

# EE-527: MicroFabrication

## Properties of Specific Chemicals

## 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.

# Sulfuric Acid ( $\text{H}_2\text{SO}_4$ ) - 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  $\text{SO}_3$  dissolved into solution; actually is  $\text{H}_2\text{S}_2\text{O}_7$ , disulfuric acid
- primary hazards:
  - when dissolved into water,  $\text{H}_2\text{SO}_4$  liberates considerable heat
    - $20 \text{ kcal/mol} = 1570.9 \text{ J/cm}^3$
  - $\text{H}_2\text{SO}_4$  is a strong acid, but only the first proton dissociates completely; second proton has  $K_i = 10^{-2}$
  - always add acid to water to avoid spattering

## Sulfuric Acid (H<sub>2</sub>SO<sub>4</sub>) - 2

- primary hazards:
  - concentrated H<sub>2</sub>SO<sub>4</sub> has a great affinity for H<sub>2</sub>O: hygroscopic
  - concentrated H<sub>2</sub>SO<sub>4</sub> will dehydrate sugars, starches, and cellulose
  - acid burns to skin dehydrate the tissue with localized evolution of heat. skin becomes charred, like burnt wood
  - concentrated H<sub>2</sub>SO<sub>4</sub> dehydrates concentrated HClO<sub>4</sub> (perchloric acid). The two can explosively decompose and must be stored in separate cabinets.
  - concentrated H<sub>2</sub>SO<sub>4</sub> 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<sub>2</sub>, I<sub>2</sub>, SO<sub>2</sub>, CO, COS, H<sub>2</sub>S
    - concentrated H<sub>2</sub>SO<sub>4</sub> will oxidize carbon, lead, and copper

# Nitric Acid (HNO<sub>3</sub>) - 1

- second most commonly used industrial chemical
- colorless liquid, often reddish-brown from dissolved NO<sub>2</sub>
  - 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 NO<sub>2</sub> produces “fuming” nitric acid
- standard reagent concentration is 68-70 %, red bottle cap
- NFPA704M code = 3-0-0-OXY

## Nitric Acid ( $\text{HNO}_3$ ) - 2

- primary hazards:
  - reacts with metals and nonmetals, releases NO and/or  $\text{NO}_2$
  - concentrated  $\text{HNO}_3$  will spontaneously ignite wood, cellulose products, and many organic materials such as turpentine, acetic acid, acetone, ethyl alcohol, nitrobenzene, and aniline
  - concentrated  $\text{HNO}_3$  oxidizes proteins
    - produces xanthoproteic acid (yellow colored, slow-healing wound)
  - concentrated  $\text{HNO}_3$  acts as both an acid and an oxidizer!!

# Hydrochloric Acid (HCl)

- pure HCl is a strong-smelling, colorless gas
  - TLV = 5 ppm, exposure to > 1500 ppm is usually fatal
  - extremely soluble in H<sub>2</sub>O
- technical grade HCl is slightly yellow due to Fe<sup>++</sup> 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

# Aqua Regia

- mixture of 3 parts conc. HCl and 1 part conc. HNO<sub>3</sub>
- also called “nitrohydrochloric acid”
- very potent oxidizing agent
- useful for dissolving Au and Pt

## Perchloric Acid (HClO<sub>4</sub>)

- 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 HClO<sub>4</sub> 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 HClO<sub>4</sub> ignites or explodes with cellulose materials and most organic compounds
  - treated differently following the 1940's Los Angeles explosion caused by its reaction with aniline

# Hydrofluoric Acid (HF) - 1

- pure HF is a colorless gas above 20C, TLV = 2.5 ppm
- similar in reactivity to  $\text{H}_2\text{SO}_4$
- a strong dehydrating agent
- has a high affinity for water (hygroscopic)
- dissolved in  $\text{H}_2\text{O}$  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

## 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

## Buffered Oxide Etch (BOE)

- a solution of HF and  $\text{NH}_4\text{F}$ , usually 10:1 ratio by volume
- $\text{NH}_4\text{F}$  is a solid crystal, but dissolved in  $\text{H}_2\text{O}$ , it produces some HF and fluoride ion
- industry standard solution for etching  $\text{SiO}_2$
- $\text{NH}_4\text{F}$  provides buffering of the fluoride ion, as  $\text{SiO}_2$  etching proceeds, the  $\text{NH}_4\text{F}$  replenishes the fluoride ion that is consumed in the creation of  $\text{SiF}_4$
- NFPA704M code = 4-0-0
- primary hazards:
  - the same as for hydrofluoric acid, HF
  - use only Trionic gloves when dealing with BOE!!

## Phosphoric Acid ( $\text{H}_3\text{PO}_4$ )

- phosphorous forms 8 different acids;  $\text{H}_3\text{PO}_4$  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  $\text{H}_3\text{PO}_4$  liberates considerable heat when diluted with water; always add the acid to the water to avoid spattering
  - concentrated  $\text{H}_3\text{PO}_4$  can cause severe skin burns, but it is generally the least hazardous of the strong mineral acids

# Acetic Acid ( $\text{CH}_3\text{COOH}$ )

- 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
  - $\text{CH}_3\text{COOH}$  freezes at  $17^\circ\text{C}$ , and like water, expands upon freezing
    - glass bottles must be protected against temperatures below  $17^\circ\text{C}$
  - $\text{CH}_3\text{COOH}$  will burn, but the autoignition temperature is  $426^\circ\text{C}$  and is generally unlikely without the presence of an ignition source

# 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

# 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<sub>2</sub>O
    - 10 kcal/mole
    - hot enough to ignite or melt some materials

# 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 ( $\text{NH}_4\text{OH}$ )

- created by dissolving  $\text{NH}_3$  into  $\text{H}_2\text{O}$
- $\text{NH}_3$  is very soluble in  $\text{H}_2\text{O}$ , 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  $\text{NH}_4\text{OH}$  will burn skin
  - $\text{NH}_3$  vapors are harmful
    - TLV = 50 ppm
    - moderately toxic, strong irritant to skin, eyes, and mucus membranes

# Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>)

- 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 %