

Appendix F

Preventing Chemical Incompatibility Hazards

Unsure if your chemicals are compatible?

Call us at 5-5518.

Consider chemical compatibility when:

- Storing chemicals
- Packaging chemicals for transport
- Pouring a variety of solvents into carboys

Avoid the hazards of chemical incompatibility. Incompatible chemical mixtures can cause violent reactions, explosions, fires or generate toxic gases. Containers that are incompatible with their contents can leak or catastrophically fail. In a fire or other disaster, containers break and chemicals could combine to fuel a fire or react to injure emergency responders. What threat would your bottles of oxidizers and flammable liquids pose if fire fighters dragged hoses through the aisles of your laboratory? Address chemical incompatibility hazards from three perspectives:

- ✓ **Containment:** proper containers and closures prevent leaks and releases.
- ✓ **Storage:** keep any aqueous acids away from cyanide salts.
- ✓ **Mixing:** oxidizers, acids, or reactives should not be mixed together in a flammable solvent waste container.

Because of the scope and complexity of this topic, this Appendix is not meant to be comprehensive. For more information consult *Bretherick's Handbook of Reactive Chemical Hazards, Fourth Edition* (L. Bretherick, Butterworth's, London 1990), and NFPA 491, *Guide to Hazardous Chemical Reactions, 1997 Edition*, or call the American Chemical Society's Health and Safety Referral Service (1-800-227-5558). This ACS service keeps records of chemical accidents and incompatibility incidents that have been reported in *Chemical and Engineering News*.

F.1 Containment to Prevent Hazards

Use the right container for the job to keep your chemicals safe. Use secondary containment whenever possible. Follow these general guidelines for safe containment of laboratory chemicals:

Do not store hydrofluoric acid in a glass container.

- ◆ Use containers that are compatible with their contents. The chemical should not react with the container material or cap liner. For example, do not store hydrofluoric acid in a glass container. Whenever possible, store chemicals in their original containers; transfer chemicals only to containers made of like materials.
- ◆ Buy smaller quantities. Chapter 6 of this *Guide* discusses waste minimization. Smaller quantities make safe storage easier, and simultaneously encourages waste minimization. Additionally, smaller bottles are less prone to break when accidentally dropped.
- ◆ Use safety cans for storage of flammable liquids. Fire codes allow only 38 liters (10 gallons) of flammable liquids in a lab if stored in conventional containers. But, if stored in UL-approved safety cans or a flammable liquid storage cabinet, up to 76 liters (20 gallons) may be stored in a single fire area (i.e., a fire area may be more than one lab rooms; ask your building manager or call Safety for an evaluation).
- ◆ Whenever possible, purchase materials in coated bottles.
- ◆ Make sure that all containers are properly labeled.
- ◆ Inspect your chemical stocks periodically to make sure the containers are sound and labels are intact.

Some chemicals require special devices such as vent caps for alleviating pressure buildup. Dibenzoyl peroxide, for example, requires a container that is non-rigid to prevent shock transfer, has a non-threaded cap to prevent friction when opening and is resistant to static electricity buildup; all of these precautions may help to prevent an explosion.

Choose Safer Containers to Reduce Breakage

Buy chemicals in plastic-coated bottles. These are coated with a thin layer of polymer to help absorb shock, prevent breakage and act as a secondary container in the event the bottle is broken. The safest container is a UL-approved safety can. The least safe is an uncoated glass container. It will shatter if dropped on the floor or if lightly tapped where there is a crack.

<i>Safest</i>	→	→	→	<i>Least Safe</i>
Safety Cans	Metal Cans	Coated Glass	Plastic	Glass

Secondary containment means using a second, outer container to collect and contain spills or leaks from a primary chemical container. Secondary containment can be a plastic tray, a bottle carrier or a wide-mouthed jar containing a smaller bottle.

Use Secondary Containment. For liquid and high hazard chemicals, secondary containers are effective tools to prevent reactions between incompatible chemicals. When storing reactive materials, secondary containment can prevent degradation and reactions that occur during storage (i.e., use a wide-mouthed jar to protect smaller bottles). For transporting bottles in hallways, place them in a specially- designed carrier or a five-gallon plastic bucket to prevent spills. It is best to use secondary containers made of materials that are non-reactive, e.g. polyethylene.

F.2 Safe Chemical Storage

Incompatibility of stored chemicals is a serious concern in the event of an accident, container breakage, a spill, a tornado or a fire. When responding to a laboratory fire with bulky equipment in a smoke filled area, firefighters may unintentionally break containers of chemicals. To minimize such risks, limit the amounts of chemicals on your benchtop to the minimum required for the day's work and safely store the remainder as described below. Also see the Chemical Storage and Management section of Chapter 4 for more information.

F.2.a Designate Cabinets / Areas for High Hazard Chemicals

Follow the specific storage requirements for flammable liquids and strong acids listed below.

Flammable Liquids

Large volumes of flammable liquids, more than ten gallons per 100 square feet of floor space, must be stored in an approved flammable liquid cabinet or safety can. Store containers of flammable liquids in these cabinets. Refer to Chapter 4 of this *Guide* for more information on flammable liquid storage cabinets.

Acid Cabinets

Bottles of acid should be stored in an acid cabinet. While acids and bases are both considered to be corrosive, do not store acids and bases in the same cabinet. It is

Glacial acetic acid is an unusual case due to its flammability. Keep glacial acetic acid in a fire safe cabinet to protect it in a fire, but place the bottle within secondary containment to separate it from other flammable liquids.

particularly important to avoid storing ammonium hydroxide and strong mineral acids in the same cabinet.

Store oxidizing acids, such as perchloric and nitric, separately in a secondary container *within* an acid cabinet. Polypropylene boxes for use in acid cabinets are available commercially. Glacial acetic acid is both corrosive and flammable; store it in secondary containment in a flammable storage cabinet.

A good guide to storage of strong, liquid acids is based upon its chemical classification. For this consideration, acids that are relatively weak (i.e., $pK_a > 2.3$), dilute aqueous or non-volatile solids are not of concern. The classification is based upon one of 9 categories the acid fall within.

Oxidizing	Ox	crossed with	Water reactive	WR
Non-oxidizing, non-reducing	NRedOx		Non-water reactive, non-aqueous	NAqWR
Reducing or organic	Red		Aqueous	Aq

Examples of acids and their resulting category are in the table, below.

Acid Categories		
Ox - WR <ul style="list-style-type: none"> ◆Chromyl chloride ◆Nitric acid 100% ◆Perchloric acid 100% ◆Bromine pentafluoride ◆Chromic - sulfuric acid mixture 	Ox - NAqWR	Ox - Aq <ul style="list-style-type: none"> ◆Nitric acid 67% ◆Perchloric acid 72% ◆Chromic acid (Chromerge solution)
NRedOx - WR <ul style="list-style-type: none"> ◆Sulfuric acid ◆Fuming sulfuric ◆Chlorosulfonic acid ◆Sulfuryl chloride ◆Fluorosulfonic acid ◆Phosphorus oxychloride ◆Trifluoroacetic anhydride or chloride ◆Trifluoromethanesulfonic anhydride or chloride ◆Boron tribromide ◆Silicon tetrachloride ◆Titanium tetrachloride ◆Antimony pentafluoride ◆Vanadium tetrachloride 	NRedOx - NAqWR <ul style="list-style-type: none"> ◆Phosphoric acid 85% ◆Fluoboric ◆Trifluoromethanesulfonic acid ◆Trifluoroacetic acid ◆Hydrofluoric 100% 	NRedOx - Aq <ul style="list-style-type: none"> ◆Hydrofluoric acid 50% ◆Hydrochloric acid 36% ◆Hydrobromic acid 48% ◆Trichloroacetic acid solution 30% ◆Fluoboric acid 50%
Red - WR <ul style="list-style-type: none"> ◆Acetyl chloride ◆Chloroformate esters ◆Oxalyl chloride ◆Methyl fluorosulfonate ◆Diethylaminosulfurtrifluoride (DAST) ◆Thionyl chloride ◆Phosphorus trichloride 	Red - NAqWR <ul style="list-style-type: none"> ◆Dichloroacetic acid 	Red - Aq <ul style="list-style-type: none"> ◆Hydroiodic acid ◆Sulfurous acid (saturated) ◆Hypophosphorus 50%

Once an acid has been classified into one of the nine categories, then storage can be done with these considerations:

- ✓ NRedOx is generally compatible with Red and Ox; NAqWR is compatible with Aq and WR.
- ✓ Generally, Red versus Ox is a worse incompatibility than Aq versus WR
- ✓ Organic acids like formic, acetic, lactic, pyruvic, acetic anhydride and dichloroacetic acid are best placed with the organic solvents.
- ✓ Chloroformates and acetyl chloride, even though they're flammable, are best with the Red - WR group

F.2.b Spatial Considerations for Safe Storage

Incompatibility risks can also be minimized by considering the configuration of your storage area and the proximity of incompatible substances. Follow the guidelines below.

Most laboratories should have:

- A flammable cabinet
- An acid cabinet
- Liquids on lower shelves within trays

Storage of Liquids

Do not store bottles of liquids above your containers of solids, and never above eye level. Keep your bottles of liquids stored close to the floor to lessen the chance of breakage and prevent them from reacting with chemicals on lower shelves. This will also prevent injuries to laboratory personnel from liquids leaking at eye level.

Compatibility Considerations for Open Stock

Keep stored incompatible chemicals apart from each another. Keep dissimilar materials apart by distance, shelf, shelving unit, drawer, or cabinet.

By using flammable and acid cabinets, and following the containment guidelines listed above, you will eliminate from your laboratory many of the compatibility risks associated with chemical storage.

F.3 Preventing Binary Mixture Hazards

Accidental mixing of chemicals may result in a vigorous and hazardous chemical reaction. Generation of toxic gases, heat, overflow or rupturing of containers, fire, and even explosions are possible consequences of such reactions. These reactions may be immediate or they might take some time or outside help to gain momentum. However, these violent reactions will occur only if the chemicals are mixed together, not when the incompatible materials are merely present in the same room at the same time. Although binary mixture compatibility is not always applicable to storage of chemicals, it must be taken into account when packaging chemicals for transport and especially when pouring a variety of solvents into carboys. An improperly packaged box of chemicals could turn into a bonfire or emit toxic gas if the box falls, the bottles break and incompatible chemicals mix.

The chemical compatibility lists in this Appendix are derived in part from *Bretherick's Handbook of Reactive Chemical Hazards*, and shows chemical combinations that can be dangerous. You should have special concern for:

- ◆ Toxic or explosive generation of gas.
- ◆ Fire from oxidizers meeting combustibles.
- ◆ Explosive liquids formed in accidental mixing.
- ◆ Heat of reaction causing boiling and/or splattering of hazardous substances.

Binary mixture compatibility applies to:

- preventing violent reactions in your lab work
- packaging chemicals for transport
- pouring a variety of solvents into waste solvent collection carboys

A graduate student sitting at a lab computer was surprised by a chemical waste bottle which burst and sprayed nitric acid and glass shards. About 2L of nitric acid waste had been accumulated in a chemical waste bottle which originally held methanol. Over a 12 - 16 hr. period, some residual methanol reacted with the nitric acid and created enough CO₂ to overpressure the container.

Accidents can result from incompatible chemical combination whether planned or unintended. Binary mixing hazards are prevented by laboratory:

- ✓ supervisors establishing standard operating procedures for chemical work.
- ✓ personnel being aware of the specific mixing hazards commonly found in their experiments.

This section also discusses some of the more common incompatible laboratory chemical risks: strong oxidizer-reducer combinations, mixtures that generate toxic gases, and water or moist air incompatibilities.

F.4 Safe Procedures for Chemical Work

One of the best ways to minimize the chance of chemical mixture hazards is to have good chemical safety procedures in place. These include:

- ◆ having a written Chemical Hygiene Plan that takes into account the specific hazards of your laboratory (See Appendix B and Appendix C).
- ◆ laboratory supervisors routinely observing hazardous processes and periodically reviewing and updating procedures.
- ◆ laboratory supervisors providing the correct protective equipment and making sure it is used correctly (See Chapter 4).
- ◆ having Material Safety Data Sheets (MSDSs) available for the chemicals that are used in your laboratory and consulting them for incompatibilities.

Chapter 4 of this *Guide* provides information on general laboratory safety.

F.5 Strong Oxidizer-Reducer Incompatibilities

The combination of a strong oxidizer and a reducer can result in a violent reaction. Take extra care to avoid accidental combination of oxidizers and reducers. By segregating oxidizers and reducers, you will further reduce the problems involved with storage of oxidizing chemicals.

Oxidizers

◆ Acidic

- Fluorine
- Chlorine
- Ozone
- Nitrogen dioxide
- Tetranitromethane
- Dichlorocyanuric acid and salts
- Trichlorocyanuric acid
- Hydrogen peroxide
- Chromium trioxide
- Chromyl chloride
- Ruthenium tetroxide
- Bromine pentafluoride
- Xenon difluoride
- Perchloric acid anhydrous
- Bismuth pentafluoride

Reducers

◆ Pyrophoric

- Phosphorus, white
- Sodium-potassium alloy
- Rubidium and cesium
- High surface area titanium, zirconium, hafnium, iron, nickel (as Raney Nickel)
- Boranes, up to penta
- Aluminum Hydride
- Silanes
- Phosphine
- Diphosphine
- Alkyl boranes
- Alkyl aluminums
- Alkyl galliums
- Alkyl phosphines
- Alkyl arsines

◆ **Basic and non-basic anions**

- Peroxide
- Superoxide (Dioxide)
- Perborate
- Percarbonate
- Nitrite
- Nitrate
- Peroxydisulfate
- Persulfate
- Hypochlorite
- Chlorite
- Chlorate
- Perchlorate
- Bromate
- Iodate
- Periodate
- Xenate
- Bismuthate
- Chromate
- Dichromate
- Permanganate

◆ **Ammonium salts (relatively stable)**

- Nitrate
- Perchlorate
- Peroxydisulfate
- Chromate
- Dichromate

◆ **Oxides**

- Manganese(IV)
- Nickel(III)
- Silver(II)
- Gold(III)
- Lead(IV)
- Bismuth(IV)

- Alkyl zincs
- Alkyl and aryl alkalines and alkaline earths
- Vanadium hexacarbonyl, Iron pentacarbonyl
- Titanium(II), Zirconium(II), Vanadium(II), Molybdenum(III) oxides and salts

◆ **Air and water reactive**

- Alkaline and alkaline earth metals, their hydrides, alkyls, aryls, carbides, acetylides, amides, phosphides
- Tetrahydridoaluminates
- Aluminum carbide, nitride and phosphide
- High surface area magnesium, aluminum, iron, zinc, rare earths, lanthanides and actinides

◆ **Water stable (not as much air resistant)**

- Titanium(III), vanadium(III), Chromium(II), Iron(II), Cerium(III), Tin(II) salts
- Borohydrides, hypoborates
- Oxalates, formates, carbon monoxide
- Formaldehyde, carbohydrates, alcohols
- Hydroquinone, ascorbic acid
- Hydroxylamine, hydrazine, ammonia
- Hypophosphites, phosphites, hydrosulfites (dithionites), sulfites, sulfides, thiosulfates
- Cyanides, thiocyanates
- Iodides

◆ **Organic compounds (other than already listed)**

- Must have at least one: Carbon to carbon bond, Carbon to hydrogen bond or Carbon to nitrogen to hydrogen bond set
- Can otherwise have a carbon bond to silicon, tin, lead germanium, mercury, nitrogen, chalcogen or halogen

◆ **Organometallic and transition metal carbonyls**

- Hexacarbonyl chromium, molybdenum and tungsten
- Metallocenes - dicyclopentadienyliron
- Triphenylphosphino metals - tetrakis(triphenylphosphino)palladium
- Infinite variety on these themes

◆ **Non-metallic elements**

- | | | |
|------------|-------------------|-------------|
| - Hydrogen | - Boron | - Carbon |
| - Silicon | - Phosphorus, red | - Sulfur |
| - Arsenic | - Antimony | - Tellurium |

◆ **and, additionally, these metals**

- The "early" transition metals (Groups 3 - 7)
- Cobalt - Nickel - Cadmium
- Gallium - Indium - Germanium

- Tin - Lead

F.6 Toxic Gas Generation

Certain compounds when mixed, as in a spill or breakage of containers in a package, may react to produce toxic gases. This danger is present when at least one component is a liquid or a dissolved solid, usually as an aqueous solution. This toxic gas can be produced from either acid or base incompatibility.

Acid Incompatibilities		
Solid ... mixed with	Liquid ... produces	Gas
Azide salts, soluble	Concentrated acid	Hydrazoic acid vapor
Bromide salts, soluble	Sulfuric acid > 95%	Sulfur dioxide and bromine
Bromate salts	Strong, conc. acid	Bromine, oxygen, hydrogen bromide and heat
Chloride salts, soluble	Sulfuric acid > 95%	Hydrogen chloride
Chlorate or chlorite salts	Strong, conc. acid	Oxygen, hydrogen chloride and heat
Cyanide salts, soluble	Any acid	Hydrogen cyanide
Cyanometal salts (potas.ferricyanide)	Strong, conc. acid	Hydrogen cyanide
Fluoride salts, soluble	Strong, conc. acid	Hydrogen fluoride
Silica or silicate salts	Hydrofluoric acid	Silicon tetrafluoride
Bleaching powder (CaCl(OCl))	Acid	Chlorine
Acid	Chlorox solution	Chlorine
Nitrite salts, soluble	Concentrated acid	Nitrogen oxides
Sulfide salts, soluble	Acid	Hydrogen sulfide
Sulfide, transition metal	Strong acid	Hydrogen sulfide
Sulfite salts, soluble	Acid	Sulfur Dioxide
Manganese dioxide Permanganate salt Cobaltic oxide Nickel sesquioxide Lead dioxide Ceric oxide Hydrogen peroxide	Hydrochloric acid, concentrated	Chlorine

There are some fine points to note when reviewing this table:

- ✓ Where the word "Acid" is listed as the incompatible liquid, aqueous solutions of these salts can slowly liberate the product gases from reaction with carbon dioxide that is normally in the air.
- ✓ Bromate, chlorate, chlorite, permanganate and nitrite salts made acidic with concentrated sulfuric acid may ignite or explode. Also, these salts, if intimately mixed with ammonium salts, may ignite or explode.
- ✓ Concentrated nitric acid used to clean metal residues or to reduce material from glass or ceramic surface will first be reduced to nitrous acid, which then decomposes to nitrogen oxides producing a brown or orange vapor that is often observed from the process.

- ✓ Chlorine bleach is made by reacting chlorine with a base solution; it produces a hypochlorite - chloride mixture which is stable as a base solution or salt mixture. Adding acid, even carbon dioxide will regenerate the chlorine.
- ✓ Hydrofluoric acid or materials that on contact with moisture produce hydrofluoric acid will react with silica in glass to form silicon tetrafluoride. If there is excess moisture in a container, this gas production can pressurize a sealed container and cause it to burst.
- ✓ Concentrated sulfuric acid appears to oxidize bromide to bromine. What seems to drive this reaction is that sulfuric acid wants water and will take it from the sulfurous acid that is produced in a weak equilibrium of bromide reduction of sulfate. This leaves the sulfur dioxide stranded with bromine. Concentrated sulfuric acid also will "char" cellulose and sugars by simply removing water and leaving the carbon molecules behind.

Base Incompatibilities		
Solid mixed with	Liquid produces	Gas
Ammonium Salts	Concentrated base solution	Ammonia
N-methyl-N-nitrosamides (Diazaald)	Base solution	Diazomethane

F.7 Water or Moist Air Incompatibilities

Some common laboratory chemicals have a great affinity for or react vigorously with water. It is important to understand situations in which water reactivity may occur and take care not to store or use these chemicals in damp areas.

The first step in understanding water reactivity is to note that there are a variety of ways in which water reacts with chemicals and a variety of outcomes; some are hazardous, some are annoying and others are desired.

Reactions include:

- ◆ **Hydrolysis** of a bond
- ◆ **Hydration**, water as a ligand
- ◆ **Solution** by water, dissociation of ions or solvation
- ◆ **Oxidation** by water, forming hydrogen
- ◆ **Reduction** by water, forming oxygen
- ◆ **Disproportionation** of an oxidation state to (a) higher and lower one(s)

Factors affecting the outcome can be kinetic and thermodynamic:

- ◆ Heat of reaction relative to the heat capacity of what is involved
- ◆ Rate of interaction or mixing with water
- ◆ Rate of reaction with water once mixed

Possible outcomes include:

- ◆ **Heat** of reaction generated
- ◆ Hydrolysis liberates a **gas**
- ◆ Hydrolysis generates **acid** protons
- ◆ Hydration **liquifies** a solid
- ◆ **Hydrogen** is generated
- ◆ **Oxygen** is generated

The specific type water interaction is also important:

- ◆ Limited water is added to material
- ◆ Material is added to water that is in excess
- ◆ Humidity in air invades a container or exposed material

The heat generated by the reaction relative to the capacity of the solution to absorb that heat will determine the maximum temperature that a possible reaction can attain. Since this section is primarily concerned with water reactivity, the heat of vaporization of the water is an important factor. The heat generation rate and the

vaporization rate interact to determine how an interaction will play out. Some factors that can limit the rate of access to water include:

- ✓ the fineness of a solid,
- ✓ viscosity of a liquid,
- ✓ density relative to water and
- ✓ solubility in water, its rate and maximum.

The water-material ratio is a key factor. Conditions which affect this ratio (e.g., if a powder flie away, a liquid readily evaporates from the reaction heat, etc.), will limit the rate of reaction.

Thus, in a reaction that produces a great amount of heat, if the rate of water reaction is fast but the rate of interaction among the materials is limited by physical factors (e.g., small diameter, tall column), not solubility, then high temperatures and splattering can result because heat is being generated in only a small amount of the material in the container. If the solubility rate (and / or extent of solubility itself) is temperature dependent, a non homogeneous mixture can at first slowly build heat and increase temperature so that it may react suddenly and energetically later.

This exact situation is seen in the neutralization of acids with sodium hydroxide pellets. In the case of both sulfuric acid and sodium hydroxide pellets, the heat of hydration is fairly high but the rate of solution is limited by the acid's viscosity and the pellets' surface area. When these are slowly added TO water, constantly stirring the mixture, heat is dissipated evenly. However, if water is added to THEM slowly, it can boil and splatter the material.

Another water reactivity issue involves storage of potentially reactive compounds in sealed containers. Humidity in air may invade a confined bulk of a water reactive substance. The humidity can react and heat can build at a rate limited only by the air intrusion. Another interesting situation that is commonly seen involves a material in an almost air tight container. Air and humidity invades the container. The heat and rates of reaction may be low, but a gas that is otherwise not trapped, dissolved or absorbed by the material is produced on hydration. While small molecules like air and water vapor can readily diffuse into the container, the larger gas molecules produced in the reaction (e.g., hydrogen chloride, carbon dioxide, etc.) diffuse out at a much slower rate. The result is that pressure builds in the container.

Chemicals that have a high heat of hydrolysis and reasonable rates of interaction and reaction and produce a flammable gas like hydrogen, methane or acetylene can ignite on contact with water because the heat produces a locally high temperature that ignites the gas.

- ✓ Active metals, their hydrides and carbides or acetylides will do this.
- ✓ Active metal phosphides need only a moderate rate of interaction and hydrolysis to ignite with water as the phosphine and diphosphine produced will ignite without much heat.
- ✓ Active metal sulfides are less prone to this because hydrogen sulfide is more water soluble than phosphine. A high heat of hydrolysis and limited water addition may cause ignition though.
- ✓ Soluble cyanide and sulfide salts can be a toxic hazard when humidity and the ubiquitous, low level, carbon dioxide in air combine to hydrolyse and liberate hydrogen cyanide and hydrogen sulfide, slowly but possibly significantly, due to mild carbonic acid action.

- ✓ Additionally, bleach, which is a mixture of hypochlorite and chloride ions, will produce chlorine on this same combination in air contact.

Aqueous solutions of the latter three examples all are susceptible to loss due to carbon dioxide contact.

While disproportionation aided by water is not common, it is worth mentioning. Potassium osmate (K_2OSO_4) can decompose to osmium dioxide and osmium tetroxide in mildly acidic water; the dioxide is insoluble and the tetroxide is volatile. A manganate salt, MnO_4^- , a green colored aqueous solution will become permanganate, purple solution and precipitate manganese dioxide; no hazard really. Ammonium thiosulfate, photo fixer, slowly becomes sulfur and ammonium sulfite, which decomposes to sulfur dioxide. Vanadium tetrachloride, on somewhat violent hydrolysis in water, will become vanadium oxychloride and vanadium trichloride, both of which further hydrolyse.

Some salts are deliquescent and will take on water beyond a few water molecules of hydration; they can take water to the extent of overflowing a container if moist air can seep in. A hazard can arise from a material becoming mobile as a water solution spilled on a storage shelf.

Water Reactions

◆ Immediate Violent Reaction with Water

- Boron tribromide
- Dichlorophenylboronate
- Trifluoroacetic anhydride
- Oxalyl chloride
- (chloromethylene)dimethyliminium chloride (Vilsmeier Reagent)
- Sodium oxide
- Magnesium chloride anhydrous
- Aluminum chloride anhydrous
- Silicon tetrachloride
- Phosphorus trichloride
- Phosphorus pentachloride
- 1,2-phenylene phosphochloridite
- Phosphorus pentaoxide
- Trifluoromethanesulfonic anhydride
- Methyl fluorosulfonate
- Fuming sulfuric acid
- Sulfur trioxide
- Chlorosulfonic acid
- Chlorosulfonyl isocyanate
- Diethylaminosulfurtrifluoride (DAST)
- Thionyl chloride
- Titanium tetrachloride

◆ High Heat of Hydrolysis but Slow Solubility

- Acetyl chloride

◆ Decomposed by Water, not Necessarily Reactive

- Lithium
- Magnesium (fine)
- Calcium
- Strontium
- Barium
- Aluminum (fine)
- Beryllium hydride, Calcium hydride
- Phenyl aluminum, Phenyl zinc
- Carbides of 2A
- Aluminum carbide
- Aluminum nitride
- Lithium amide

◆ Pressure Buildup in Container from Humidity Intrusion

- Chloroformate esters
- Chloroacetone
- Aluminum chloride anhydrous
- Cyanogen bromide
- Dichlorodimethylsilane
- Oxalyl chloride
- Trimethyloxonium hexafluorophosphate
- Diethyl pyrocarbonate
- Phenyl isocyanates
- Beryllium carbide

- Methanesulfonyl chloride
- Phosphoryl chloride
- Sulfuryl chloride
- ◆ **Ignites in Air if made Moist or Wet**
 - Sodium, Potassium, Rubidium, Cesium
 - Calcium, Strontium (powders)
 - Hydrides of 1 A, Magnesium hydride, Barium hydride
 - Lithium Aluminum Hydride, Aluminum borohydride
 - Alkyls of 1A, 2A, 3A (13) metals, Zinc and Cadmium
 - Phenyls of 1A, 2A metals
 - Carbides or acetylides of 1A metals
 - Calcium carbide (phosphide traces)
 - Sodium amide
 - Nitrides of 1A
 - Calcium nitride (powder)
 - Phosphides of 1A, 2A metals, Zinc
- ◆ **Pressure buildup without Humidity**
 - Diisopropyl fluorophosphate in glass
 - Pyruvic acid
 - Formic acid
 - Iron and Nickel carbonyls
 - Nitrite esters
 - Trichloroacetic acid aqueous solutions (< 30%)
 - MEK peroxide in dimethyl phthalate
 - Ammonium peroxydisulfate
 - Hydrogen peroxide
 - AIBN (azobis(isobutyronitrile))
 - Hydrogen chloride in methanol (anhydrous)
 - Diphosgene (trichloromethyl chloroformate)
 - Triphosgene (trichloromethyl carbonate)
 - Used chromic acid cleaning solutions
- ◆ **Observations of Deliquescence Overflowing a Container**
 - Antimony trichloride
 - Ferric perchlorate
 - Mercuric nitrate
 - Zinc chloride
 - Sodium sulfide nonahydrate
 - Trichloroacetic acid

