

LABORATORY SAFETY

A. General Considerations

In the laboratory the chemist works with many potentially dangerous substances. Yet, with constant alertness, awareness of potential hazards, and a few common-sense precautions, laboratory operations can be carried out with a high degree of safety.

Most of the responsibility for the personal safety of the laboratory worker rests on the worker himself. In the event of an accident resulting from his neglect of appropriate precautions or disregard of laboratory regulations he is in a poor position to collect damages for his own injuries, and may even find himself the target of civil or criminal action if his negligence results in injury to others. Worse, injuries sustained in laboratory accidents can result in permanent disability, disfigurement, blindness, or death a fact that far transcends legal considerations.

The basic rule of safety in the laboratory is: **be alert stay alert.**

The laboratory is no place for the "absent-minded professor" or the "absent-minded student" for that matter. Beyond this, take the trouble to understand what you are doing and to know what the hazards are, take the appropriate precautions, and use the appropriate protective equipment.

We summarize here some of the more important specific laboratory rules and precautions.

(1) Never work in the laboratory alone. Before working in the laboratory outside regular hours make sure that this is permissible and be certain that someone else will be in the same room to provide assistance in case of need.

(2) At all times wear approved eye protection: "safety glasses" with impact-resistant lenses in approved frames, or protective goggles, or a face shield, or some combination of these - It should be borne in mind that this is required by Maryland state law. Safety glasses may be obtained either ground to prescription or non-refracting. Side shields of transparent plastic may be clipped on for additional protection. Ordinary prescription glasses provide about the same protection against spatter as do safety glasses but in the event of an explosion the lenses of ordinary glasses are much more easily shattered and the glass fragments may be driven into the eyeball; in such a case they can be worse than no glasses at all. Contact lenses (especially the corneal type) provide negligible protection, and indeed their use may seriously aggravate hazards from spatter since they will impede washing the cornea free of caustic liquids that creep or diffuse under them. It is inadvisable to wear them even under safety glasses, which (it must always be remembered) do not by themselves provide one hundred percent protection from spatter at top, sides, and bottom.

(3) Use the fume hood for all operations involving poisonous or offensive gases or fumes as well as for operations involving highly inflammable or potentially explosive materials. A combination of a fume hood and a safety shield (see below) will provide the maximum readily available protection against minor laboratory explosions.

(4) Guard against injury from explosion, implosion, flash fires, and spatter of dangerous liquids by interposing a "safety shield" or other effective barrier between all personnel and any setup presenting such hazards. Vacuum distillations of more than small (about 100 ml) quantities should be shielded, as should gas scrubbing trains containing significant amounts of corrosive solutions and all evacuated equipment of any significant size such as vacuum desiccators.

(5) Use a metal safety pail with a well-fitting cover to transport any dangerous liquid, or more than a small quantity (a pint) of any solvent. Several years ago the writer (someone at MIT) was a witness to a fatal

accident in which a sealed bottle of ethyl chlorocarbonate, C_2H_5OCOCl , blew up (from internal CO_2 pressure) in the face of a technician who was carrying it in one hand from the dangerous chemicals vault. A safety pail would probably have saved her life.

(6) Never heat an organic solvent in an open vessel over an open flame; keep a respectable distance between open vessels containing organic solvents and any open flames or sources of sparks. Except under special circumstances, an open flame should not be used to heat a reaction apparatus containing inflammable materials.

(7) Never place beakers or unstoppered flasks containing chemicals in a refrigerator, even if it is of the "explosive proof" type, or in any other unventilated enclosure. Never store volatile toxic materials in a refrigerator or other unventilated enclosure even in a "stoppered" vessel. The first breath a person takes after opening the refrigerator door could be his/her last.

(8) Do not work with large quantities of reactants (i.e. more than about 100g) unless you have received special instruction regarding large-scale reactions.

(9) Always be careful to avoid pointing the mouth of a vessel being heated toward any person, including yourself.

(10) Except for certain operations for which special instruction should be obtained beforehand (reduced-pressure distillations, reactions in bombs or sealed tubes, etc.) never heat reactants of any kind in a fully closed system; be sure the system is open to the air at some point to prevent pressure buildup from boiling or gas evolution.

(11) Never add anything TO a concentrated acid, caustic, or strong oxidant; instead add the acid, caustic, or oxidant slowly and cautiously to the other ingredients, preferably no faster than it is consumed by reaction.

(12) Never add solids (boiling chips, charcoal, etc.) to a hot liquid as this may result in violent boiling if the liquid happens to be superheated. Perform such additions (or put in an appropriate ebullator) when the liquid is still at room temperature.

(13) Never pipette by mouth any toxic or corrosive substance or (preferably) anything else. Use an automatic pipette or fill a conventional pipette with a rubber bulb. (Exceptions to this can be made for certain dilute non-toxic or slightly toxic solutions used in analytical work: HCl , $NaOH$, $NaCl$, $NaHCO_3$, $Na_2S_2O_3$, etc. If some of any such solution gets into the mouth it will be sufficient to spit it out and wash the mouth out well with water.) Assume any unfamiliar substance to be toxic unless you know definitely to the contrary.

(14) Be sure all chemical containers are correctly and clearly labeled. Labels for your -preparations should contain, besides the name or formula of the contents your name, the date, and a sample number by which it can be identified in your notebook.

(15) Never pour anything back into a reagent bottle.

(16) Protect your clothing with a laboratory apron or a laboratory coat.

(17) Protect your hands: with rubber or polyethylene gloves when handling caustic liquids, with canvas or asbestos gloves when handling hot objects. Remember that some highly toxic substances can penetrate rubber or polyethylene gloves; do not hesitate to discard gloves (or aprons, or coats, even shoes) that become dangerously contaminated.

(18) Dangling neckties, unrestrained long hair, and fluffy or floppy clothing (including over-large or ragged laboratory coat sleeves) can easily catch fire, dip into chemicals on the laboratory bench, get ensnarled in apparatus and moving machinery, etc. Remove or restrain your long necktie; put up long hair or at least restrain it with a rubber band.

(19) Know and observe the approved procedures for disposal of the chemicals and laboratory refuse associated with your experiment (see Section F). In particular, never throw chemical wastes into a waste crock, or water-insoluble solids into the sink; flush down soluble substances with a great excess of water; never dispose of cyanides or mercury or alkali metals in the sink or crock; package hazardous chemical wastes in suitable containers appropriately labeled; these are taken away every Thursday at the chemical waste disposal site at Mudd Hall. If in doubt about the waste call the Safety Office to take them away.

(20) Know the location of exits, fire extinguishers, fire blankets, safety showers, gooseneck faucets for douching eyes, and other safety devices; familiarize yourself with the purposes of these devices and with-the procedures for their use.

(21) Before beginning any procedure with which you have not had adequate previous experience and thorough knowledge of the hazards, find out what the hazards and appropriate precautions are by reading the literature and/or conferring with someone having such knowledge and experience.

This list of twenty-one safety rules and precautions has been chosen somewhat arbitrarily and is by no means complete. However, it represents a selection that contains the most important precautions. It should be reread periodically until observance of these precautions has become second nature. These same precautions and some additional ones will be treated in specific contexts in the following sections, which should be read in advance of performing the corresponding laboratory operations and reviewed from time to time. Since observance of the precautions here presented can be of crucial importance, we do not apologize for being occasionally repetitious.

B. Fire Protection

Fire is the principal cause of serious laboratory accidents. Nearly all organic solvents are inflammable., some of them extremely so, as are many gases such as hydrogen, acetylene, ammonia, and light hydrocarbons. These gases and solvent vapors can form explosive mixtures with air.

(1) Solvents

The auto-ignition temperature of a liquid is the minimum liquid temperature necessary to initiate self-sustained combustion independently of the heating element. The flash point of a liquid is the minimum liquid temperature at which the liquid vapor pressure is sufficient to form a flammable mixture with air, so that once initiated the flame will propagate through the vapor, often without the liquid itself giving rise to continued combustion. Flammable limits are the composition limits of a gas mixture within which a flame, once initiated, will propagate itself. The lower flammable limit for many solvents (CS₂, hydrocarbons) in air is as little as one or two percent by volume.

In the absence of a flame, a spark, or an incandescent electric heating element the auto-ignition temperature is ordinarily of serious concern only with a few substances. Carbon disulfide has an auto-ignition temperature of about 100 °C, and the vapors can be ignited by contact with an ordinary low-pressure steam line; the auto-ignition temperature for ethyl ether is 180 °C low enough so that use of an electric hot plate may provide a significant hazard. Such liquids should be heated with a water bath or a steam bath in a hood so that vapor from the boiling liquid does not accumulate.

Of more frequent concern is the flash point. If the flash point of a solvent is below room temperature (25 °C) the solvent is termed a Class I solvent. Examples of Class I solvents are the commonly used organic solvents ether, benzene, methanol, ethanol, acetone, petroleum ether, ethyl acetate. Precautions to be observed in all operations with Class I solvents include the following:

a. Never handle solvents near an open flame. If large quantities are being handled, set up "NO FLAME" signs. Deliberately scout the working area for lighted burners, pilot lights, electric motors, switches and other sparking electrical contacts, etc., before beginning your operations and periodically while they are in progress. Operations in which solvents are escaping from the reaction vessel should always be conducted in a hood.

b. Conduct recrystallizations on a steam bath or a hot plate (see above with regard to CS₂ and ethyl ether), either in a hood or with a condenser to contain vapors from the boiling liquid. Use an Erlenmeyer flask (never a beaker) for recrystallization.

c. Before a liquid is heated to boiling add a boiling chip or some other device to serve as an ebullator. A superheated liquid may suddenly "bump" or boil violently, and often will overflow the container and create a fire hazard. The same may happen if a solid is added to a superheated liquid, therefore never add solids to a hot liquid.

d. Make sure that reflux and distillation apparatus is tightly assembled and firmly clamped, with all ground joints well seated. Be certain that somewhere (at the top of the reflux condenser or at the distillate receiver) the system is open to the air (except in reduced-pressure distillations). Use a mantle, oil bath, hot plate, or steam for heating. The use of a free flame is never desirable; if a microburner must be used to melt solidified distillate in some part of the system or for some other purpose make doubly sure the joints are tight; in this case the vent to the air should be through a rubber tube with its open end several feet away and below the flame level.

- e. Any quantity of solvent amounting to more than one pint must be transported in a safety pail and stored in the pail either on a side shelf (not on a shelf over the laboratory bench) or in a designated cabinet.
- f. Never work in a solvent storage area; avoid having large quantities of solvents in a working area.
- g. Eliminate the possibility of sparks of all kinds in the working area. Electric sparks may come from switches, relay contacts, and thermostatic devices; the latter are found in heaters, hot plates, and refrigerators. For this reason these devices whenever possible should be sealed so that solvent vapors cannot get in or sparks or flame get out; refrigerators used in the laboratory should be of the "explosion-proof" type, with switches and thermostat contacts sealed or mounted outside the box. Electric sparks from electric motors can be avoided by employing induction motors for stirrers and pumps instead of series-wound and other brush-containing motors. Electric sparks can also arise from the buildup of "static electricity". Avoid excessive wiping or swirling of flasks or bottles containing solvents before pouring; when dealing with more than about a liter of Class I solvents in metallic systems, ground the apparatus and the container. Sparks can arise also from metal striking metal or concrete, and, since solvent vapors are denser than air, a fire could be produced from a metal object falling onto a concrete floor or even shoe nails scraping on the concrete. This fact is particularly to be remembered if there is any spillage of solvents.
- h. Never place beakers or unstoppered flasks containing solvents in a refrigerator.
- i. Do not smoke, or permit others to do so, while working with solvents, or (preferably) at any other time in the laboratory. Smoking inside public buildings, including classrooms and laboratories is not permitted in the State of Maryland.

(2) Other fire hazards

Clothing and hair can catch fire from a forgotten Bunsen burner, or be ignited by a flash fire. Avoid fluffy or floppy or ragged clothing, especially of rayon or cotton, and unrestrained hair or necktie. A person with hair or clothing on fire may suffer very serious or even fatal burns unless prompt action is taken. Douse him/her with water at the safety shower and/or roll him in a fire blanket immediately. Know where the showers and blankets are, so that the victim will not be a cinder by the time they are found. If too far from either, use any available source of water or roll the victim on the floor to snuff out flames. A person who is a fire should not run as this fans the flames.

A number of chemical substances and mixtures are spontaneously combustible. These include white phosphorus, pyrophoric metals (including hydrogenation catalysts such as Raney nickel or platinum whose surface is saturated with hydrogen, palladium and methanol, platinum oxide and alcohol vapors or hydrogen, finely divided alkali metals), metal alkyls such as dry Grignard or organolithium reagents, low molecular weight phosphines and boranes, arsine, and iron carbonyl. White phosphorus can be transported and stored for a time under water, but after long periods acidity builds up in the water due to slow air oxidation. Beware of storing phosphorus under water of high alkalinity; if the pH of the water is above 9 the poisonous and spontaneously flammable gas phosphine, PH_3 , may be evolved.

Alkali metals are spontaneously combustible in the presence of water (owing to evolution of both hydrogen and heat) and of certain other substances such as chlorinated hydrocarbons. Alkali metals should be stored under purified kerosene or mineral oil (Nujol). Metallic sodium may be used to dry certain solvents (e.g. ether, dioxane) that contain no active hydrogen or halogen, for which purpose the metal is usually introduced in the form of wire extruded from a sodium press directly into the solvent bottle. Scraps of sodium wire in an empty solvent bottle should be immediately destroyed under a flow of nitrogen by cautious addition of ethanol or methanol to the bottle, which is contained in a clean, dry pan or pail;

other alkali metal scraps can be disposed of similarly or placed under mineral oil in a bottle provided for that purpose. CAUTION: Never put alkali metal into water, CCl₄, or other chlorinated hydrocarbons

(3) Extinguishing a fire

If a fire breaks out, retreat to safety and do not approach to extinguish the fire until you are sure that it is safe to do so; the fire extinguishers are usually at or just outside the laboratory doors. When approaching to extinguish the fire (a) be very careful to leave yourself an avenue of retreat, (b) take into account the possibility of explosion or rapid spread of the fire, and (c) be alert for any sign of toxic gases, particularly phosgene which can be present when chlorinated hydrocarbons are involved. Unless the fire is very minor and---. burns itself out very quickly, call the JHU -emergency number (dial **x7777**). The principal classes of fires and the appropriate extinguishers for them are listed in the following table.

Table 1.1 Fires and Extinguishers

Class of fire	Materials burning, or conditions	Preferred extinguisher	Never use
A	Wood, paper, cloth	Water, CO ₂ , Dry NaHCO ₃ -type*	CCl ₄ **
B	Flammable liquids and gases, hydrocarbon solids, rubber, plastics	Dry NaHCO ₃ -type*, CO ₂	CCl ₄
C	The above, whenever electrical contacts must be taken into consideration	Dry NaHCO ₃ -type*, CO ₂ Soda-acid,	Water, Foam, CCl ₄
D	Alkali metals (also alkaline earths, Al)	Dry NaHCO ₃ -type*, Dry graphite*, (for Li) Dry NaCl* (for Na or K)	Water, Soda-acid, Foam, CO ₂ , CCl ₄

* Dry solids in cylinder pressurized with N₂, a CO₂ cartridge, or a propellant such as freon.

** May be used on small fires with adequate ventilation, if the only type available; not recommended.

The preferred all-round extinguisher, and the most effective in the particularly important Class B type, is the dry NaHCO₃-type or "dry chemical" type. This is also the best all-around extinguisher for home or automobile. However, many laboratories are equipped with the CO₂-type, which is reasonably effective although in a confined area the CO₂ gas released adds somewhat to the hazard of suffocation always present to some degree at a fire. Soda-acid extinguishers are messy, and even hazardous when electric appliances or outlets are involved, the use of CCl₄-type extinguishers carries the hazard of producing the very poisonous gas phosgene, and the CCl₄ fumes are themselves toxic. The use of these two types is to be discouraged in general. In the absence of the recommended extinguishers, a small class D fire can be smothered by other inert (non-reducible), dry materials: reagent sodium chloride or sodium bicarbonate from a previously unopened bottle, or dry sand.

Whenever an extinguisher has been used, the usage must be reported without delay so that the extinguisher can be refilled. All extinguishers should be periodically inspected to insure their readiness for use at any time.

C. Explosions

The term "explosion" is used loosely to denote any reaction in which a pressure buildup is sufficiently rapid and violent to shatter the reaction container. Detonations are explosions in which the decomposition, once initiated by mechanical shock or temperature, propagates at hypersonic velocity through the medium and results in a destructive shock wave. Ordinary protective equipment such as safety shields, face shields, and safety glasses provide at best uncertain protection against detonations, even with small quantities of material, though they may be better than nothing. Where detonation is a possibility the reaction should be carried out behind an adequate barricade or in a remote location, and warning signs should be posted throughout the area.

Also under the heading of explosions are non-detonating reactions that get out of control in such a way that the rapid pressure buildup results in bursting of the reaction vessel and spattering of the contents, or where a flammable gas mixture inside a vessel becomes ignited with similar results. Such occurrences are much more common than detonations, and fortunately have less "brisanse". Safety shields and face masks and placement of the apparatus in a hood usually give adequate protection when the quantities involved are not large. However, some reactions that may be carried out safely when under good control at ordinary temperatures may result in detonation when the reaction gets out of control and the temperature rises above the detonation level.

Compounds having oxidizing elements -oxygen or halogen- attached to nitrogen or oxygen may be potential detonating explosives; this is particularly true of nitrogen compounds, since the great stability of the N_2 molecule which is an important detonation product contributes to the driving force of the reaction. Groups which may contribute to explosiveness are: azide ($-N_3$), diazo ($-N=N-$), diazonium ($-N_2$), nitro ($-NO_2$), nitroso ($-NO$), nitrite ($-ONO$), nitrate ($-ONO_2$), fulminate ($-ONC$), peroxide ($-O-O-$), peracid (CO_3H), hydroperoxide ($-O-O-H$), ozonide ($-O_3-$), N-haloamine ($-NHCl$), aline oxide ($=NO$), hypohalites (OX^-), chlorates (ClO_3^-), and perchlorates (ClO_4^-). Ether and conjugated olefins may form explosive peroxides on prolonged exposure to air; many explosions have resulted from distilling ether to dryness. Always test a small portion of such a solution with moist starch-potassium iodide paper before distillation; the slightest blue coloration indicates the presence of peroxide. Heavy metal acetylides, fulminates, and azides are highly explosive, a fact to be remember if a heavy metal salt is present in a reaction where acetylene is to be used. The presence of ammonia and iodine in the same reaction mixture can lead inadvertently to the formation of nitrogen iodide which is a powerful explosive so sensitive when dry that the slightest shock -- such as that resulting from merely picking up the container -- can set it off.

Compounds of the above types vary widely in sensitivity to shock and temperature; nitrogen iodide, ether peroxides, and heavy metal azides are extremely sensitive, while ammonium nitrate is a powerful explosive that can be set off only with another explosive.

Oxidizing agents such as hydrogen peroxide, sodium peroxide, potassium permanganate, perchloric acid, nitric acid, chromium trioxide, nitrogen tetroxide, tetranitromethane, acetyl peroxide, acetyl nitrate, and Tollens reagent, as well as many compounds of types already mentioned, can yield explosive mixtures with oxidizable substances. Carbon tetrachloride and nitromethane may explode during a sodium fusion test. Liquid oxygen, liquid air, or gaseous fluorine in contact with organic substances may lead to spontaneous explosion. Traps cooled with liquid nitrogen are capable of condensing liquid air inside them, which will create a hazard if organic substances are later condensed; a trap on a vacuum system should not be chilled with liquid nitrogen until the pressure has been reduced below 1 torr.

Among reactions that may require careful attention to control, to prevent possible explosion, are: nitrations, oxidations (especially with per-acids, per-salts, peroxides), condensations (Friedel-Crafts, Claissen, Cannizzaro, Reppe), reductions (Wolff-Kishner, metal hydride), and polymerizations (such substances as butadiene, acrolein, and acrylonitrile can polymerize

spontaneously and explosively in the presence of a catalyst which may be an unintended impurity; the same is true of liquid H₂O₂ and liquid acetylene). Some intrinsically slow reactions can be speeded up explosively by the presence of a solubilizer (e.g., NaOH + CHCl₃ in the presence of methanol).

It is not possible to avoid altogether working with potentially explosive substances. Explosion hazard may however be reduced below acceptable limits by following sensible precautions:

- (1) Ascertain the degree of hazard, where possible, by reference to the literature.
- (2) Try any unknown reaction with small quantities, with all reasonable precautions, then scale up. (Beware, however, of the essential unpredictability and non reproducibility of detonations.)
- (3) Compounds that may be prone to detonation should be prepared and handled only in dilute solution; if then they should decompose, even violently, the energy of decomposition is largely absorbed by the solvent. Be sure that transfers are quantitative and washings meticulous so that explosive residues are not left in vessels or on the desk top by evaporation.
- (4) Have adequate means on hand for moderating the reaction (control of heat, cooling water, rate of addition of reagents or quenches); if working behind a barrier, controls should be outside. Always arrange the apparatus with enough space below so that the heating device can be quickly lowered and a cooling bath substituted without moving the apparatus itself.
- (5) Try to avoid adding a reagent faster than it is consumed, especially in oxidation, free-radical, and heterogeneous reactions. Never add organic or other oxidizable materials to a strong oxidant; rather, add the oxidant slowly and with caution to the other substances.
- (6) Be especially alert for indications that something is about to go out of control: a sudden rise in temperature or pressure, the unanticipated appearance of fumes or discoloration, evolution of gas, unexpected boiling, reflux high in the condenser. Any of these may be sufficient cause to quench the reaction if this can be done in time safely (the procedure having been well thought out ahead of time); otherwise it should be the signal to beat a hasty retreat to safe cover, warning others as you go. The same may be said for a situation where a cracked flask, flame around a joint, or a loose connection or stopcock appears to foretell immediate serious trouble. From a safe place, with aid present, carefully appraise the situation and attempt to control the situation at a distance by disconnecting heat and/or discontinuing the addition of reagents. With suitable protective equipment and with help present take whatever additional steps can be carried out safely to mitigate the explosion and fire hazards.

D. Caustic liquids

Although the term "caustic" is often reserved for strong bases, the term is applicable to strong acids and oxidants as well. Concentrated acids (hydrofluoric, hydrochloric, sulfuric, chlorosulfonic, nitric, chromic, phosphoric, trichloroacetic, glacial acetic, phenol) as well as concentrated bases (sodium, potassium, and ammonium hydroxides) are injurious to the human skin and especially to eyes, corrosive to laboratory apparatus and furniture, and destructive of clothing. If taken into the mouth or digestive tract they produce widespread destruction of the mucous membranes and other tissues, which may be fatal. Fumes from some of them (particularly nitric acid and hydrochloric acid) are injurious to the respiratory tract and lung tissue if inhaled, and may result in fatal pulmonary edema.

Some of these substances have high heats of hydration; the thoughtless addition of water to concentrated sulfuric acid or to solid sodium hydroxide may result in a violent reaction with dangerous spatter. In reaction mixtures several of them, particularly the oxidizing acids, may be

involved in run-away reactions which may result in eruption or explosion with considerable spatter and the possibility of harm to eyes and skin.

Chromic acid cleaning solution, which is often used to remove residual hydrophobic films (oil, grease) from laboratory glassware, should be treated with respect. It is made up by the mixing with stirring, of sodium dichromate with concentrated sulfuric acid; caution is required because considerable heat is evolved. Contact with the skin rapidly produces severe burns; contact with wood, paper, cloth, and other organic substances can produce a fire. Use only where necessary (e.g., with volumetric glassware; for other purposes use a phosphate-base laboratory detergent instead. Chromic acid cleaning solution should not be used to remove more than very small amounts of intractable organic residues in flasks, as a violent reaction may take place. During use, the solution container and glassware should be standing in a tray large enough to contain the entire amount in case of spillage or breakage.

Sensible precautions in handling caustic liquids include the following:

- (1) Where there is significant spatter hazard, wear a face shield.
- (2) Protect your clothes with a rubber apron or a laboratory coat.
- (3) Wear rubber gloves when handling containers.
- (4) Work in a hood when any fumes (e.g., HCl oxides of nitrogen) may be evolved.
- (5) Never pipette such substances (or any other toxic or harmful materials) by mouth.
- (6) Use a funnel if pouring into a narrow-mouth vessel.
- (7) Never pour water or a reaction mixture into concentrated acid; pour the acid slowly, or a small amount at a time, into the mixture.
- (8) Wipe up small spills and bottle rings immediately, using rubber gloves and a wet cloth. A large spill constitutes an emergency that requires notification of the laboratory instructor. Strong acids on the table top or floor should be diluted with water and washed down the floor drain, if one is available; otherwise the diluted acid can be neutralized cautiously with sodium bicarbonate (which is applied in solid form) and mopped up. Strong bases should be diluted and washed away or neutralized with solid sodium bisulfate or sodium dihydrogen phosphate. Beware of spatter in either case. Toxic acids such as chromic acid cleaning solution should not be neutralized in any significant quantity with bicarbonate as this may produce an airborne mist of chromic acid. A large spill of cleaning solution may be soaked up in a heavily applied layer of dry sand, which is then shoveled into a metal container and carried immediately outside the building where it can be shoveled, a little at a time, into a pail of water. The site of the spillage should then be washed thoroughly; a neutralizer such as bicarbonate can be applied at this stage.
- (9) In case of skin contact, wash the affected part immediately in running water. A dilute (3%) acetic acid solution or vinegar may then be safely applied in the case of strong alkali, or sodium bicarbonate or laboratory soap in the case of strong acid, followed by more washing with water. Obtain medical help if a chemical burn results.
- (10) In case of eye contact, immediately bathe the eyes copiously in running water: subject the eyes to a copious (but not forceful) flow of water from one of the gooseneck faucets at the laboratory sink; hold the eyelids thoroughly open to bathe the eyeballs and undersides of eyelids. Summon medical help immediately. If alkali is involved, follow the washing with application of a saturated solution of boric acid. Time is of the essence; a caustic alkali can destroy the cornea in as little as five minutes. CAUTION: Boric acid is very toxic and should be used for the eyes only, never taken internally as an antidote for a base or for any other reason.

(11) In case of ingestion of caustics or inhalation of their fumes get medical aid immediately - Before aid arrives, a person who has ingested acid or alkali should be given a considerable amount of water to drink; sodium bicarbon or magnesia can then be safely administered in case of acid ingestion, or dilute (3%) acetic acid or vinegar or lemon juice (NEVER boric acid) in case of alkali.

E. Toxic substances

Almost all chemical substances that are dealt with in the laboratory are toxic to humans when ingested as liquids or solids or inhaled as gases or dusts. It makes sense to take normal precautions with all substances to keep them out of mouth, nose, and eyes, and even off the skin. Some poisons can be absorbed into the body through the skin, others, -- known as vesicants -- can attack the skin and underlying tissues causing dangerous chemical "burns" which are very painful and slow to heal.

Certain substances, because of the high degree of toxicity or the insidiousness of their action, deserve special mention.

(1) Gases: Carbon monoxide (CO) is universally recognized as dangerous because it is colorless, odorless, and tasteless, and physiological symptoms come often too late to give warning. Also in this category for practical purposes are H₂S, HCN, NO, PH₃, AsH₃, SbH₃, and COCl₂ (phosgene), since any of these may be present above the permissible concentration limit before it is detected by odor. This may be a surprise in respect to H₂S, with its familiar "rotten egg" odor, but there is evidence that small amounts quickly deaden the sense of smell; this gas is toxic in lower concentrations than is CO and in not much higher concentrations than HCN. Other particularly hazardous gases are: acrolein, halogens (F₂, Cl₂, Br₂, I₂), hydrogen halides (HF, HCl, HBr, HI), methyl halides (CH₃Cl, CH₃Br), NO₂, O₃ (ozone), CS₂, SO₂, CH₂N₂ (diazomethane), and metal carbonyls. Most of the gases named are extremely dangerous or fatal for exposures of a few minutes at concentrations of the order of 100 ppm (parts per million). The maximum allowable concentration" (often abbreviated MAC) is for most of these gases of the order of 1 ppm, although for phosphine and its analogues it is only 0.05 ppm. Ammonia is also toxic but less so on a concentration basis. Also toxic are ethylene oxide, ethyleneimine, and ketene.

(2) Vapors. The vapors of solvents, particularly benzene, chlorinated (and brominated and iodinated) hydrocarbons, and esters of mineral acids (e.g., dimethyl sulfate) are more dangerous than is commonly recognized. Benzene is a cumulative poison affecting the blood-forming tissues; it has been claimed even to cause leukemia. Chlorinated hydrocarbons affect the heart, circulatory system, and the liver. Even saturated hydrocarbon vapors can have toxic effects. The vapors of nearly all organometallic compounds such as tetraethyl lead and dimethyl mercury are toxic in very low concentrations; the vapor of osmium tetroxide is extraordinarily toxic with MAC as low as 0.002 ppm. The vapors of Br₂, I₂, and CS₂ have already been discussed under gases. Prolonged inhalation of mercury vapor may result in damage to kidneys, eyes, and other organs. The saturation vapor pressure of mercury at room temperature, about 1.8×10^{-3} torr (i.e., about 2.4×10^{-6} atm or about 20 mg per cubic meter), is about 200 times the MAC (0.1 mg/m³ or about 1.2×10^{-8} atm).

(3) Airborne dusts. Beryllium metal and its compounds (MAC: 0.002 ppm), heavy-metal compounds, naphthylamines, and certain alkaloids present a high degree of hazard when they can be inhaled as dusts. Beryllium has a complex toxicology; some effects of chronic exposure may be delayed as much as 15 years.

(4) Vesicants - Liquid bromine, bis-(beta-chloroethyl) sulfide ("mustard gas"), the nitrogen mustards beta-haloethylamine derivatives), a-halo ketones and esters, benzylic and allylic halides, and phenol attack the skin on contact, producing chemical burns and in some cases internal poisoning as well.

(5) Other substances. We now come to substances that are most likely to exert their toxic effect through ingestion or skin absorption. The list is long and we can give here only a sampling. Among inorganic compounds

cyanide salts, mercuric salts (which even in small quantity may produce irreversible kidney damage, and probable death) other heavy metal compounds (Ba, Pb, Cu, Ag, Zn, Cd, Co, Ni, Os, and others), chromates, and beryllium salts must be mentioned. Ferricyanides, ferrocyanides, and thiocyanates are less hazardous than cyanide salts as they do not give rise to free HCN in the body. Beryllium compounds may be absorbed in dangerous amounts through the skin. Oxidizing salts (AgNO₃, chromates) may produce skin damage. Poisonous organic compounds include certain alkaloids and biologically produce toxins, organometal compounds, compounds of hydrazoic acid, esters of inorganic acids such as diisopropyl fluorophosphate, tetraethyl pyrophosphate, dimethyl sulfate, and methyl iodide; several of these can penetrate the unbroken skin. Aromatic amines such as aniline and nitro compounds such as nitrobenzene are particularly dangerous because they are readily absorbed through the skin, where they react in the blood to convert hemoglobin to methemoglobin; in addition they can produce severe damage to the nervous system. Less toxic but still significantly so are benzene, chlorinated hydrocarbons, methanol, and butanol. beta-Naphthylamine, which can be absorbed through the skin, has been incriminated as a carcinogen; one should also be aware that crude alpha-naphthylamine may contain some beta. These are especially dangerous as dusts that may be inhaled. Other carcinogens are benzpyrene and certain other aromatic fused-ring hydrocarbons.

Radioactive substances involve exceptional dangers that are beyond the scope of this review. Examples of radioisotope use are isotope tracer studies, activation analysis with neutron irradiation, fission and nuclear decay studies, "hot-atom" chemistry, and Mossbauer spectroscopy. In all cases the Radiological Safety office must be consulted before such an experiment is undertaken; the handling of and storage of radioisotopes is in nearly all cases subject to terms of A.E.C. licences.

(6) When dealing with toxic substances take proper precautions:

- a. Assume that any substance is toxic unless you know positively to the contrary; when in doubt, consult the Merck index or other toxicology reference works (see Section I below).
- b. Avoid pipetting by mouth.
- c. In dealing with any substance that can attack or penetrate the skin, use rubber gloves and a face mask.
- d. All operations utilizing or giving off toxic or malodorous gases or vapors must be carried out in the fume hood.
- e. Never evaporate solvents in the open; do it in the hood, and in small amounts only (less than 500 ml), using a steam bath. Remove large amounts of solvents by distillation in a hood.
- f. Highly hazardous gases (e.g., Cl₂ phosgene) should be obtained in small cylinders and used only in the hood. When not in use they should be stored in a well ventilated area (never in the hood) or returned.
- g. Operations involving beryllium and its compounds or other substances with highly dangerous dusts should be performed in a "dry box" or glove bag.
- h. Be particularly careful to see that all vessels containing chemicals (hazardous or otherwise) are properly labeled. Never place vessels containing hazardous volatile chemicals or unlabelled or unstopped vessels containing any chemicals, in a refrigerator.
- i. In the event of a mercury spill, regardless how small, pick up as much of the mercury as possible (use a glass or metal capillary tube connected to a trap bottle and an aspirator). In the case of large spills, call the Occupational Medical Service for assistance or advice. Be particularly concerned about mercury in the vicinity of heated objects (steam lines, steam radiators, hot plates) where the vapor pressure will be much higher. Sprinkle any contaminated area with "flowers of sulfur", and after 48 hours sweep up as much of it as possible. Place sweepings in a container and

arrange for it to be picked up by the Safety Office for disposal as described in Section F. Inaccessible mercury droplets in crevasses should be covered lightly with sulfur. Waste mercury (including that recovered from spills) should be accumulated in a stoppered bottle; 'when an appreciable amount has been collected it may be turned in to the stockroom for credit. Do not leave mercury in uncovered vessels.

F. Storage, Transportation, and Disposal of Chemicals

(1) Storage

Small quantities of ordinary chemicals in stoppered, properly labeled bottles may be kept in the laboratory desk; the same is true of solvents in amounts not exceeding more than about a pint. Larger amounts of solvent and all dangerous chemicals in any amount should be stored in safety pails on laboratory shelves (not over the laboratory desk) or in special well-ventilated storage rooms. Never store any chemical in an unstoppered or unlabelled container. Never work in a storage area or store appreciable quantities of chemicals in a working area; do not store chemicals in the hood, where they might make the consequence of a fire or explosion that much worse. Store and use gas cylinders in an upright position, restrained by a chain or clamp to prevent upset. Cylinders should be closed at the main valve and capped when not in use. Cylinders containing toxic gases should be stored in well ventilated place. Promptly return empty gas cylinders, especially those containing toxic gases, to the stockroom. The refrigerator should be used for storage only when necessary, and not for volatile toxic substances.

In general, store chemicals only in amounts for which you see a foreseeable need. Dispose of the contents of any unlabelled bottles you find in your own storage or working areas. Be wary of "old chemicals" that may have deteriorated, decomposed, oxidized, hydrated, formed explosive peroxides, etc.; if you have no foreseeable use for them get rid of them.

(2) Transportation

Solvents (in quantities exceeding about a pint) and all dangerous chemicals should be carried in metal safety pails with well-fitting covers. When putting a bottle into a safety pail or taking-it out, especially while in a dangerous chemicals vault, wear a face shield.

Gas cylinders weighing more than a few pounds should be transported with a hand truck, with protective caps in place. Be very careful not to drop cylinders or permit them to strike each other violently.

(3) Disposal

Most chemical wastes can be disposed of without resort to special procedures, but it is important to know the exceptions. The laboratory sinks can be used for most materials of not excessive toxicity that are soluble in water. If liquid they may be poured down the drain with a copious flow of water; if solid they should be dissolved in water first. Acids and alkalis (including chromic acid cleaning solution) in amounts not exceeding about a pint should be poured slowly into a sink about half full of water after opening the sink drain; after the sink is empty it should be flushed thoroughly for several minutes.

Solvents that are not miscible with water may be flushed down the sink with a considerable amount of water if they amount only to "a few drops"; in any significant quantity they should be poured into waste bottles that are suitably stoppered and labeled. They may later be distilled for re-use, or disposed of as described subsequently.

Hazardous chemical wastes of all descriptions may be disposed of by calling the Safety Office for pickup and transportation to the Waste Chemicals facility (Mudd Hall) which is maintained by the Office of Laboratory Supplies and the Safety Engineer. These wastes must be in suitable containers, properly labeled and stoppered, and if of any considerable size they should be packed in boxes or safety pails with vermiculite to prevent accidental breakage during handling. Among wastes that should be handled

routinely in this way are: any large quantities of acids and alkalis, unrecoverable solvents that are immiscible with water, all kinds of toxic chemicals, especially those insoluble in water., "old chemicals". unlabelled or suspicious bottles of chemicals, all cyanides, alkali metal wastes (covered with Nujol in a suitable container and sealed to prevent accidental contact with water), floor sweepings containing mercury or other hazardous chemicals, and rags, gloves, and other objects that may have become dangerously contaminated.

Mercury should never be allowed to run down a drain, as it will settle in traps where it may not only obstruct liquid flow but also amalgamate with the drain-pipe metal. This may have serious consequences for a plumber who might later heat the pipe with a blow torch.

Cyanides must never be flushed down a drain because of the danger of contact with acids flushed down somewhere else and the consequent evolution of HCN. The hazard is particularly great when several sink drains lead to a common trap.

The waste crocks may be used for inert solid wastes such as paper, cloth, and broken glass. Rags and paper towels that have been in contact with acids, bases, and especially cleaning solution should be thoroughly rinsed first; if dangerously contaminated with highly toxic chemicals they should be put in a wide-mouth bottle or safety pail with appropriate label, for disposal by the Safety Office. In general, chemical wastes are not to be put in the crocks, even in sealed containers; they create too much hazard in the handling of trash by University employees. It goes without saying that alkali metal wastes should never be put in the crock or the sink.

When in doubt as to procedures for disposal, consult the Safety Office.

G. Other Hazards

(1) Pressure and vacuum

Dangers from explosion and implosion will be treated in connection with the techniques of pressure and vacuum operations themselves. In brief: use tank clamps or chains to prevent upset of gas cylinders, which could result in breakage at the valve; use the correct regulators and fittings; use no oil or grease with valves or regulators - especially with oxygen; never admit gas from a pressurized vessel to a closed system without providing an adequate safety relief; carry out all vacuum operations (reduced pressure distillation, vacuum-line manipulation, desiccator evacuation) behind a safety shield; do not move an evacuated apparatus such as a distillation set-up or desiccator; put electrician's tape on all dewar flasks and vacuum desiccators before using. Compressed air from the laboratory line should be used only when necessary, and not routinely for cleaning off machinery, your desk, the floor, or your clothes. The sixty-pound blast can easily burst an eardrum or drive particles deep into the eyeball. Never point a compressed air blast at anyone, including yourself. Never connect the compressed air to a closed system (or one that could by accident become closed) that contains glass bulbs or rubber tubing that is not rated at at least twice the pressure.

(2) Electrical hazards

Most people are aware of electrical hazards in general. It is worth pointing out, however, that the laboratory environment amplifies the hazards somewhat: voltages in some laboratory apparatus are frequently higher than normally encountered (although the familiar 115 volts can be lethal with a good ground and wet hands); metal desk tops and fixtures provide body grounds; water lines and spills can furnish conduction paths. Disconnect apparatus from the electric mains (and in certain apparatus, discharge condensers) before tinkering, use insulating gloves and insulated tools where appropriate, be sure the floor is dry. Do not defeat the purpose of interlocks, fuses, or circuit breakers designed to protect supply lines, equipment, and people. "One hand in the pocket" is good insurance when electric shock is a possibility, and should be adhered to rigidly when throwing open-type switches, removing leads from terminal boards, pulling plug leads from a distribution board, operating line-power

rheostats, etc. Always be sure your hands are dry. Ground exposed parts of all electrical apparatus where possible. Beware of single-pole double-throw switches that may leave part of an apparatus at an AC potential with respect to ground when the switch is off. Beware also of "polarized plugs" with prongs slightly different in width, designed to go into a similarly designed outlet in only one way so as to ground the chassis to the "grounded" side of an AC line; the "grounded" side actually is found quite often to carry a significant voltage with respect to true ground. Moreover, in an unpolarized receptacle or extension cord the plug will frequently go in the wrong way. It is better to use a plug with a third prong for grounding in the appropriate outlet or to provide a positive ground to a clamp on a water pipe. Be sure that power cords, insulators, and ground connections are in good condition, and that fuses used are of the appropriate rating. Avoid temporary wiring as much as possible; use it 'with caution. Be very careful with electrical apparatus that may be wet, especially heating mantles and devices with exposed conductors.

Very high voltages carry special hazards. In dry air a spark can jump approximately one centimeter for each 10,000 volts; the distance is greater with wet air or with sharp-pointed electrodes. X-rays may be a significant hazard when the voltage exceeds about 15,000 volts; this hazard can be present in oscilloscopes, electron microscopes, and electron diffraction apparatus as well as from high voltage rectifier tubes.

(3) Radiation

Aside from radioactivity, with which we will not deal further here, injurious radiation in the laboratory comes under four principal headings: X-ray, ultraviolet, laser, and radio-frequency power.

(a) X-Rays are used by chemists primarily in crystallographic diffraction work. Such work should be performed only by persons who have been adequately trained in the procedures and precautions, or under the immediate and responsible direction of such a person. An X-ray generator and diffraction apparatus must be shielded with 2 mm of lead (or equivalent) so that no direct radiation escapes into the room from either of them or the junction between them, and so that scattered radiation arising from the junction, the crystal, and the beam stop are at the lowest possible levels. Every diffraction experiment should be monitored with a counter-type survey meter and it should be ascertained that the radiation level at all points around the apparatus is no more than 10 mrem/hr (millirem/ hour), and preferably less. The allowed occupational dosage of whole-body X-radiation is 300 mrem/week (but no more than 5000/year hands or forearms are allowed several times than much. The output of the X-ray tube at the window may be 10^4 rem or 10^7 mrem/min! Local exposures of more than 1000 rem (easily obtained on the fingers when working on the apparatus with a tube port open) can produce serious skin burns; probably much smaller exposures can cause eye cataracts. A whole-body one-time exposure of 500 rem (500,000 mrem) of penetrating X-rays is usually fatal, but difficult to imagine as coming from a diffraction X-ray generator since the beam is somewhat confined; also, the principal component of X-rays used in diffraction penetrates only a few millimeters into the body. However, an insidious hazard with some X-ray units is back-conduction of a gassy rectifier tube during the non-rectification halfcycle of a full-cycle rectifier circuit; this can result in radiation of twice the nominal maximum energy as the beam from the X-ray tube, and of greater penetrating power. Adequate shielding of the transformer-rectifier unit (1/8 inch of lead), good periodic maintenance, and routine monitoring of the radiation background are essential. Walls, ceilings, and floors do not provide reliable isolation of crystallographic X-rays unless at least equivalent to five inches of solid concrete; wooden doors and plasterboard partitions are not to be trusted.

The laboratory should be equipped with film badges mounted at appropriate positions to detect escaping direct radiation. Before the X-ray unit is turned on answer the question: are all X-ray ports adequately covered? Before leaving the room, be sure that no mechanical malfunction of the diffraction camera can possibly lead to radiation hazard during the run (by slippage of a shield, displacement of a collimator, etc.). A woman in the first few weeks of pregnancy should avoid any exposures to X-rays as the

foetus is extraordinarily sensitive to injury that is likely to result in subsequent malformation.

(b) Ultraviolet radiation (such as is used in spectroscopic and fluorescence experiments) can provide skin burns (akin to sunburn) and, more especially eye damage (particularly cornea and lens). Eyeglasses provide some protection; special goggles (with side protection) are better. In any case, careful attention should be given to shielding the experiment to prevent the escape of any direct beam or any significant amount of scattered radiation.

(c) Laser radiation is potentially dangerous to the eyes (retina) because of the high energy content available in the laser beam and because, being coherent and parallel, the beam can be focused to provide exceedingly high local intensities. Adequate shielding must be provided. Eyeglasses, of course, give no protection from lasers in the visible range.

(d) Radio-frequency power such as is used in induction melting of alloys and certain microwave applications can be absorbed deeply in human tissues, "cooking" them quickly and causing deep burns. Shield induction units as well as possible; keep your body out of a microwave beam.

Eye damage can also be produced by flash tubes, very bright sparks, and arcs.

(4) Centrifugation

A centrifuge contains a high-speed rotor which is under considerable stress owing to centrifugal force. In a well-designed centrifuge properly operated, these stresses are well below those required to rupture the rotor. However, abuse of this apparatus can result in the rotor being more susceptible to rupture at a given stress; moreover, the stresses can be considerably increased by vibrations arising from imbalance. When the rotor does rupture, its fragments become dangerous high-speed projectiles similar to bullets or shrapnel that can in some circumstances rip through the steel outer jacket, through partitions between rooms and then through human flesh. A high-speed centrifuge should have an adequate barrier against such a possibility; for an "ultracentrifuge" this might be a reinforced concrete wall about a foot thick.

Besides providing an adequate barrier against bursting, it is important to guard against imbalance which is the principal cause of rotor failure. Each centrifuge tube containing a sample must be balanced with another of this same gross weight (or rather, moment of inertia) diametrically opposite. Be careful that imbalance does not occur during the run owing to differential evaporation of solvent. This can easily happen when two liquids of different vapor pressure are present diametrically opposite, or when a concentrated solution is initially balanced with the same weight of pure solvent. It is best to balance each sample with another identical to it.

While the centrifuge is operating, and especially while it is approaching its operating speed, be alert for unusual noises or other evidence of excessive vibration; turn it off if any should arise. Never attempt to stop a centrifuge by mechanical interference; never put your hands into the centrifuge until the rotor is absolutely stationary.

H. Procedures in case of accident

First priority is to get all persons injured and uninjured out of the dangerous environment; second is to provide any emergency action needed to minimize injuries (washing of eyes or skin, antidotes in certain cases); third is to summon medical help if needed. Since a modern-day chemical laboratory is seldom (and should be never) more than a very few minutes away from competent medical aid, first-aid measures by those on the spot are in general inadvisable. Exceptions are immediate precautions to minimize effects of shock, electrical or other; artificial respiration when breathing has stopped; prompt staunching of any serious flow of blood by use of a pressure compress (not a tourniquet); use of the cyanide kit in cyanide poisoning; measures described elsewhere to deal with caustic substances in the eyes or ingested. Leave mechanical eye injuries to be

dealt with by the doctor (restrain the patient if necessary from aggravating the injuries by blinking). Likewise leave to the doctor the treatments of burns of all kinds and (in general) the administration of antidotes in all cases of poisoning.

The Johns Hopkins University emergency number is x7777.

In summoning medical help be as explicit concerning the nature of the injury; before calling, take particular note whether the eyes are involved and whether shock is evident. If the injured is clearly ambulatory (showing no signs of shock), arrange for him to be received at the medical center as soon as he gets there, and accompany him there. Shock is always a dangerous possibility in cases of severe injury or trauma, and may result quite unexpectedly in sudden heart stoppage and death. A person in shock has a weak pulse and low blood pressure, his face and extremities will be pale and cold, he may be nauseated and may vomit, he may be light-headed, or feel faint, his breathing may be shallow and rapid and perhaps irregular. In the case of irregular breathing or unconsciousness, there may be serious danger to life. Keep the victim warm and quiet lying flat. Loosen any tight clothing at neck and waist. Give the victim nothing by mouth, but his lips may be moistened. Especially important:

- (1) never give stimulants of any kind when shock is present or a possibility, and
- (2) never give anything by mouth to an unconscious person.

After all possible has been done to remove personnel from danger and assure needed care for any injured persons, attention can be directed to minimizing other destructive effects of the accident. In any but the most minor of fires or other accidents, and in all cases where there is injury to personnel, emergency aid should be called by JHU extension **x 7777**.

The Safety Officer **x8798** should be called also and should supervise the decontamination of the area in the event of the presence of toxic, flammable, or caustic chemicals in the environment. The Radiation Safety Office (ext. 8798) should be called in the event of any known or suspected X-ray exposure.

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