<b>8. Ecological Information</b> none



## 8. WORKING WITH LASERS

The term “laser” is the abbreviation of “**L**ight **A**mplification by **S**timulated **E**mission of **R**adiation“. Laser devices serve to amplify light of a specific wavelength such as the production of tightly bundled light emissions of same wavelength. For the production of the laser light, a medium (e.g., a ruby crystal with a solid state laser) is shifted into an excited state, from which it returns with light emission to its original condition. The emitted light is strengthened and bundled.

Lasers are used at ETHZ, for example, for material processing and testing and for structural and electrical analysis. Moreover, you encounter weaker lasers also in laser printers, CD players or laser pointers.

Lasers are divided according to the strength of its power spectrum (performance and radiation emissions) into **4 classes**:

**Class 1:** Harmless to the human eye  
< 1 mW  
e.g.: laser pointer

**Class 2:** Harmless to the human eye with brief exposure due to blinking reflex (until 0.25 seconds)  
Until 50mW  
e.g.: laser printer

**Class3A:** Harmless to the human eye with exposure time of 0.25 seconds, dangerous for the human eye when using optical instruments which make the radiated light diameter smaller.  
Until 500 mW  
e.g.: technical applications, researched.

**Class3B:** Dangerous to the human eye and in some cases, to the human skin e.g.,:  
technical applications, researched.

**Class 4:** Very dangerous to the human eye and dangerous to the human skin e.g.,:  
> 500mW  
technical applications, research etc.

Thus, at ETHZ, all laser classes are represented. The following, however, particularly addresses the danger of lasers belonging to classes 3 and 4.

The direct danger to the human eye by lasers arises as a result of the extremely high power intensity of the laser beam (see below). While a conventional source of light radiates into the full area, the laser beam is bundled on a very small solid angle.

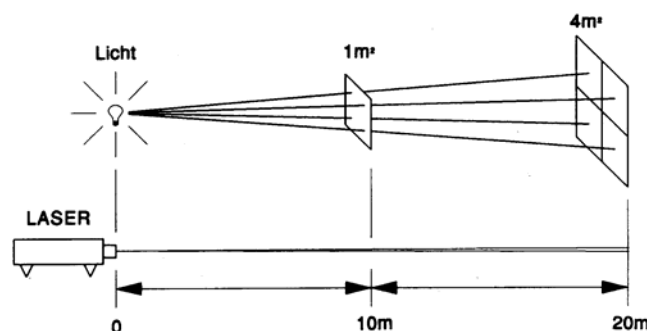


Fig. 9.1: Comparison of the radiation angle of conventional sources of light and lasers

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Due to their high power intensity, reflected rays can also be dangerous. Thereby, the weight of the damage depends on:

- the strength of the radiation,
- the wavelength used,
- the impact time of the laser light, and
- The absorption behaviour of the illuminated materials.

The wavelength is crucial for the damaged region of the eye. Radiation within the visible and near the limits of the infrared range (400 to 1400 Nm) can endanger the retina. UV and far infrared radiation (100 to 400 or over 2500 Nm), however, damages the lens and the cornea.

The **largest danger for the eye** comes from **lasers with high power intensity** and **lasers with wavelengths between 400 and 1400 Nm** . On one hand, lights of these wavelengths, which reach the retina, are focused further by the refractive eye media. On the other hand, lights with wavelengths over 700 Nm are not visible to the human eye, which increases the probability of an accident. High intensity radiation causes tissue vaporization, in this case, retina coagulation. Pulsed lasers are particularly dangerous in this way because of their capacity to produce from and up to several TW (=  $10^{12}$  Watt) in a short time. The effects of retina injury depend on the location of the damage. Particularly serious damage arises upon viewing directly into the beam since in this case; light is focused on the “yellow spot,” the part of the retina where one uses to see sharply. The further the damage is from the yellow spot, the lesser the impairment to the vision.

Laser radiation on the **human skin** has, on the one hand, photochemical and, on the other hand, thermal effects. Skin injuries caused by lasers are reversible, as a rule. Usually only the epidermis is damaged. Light with wavelengths of 400 to 1400 Nm can penetrate down to the subcutaneous tissue; therefore, also mutagenic effects cannot be excluded.

However, **indirect dangers** can also result from lasers. The efficiency of energy conversion is very small, which is why most devices are operated with high power. Different components of the laser, e.g., the stimulated medium or the optical components, can be toxic. With the treatment of materials (e.g., when cutting metals) toxic materials can, likewise, develop. Not to be forgotten are also the constant danger of fire and explosion, which can arise as a result of the possible ignition of liquids and gases upon irradiation of the laser.

Lasers are, thus, not completely harmless devices. The following general behavioral rules help you to avoid risks and accidents with lasers. Chapter 9.2 describes correct behavior in case of accidents with lasers. For general questions regarding first aid, refer to Chapter 2.

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## 8.1 General Behavior

- Never** work **alone** with lasers (exception: permanently installed machines).
- When working with lasers, **consistently** wear **laser eye protectors** for type of laser. Goggles are located at the entrance of the room.
- Perform adjustments only when wearing the appropriate **laser adjusting glasses**
- Never look directly at a laser beam.**
- If possible, always work with **sufficient lighting**. The pupils close with brightness and, thus, the probability of an accident so decreases.
- When operating lasers **do not wear watches, rings, eyeglasses** or reflective objects that could reflect (deflect) the laser.
- When laser work is done in the dark, keeping **order in the laboratory to prevent** accidents (stumbling, etc.).
- Equipment assembly:**
  - The laser beam may run only above or below **eye level**. If the laser apparatus absolutely needs to be at eye level, shields must be placed which block the path of the rays.
  - Never direct a laser beam toward the entrance of a room, a window (reflection) or chemicals (fire and danger of explosion).
  - Rule of thumb: **No laser beam leaves the table boundaries uncontrolled**. Use non-scattering, non-reflecting protection shields and light-absorbing covers for the protection of visitors.
  - Should a laser beam have to leave the table boundaries, it should only be directed at **non-reflective wall elements**.
- Pay special attention the **warning light** located at the entrance of the laboratory. Also use them yourself.

The following apply:

**Red: Do not enter.** Knock and wait.

(Possible danger to visitors due to work with high energy laser beams, by measurements, recordings, calibrations, etc.)

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## 8.2 Behavior in Case of Accidents

If a laser beam has caused an injury, it is **not possible to minimize the damage through immediate first aid!** More important than the immediate seeking of aid in an emergency station is the prevention of further accidents. Therefore, heed the following instructions:

- Remain calm, do not immediately run away.
- Switch off laser .Likewise, switch off the possible sources of danger
- Inform responsible persons.
- Only now, with accompaniment, should you seek help at the ophthalmic.
- after the examination, inform responsible persons, as well as the Dept. about the extent of the damage.

### Burning of the skin:

- Soak affected skin immediately in cold water until the pain is relieved.
- Proceed as described above.
- Burns caused by should be treated in each case by a physician.
- After the examination, inform responsible persons, as well as the Dept. about the extent of the damage.

## 9. WORKING AT THE MACHINESHOP

### 9.1 General conduct

- Wear **safety glasses** when in the workshop.
- for the protection of clothes and to prevent loose articles of clothing from being seized by a machine, wearing **overcoats or dresses** is recommended.
- Reduce **arm, throat, and finger jewelry** to a minimum.
- Hearing damage is irreversible! Therefore, **protect your hearing** when you are within the range of loud machines (also refer to Chapter 1.2.4). Consistently wear hearing protection at noisy workspaces because even short noise events can lead to hearing damage. Whistling or humming in the ears in calm environ mentare already indications of as light damage.
- Close **drawers** of toolboxes, etc., as soon as you take out what you danger of injury for you and others).
- Always immediately remove shavings, material remains, oil or water spills That are lying about on the floor (danger of slipping and stumbling).
- Interrupt the current supply** (cableorfuse)**before each manipulation** of an equipment or a machine. If the fuse is removed, attach a **warning sign** on the fuse box so that no one in advertently replaces the fuse to early.

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### 10.1.1 Sharp Cutting Tools

- When working with sharp cutting tools, **proper cutting technique** is of most importance:
  1. The tips of the forefinger and middle finger must be at the same height as the tip of the thumb
  2. The fingers should be bent when holding a work piece, not extended out.

If possible, blades should not be pulled directly alongside the fingertips but some centimeters away. If

### 10.1.2 Compressed Air

Compressed air is often used for blowing off work pieces or for cleaning the working place of splinters and other dirt.

- Always wear eye protection when working with compressed air (danger of injuries from flying particles).
- Never direct compressed air to yourself or others. It can result in serious injury such as hearing loss or small wounds enlarging to involve of large parts of the body.
- Vacuum the machines before they are cleaned with compressed air.
- Use caution when cleaning off metal shavings coming from stainless steel.  
Do not touch with bare hands!

### 10.1.3 Welding, Brazing

- Always wear special **welding eye shields** when doing welding or brazing. Otherwise, there is the danger of blinding or eye inflammation by the strong light radiation of the flame and the welded joint (high amounts of UV).
- Since glowing metal sprays or drip is inevitable when gas welding, an overcoat must be worn. Pay attention that it is oil- and grease-free. Avoid wearing easily flammable textiles (artificial fibers).
- Make sure that the **welding or brazing area is clear of oil or solvent containers**. Do not work on areas that are flammable.
- Never oil bolt connections** of welding equipment's.
- Do not lay a burner on to flammable pieces such as rags, etc. Instead of light on its designated space.
- Hoses** of a burner apparatus may not be **laid out** in such a way that you could stumble over them.
- Make sure that **the hoses are in perfect condition**. Immediately report tears and other damages to responsible persons (danger of injury and explosion)

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### Procedures for start of welding:

1. Open the valves of the gas bottles slowly and without jerking (only by hand!). Examine afterwards whether the bolt connection between bottle safety valve and pressure release valve is tight (e.g., with soapy water, never with open flame). Leakages are to be repaired immediately.
2. Open fuel bottle valve (could be necessary to leave in square socket wrench).
3. Set operating pressure, check the operating pressure manometer (indicated on burner insert or in the manual). Do not set too high, danger of exploding hose!
4. Open oxygen valve.
5. Open combustible gas regulator, ignite gas mixture, and regulate flame.

### Procedures for end of welding:

1. Close combustible gas regulator (flame expires).
2. Empty gas hoses (close tank valve, open fuel valve, open and close oxygen valve; never open both valves at the same time, danger of explosion when restarting).
3. Relieve diaphragms in the pressure reduction valves with the head adjusting screws.

#### 10.1.4 Machines with Rotating Parts

When working with machines with rotating parts, wear **tight-fitting**, belt-less **overalls**. Button the sleeves or push them inwards and up.

- **Long hair** must be worn so that it does not, under any circumstance, come into contact with rotating machinery (e.g. Hats)
- **Do not wear gloves**. They could get caught on the machine.
- Never support yourself with the hands on machine parts or workpieces. never grab a running **machine with your hand** (e.g., use a rag on a circulating spindle).
- Never work without a protective cover, safety net, on unsecured lathe dogs.
- Remove the **lathe chuckkey** before you start the machine (danger of injury from the flying key).
- Check on the **secure attachment of work pieces** (use vice, etc).
- Avoid direct skin contact with cooling agents (boric acid solution, dilute oil, cutting oil, etc.; use skin protection ointments).
- Use gloves when **removing shavings**. Use special caution with shavings for stainless steel (danger of hand injuries).

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## **Types of waste and their management**

The following information is commonly required by treatment disposal facilities before they will consider handling unknown materials:

- physical description,
- water reactivity,
- water solubility,
- pH and possibly also neutralization information,
- ignitability (flammability),
- presence of oxidizer,
- presence of sulfides or cyanides,
- presence of halogens,
- presence of radioactive materials,
- presence of biohazardous materials, and
- presence of toxic constituents.

### **1. Peroxide forming chemicals**

Peroxide-forming chemicals are a class of materials that have the ability to form shock-sensitive and explosive peroxide crystals. When triggered by friction or shock the peroxides will explode. Peroxide forming chemicals include solids, liquids and gases. These chemicals may also be flammable or reactive so other SOPs will likely apply to their use in the laboratory.

Peroxide formers fall into three classes according to its expiry

Class A peroxide forming chemicals can form explosive levels of peroxides while sitting on the shelf. Disposed of through the chemical waste system three months after opening or at the expiration date on the container if unopened

Class B peroxide formers are only a hazard if the peroxides are concentrated, which may happen upon evaporation or distillation of the solvent. Materials should be disposed of 1 year after opening or at the expiration date on the container if unopened.

Class C peroxide formers may auto-polymerize as a result of peroxide formation. Materials should be disposed of 1 year after opening or at the expiration date on the container if unopened.

Isopropyl ether	Sodium amide	Class A
Butadiene	Tetrafluoroethylene	
Chlorobutadiene (chloroprene, liquid monomer)	Divinyl acetylene	
Potassium amide	Vinylidene chloride	
Benzyl alcohol & Other Secondary Alcohols	Decahydro naphthalene (decalin)	Class B
2-Butanol Dioxanes	Ethers	
Chlorofluoroethylene	THF	
Diethyl ether	4-Methyl-2-pentanol	
Butadiene	Vinylidene Chloride	Class C
Chlorobutadiene	Vinyl Chloride	
Chloroprene	Vinyl Pyridine	
Vinyl Acetate	Styrene	
Chlorotrifluoroethylene	Vinyl Acetylene	

## 2. Waste oil

- Waste oil should be collected in a proper waste container.
- If the oil are contaminated with metal or other specific chemicals then please include this information on the chemical waste label.

## 3. Gas producing waste streams

- Several laboratory chemical compounds produce gas, thus they must be carefully handled to avoid over pressurizing or exploding containers.
- **Aquaregia** is a mixture of concentrated nitric acid (HNO<sub>3</sub>) & hydrochloric acid (HCl)
- **Piranha solution** is a mixture of sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) & hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>).
- All gas-producing wastes must be stored in poly containers that have special vented caps.
- Glass containers must never be used for any gas-producing waste streams due to the risk of explosion from over pressurization.
- These waste streams should also be stored in a special reactive waste bucket.

## 4. Compressed gas cylinders

- In general, the vendor who provides and refills compressed gas cylinders for the laboratory is the operator of these cylinders. When a compressed gas cylinder is empty or no longer needed, it must be returned to the vendor.
- While being stored or in use, compressed gas cylinders must be firmly affixed to benches



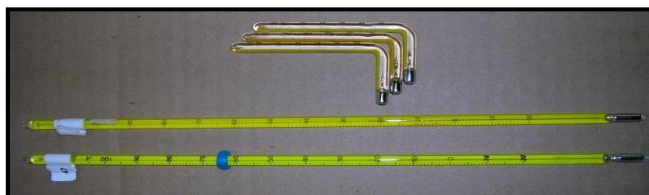
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or walls with appropriate strapping. The contents of all compressed gas cylinders must be clearly labeled.



## 5. Mercury containing items

- Mercury containing items such as thermometers, thermostat switches and manometers must be collected for proper disposal and not place in the regular trash.



Thermometer

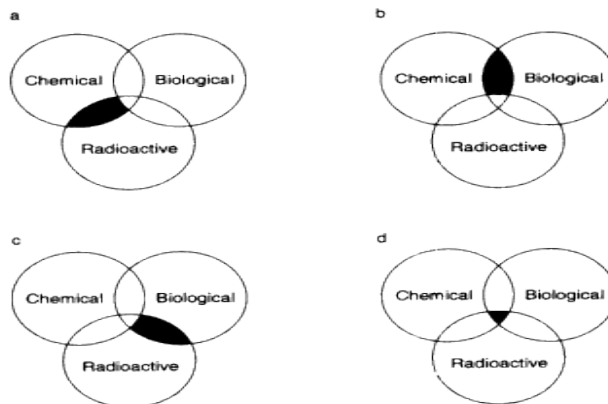
## 6. Pure & Mixed waste

- Pure chemicals are any partially used or unused chemical with a single chemical constituent. Aqueous solutions of pure chemicals are also considered pure chemicals. Compressed gases are considered pure chemicals.
- Mixed chemicals are any mixture of two or more chemicals not including water. Mixed chemicals should contain like states of either liquid or solid chemicals.

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Some precipitate due to mixing of chemicals is allowable.

- There are few types of mixed waste shown below



(a) Chemical-radioactive waste, or 'mixed waste," (b) Chemical-biological waste, (c) Radioactive biological waste (d) chemical-radioactive biological waste.

A mixed waste is a material that is both a chemical hazardous waste and is also radioactive. These types of waste can be extremely expensive to dispose of. Discuss and follow general guideline of institute for disposal purpose.

## 7. Empty containers

- All empty chemical containers must be “triple rinsed” before disposal except bio hazardous material.
- Odoriferous materials should be placed into a bag and stored inside a fume hood until institute collects them for disposal.

While institute collects the hazardous materials please ensure that:

- The paperwork is completed accurately and located with the waste. All chemical containers must have a properly labelled.
- The containers’ exterior is free of contamination.
- The containers are not overfilled.



19-Liter carboy



1-Liter bottle

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## 8. Disposal of chemically contaminated needles & syringes

Dispose of all chemically contaminated needles, syringes and razor blades as infectious waste by placing them inside a proper sharps container.

## 9. Bio-hazard and Bio-waste

- Biohazard waste includes biohazard-contaminated items such as absorbent materials (e.g. paper towels), gloves, and/or plastics (e.g. micro centrifuge tubes, Petri plates and tissue culture flasks containing small volumes of biohazards).
- Place biohazards in the bag; do not fill more than 2/3 the capacity of the bag. Secure the neck of the bag with tape allowing an opening for steam to penetrate the bag.
- Transport the bag in a tray on a cart to the nearest autoclave. Once autoclaved, place the autoclave bag inside a garbage bag for disposal with regular garbage.



Bio-hazard waste container

## 10. Batteries

- Collects all types of batteries (lead-acid, alkaline, lithium, nickel-Metal hydride, etc.) For recycling or disposal.
- For laboratories, workshops and offices a single use container is the best choice for collecting batteries.
- Terminals on 9V batteries need to be taped to prevent an electrical short that could cause a fire.



## 11. Radioactive waste

- The Radioisotope Permit Holder and Nuclear Energy Workers must dispose of all radioactive waste generated according to the procedures set out by the University.
- Document the disposal of radioactive materials on the radioactive inventory sheet as wastes are placed in the radioactive waste containers
- Radioactive Solid Waste Container  
Radioactive solid waste containers issued by university to laboratories for radioactive solid waste excluding animal carcasses. The radioactive solid waste container includes a white plastic liner with a black garbage bag. When full the garbage bag is closed with tape that does not display radioactive warnings or symbols. Take care to avoid overfilling the can. The lid must fit securely on the top of the can.



Radioactive Solid Waste Container

# 11. LABORATORY-SCALE TREATMENT OF SURPLUS & WASTE CHEMICALS

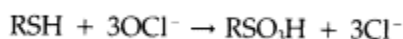
## 1. Acids and Bases

- Neutralization of acids and bases (corrosives) is generally exempt from a RCRA treatment permit. However, because the products of the reaction are often disposed of in the sanitary sewer, it is important to ensure that hazardous waste such as toxic metal ions is not a part of the effluent.
- In most laboratories, both waste acids and waste bases are generated, and so it is most economical to collect them separately and then neutralize one with the other. If additional acid or base is required, sulfuric or hydrochloric acid and sodium or magnesium hydroxide, respectively, can be used.
- If the acid or base is highly concentrated, it is prudent to first dilute it with cold water (adding the acid or base to the water) to a concentration below 10%. Then the acid and base are mixed, and the additional water is slowly added when necessary to cool and dilute the neutralized product. The concentration of neutral salts Bottom of Form disposed of in the sanitary sewer should generally be below 1%.

## 2. Organic Chemicals

### Thiols and Sulfides

- Small quantities of thiols (mercaptans) and sulfides can be destroyed by oxidation to a sulfonic acid with sodium hypochlorite. If other groups that can be oxidized by hypochlorite are also present, the quantity of this reagent used must be increased accordingly.
- Procedure for oxidizing 0.1 mol of a liquid thiol:

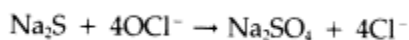


- Five hundred milliliters (0.4 mol, 25% excess) of commercial hypochlorite laundry bleach (5.25% sodium hypochlorite) is poured into a 5-L three-necked flask located in a fume hood. The flask is equipped with a stirrer, thermometer, and dropping funnel. The thiol (0.1 mol) is added dropwise to the stirred hypochlorite solution, initially at room temperature. A solid thiol can be added gradually through a neck of the flask or can be dissolved in tetrahydrofuran or other appropriate nonoxidizable solvent and the solution added to the hypochlorite. (The use of tetrahydrofuran introduces a flammable liquid that could alter the final disposal method.) Traces of thiol can be rinsed from the reagent bottle and dropping funnel with additional hypochlorite solution. Oxidation, accompanied by a rise in temperature and dissolution of the thiol, usually starts after a small amount of the thiol has been added. If the reaction has not started spontaneously after about 10% of the thiol has been added, addition is stopped and the mixture warmed to about 50 °C to initiate this reaction. Addition is resumed only after it is clear that oxidation is occurring. The

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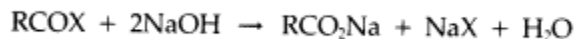
temperature is maintained at 45 to 50 °C by adjusting the rate of addition and using an ice bath for cooling if necessary. Addition requires about 15 minutes. If the pH drops below 6 because of generation of the sulfonic acid, it may be necessary to add some sodium hydroxide or additional bleach because hypochlorite is destroyed under acidic conditions. Stirring is continued for 2 hours while the temperature gradually falls to room temperature. The mixture should be a clear solution, perhaps containing traces of oily by-products. The reaction mixture can usually be flushed down the drain with excess water. The unreacted laundry bleach need not be decomposed.

- Because sodium hypochlorite solutions deteriorate on storage, it is advisable to have relatively fresh material available. A 5.25% solution of sodium hypochlorite has 25 g of active chlorine per liter. If determination of the active hypochlorite content is justified, it can be accomplished as follows. Ten milliliters of the sodium hypochlorite solution is diluted to 100.0 mL, and then 10.0 mL of this diluted reagent is added to a solution of 1 g of potassium iodide and 12.5 mL of 2 M acetic acid in 50 mL of distilled water. Using a starch solution as indicator, titrate the solution with 0.1 N sodium thiosulfate. One milliliter of titrant corresponds to 3.5 mg of active chlorine. A 5.25% solution of sodium hypochlorite requires approximately 7 mL of titrant.
- Calcium hypochlorite may be used as an alternative to sodium hypochlorite and requires a smaller volume of liquid. For 0.1 mol of thiol, 42 g (25% excess) of 65% calcium hypochlorite (technical grade) is stirred into 200 mL of water at room temperature. The hypochlorite soon dissolves, and the thiol is then added as in the above procedure.
- Laboratory glassware, hands, and clothing contaminated with thiols can be deodorized by a solution of Diaperene<sup>®</sup>, a tetraalkylammonium salt used to deodorize containers in which soiled diapers have been washed.
- Small amounts of sulfides, RSR', can be oxidized to sulfones (RSO<sub>2</sub> R') to eliminate their disagreeable odors. The hypochlorite procedure used for thiols can be employed for this purpose, although the resulting sulfones are often water-insoluble and may have to be separated from the reaction mixture by filtration.
- Small amounts of the inorganic sulfides, sodium sulfide or potassium sulfide, can be destroyed in aqueous solution by sodium or calcium hypochlorite using the procedure described for oxidizing thiols.



### **Acyl Halides and Anhydrides**

- Acyl halides, sulfonyl halides, and anhydrides react readily with water, alcohols, and amines. They should never be allowed to come into contact with waste that contains such substances. Most compounds in this class can be hydrolyzed to water-soluble products of low toxicity.
- Procedure for hydrolyzing 0.5 mol of RCOX, RSO<sub>2</sub>X, or (RCO)<sub>2</sub>O:



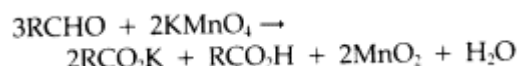
A 1-L three-necked flask equipped with a stirrer, dropping funnel, and thermometer is placed on a steam bath in a hood, and 600 mL of 2.5 M aqueous sodium hydroxide (1.5 mol, 50% excess) are poured into the flask. A few milliliters of the acid derivative are added drop wise

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with stirring. If the derivative is a solid, it can be added in small portions through a neck of the flask. If reaction occurs, as indicated by a rise in temperature and dissolution of the acid derivative, addition is continued at such a rate that the temperature does not rise above 45 °C. If the reaction is sluggish, as may be the case with less soluble compounds such as p-toluenesulfonyl chloride, the mixture is heated before adding any more acid derivative. When the initial added material has dissolved, the remainder is added drop wise. As soon as a clear solution is obtained, the mixture is cooled to room temperature, neutralized to about pH 7 with dilute hydrochloric or sulfuric acid, and washed down the drain with excess water.

## Aldehydes

- Many aldehydes are respiratory irritants, and some, such as formaldehyde and acrolein, are quite toxic. There is sometimes merit in oxidation of aldehydes to the corresponding carboxylic acids, which are usually less toxic and less volatile.
- Procedure for permanganate oxidation of 0.1 mol of aldehyde:



- A mixture of 100 mL of water and 0.1 mol of aldehyde is stirred in a 1-L round-bottomed flask equipped with a thermometer, dropping funnel, stirrer, steam bath, and, if the aldehyde boils below 100 °C, a condenser. Approximately 30 mL of a solution of 12.6 g (0.08 mol, 20% excess) of potassium permanganate in 250 mL of water is added over a period of 10 minutes. If the temperature rises above 45 °C, the solution should be cooled. If this addition is not accompanied by a rise in temperature and loss of the purple permanganate color, the mixture is heated by the steam bath until a temperature is reached at which the color is discharged. The rest of the permanganate solution is added slowly at within 10 °C of this temperature. The temperature is then raised to 70 to 80 °C, and stirring continued for 1 hour or until the purple color has disappeared, whichever occurs first. The mixture is cooled to room temperature and acidified with 6 N sulfuric acid. (**CAUTION: Do not add concentrated sulfuric acid to permanganate solution because explosive manganese oxide (Mn<sub>2</sub>O<sub>7</sub>) may precipitate.**) Enough solid sodium hydrogen sulfite (at least 8.3 g, 0.08 mol) is added with stirring at 20 to 40 °C to reduce all the manganese, as indicated by loss of purple color and dissolution of the solid manganese dioxide. The mixture is washed down the drain with a large volume of water.
- If the aldehyde contains a carbon-carbon double bond, as in the case of the highly toxic acrolein, 4 mol (20% excess) of permanganate per mol of aldehyde is required to oxidize the alkene bond and the aldehyde group.
- Formaldehyde is oxidized conveniently to formic acid and carbon dioxide by sodium hypochlorite. Thus 10 mL of formalin (37% formaldehyde) in 100 mL of water is stirred into 250 mL of hypochlorite laundry bleach (5.25% NaOCl) at room temperature and allowed to stand for 20 minutes before being flushed down the drain. This procedure is not recommended for other aliphatic aldehydes because it leads to chloro acids, which are more toxic and less biodegradable than corresponding unchlorinated acids.

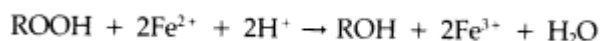
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## Amines

- Acidified potassium permanganate efficiently degrades aromatic amines. Diazotization followed by hypophosphorus acid protonation is a method for deamination of aromatic amines, but the procedure is more complex than oxidation.
- Procedure for permanganate oxidation of 0.01 mol of aromatic amine:
- A solution of 0.01 mol of aromatic amine in 3 L of 1.7 N sulfuric acid is prepared in a 5-L flask; 1 L of 0.2 M potassium permanganate is added, and the solution allowed to stand at room temperature for 8 hours. Excess permanganate is reduced by slow addition of solid sodium hydrogen sulfite until the purple color disappears. The mixture is then flushed down the drain.

## Organic Peroxides and Hydroperoxides

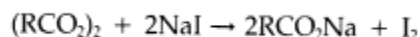
- **(CAUTION: Peroxides are particularly dangerous. These procedures should be carried out only by knowledgeable laboratory workers.)** Peroxides can be removed from a solvent by passing it through a column of basic activated alumina, by treating it with indicating Molecular Sieves<sup>®</sup>, or by reduction with ferrous sulfate. Although these procedures remove hydroperoxides, which are the principal hazardous contaminants of peroxide-forming solvents, they do not remove dialkyl peroxides, which may also be present in low concentrations. Commonly used peroxide reagents, such as acetyl peroxide, benzoyl peroxide,
- t-butyl hydroperoxide, and di-t-butyl peroxide, are less dangerous than the adventitious peroxides formed in solvents.
- Removal of peroxides with alumina:
- A 2 x 33 cm column filled with 80 g of 80-mesh basic activated alumina is usually sufficient to remove all peroxides from 100 to 400 mL of solvent, whether water-soluble or water-insoluble. After passage through the column, the solvent should be tested for peroxide content. Peroxides formed by air oxidation are usually decomposed by the alumina, not merely absorbed on it. However, for safety it is best to slurry the wet alumina with a dilute acidic solution of ferrous sulfate before it is discarded.
- Removal of peroxides with Molecular Sieves<sup>®</sup>:
- Reflux 100 mL of the solvent with 5 g of 4- to 8-mesh indicating activated 4A Molecular Sieves<sup>®</sup> for several hours under nitrogen. The sieves are separated from the solvent and require no further treatment because the peroxides are destroyed during their interaction with the sieves.
- Removal of peroxides with ferrous sulfate:



- A solution of 6 g of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , 6 mL of concentrated sulfuric acid, and 11 mL of water is stirred with 1 L of water-insoluble solvent until the solvent no longer gives a positive test for peroxides. Usually only a few minutes are required.
- Diacyl peroxides can be destroyed by this reagent as well as by aqueous sodium hydrogen sulfite, sodium hydroxide, or ammonia. However, diacyl peroxides with low solubility in water, such as dibenzoyl peroxide, react very slowly. A better reagent is a solution of sodium iodide or potassium iodide in glacial acetic acid.



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- Procedure for destruction of diacyl peroxides:



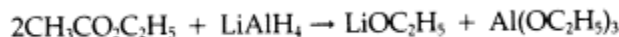
- For 0.01 mol of diacyl peroxide, 0.022 mol (10% excess) of sodium or potassium iodide is dissolved in 70 mL of glacial acetic acid, and the peroxide added gradually with stirring at room temperature. The solution is rapidly darkened by the formation of iodine. After a minimum of 30 minutes, the solution is washed down the drain with a large excess of water.
- Most dialkyl peroxides (ROOR) do not react readily at room temperature with ferrous sulfate, iodide, ammonia, or the other reagents mentioned above. However, these peroxides can be destroyed by a modification of the iodide procedure.
- Procedure for destruction of dialkyl peroxides:
- One milliliter of 36% (w/v) hydrochloric acid is added to the above acetic acid/potassium iodide solution as an accelerator, followed by 0.01 mol of the dialkyl peroxide. The solution is heated to 90 to 100 °C on a steam bath over the course of 30 minutes and held at that temperature for 5 hours.

### 3. Inorganic Chemicals

#### Metal Hydrides

- Most metal hydrides react violently with water with the evolution of hydrogen, which can form an explosive mixture with air. Some, such as lithium aluminum hydride, potassium hydride, and sodium hydride, are pyrophoric. Most can be decomposed by gradual addition of (in order of decreasing reactivity) methyl alcohol, ethyl alcohol, n-butyl alcohol, or t-butyl alcohol to a stirred, ice-cooled solution or suspension of the hydride in an inert liquid, such as diethyl ether, tetrahydrofuran, or toluene, under nitrogen in a three-necked flask. Although these procedures reduce the hazard and should be a part of any experimental procedure that uses reactive metal hydrides, the products from such deactivation may be hazardous waste that must be treated as such on disposal.
- Hydrides commonly used in laboratories are lithium aluminum hydride, potassium hydride, sodium hydride, sodium borohydride, and calcium hydride. The following methods for their disposal demonstrate that the reactivity of metal hydrides varies considerably. Most hydrides can be decomposed safely by one of the four methods, but the properties of a given hydride must be well understood in order to select the most appropriate method. **(CAUTION: Most of the methods described below produce hydrogen gas, which can present an explosion hazard. The reaction should be carried out in a hood, behind a shield, and with proper safeguards to avoid exposure of the effluent gas to spark or flame. Any stirring device must be spark-proof.)**
- Decomposition of lithium aluminum hydride:
- Lithium aluminum hydride ( $\text{LiAlH}_4$ ) can be purchased as a solid or as a solution in toluene, diethyl ether, tetrahydrofuran, or other ethers. Although drop-

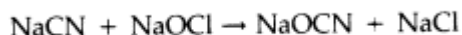
wise addition of water to its solutions under nitrogen in a three-necked flask has frequently been used to decompose it, vigorous frothing often occurs. An alternative is to use 95% ethanol, which reacts less vigorously than water. A safer procedure is to decompose the hydride with ethyl acetate, because no hydrogen is formed.



- To the hydride solution in a flask equipped with a stirrer, ethyl acetate is added slowly. The mixture sometimes becomes so viscous after the addition that stirring is difficult and additional solvent may be required. When the reaction with ethyl acetate has ceased, a saturated aqueous solution of ammonium chloride is added with stirring. The mixture separates into an organic layer and an aqueous layer containing inert inorganic solids. The upper, organic layer should be separated and disposed of as a flammable liquid. The lower, aqueous layer can often be disposed of in the sanitary sewer.
- Decomposition of potassium or sodium hydride:
- Potassium and sodium hydride (KH, NaH) in the dry state are pyrophoric, but they can be purchased as a relatively safe dispersion in mineral oil. Either form can be decomposed by adding enough dry hydrocarbon solvent (e.g., heptane) to reduce the hydride concentration below 5% and then adding excess t-butyl alcohol drop wise under nitrogen with stirring. Cold water is then added drop wise, and the resulting two layers are separated. The organic layer can be disposed of as a flammable liquid. The aqueous layer can often be neutralized and disposed of in the sanitary sewer.
- Decomposition of sodium borohydride:
- Sodium borohydride ( $\text{NaBH}_4$ ) is so stable in water that a 12% aqueous solution stabilized with sodium hydroxide is sold commercially. In order to effect decomposition, the solid or aqueous solution is added to enough water to make the borohydride concentration less than 3%, and then excess equivalents of dilute aqueous acetic acid are added drop wise with stirring under nitrogen.
- Decomposition of calcium hydride:
- Calcium hydride ( $\text{CaH}_2$ ), the least reactive of the materials discussed here, is purchased as a powder. It is decomposed by adding 25 mL of methyl alcohol per gram of hydride under nitrogen with stirring. When reaction has ceased, an equal volume of water is gradually added to the stirred slurry of calcium methoxide. The mixture is then neutralized with acid and disposed of in the sanitary sewer.

## **Inorganic Cyanides**

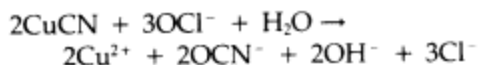
- Inorganic cyanides can be oxidized to cyanate using aqueous hypochlorite following a procedure similar to the oxidation of thiols. Hydrogen cyanide can be converted to sodium cyanide by neutralization with aqueous sodium hydroxide, and then oxidized.
- Procedure for oxidation of cyanide:



- An aqueous solution of the cyanide salt in an ice-cooled, three-necked flask equipped with a stirrer, thermometer, and dropping funnel is cooled to 4 to 10 °C. A 50% excess of commercial hypochlorite laundry bleach containing 5.25% (0.75 M) sodium hypochlorite is added slowly with stirring while maintaining the low temperature. When the addition is complete and heat is no longer being evolved, the solution is allowed to warm to room temperature and stand for several hours. The mixture can then be washed down the drain with excess water. The same procedure can be applied to insoluble cyanides such as cuprous cyanide (though copper salts should not be disposed of in the sanitary sewer). In

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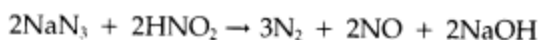
calculating the quantity of hypochlorite required, the experimenter should remember that additional equivalents may be needed if the metal ion can be oxidized to a higher valence state, as in the reaction,



- A similar procedure can be used to destroy hydrogen cyanide, but precautions must be taken to avoid exposure to this very toxic gas. Hydrogen cyanide is dissolved in several volumes of ice water. Approximately 1 molar equivalent of aqueous sodium hydroxide is added at 4 to 10 °C to convert the hydrogen cyanide into its sodium salt, and then the procedure described above for sodium cyanide is followed. (**CAUTION: Sodium hydroxide or other bases, including sodium cyanide, must not be allowed to come into contact with liquid hydrogen cyanide because they may initiate a violent polymerization of the hydrogen cyanide.**)
- This procedure also destroys soluble ferrocyanides and ferricyanides. Alternatively, these can be precipitated as the ferric or ferrous salt, respectively, for possible landfill disposal.

### Metal Azides

- Heavy metal azides are notoriously explosive and should be handled by trained personnel. Silver azide (and also fulminate) can be generated from Tollens reagent, which is often found in undergraduate laboratories. Sodium azide is explosive only when heated to near its decomposition temperature (300 °C), but heating it should be avoided. Sodium azide should never be flushed down the drain. This practice has caused serious accidents because the azide can react with lead or copper in the drain lines to produce an azide that may explode. It can be destroyed by reaction with nitrous acid:



- Procedure for destruction of sodium azide:
- The operation must be carried out in a hood because of the formation of toxic nitric oxide. An aqueous solution containing no more than 5% sodium azide is put into a three-necked flask equipped with a stirrer and a dropping funnel. Approximately 7 mL of 20% aqueous solution of sodium nitrite (40% excess) per gram of sodium azide is added with stirring. A 20% aqueous solution of sulfuric acid is then added gradually until the reaction mixture is acidic to litmus paper. (**CAUTION: The order of addition is essential. Poisonous, volatile hydrazoic acid (HN<sub>3</sub>) will evolve if the acid is added before the nitrite.**) When the evolution of nitrogen oxides ceases, the acidic solution is tested with starch iodide paper. If it turns blue, excess nitrite is present, and the decomposition is complete. The reaction mixture is washed down the drain.

### Alkali Metals

- Alkali metals react violently with water, with common hydroxylic solvents, and with halogenated hydrocarbons. They should always be handled in the absence of these materials. The metals are usually destroyed by controlled reaction with an alcohol. The final aqueous alcoholic material can usually be disposed of in the sanitary sewer.
- Procedure for destruction of alkali metals:

- 
- Waste sodium is readily destroyed with 95% ethanol. The procedure is carried out in a three-necked, round-bottomed flask equipped with a stirrer, dropping funnel, condenser, and heating mantle. Solid sodium should be cut into small pieces with a sharp knife while wet with a hydrocarbon, preferably mineral oil, so that the unoxidized surface is exposed. A dispersion of sodium in mineral oil can be treated directly. The flask is flushed with nitrogen and the pieces of sodium placed in it. Then 13 mL of 95% ethanol per gram of sodium are added at a rate that causes rapid refluxing. **(CAUTION: Hydrogen gas is evolved and can present an explosion hazard. The reaction should be carried out in a hood, behind a shield, and with proper safeguards (such as in Chapter 5, sections 5.G.4 and 5.G.5) to avoid exposing the effluent gas to spark or flame. Any stirring device must be spark-proof.)** Stirring is commenced as soon as enough ethanol has been added to make this possible. The mixture is stirred and heated under reflux until the sodium is dissolved. The heat source is removed, and an equal volume of water added at a rate that causes no more than mild refluxing. The solution is then cooled, neutralized with 6 M sulfuric or hydrochloric acid, and washed down the drain.
  - To destroy metallic potassium, the same procedure and precautions as for sodium are used, except that the less reactive t-butyl alcohol is used in the proportion of 21 mL/g of metal. **(CAUTION: Potassium metal can form explosive peroxides. Metal that has formed a yellow oxide coating from exposure to air should not be cut with a knife, even when wet with a hydrocarbon, because an explosion can be promoted.)** If the potassium is dissolving too slowly, a few percent of methanol can be added gradually to the refluxing t-butyl alcohol. Oxide-coated potassium sticks should be put directly into the flask and decomposed with t-butyl alcohol. The decomposition will require considerable time because of the low surface/volume ratio of the metal sticks.
  - Lithium metal can be treated by the same procedure, but using 30 mL of 95% ethanol per gram of lithium. The rate of dissolution is slower than that of sodium.

### **Metal Catalysts**

- Metal catalysts such as Raney nickel and other fine metal powders can be slurried into water; dilute hydrochloric acid is then added carefully until the solid dissolves. Depending on the metal and on local regulations, the solution can be discarded in the sanitary sewer or with other hazardous or nonhazardous solid waste. Precious metals should be recovered from this process.

### **Water-Reactive Metal Halides**

Liquid halides, such as  $\text{TiCl}_4$  and  $\text{SnCl}_4$ , can be added to well-stirred water in a round-bottomed flask cooled by an ice bath as necessary to keep the exothermic reaction under control. It is usually more convenient to add solid halides, such as  $\text{AlCl}_3$  and  $\text{ZrCl}_4$ , to stirring water and crushed ice in a flask or beaker. The acidic solution can be neutralized and, depending on the metal and local regulations, discarded in the sanitary sewer or with other hazardous or nonhazardous solid waste.

### **Halides and Acid Halides of Nonmetals**

- Halides and acid halides such as  $\text{PCl}_3$ ,  $\text{PCl}_5$ ,  $\text{SiCl}_4$ ,  $\text{SOCl}_2$ ,  $\text{SO}_2\text{Cl}_2$ , and  $\text{POCl}_3$  are water-reactive. The liquids can be hydrolyzed conveniently using 2.5 M sodium hydroxide by the

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procedure described earlier for acyl halides and anhydrides. These compounds are irritating to the skin and respiratory passages and, even more than most chemicals, require a good hood and skin protection when handling them. Moreover,  $\text{PCl}_3$  may give off small amounts of highly toxic phosphine ( $\text{PH}_3$ ) during hydrolysis.

- Sulfur monochloride ( $\text{S}_2\text{Cl}_2$ ) is a special case. It is hydrolyzed to a mixture of sodium sulfide and sodium sulfite, so that the hydrolyzate must be treated with hypochlorite as described earlier for sulfides before it can be flushed down the drain.
- The solids of this class (e.g.,  $\text{PCl}_5$ ) tend to cake and fume in moist air and therefore are not conveniently hydrolyzed in a three-necked flask. It is preferable to add them to a 50% excess of 2.5 M sodium hydroxide solution in a beaker or wide-mouth flask equipped with a stirrer and half-filled with crushed ice. If the solid has not all dissolved by the time the ice has melted and the stirred mixture has reached room temperature, the reaction can be completed by heating on a steam bath, and then the acidic solution neutralized and disposed of in the sanitary sewer.

## **Inorganic Ions**

- Many inorganic wastes consist of a cation (metal or metalloid atom) and an anion (which may or may not contain a metalloid component). It is often helpful to examine the cationic and anionic parts of the substance separately to determine whether either possesses a hazard.
- If a substance contains a "heavy metal," it is often assumed that it is highly toxic. While salts of some heavy metals, such as lead, thallium, and mercury, are highly toxic, those of others, such as gold and tantalum, are not. On the other hand, compounds of beryllium, a "light metal," are highly toxic. In [Table 5.1](#), cations of metals and metalloids are listed alphabetically in two groups: those whose toxic properties as described in the toxicological literature present a significant hazard, and those whose properties do not. The basis for separation is relative, and the separation does not imply that those in the second list are "nontoxic." Similarly, [Table 5.2](#) lists anions according to their level of toxicity and other dangerous properties, such as strong oxidizing power (e.g., perchlorate), flammability (e.g., amide), water reactivity (e.g., hydride), and explosivity (e.g., azide).
- Materials that pose a hazard because of significant radioactivity are outside the scope of this volume, although they may be chemically treated in a manner similar to the nonradioactive materials discussed in this chapter. Their handling and disposal are highly regulated in most countries. Low-level radioactive mixed waste is discussed in [section 5.C](#) above.
- Chemicals in Which Neither the Cation nor the Anion Presents a Significant Hazard
- Chemicals in which neither the cation nor the anion presents a significant hazard consist of those chemicals composed of ions from the right-hand columns of [Tables 5.1](#) and [5.2](#). Those that are soluble in water to the extent of a few percent can usually be disposed of in the sanitary sewer. Only laboratory quantities should be disposed of in this manner, and at least 100 parts of water per part of chemical should be used. Local regulations should be checked for possible restrictions. Dilute slurries of insoluble materials, such as calcium sulfate or aluminum oxide, also can be handled in this way, provided the material is finely divided and not contaminated with tar, which might clog the piping. Some incinerators can handle these chemicals. If time and space permit, dilute aqueous solutions can be boiled down or allowed to evaporate to leave only a sludge of the inorganic solid for landfill

disposal. However, appropriate precautions, including the use of traps, must be considered to ensure that toxic or other prohibited materials are not released to the atmosphere.

- An alternative procedure is to precipitate the metal ion by the agent recommended in [Table 5.1](#). The precipitate can often be disposed of in a secure landfill. The most generally applicable procedure is to precipitate the cation as the hydroxide by adjusting the pH to the range.

## **Precipitation of Cations as Their Hydroxides**

- Because the pH range for precipitation varies greatly among metal ions, it is important to control it carefully. The aqueous solution of the metal ion is adjusted to the recommended pH ([Table 5.3](#)) by addition of a solution of 1 M sulfuric acid, or 1 M sodium hydroxide or carbonate. The pH can be determined over the range 1 through 10 by use of pH test paper.
- The precipitate is separated by filtration, or as a heavy sludge by decantation, and packed for disposal. Some gelatinous hydroxides are difficult to filter. In such cases, heating the mixture close to 100 °C or stirring with diatomaceous earth, approximately 1 to 2 times the weight of the precipitate, often facilitates filtration.
- As shown in [Table 5.1](#), precipitants other than a base may be superior for some metal ions, such as sulfuric acid for calcium ion. For some ions, the hydroxide precipitate will redissolve at a high pH. For a number of metal ions the use of sodium carbonate will result in precipitation of the metal carbonate or a mixture of hydroxide and carbonate.

**TABLE 5.1** High-and Low-Toxicity Cations and Preferred Precipitants

High Toxic Hazard	Precipitant <sup>a</sup>	Low Toxic Hazard	Precipitant <sup>a</sup>
Cation		Cation	
Antimony	OH <sup>-</sup> , S <sup>2-</sup>	Aluminium	OH <sup>-</sup>
Arsenic	S <sup>2-</sup>	Bismuth	OH <sup>-</sup> , S <sup>2-</sup>
Barium	SO <sub>4</sub> <sup>2-</sup> , CO <sub>3</sub> <sup>2-</sup>	Calcium	SO <sub>4</sub> <sup>2-</sup> , CO <sub>3</sub> <sup>2-</sup>
Beryllium	OH <sup>-</sup>	Cerium	OH <sup>-</sup>
Cadmium	OH <sup>-</sup> , S <sup>2-</sup>	Cesium	
Chromium(III) <sup>b</sup>	OH <sup>-</sup>	Copper <sup>c</sup>	OH <sup>-</sup> , S <sup>2-</sup>
Cobalt(II) <sup>b</sup>	OH <sup>-</sup> , S <sup>2-</sup>	Gold	OH <sup>-</sup> , S <sup>2-</sup>
Gallium	OH <sup>-</sup>	Iron <sup>c</sup>	OH <sup>-</sup> , S <sup>2-</sup>
Germanium	OH <sup>-</sup> , S <sup>2-</sup>	Lanthanides	OH <sup>-</sup>
Hafnium	OH <sup>-</sup>	Lithium	
Indium	OH <sup>-</sup> , S <sup>2-</sup>	Magnesium	OH <sup>-</sup>
Iridium <sup>d</sup>	OH <sup>-</sup> , S <sup>2-</sup>	Molybdenum(VI) <sup>b,e</sup>	
Lead	OH <sup>-</sup> , S <sup>2-</sup>	Niobium(V)	OH <sup>-</sup>
Manganese(II) <sup>b</sup>	OH <sup>-</sup> , S <sup>2-</sup>	Palladium	OH <sup>-</sup> , S <sup>2-</sup>
Mercury	OH <sup>-</sup> , S <sup>2-</sup>	Potassium	
Nickel	OH <sup>-</sup> , S <sup>2-</sup>	Rubidium	
Osmium(IV) <sup>b,f</sup>	OH <sup>-</sup> , S <sup>2-</sup>	Scandium	OH <sup>-</sup>
Platinum(II) <sup>b</sup>	OH <sup>-</sup> , S <sup>2-</sup>	Sodium	
Rhenium(VII) <sup>b</sup>	S <sup>2-</sup>	Strontium	SO <sub>4</sub> <sup>2-</sup> CO <sub>3</sub> <sup>2-</sup>
Rhodium(III) <sup>b</sup>	OH <sup>-</sup> , S <sup>2-</sup>	Tantalum	OH <sup>-</sup>
Ruthenium(II) <sup>b</sup>	OH <sup>-</sup> , S <sup>2-</sup>	Tin	OH <sup>-</sup> , S <sup>2-</sup>

Selenium	S <sup>2-</sup>	Titanium	OH <sup>-</sup>
Silver <sup>d</sup>	Cl, OH <sup>-</sup> , S <sup>2-</sup>	Yttrium	OH <sup>-</sup>
Tellurium	S <sup>2-</sup>	Zinc <sup>e</sup>	OH <sup>-</sup> , S <sup>2-</sup>
Thallium	OH <sup>-</sup> , S <sup>2-</sup>	Zirconium	OH <sup>-</sup>
Tungsten(VI) <sup>b,e</sup>			
Vanadium	OH <sup>-</sup> , S <sup>2-</sup>		

<sup>a</sup> Precipitants are listed in order of preference: OH<sup>-</sup>, CO<sub>3</sub><sup>2-</sup> =base (sodium hydroxide or sodium carbonate), S<sup>2-</sup> = sulfide, SO<sub>4</sub><sup>2-</sup> = sulfate, and Cl<sup>-</sup> = chloride.

<sup>b</sup> The precipitant is for the indicated valence state.

<sup>c</sup> Very low maximum tolerance levels have been set for these low-toxicity ions in some countries, and large amounts should not be put into public sewer systems. The small amounts typically used in laboratories will not normally affect water supplies, although they may be prohibited by the local publicly owned treatment works (POTW).

<sup>d</sup> Recovery of these rare and expensive metals may be economically favorable.

<sup>e</sup> These ions are best precipitated as calcium molybdate(VI) or calcium tungstate(VI).

<sup>f</sup> CAUTION: Osmium tetroxide, OsO<sub>4</sub>, a volatile, extremely poisonous substance, is formed from almost any osmium compound under acid conditions in the presence of air. Reaction with corn oil or powdered milk will destroy it.

### **Chemicals in Which the Cation Presents a Relatively High Hazard from Toxicity**

- In general, waste chemicals containing any of the cations listed as highly hazardous in [Table 5.1](#) can be precipitated as their hydroxides or oxides. Alternatively, many can be precipitated as insoluble sulfides by treatment with sodium sulfide in neutral solution (Table 5.3). Several sulfides will redissolve in excess sulfide ion, and so it is important that the sulfide ion concentration be controlled by adjustment of the pH.
- Precipitation as the hydroxide is achieved as described above. Precipitation as the sulfide is accomplished by adding a 1 M solution of sodium sulfide to the metal ion solution, and then adjusting the pH to neutral with 1 M sulfuric acid. (**CAUTION: Avoid acidifying the mixture because hydrogen sulfide could be formed.**) The precipitate is separated by filtration or decantation and packed for disposal. Excess sulfide ion can be destroyed by the addition of hypochlorite to the clear aqueous solution.
- The following ions are most commonly found as oxyanions and are not precipitated by base: As<sup>3+</sup>, As<sup>5+</sup>, Re<sup>7+</sup>, Se<sup>4+</sup>, Se<sup>6+</sup>, Te<sup>4+</sup>, and Te<sup>6+</sup>. These elements can be precipitated from their oxyanions as the sulfides by the above procedure. Oxyanions of Mo<sup>6+</sup> and W<sup>6+</sup> can be precipitated as their calcium salts by the addition of calcium chloride. Some ions can be absorbed by passing their solutions over ion-exchange resins. The resins can be landfilled, and the effluent solutions poured down the drain.
- Another class of compounds whose cations may not be precipitated by the addition of hydroxide ions are the most stable complexes of metal cations with Lewis bases, such as ammonia, amines, and tertiary phosphines. Because of the large number of these compounds and their wide range of properties, it is not possible to give a general procedure for separating the cations. In many cases, metal sulfides can be precipitated directly from aqueous solutions of the complexes by the addition of aqueous sodium sulfide. If a test-tube experiment shows that other measures are needed, the addition of hydrochloric acid to produce a slightly acidic solution will often decompose the complex by protonation of

the basic ligand. Metal ions that form insoluble sulfides under acid conditions can then be precipitated by drop wise addition of aqueous sodium sulfide.

- A third option for this waste is incineration, provided that the incinerator ash is to be sent to a secure landfill. Incineration to ash reduces the volume of neutral with 1 M sulfuric acid. (**CAUTION: Avoid acidifying the mixture because hydrogen sulfide could be formed.**) The precipitate is separated by filtration or decantation and packed for disposal. Excess sulfide ion can be destroyed by the addition of hypochlorite to the clear aqueous solution.
- The following ions are most commonly found as oxyanions and are not precipitated by base:  $\text{As}^{3+}$ ,  $\text{As}^{5+}$ ,  $\text{Re}^{7+}$ ,  $\text{Se}^{4+}$ ,  $\text{Se}^{6+}$ ,  $\text{Te}^{4+}$ , and  $\text{Te}^{6+}$ . These elements can be precipitated from their oxyanions as the sulfides by the above procedure. Oxyanions of  $\text{Mo}^{6+}$  and  $\text{W}^{6+}$  can be precipitated as their calcium salts by the addition of calcium chloride. Some ions can be absorbed by passing their solutions over ion-exchange resins. The resins can be landfilled, and the effluent solutions poured down the drain.
- Another class of compounds whose cations may not be precipitated by the addition of hydroxide ions are the most stable complexes of metal cations with Lewis bases, such as ammonia, amines, and tertiary phosphines. Because of the large number of these compounds and their wide range of properties, it is not possible to give a general procedure for separating the cations. In many cases, metal sulfides can be precipitated directly from aqueous solutions of the complexes by the addition of aqueous sodium sulfide. If a test-tube experiment shows that other measures are needed, the addition of hydrochloric acid to produce a slightly acidic solution will often decompose the complex by protonation of the basic ligand. Metal ions that form insoluble sulfides under acid conditions can then be precipitated by drop wise addition of aqueous sodium sulfide.
- A third option for this waste is incineration, provided that the incinerator ash is to be sent to a secure landfill. Incineration to ash reduces the volume of waste going to a landfill. Waste that contains mercury, thallium, gallium, osmium, selenium, or arsenic should not be incinerated because volatile, toxic combustion products may be emitted.

**TABLE 5.2** High- and Low-Hazard Anions and Preferred Precipitants

High-Hazard Anions	Hazard Type <sup>a</sup>	Precipitant	Low-Hazard Anions
Aluminium hydride, $\text{AlH}_4^-$	F, W	—	Bisulfite, $\text{HSO}_3^-$
Amide, $\text{NH}_2^-$	F, E <sup>b</sup>	—	Borate, $\text{BO}_3^{3-}$ , $\text{B}_4\text{O}_7^{2-}$
Arsenate, $\text{AsO}_3^-$ , $\text{AsO}_4^{3-}$	T	$\text{Cu}^{2+}$ , $\text{Fe}^{2+}$	Bromide, $\text{Br}^-$
Arsenite, $\text{AsO}_2^-$ , $\text{AsO}_3^{3-}$	T	$\text{Pb}^{2+}$	Carbonate, $\text{CO}_3^{2-}$



Azide, $N_3^-$	E, T	—	Chloride, $Cl^-$
Borohydride, $BH_4^-$	F	—	Cyanate, $OCN^-$
Bromate, $BrO_3^-$	O, F, E	—	Hydroxide, $OH^-$
Chlorate, $ClO_3^-$	O, E	—	Iodide, $I^-$
Chromate, $CrO_4^{2-}$ , $Cr_2O_7^{2-}$	T, O	<sup>c</sup>	
Oxide, $O^-$			
Cyanide, $CN^-$	T	—	Phosphate, $PO_4^{3-}$
Ferricyanide, $\{Fe(CN)_6\}^{3-}$	T	$Fe^{2+}$	Sulfate, $SO_4^{2-}$
Ferrocyanide, $\{Fe(CN)_6\}^{4-}$	T	$Fe^{3+}$	Sulfite, $SO_3^{2-}$
Fluoride, $F^-$	T	$Ca^{2+}$	Thiocyanate, $SCN^-$
Hydride, $H^-$	F, W	—	
Hydroperoxide, $O_2H^-$	O, E	—	
Hydrosulfide, $SH^-$	T	—	
Hypochlorite, $OCl^-$	O	—	
Iodate, $IO_3^-$	O, E	—	
Nitrate, $NO_3^-$	O	—	
Nitrite, $NO_2^-$	T, O	—	
Perchlorate, $ClO_4^-$	O, E	—	
Permanganate, $MnO_4^-$	T, O	—	
Peroxide, $O_2^{2-}$	O, E	<sup>d</sup>	
Persulfate, $S_2O_8^{2-}$	O	—	
Selenate, $SeO_4^{2-}$	T	$Pb^{2+}$	
Selenide, $Se^{2-}$	T	$Cu^{2+}$	
Sulfide, $S^{2-}$	T	<sup>e</sup>	

<sup>a</sup> T = toxic; O = oxidant; F = flammable; E = explosive; and W = water reactive.

<sup>b</sup> Metal amides readily form explosive peroxides on exposure to air.

<sup>c</sup> Reduce and precipitate as Cr(III).

<sup>d</sup> Reduce and precipitate as Mn(II); see [Table 5.1](#).

**TABLE 5.3** Precipitation of Sulfides

Precipitated at pH 7	Not Precipitated at Low pH	Soluble Complex at High pH
$Ag^+$		
$As^{3+a}$		X
$Au^{+a}$		X
$Bi^{3+}$		
$Cd^{2+}$		

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Co <sup>2+</sup>	X	
Cr <sup>3+a</sup>		
Cu <sup>2+</sup>		
Fe <sup>2+a</sup>	X	
Ge <sup>2+</sup>		X
Hg <sup>2+</sup>		X
In <sup>3+</sup>	X	
Ir <sup>4+</sup>		X
Mn <sup>2+a</sup>	X	
Mo <sup>3+</sup>		X
Ni <sup>2+</sup>	X	
Os <sup>4+</sup>		
Pb <sup>2+</sup>		
Pd <sup>2+a</sup>		
pt <sup>2+a</sup>		X
Re <sup>4+</sup>		
Rh <sup>2+a</sup>		
Ru <sup>4+</sup>		
Sb <sup>3+a</sup>		X
Se <sup>2+</sup>		X
Sn <sup>2+</sup>		X
Te <sup>4+</sup>		X
Tl <sup>+a</sup>	X	
V <sup>4+a</sup>		
Zn <sup>2+</sup>	X	

NOTE: Precipitation of ions listed without an x is usually not pH-dependent.

<sup>a</sup> Higher oxidation states of this ion are reduced by sulfide ion and precipitated as this sulfide.

SOURCE: Swift and Schaefer (1961)

### **Chemicals in Which an Anion Presents a Relatively High Hazard**

- The more common dangerous anions are listed in [Table 5.2](#). Many of the comments made above about the disposal of dangerous cations apply to these anions. The hazard associated with some of these anions is their reactivity or potential to explode, which makes them unsuitable for landfill disposal. Most chemicals containing these anions can be incinerated, but strong oxidizing agents and hydrides should be introduced into the incinerator only in containers of not more than a few hundred grams. Incinerator ash from anions of chromium or manganese should be transferred to a secure landfill.
- Some of these anions can be precipitated as insoluble salts for landfill disposal, as indicated in [Table 5.2](#). Small amounts of strong oxidizing agents, hydrides, cyanides, azides, metal amides, and soluble sulfides or fluorides can be converted into less hazardous substances in the laboratory before being disposed of. Suggested procedures are presented in the following paragraphs.

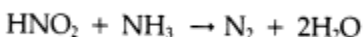
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## Procedure for Reduction of Oxidizing Salts

- Hypochlorites, chlorates, bromates, iodates, periodates, inorganic peroxides and hydroperoxides, persulfates, chromates, molybdates, and permanganates can be reduced by sodium hydrogen sulfite. A dilute solution or suspension of a salt containing one of these anions has its pH reduced to less than 3 with sulfuric acid, and a 50% excess of aqueous sodium hydrogen sulfite is added gradually with stirring at room temperature. An increase in temperature indicates that the reaction is taking place. If the reaction does not start on addition of about 10% of the sodium hydrogen sulfite, a further reduction in pH may initiate it. Colored anions (e.g., permanganate and chromate) serve as their own indicators of completion of the reduction. The reduced mixtures can often be washed down the drain. However, if large amounts of permanganate have been reduced, it may be necessary to transfer the manganese dioxide to a secure landfill, possibly after a reduction in volume by concentration or precipitation. Do not dispose of chromium salts in the sanitary sewer.
- Hydrogen peroxide can be reduced by the sodium hydrogen sulfite procedure or by ferrous sulfate as described earlier for organic hydroperoxides. However, it is usually acceptable to dilute it to a concentration of less than 3% and dispose of it in the sanitary sewer. Solutions with a hydrogen peroxide concentration greater than 30% should be handled with great care to avoid contact with reducing agents, including all organic materials, or with transition metal compounds, which can catalyze a violent reaction.

Concentrated perchloric acid (particularly when stronger than 60%) must be kept away from reducing agents, including weak ones such as ammonia, wood, paper, plastics, and all other organic substances, because it can react violently with them. Dilute perchloric acid is not reduced by common laboratory reducing agents such as sodium hydrogen sulfite, hydrogen sulfide, hydriodic acid, iron, or zinc. Perchloric acid is most easily disposed of by stirring it gradually into enough cold water to make its concentration less than 5%, neutralizing it with aqueous sodium hydroxide, and washing the solution down the drain with a large excess of water.

- Nitrate is most dangerous in the form of concentrated nitric acid (70% or higher), which is a potent oxidizing agent for organic materials and all other reducing agents. It can also cause serious skin burns. Dilute aqueous nitric acid is not a dangerous oxidizing agent and is not easily reduced by common laboratory reducing agents. Dilute nitric acid should be neutralized with aqueous sodium hydroxide before disposal down the drain; concentrated nitric acid should be diluted carefully by adding it to about 10 volumes of water before neutralization. Metal nitrates are generally quite soluble in water. Those of the metals listed in [Table 5.1](#) as having a low toxic hazard, as well as ammonium nitrate, should be kept separate from oil or other organic materials because on heating such a combination, fire or explosion can occur. Otherwise, these can be treated as chemicals that present no significant hazard.
- Nitrites in aqueous solution can be destroyed by adding about 50% excess aqueous ammonia and acidifying with hydrochloric acid to pH 1:



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