

Sulfuric Acid (H_2SO_4) - 1

- most commonly used industrial chemical
- also called "oil of vitriol"
- colorless, oily, syrupy liquid, specific gravity = 1.84
- standard reagent concentration is 98 %, yellow bottle cap
- NFPA704M code = 3-0-2-W
- "fuming sulfuric acid" or "oleum" has additional SO_3 dissolved into solution; actually is $\text{H}_2\text{S}_2\text{O}_7$, disulfuric acid
- **primary hazards:**
 - when dissolved into water, H_2SO_4 liberates considerable heat
 - $20 \text{ kcal/mol} = 1570.9 \text{ J/cm}^3$
 - H_2SO_4 is a strong acid, but only the first proton dissociates completely; second proton has $K_2 = 10^{-2}$
 - always add acid to water to avoid spattering

Fundamentals of Micromachining

Properties of Micromachining Chemicals

Sulfuric Acid (H_2SO_4) - 2

- **primary hazards:**
 - concentrated H_2SO_4 has a great affinity for H_2O : hygroscopic
 - concentrated H_2SO_4 will hydrate sugars, starches, and cellulose
 - acid burns to skin dehydrate the tissue with localized evolution of heat. skin becomes charred, like burnt wood
 - concentrated H_2SO_4 dehydrates concentrated HClO_4 (perchloric acid). The two can explosively decompose and must be stored in separate cabinets.
 - concentrated H_2SO_4 can react to form hazardous compounds
 - chlorine containing oxidizers will react explosively
 - will decompose salts into other acids
 - $2\text{NaF} + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + 2\text{HF}$
 - may produce toxic gases, e.g. Br_2 , I_2 , SO_2 , CO , COS , H_2S
 - concentrated H_2SO_4 will oxidize carbon, lead, and copper

Be Careful and Know Some Chemistry

- "On April 16, 1947, 2200 tons of ammonium nitrate [fertilizer] was stored on board the S. S. Grandcamp along with 1500 tons of fuel oil. While docked at Texas City, Texas, a fire was detected in the hold. An order was given to close hatches and to apply steam throughout the hold. Under these conditions, the fire could not extinguish. Instead, the internal pressure built up at an uncontrollable rate, causing the cargo vessel to explode. Six hundred people were killed and another 3500 were injured. The property damage was comparable to that experienced during a major wartime bombing incident. The total property loss was estimated as \$33 million based upon 1947 costs."
- Eugene Meyer, *The Chemistry of Hazardous Materials*, 2nd ed.

Hydrochloric Acid (HCl)

- pure HCl is a strong-smelling, colorless gas
 - TLV = 5 ppm, exposure to > 1500 ppm is usually fatal
 - extremely soluble in H₂O
- technical grade HCl is slightly yellow due to Fe⁺⁺ impurities
- also known as "muriatic acid"
- standard reagent concentration is 37 %, blue bottle cap
- NFPA704M code = 3-0-0
- **primary hazards:**
 - corrosive effect on metals
 - vapor toxicity:
 - 1-5 ppm = limit of odor
 - 35 ppm = irritation of throat
 - 50 ppm = barely tolerable
 - 1000 ppm = fatal via lung edema

Nitric Acid (HNO₃) - 1

- second most commonly used industrial chemical
- colorless liquid, often reddish-brown from dissolved NO₂
 - light exposure produces: $4\text{HNO}_3 \rightarrow 4\text{NO}_2 + 2\text{H}_2\text{O} + \text{O}_2$
- also called "aqua fortis" in art engraving
- excess dissolved NO₂ produces "fuming" nitric acid
- standard reagent concentration is 68-70 %, red bottle cap
- NFPA704M code = 3-0-0-OXY

Aqua Regia

- mixture of 3 parts conc. HCl and 1 part conc. HNO₃
- also called "nitrohydrochloric acid"
- very potent oxidizing agent
- useful for dissolving Au and Pt

Nitric Acid (HNO₃) - 2

- **primary hazards:**
 - reacts with metals and nonmetals, releases NO and/or NO₂
 - concentrated HNO₃ will spontaneously ignite wood, cellulose products, and many organic materials such as turpentine, acetic acid, acetone, ethyl alcohol, nitrobenzene, and aniline
 - concentrated HNO₃ oxidizes proteins
 - produces xanthoproteic acid (yellow colored, slow-healing wound)
 - concentrated HNO₃ acts as both an acid and an oxidizer!!

Hydrofluoric Acid (HF) - 2

- **primary hazards:**
 - HF vapor produces edema of the lungs and can permanently damage the cornea
 - HF is extremely dangerous to skin contact, the worst of all acids in terms of damage to tissue, can produce very severe, painful burns
 - HF has a slight anesthetizing effect, pain is often not noticed until the acid has penetrated a large distance into tissue, often down into bone material where it reacts with Ca and Mg to form fluorides
 - because of small size of molecule, HF dissolves easily through pores of skin and cell membranes, and also through many plastics
 - use only Trionic gloves when dealing with HF!!
 - at present there exists no real remedy for HF burns
 - some suggest an ointment of 3 oz. magnesium oxide, 4 oz. heavy mineral oil, and 11 oz. white vaseline is helpful

Perchloric Acid (HClO₄)

- strongest of all of the common acids
- anhydrous form is unstable
- standard reagent concentration is 72 %
- NFPA704M code = 3-0-3-OXY
- must be used and stored in specially designed facilities
- **primary hazards:**
 - concentrated HClO₄ when heated to 92C explodes
 - $4\text{HClO}_4 \rightarrow 2\text{Cl}_2 + 7\text{O}_2 + 2\text{H}_2\text{O}$
 - concentrated HClO₄ ignites or explodes with cellulose materials and most organic compounds
 - treated differently following the 1940s Los Angeles explosion caused by its reaction with aniline

Buffered Oxide Etch (BOE)

- a solution of HF and NH₄F, usually 10:1 ratio by volume
- NH₄F is a solid crystal, but dissolved in H₂O, it produces some HF and fluoride ion
- industry standard solution for etching SiO₂
- NH₄F provides buffering of the fluoride ion, as SiO₂ etching proceeds, the NH₄F replenishes the fluoride ion that is consumed in the creation of SiF₄
- NFPA704M code = 4-0-0
- **primary hazards:**
 - the same as for hydrofluoric acid, HF
 - use only Trionic gloves when dealing with BOE!!

Hydrofluoric Acid (HF) - 1

- pure HF is a colorless gas above 20C, TLV = 2.5 ppm
- similar in reactivity to H₂SO₄
- a strong dehydrating agent
- has a high affinity for water (hygroscopic)
- dissolved in H₂O it becomes a weak acid (it partially dissociates)
 - BUT IT IS STILL EXTREMELY DANGEROUS!!
- standard reagent concentration is 49 %
- NFPA704M code = 4-0-0
- HF dissolves glasses:
 - $\text{CaSiO}_3 + 6\text{HF} \rightarrow \text{CaF}_2 + \text{SiF}_4 + 3\text{H}_2\text{O}$
 - $\text{SiO}_2 + 4\text{HF} \rightarrow \text{SiF}_4 + 2\text{H}_2\text{O}$
- concentrated HF must be stored in polypropylene containers!!
- commercially used for etching glass

Sodium Hydroxide (NaOH) - 1

- most common alkali
- also called “lye” or “caustic soda”
- produced by electrolysis of brine
 - $2\text{NaCl} + 2\text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{H}_2 + \text{Cl}_2$
- at room temp., NaOH is a white solid, usually pellets or powder
- very hygroscopic
- weak solutions have a bitter or caustic taste, and a slippery or soapy feeling, typical of all alkalis
- like all alkalis, it can destroy or burn tissues, leaving serious wounds that heal very slowly
- standard reagent concentration is 97 %
- NFPA704M code = 3-0-1

Phosphoric Acid (H_3PO_4)

- phosphorous forms 8 different acids; H_3PO_4 is the most common
- clear, odorless, sparkling liquid or transparent solid
- phosphorous anhydride is a strong dehydrator and has a great affinity for water. Dissolved in water it produces phosphoric acid:
 - $\text{P}_4\text{O}_{10} + 6\text{H}_2\text{O} \rightarrow 4\text{H}_3\text{PO}_4$
- standard reagent concentration is 85 %, white bottle cap
- NFPA704M code = 2-0-0
- **primary hazards:**
 - concentrated H_3PO_4 liberates considerable heat when diluted with water; always add the acid to the water to avoid spattering
 - concentrated H_3PO_4 can cause severe skin burns, but it is generally the least hazardous of the strong mineral acids

Sodium Hydroxide (NaOH) - 2

- **primary hazards:**
 - can cause extremely severe burns to the skin
 - treat with 1 % acetic acid solution or common household vinegar
 - tissues have no natural defense to strong bases, so tissue damage can be greater than that of a strong acid
 - strong acids create impermeable damage zone with limits spread
 - strong bases do not create this reaction and can diffuse much farther
 - can cause extremely severe burns to the cornea
 - treat with 1 % boric acid to neutralize after several minutes of irrigation with water
 - nonflammable by itself, but can trigger the ignition of other materials
 - very exothermic upon dissolving in H_2O
 - 10 kcal/mole
 - hot enough to ignite or melt some materials

Acetic Acid (CH_3COOH)

- most common organic acid
- causes the sour taste and odor of vinegar (typ. 3-6 % acetic acid)
- “glacial” acetic acid is about 99.5 % acetic acid, derived from the decomposition of acetylene, used in photography
- standard reagent concentration is 99 %, brown bottle cap
- NFPA704M code = 2-2-1
- **primary hazards:**
 - primary hazard is its corrosiveness
 - vapors are harmful, TLV = 10 ppm
 - CH_3COOH freezes at 17C, and like water, expands upon freezing
 - glass bottles must be protected against temperatures below 17C
 - CH_3COOH will burn, but the autoignition temperature is 426C and is generally unlikely without the presence of an ignition source

Hydrogen Peroxide (H₂O₂)

- resembles water, but with a slightly sharp odor
- a very strong oxidizer
- inherently unstable, decomposes from sunlight or UV radiation
 - $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$
 - typically lasts only a few months under refrigeration
- standard reagent concentration is 30 %, white bottle cap
- NFPA704M code = 2-0-1-OXY
- **primary hazards:**
 - decomposes violently at 144C
 - readily provides oxygen in redox reactions
 - can cause spontaneous ignition of combustible materials when > 50 %
 - greatly speeds up many reactions, turning some toward explosions
 - can cause severe skin burns or bleaching
 - drug store hydrogen peroxide is only 1-3 %

Potassium Hydroxide (KOH)

- also called "potash" or "caustic potash"
- very similar to NaOH
- considered a slightly stronger base
- at room temp., NaOH is a white solid, usually pellets or powder
- very hygroscopic
- standard reagent concentration is 97 %
- NFPA704M code = 3-0-1
- **primary hazards:**
 - very similar to NaOH

Ammonium Hydroxide (NH₄OH)

- created by dissolving NH₃ into H₂O
- NH₃ is very soluble in H₂O, forms a weak base (partially ionizes)
- neutralizes acids, but is generally unreactive with most metals
- standard reagent concentration is 30 %, green bottle cap
- NFPA704M code = 3-1-0
- **primary hazards:**
 - concentrated NH₄OH will burn skin
 - NH₃ vapors are harmful
 - TLV = 50 ppm
 - moderately toxic, strong irritant to skin, eyes, and mucus membranes