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MULTIPURPOSE INORGANIC MINERAL ACIDS AND THEIR R-PHRASE AND S-PHRASE VALUES

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ABSTRACT

A mineral acid (or inorganic acid) is an acid derived from one or more inorganic compounds. All mineral acids form hydrogen ions and the conjugate base ions when dissolved in water. Commonly used mineral acids are sulfuric acid, hydrochloric acid and nitric acid (they are also known as bench acids). These mineral acids range from acids of great strength (sulfuric acid) to very weak (boric acid). These have tendency to be very soluble in water and insoluble in organic solvents. These are used in many sectors of the chemical industry as feed stocks for the synthesis of other chemicals, both organic and inorganic. Large quantities of these acids – especially sulfuric acid, nitric acid and hydrochloric acid – are manufactured for commercial use in large plants. These acids are also used directly for their corrosive properties. For example, a dilute solution of hydrochloric acid is used for removing the deposits from the inside of boilers, with precautions taken to prevent the corrosion of the boiler by the acid. This process is known as descaling. Examples of mineral acids: Hydrochloric acid (HCl), Nitric acid (HNO_3), Phosphoric acid (H_3PO_4), Sulfuric acid (H_2SO_4), Boric acid (H_3BO_3), Hydrofluoric acid (HF), Hydrobromic acid (HBr), Perchloric acid ($HClO_4$) and Hydroiodic acid (HI).

KEYWORDS: R-phrases, S-phrases, HCl, HNO_3, H_3PO_4, H_2SO_4, H_3BO_3, HF, HBr, $HClO_4$, HI, Irritant, Corrosive, Fuming, Aqua Regia, Oleum, RFNA, IRFNA, WFNA, S-Stoff, SV-Stoff, Vitriol.

INTRODUCTION

R-phrases (Risk Phrases) are defined in Annex III of European Union Directive 67/548/EEC: Nature of special risks attributed to dangerous substances and preparations. The list was consolidated and republished in Directive 2001/59/EC, where translations into other EU languages may be found. These risk phrases are used internationally, not just in Europe, and there is an ongoing effort towards complete international harmonization. **S-phrases** (Safety Phrases) are defined in Annex IV of European Union Directive 67/548/EEC: Safety advice concerning dangerous substances and preparations. The list was consolidated and republished in Directive 2001/59/EC, where translations into other EU languages may be found. The list was subsequently updated and republished in Directive 2006/102/EC, where translations to additional European languages were added. These safety phrases are used internationally and not just in Europe and there is an ongoing effort towards complete international harmonization.

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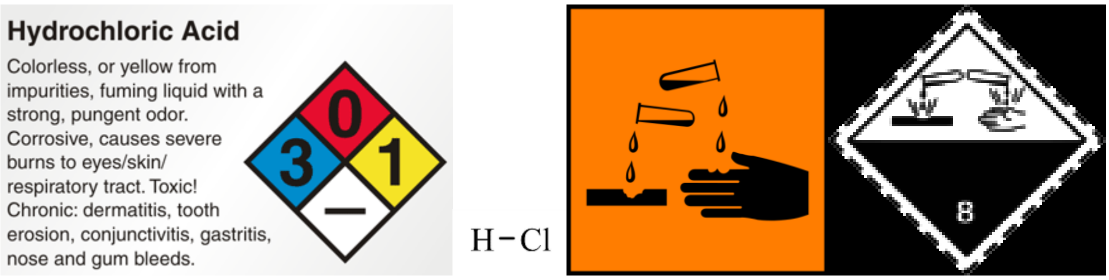
Table: 1 Acid categories

Flammability (red)	
0	Materials that will not burn under typical fire conditions (e.g. carbon tetrachloride), including intrinsically noncombustible materials such as concrete, stone and sand (Materials that will not burn in air when exposed to a temperature of 820°C (1,500°F) for a period of 5 minutes)
1	Materials that require considerable preheating, under all ambient temperature conditions, before ignition and combustion can occur (e.g. mineral oil). Includes some finely divided suspended solids that do not require heating before ignition can occur. Flash point at or above 93.3°C (200°F).
2	Must be moderately heated or exposed to relatively high ambient temperature before ignition can occur (e.g. diesel fuel) and multiple finely divided suspended solids that do not require heating before ignition can occur. Flash point between 37.8 and 93.3°C (100 and 200°F).
3	Liquids and solids (including finely divided suspended solids) that can be ignited under almost all ambient temperature conditions (e.g. gasoline, acetone). Liquids having a flash point below 22.8°C (73°F) and having a boiling point at or above 37.8°C (100°F) or having a flash point between 22.8 and 37.8°C (73 and 100°F).
4	Will rapidly or completely vaporize at normal atmospheric pressure and temperature, or is readily dispersed in air and will burn readily (e.g. acetylene, propane, liquid hydrogen). Includes pyrophorics substances. Flash point below room temperature at 22.8°C (73°F).
Health (blue)	
0	Poses no health hazard, no precautions necessary and would offer no hazard beyond that of ordinary combustible materials (e.g. wood, paper)
1	Exposure would cause irritation with only minor residual injury (e.g. acetone, sodium bromate)
2	Intense or continued but not chronic exposure could cause temporary incapacitation or possible residual injury (e.g. diethyl ether, ammonium phosphate)
3	Short exposure could cause serious temporary or moderate residual injury (e.g. liquid hydrogen, carbon monoxide)
4	Very short exposure could cause death or major residual injury (e.g. hydrogen cyanide, phosgene, methyl isocyanate, hydrofluoric acid)
Instability/reactivity (yellow)	
0	Normally stable, even under fire exposure conditions and is not reactive with water (e.g. helium, N_2)
1	Normally stable, but can become unstable at elevated temperatures and pressures (e.g. propene)
2	Undergoes violent chemical change at elevated temperatures and pressures, reacts violently with water, or may form explosive mixtures with water (e.g. white phosphorus, potassium, sodium)
3	Capable of detonation or explosive decomposition but requires a strong initiating source, must be heated under confinement before initiation, reacts explosively with water, or will detonate if severely shocked (e.g. ammonium nitrate, chlorine trifluoride)
4	Readily capable of detonation or explosive decomposition at normal temperatures and pressures (e.g. nitroglycerin, chlorine azide, chlorine dioxide, nitrogen triiodide)
SPECIAL NOTICE (WHITE)	
The white "special notice" area can contain several symbols. The following symbols are defined by the NFPA 704 standard.	
OX	Oxidizer, allows chemicals to burn without an air supply (e.g. potassium perchlorate, ammonium nitrate, hydrogen peroxide)
~~W~~	Reacts with water in an unusual or dangerous manner (e.g. cesium, sodium, sulfuric acid)
SA	Simple asphyxiant gas. Specifically limited to the following gases: nitrogen, helium, neon, argon, krypton and xenon
Non-standard symbols (white)	
COR **ACID**, **ALK**	Corrosive; strong acid or base (e.g. sulfuric acid, potassium hydroxide), Acid or alkaline, to be more specific
BIO	Biological hazard (e.g. flu virus, rabies virus)
POI	Poisonous (e.g. strychnine, alpha-amanitin)
RA, RAD	Radioactive (e.g. plutonium, cobalt-60)
CRY or **CRYO**	Cryogenic (e.g. liquid nitrogen)

Hydrochloric acid (HCl) is a corrosive, strong mineral acid with many industrial uses. Muriatic acids, Spirits of salt, Hydronium chloride, Chlorhydric Acid are the synonyms. A colorless, highly pungent gas solution of hydrogen chloride (HCl) in water, when it reacts with an inorganic/organic base it forms a hydrochloride salt. Hydrochloric acid was historically called acidum salis, muriatic acid and spirits of salt because it was produced from rock salt and green vitriol (by Basilius Valentinus in the 15th century) and later from the chemically similar common salt and sulfuric acid (by Johann Rudolph Glauber in the 17th century). Free hydrochloric acid was first formally described in the 16th century by Libavius. Later, it was used by chemists such as Glauber, Priestley and Davy in their scientific research. With major production starting in the Industrial Revolution, hydrochloric acid is used in the chemical industry as a chemical reagent in the large-scale production of vinyl chloride for PVC plastic and MDI (Methylene diphenyl diisocyanate)/TDI (Toluene diisocyanate) for polyurethane. It has numerous smaller-scale applications, including household cleaning, production of gelatin and other food additives, descaling and leather processing. About 20 million tonnes of hydrochloric acid are produced worldwide annually. It is also found naturally in gastric acid.[1]


Hydrochloric Acid

Colorless, or yellow from impurities, fuming liquid with a strong, pungent odor. Corrosive, causes severe burns to eyes/skin/ respiratory tract. Toxic! Chronic: dermatitis, tooth erosion, conjunctivitis, gastritis, nose and gum bleeds.

Figure-1: Hydrochloric acid

Safety

Concentrated hydrochloric acid (fuming hydrochloric acid) forms acidic mists. Both the mist and the solution have a corrosive effect on human tissue, with the potential to damage respiratory organs, eyes, skin and intestines irreversibly. Upon mixing hydrochloric acid with common oxidizing chemicals, such as sodium hypochlorite (bleach, NaClO) or potassium permanganate ($KMnO_4$), the toxic gas chlorine is produced.


WARNING

Hydrochloric Acid

Can cause severe burns, eye damage or other injury.

Wear proper protective equipment before handling.

Figure-2: Hydrochloric acid as corrosive agent

Concentration by weight: 10–25% (irritant=X_i); R-phrase (R36/R37/R38: R36=Irritating to eyes, irritating to respiratory system and irritating to skin) and Concentration by weight: >25% (corrosive=C); R-phrase (R34/R37=Causes burns and irritating to respiratory system). S-phrase (S1/S2=Keep locked out and out of the reach of children), S26=In case of contact with eyes, rinse immediately with plenty of water and seek medical advice, S45=In case of accident or if you feel unwell seek medical advice immediately). Personal protective equipment such as latex gloves, protective eye goggles and chemical-resistant clothing and shoes will minimize risks when handling hydrochloric acid.[2]

Nitric acid (HNO_3), (Aqua fortis, Spirit of niter, Eau forte, Hydrogen nitrate, Acidum nitricum) also known as aqua fortis and spirit of niter, is a highly corrosive mineral acid. The pure compound is colorless, but older samples tend to acquire a yellow cast due to decomposition into oxides of nitrogen and water. Most commercially available nitric acid has a concentration of 68% in water. When the solution contains more than 86% HNO_3, it is referred to as *fuming nitric acid*. Depending on the amount of nitrogen dioxide (NO_2) present, fuming nitric acid is further characterized as white fuming nitric acid or red fuming nitric acid, at concentrations above 95%. Nitric acid is the primary reagent used for nitration – the addition of a nitro group, typically to an organic molecule. While some resulting nitro compounds are shock- and thermally-sensitive explosives, a few are stable enough to be used in munitions and demolition, while others are still more stable and used as pigments in inks and dyes. Nitric acid is also commonly used as a strong oxidizing agent.

Figure-3: Corrosions by nitric acid

R-phrases: R8=Contact with combustible material may cause fire, R35=Causes severe burns.

S-phrases: S1/S2=Keep locked up and keep out of the reach of children, S23=Do not breathe gas/fumes/vapour/spray, S26=In case of contact with eyes, rinse immediately with plenty of water and seek medical advice, S36=Wear suitable protective clothing, S45=In case of accident or if you feel unwell seek medical advice immediately.[3]

Xanthoproteic test

Nitric acid reacts with proteins to form yellow nitrated products. This reaction is known as the xanthoproteic reaction. This test is carried out by adding concentrated nitric acid to the substance being tested and then heating the mixture. If proteins that contain amino acids with aromatic rings are present, the mixture turns yellow. Upon adding a strong base such as ammonia, the color turns orange. These color changes are caused by nitrated aromatic rings in the protein. Xanthoproteic acid is formed when the acid contacts epithelial cells. Respective local skin color changes are indicative of inadequate safety precautions when handling nitric acid.

Figure-4: Red fuming nitric acid

Red fuming nitric acid (RFNA)

It is a storable oxidizer used as a rocket propellant. It consists of 84% nitric acid (HNO_3), 13% dinitrogen tetroxide (N_2O_4) and 1–2% water. The color of red fuming nitric acid is due to the dinitrogen tetroxide, which breaks down partially to form nitrogen dioxide. The nitrogen dioxide dissolves until the liquid is saturated and evaporates off into fumes with a suffocating odor. RFNA increases the flammability of combustible materials and is highly exothermic when reacting with water. It is usually used with an inhibitor (with various, sometimes secret, substances, including hydrogen fluoride; any such combination is called "inhibited RFNA"**IRFNA**) because nitric acid attacks most container materials. It can also be a component of a monopropellant; with substances like amine nitrates dissolved in it, it can be used as the sole fuel in a rocket. It is not normally used this way however. During World War II, the German military used RFNA in some rockets. The mixtures used were called **S-Stoff** (96% nitric acid with 4% ferric chloride as an ignition catalyst) and **SV-Stoff** (94% nitric acid with 6% dinitrogen tetroxide) and nicknamed *Salbei* (sage). Inhibited RFNA was the oxidizer of the world's most-launched light orbital rocket, the Kosmos-3M. Other uses for RFNA include fertilizers, dye intermediates, explosives and pharmaceutical aids as acidifier. It can also be used as a laboratory reagent in photoengraving and metal etching. A commercial grade of fuming nitric acid contains 90% HNO_3 and has a density of 1.50 g/cm^3. This grade is often used in the explosives industry. It is neither as volatile nor as corrosive as the anhydrous acid and has the approximate concentration of 21.4 molar. Red Fuming nitric acid, or RFNA, contains substantial quantities of dissolved nitrogen dioxide (NO_2) leaving the solution with a reddish-brown color. Due to the dissolved nitrogen dioxide, the density of red fuming nitric acid is lower at 1.490 g/cm^3. An *inhibited* fuming nitric acid (either IWFNA, or IRFNA) can be made by the addition of 0.6 to 0.7% hydrogen fluoride (HF). This fluoride is added for corrosion resistance in metal tanks. The fluoride creates a metal fluoride layer that protects the metal. Compositions: **IRFNA IIIa**: 83.4% HNO_3, 14% NO_2, 2% H_2O, 0.6% HF, **IRFNA IV HDA**: 54.3% HNO_3, 44% NO_2, 1% H_2O, 0.7% HF, **S-Stoff**: 96% HNO_3, 4% $FeCl_3$, **SV-Stoff**: 94% HNO_3, 6% N_2O_4, **AK20**: 80% HNO_3, 20% N_2O_4, **AK20F**: 80% HNO_3, 20% N_2O_4, fluorine-based inhibitor, **AK20I**: 80% HNO_3, 20% N_2O_4, iodine-based inhibitor, **AK20K**: 80% HNO_3, 20% N_2O_4, fluorine-based inhibitor, **AK27I**: 73% HNO_3, 27% N_2O_4, iodine-based inhibitor, **AK27P**: 73% HNO_3, 27% N_2O_4, fluorine-based inhibitor.

White fuming nitric acid (**WFNA**) is a storable liquid oxidizer used with kerosene and hydrazine rocket fuel. It consists of nearly pure nitric acid (HNO_3). WFNA is commonly specified as containing no more than 2% water and less than 0.5% dissolved nitrogen dioxide or dinitrogen tetroxide. WFNA was sometimes used with an inhibitor compound to reduce corrosiveness, often hydrogen fluoride. Without inhibitors, WFNA will corrode nearly all structural metals. Inhibited WFNA is often called **IWFNA**. The hydrogen fluoride addition causes formation of protective layer of fluoride on the metal surfaces. WFNA as an oxidizer has somewhat less performance than red fuming nitric acid (RFNA) but is considerably safer (though extremely corrosive), as it has little to no dissolved nitrogen tetroxide, which is an extremely toxic and volatile chemical. If not inhibited, it will form nitrogen tetroxide on contact with most metals and some organic materials. WFNA can be converted from RFNA by simply leaving the RFNA out in low temperature for a couple of hours. WFNA is also used in the manufacture of nitroglycerin, an explosive, by mixing it with concentrated sulfuric acid to produce the nitro group ester and then by the slow addition of glycerol. This has now mostly been replaced by the less expensive procedure that uses a nearly 1:1 solution of oleum and azeotropic nitric acid (70%). WFNA and IWFNA are hypergolic with a long list of other propellants, including: Unsymmetrical dimethyl hydrazine, hydrazine, furfuryl alcohol, gasoline and aniline. Pure nitric acid or WFNA, is very close to anhydrous nitric acid. It is available as 99.9% nitric acid by assay. One specification for white fuming nitric acid is that it has a maximum of 2% water and a maximum of 0.5% dissolved NO_2. Anhydrous nitric acid has a density of 1.513 g/cm^3 and has the approximate concentration of 24 molar. Anhydrous nitric acid is a colorless mobile liquid with a density of 1.512 g/cm^3, which solidifies at −42°C to form white crystals. As it decomposes to NO_2 and water, it obtains a yellow tint. It boils at 83°C. It is usually stored in a glass shatter-proof amber bottle with twice the volume of head space to allow for pressure build up. When received, the pressure must be released and repeated monthly until finished. The molecule is planar. Two of the N–O bonds are equivalent and relatively short (this can be explained by theories of resonance; the canonical forms show double-bond character in these two bonds, causing them to be shorter than typical N–O bonds) and the third N–O bond is elongated because the O atom is also attached to a proton.

Hazards

Nitric acid is a corrosive acid and a powerful oxidizing agent. The major hazard posed by it is chemical burns as it carries out acid hydrolysis with proteins (amide) and fats (ester) which consequently decomposes living tissue (e.g. skin and flesh). Concentrated nitric acid stains human skin yellow due to its reaction with the keratin. These yellow stains turn orange when neutralized by ammonia. Systemic effects are unlikely, however and the substance is not considered a carcinogen or mutagen. The standard first aid treatment for acid spills on the skin is, as for other corrosive agents, irrigation with large quantities of water. Washing is continued for at least ten to fifteen minutes to cool the tissue surrounding the acid burn and to prevent secondary damage. Contaminated clothing is removed immediately and the underlying skin washed thoroughly. Being a strong oxidizing agent, reactions of nitric acid with compounds such as cyanides, carbides, metallic powders can be explosive and those with many organic compounds, such as turpentine, are violent and hypergolic (i.e. self-igniting). Hence, it should be stored away from bases and organics. The main industrial use of nitric acid is for the production of fertilizers. Nitric acid is neutralized with ammonia to give ammonium nitrate. This application consumes 75–80% of the 26M tons produced annually (1987). The other main applications are for the production of explosives, nylon precursors and specialty organic compounds.

Uses: Precursor to organic nitrogen compounds

In organic synthesis, industrial and otherwise, the nitro group is a versatile functional group. Most derivatives of aniline are prepared via nitration of aromatic compounds followed by reduction. Nitrations entail combining nitric and sulfuric acids to generate the nitronium ion, which electrophilically reacts with aromatic compounds such as benzene. Many explosives, e.g. TNT, are prepared in this way. The precursor to nylon, adipic acid, is produced on a large scale by oxidation of cyclohexanone and cyclohexanol with nitric acid.

Rocket propellant

Nitric acid has been used in various forms as the oxidizer in liquid fuled rockets. These forms include red fuming nitric acid, white fuming nitric acid, mixtures with sulfuric acid and these forms with HF inhibitor. IRFNA (inhibited red fuming nitric acid) was one of 3 liquid fuel components for the BOMARC missile.

Analytical reagent

In elemental analysis by ICP-MS (Inductively coupled plasma mass spectrometry), ICP-AES (Inductively Coupled Plasma Atomic Emission Spectroscopy), ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy), GFAA (Graphite Furnace Atomic Absorption) and Flame AA (Flame Atomic Absorption Spectroscopy), dilute nitric acid (0.5 to 5.0%) is used as a matrix compound for determining metal traces in solutions. Ultrapure trace metal grade acid is required for such determination, because small amounts of metal ions could affect the result of the analysis. It is also typically used in the digestion process of turbid water samples, sludge samples, solid samples as well as other types of unique samples which require elemental analysis. Typically these digestions use a 50% solution of the purchased HNO_3 mixed with Type 1 DI Water. In electrochemistry, nitric acid is used as a chemical doping agent for organic semiconductors and in purification processes for raw carbon nanotubes.

Woodworking: In a low concentration (approximately 10%), nitric acid is often used to artificially age pine and maple. The color produced is a grey-gold very much like very old wax or oil finished wood (wood finishing).

Etchant and cleaning agent
The corrosive effects of nitric acid are exploited for a number of specialty applications, such as pickling stainless steel or cleaning silicon wafers in electronics. A solution of nitric acid, water and alcohol, nital, is used for etching of metals to reveal the microstructure. ISO 14104 is one of the standards detailing this well known procedure. Commercially available aqueous blends of 5–30% nitric acid and 15–40% phosphoric acid are commonly used for cleaning food and dairy equipment primarily to remove precipitated calcium and magnesium compounds (either deposited from the process stream or resulting from the use of hard water during production and cleaning). The phosphoric acid content helps to passivate ferrous alloys against corrosion by the dilute nitric acid. Nitric acid can be used as a spot test for alkaloids like LSD, giving a variety of colours depending on the alkaloid.[4]

Sulfuric acid (H_2SO_4)
In chemistry, vitriol is an archaic name for a sulfate. The name comes from the Latin word "vitriolum" for glassy, as crystals of several metallic sulfates resemble pieces of colored glass. *Vitriol* with no further qualification often means sulfuric acid. In particular: *Black vitriol*, a mixture of iron(II) sulfate and iron sulfide, *Blue vitriol*, copper(II) sulfate pentahydrate, *Green vitriol*, iron(II) sulfate heptahydrate, *Oil of vitriol*, sulfuric acid, *Red vitriol*, cobalt(II) sulfate heptahydrate, *Roman vitriol*, copper(II) sulfate pentahydrate, *Spirit of vitriol*, sulfuric acid, *Sweet oil of vitriol*, diethyl ether *(not a sulfate)*, *Vitriol of argile* or vitriol of clay, aluminium sulfate (alum), *Vitriol of Cyprus*, copper(II) sulfate pentahydrate, *Vitriol of Mars* or vitriol martial, iron(III) sulfate, *White vitriol*, zinc sulfate heptahydrate.[5]

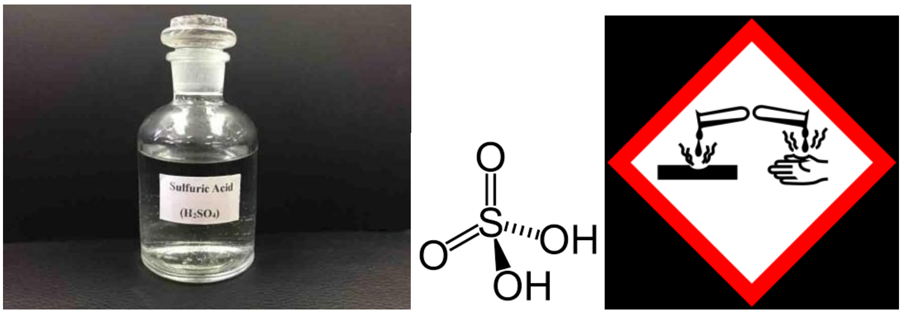


Figure-5: Sulfuric acid corrosions

Many other names have the obvious meaning given that "vitriol" means "sulfate": for example, *vitriol of lead* is lead sulfate and so on.

Hazards
R-phrases: R35=Causes severe burns.

S-phrases: S1/S2=Keep locked up and keep out of the reach of children, S26=In case of contact with eyes, rinse immediately with plenty of water and seek medical advice, S30=Never add water to this product, S45=In case of accident or if you feel unwell seek medical advice immediately.

Table: 2: Sulfuric acid concentrations

Mass fraction H_2SO_4	Density (kg/L)	Concentration (mol/L)	Common name
10%	1.07	~1	dilute sulfuric acid
29–32%	1.25–1.28	4.2–5	battery acid (used in lead-acid batteries)
62–70%	1.52–1.60	9.6–11.5	chamber acid, fertilizer acid
78–80%	1.70–1.73	13.5–14	tower acid, Glover acid
98%	1.84	~18	concentrated sulfuric acid

Sulfuric acid is capable of causing very severe burns, especially when it is at high concentrations. In common with other corrosive acids and alkali, it readily decomposes proteins and lipids through amide and ester hydrolysis upon contact with living tissues, such as skin and flesh. In addition, it exhibits a strong dehydrating property on carbohydrates, liberating extra heat and causing secondary thermal burns. Accordingly, it rapidly attacks the cornea and can induce permanent blindness if splashed onto eyes. If ingested, it damages internal organs irreversibly and may even be fatal. Protective equipment should hence always be used when handling it. Moreover, its strong oxidizing property makes it highly corrosive to many metals and may extend its destruction on other materials. Because of such reasons, damage posed by sulfuric acid is potentially more severe than that by other comparable strong acids, such as hydrochloric acid and nitric acid. Sulfuric acid must be stored carefully in containers made of nonreactive material (such as glass). Solutions equal to or stronger than 1.5 M are labeled "CORROSIVE", while solutions greater than 0.5 M but less than 1.5 M are labeled "IRRITANT". However, even the normal laboratory "dilute" grade (approximately 1 M, 10%) will char paper if left in contact for a sufficient time. The standard first aid treatment for acid spills on the skin is, as for other corrosive agents, irrigation with large quantities of water. Washing is continued for at least ten to fifteen minutes to cool the tissue surrounding the acid burn and to prevent secondary damage. Contaminated clothing is removed immediately and the underlying skin washed thoroughly. Preparation of the diluted acid can also be dangerous due to the heat released in the dilution process. The concentrated acid is always added to water and not the other way around, to take advantage of the relatively high heat capacity of water. Addition of water to concentrated sulfuric acid leads to the dispersal of a sulfuric acid aerosol or worse, an explosion. Preparation of solutions greater than 6 M (35%) in concentration is most dangerous, as the heat produced may be sufficient to boil the diluted acid: efficient mechanical stirring and external cooling (such as an ice bath) are essential. On a laboratory scale, sulfuric acid can be diluted by pouring concentrated acid onto crushed ice made from de-ionized water. The ice melts in an endothermic process while dissolving the acid. The amount of heat needed to melt the ice in this process is greater than the amount of heat evolved by dissolving the acid so the solution remains cold. After all the ice has melted, further dilution can take place using water.

Industrial hazards

Although sulfuric acid is non-flammable, contact with metals in the event of a spillage can lead to the liberation of hydrogen gas. The dispersal of acid aerosols and gaseous sulfur dioxide is an additional hazard of fires involving sulfuric acid. The main occupational risks posed by this acid are skin contact leading to burns and the inhalation of aerosols. Exposure to aerosols at high concentrations leads to immediate and severe irritation of the eyes, respiratory tract and mucous membranes: this ceases rapidly after exposure, although there is a risk of subsequent pulmonary edema if tissue damage has been more severe. At lower concentrations, the most commonly reported symptom of chronic exposure to sulfuric acid aerosols is erosion of the teeth, found in virtually all studies: indications of possible chronic damage to the respiratory tract are inconclusive as of 1997. Repeated occupational exposure to sulfuric acid mists may increase the chance of lung cancer by up to 64%. In the United States, the permissible exposure limit (PEL) for sulfuric acid is fixed at 1 mg/m^3: limits in other countries are similar. There have been reports of sulfuric acid ingestion leading to vitamin B12 deficiency with subacute combined degeneration. The spinal cord is most often affected in such cases, but the optic nerves may show demyelination, loss of axons and gliosis.

Oleum

(Latin *oleum* = "oil"), or fuming sulfuric acid (H_2SO_4+SO_3=$H_2S_2O_7$), is a solution of various compositions of sulfur trioxide in sulfuric acid, or sometimes more specifically to disulfuric acid (also known as pyrosulfuric acid). Oleum is identified by the CAS number 8014-95-7. Oleums can be described by the formula $ySO_3.H_2O$ where y is the total molar sulfur trioxide content. The value of y can be varied, to include different oleums. They can also be described by the formula $H_2SO_4.xSO_3$ where x is now defined as the molar free sulfur trioxide content. Oleum is generally assessed according to the free SO_3 content by mass. It can also be expressed as a percentage of sulfuric acid strength; for oleum concentrations, that would be over 100%. For example, 10% oleum can also be expressed as $H_2SO_4.\mathit{0.13611}SO_3$, $\mathit{1.0225}SO_3.H_2O$ or 102.25% sulfuric acid. The conversion between % acid and % oleum is: % acid=100+18/80×% oleum. A value for x of 1 gives the empirical formula $H_2S_2O_7$ for disulfuric (pyrosulfuric) acid. Pure disulfuric acid itself is a solid at room temperature, melting at 36°C and rarely used either in the laboratory or industrial processes. Oleum is produced in the contact process, where sulfur is oxidized to sulfur trioxide which is subsequently dissolved in concentrated sulfuric acid. Sulfuric acid itself is regenerated by dilution of part of the oleum. The lead chamber process for sulfuric acid production was abandoned partly because it could not produce sulfur trioxide or concentrated sulfuric acid directly due to corrosion of the lead and absorption of NO_2 gas. Until this process was made obsolete by the contact process, oleum had to be obtained through indirect methods. Historically, the biggest production of oleum came from the distillation of iron sulfates at Nordhausen, Germany, from which the historical name Nordhausen sulfuric acid is derived.[6]

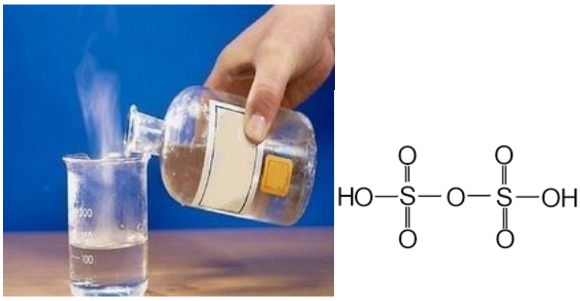


Figure-6: Oleum

Uses: Sulfuric acid production

Oleum is an important intermediate in the manufacture of sulfuric acid due to its high enthalpy of hydration.

When SO_3 is added to water, rather than simply dissolving, it tends to form a fine mist of sulfuric acid, which is difficult to manage. However, SO_3 added to concentrated sulfuric acid readily dissolves, forming oleum which can then be diluted with water to produce additional concentrated sulfuric acid.

As an intermediate for transportation

Oleum is a useful form for transporting sulfuric acid compounds, typically in rail tank cars, between oil refineries (which produce various sulfur compounds as a byproduct of refining) and industrial consumers. Certain compositions of oleum are solid at room temperature and thus are safer to ship than when liquid. Solid oleum can then be converted into liquid at the destination through steam heating or dilution or concentration. This requires some care to prevent overheating and evaporation of sulfur trioxide. To extract it from a tank car requires careful heating using steam conduits within the tank car. Great care must be taken to avoid overheating, as this can increase the internal pressure within the tank car to a value exceeding the limit of the tank's safety valve. In addition, oleum is less corrosive to metals than sulfuric acid, because there is no free water to attack the surfaces. Because of that, sulfuric acid is sometimes concentrated to oleum for in-plant pipelines and then diluted back to acid for use in industrial reactions.

Organic chemistry

Oleum is a harsh reagent and is highly corrosive. One important use of oleum as a reagent is the secondary nitration of nitrobenzene. The first nitration can occur with nitric acid in sulfuric acid, but this deactivates the ring towards further electrophilic substitution. A stronger reagent, oleum, is needed to introduce the second nitro group onto the aromatic ring.[7]

Explosives manufacture

Oleum is used in the manufacture of many explosives with the notable exception of nitrocellulose. (In modern manufacturing of nitrocellulose, the H_2SO_4 concentration is often adjusted using oleum) The chemical requirements for explosives manufacture often call for anhydrous mixtures containing nitric acid and sulfuric acid. Ordinary commercial grade nitric acid consists of the constant boiling azeotrope of nitric acid and water and contains 68% nitric acid. Mixtures of ordinary nitric acid in sulfuric acid therefore contain substantial amounts of water and are unsuitable for processes such as those that occur in the manufacture of trinitrotoluene. RDX synthesis does not require oleum. Some other explosive syntheses do not require oleum. Anhydrous nitric acid, referred to as white fuming acid, can be used to prepare water-free nitration mixtures and this method is used in laboratory scale operations where the cost of material is not of primary importance. Fuming nitric acid is very hazardous to handle and transport, because it is extremely corrosive and volatile. For industrial use, such strong nitration mixtures are prepared by mixing oleum with ordinary commercial nitric acid so that the free sulfur trioxide in the oleum consumes the water in the nitric acid.[8]

Aqua regia

(Latin, lit. "royal water" or "king's water") is a mixture of nitric acid and hydrochloric acid, optimally in a molar ratio of 1:3. Aqua regia is a yellow-orange fuming liquid. Aqua regia was so named by alchemists because it can dissolve the noble metals gold and platinum. However, aqua regia does not dissolve or corrode all metals. Aqua regia is primarily used to produce chloroauric acid, the electrolyte in the Wohlwill process. This process is used for refining the highest quality (99.999%) gold.

Aqua regia is also used in etching and in specific analytic procedure. It is also used in some laboratories to clean glassware of organic compounds and metal particles. This method is preferred over the "traditional" chromic acid bath for cleaning NMR tubes, because no traces of paramagnetic chromium can remain to spoil spectra. While chromic acid baths are discouraged because of the high toxicity of chromium and the potential for explosions, aqua regia is itself very corrosive and has been implicated in several explosions due to mishandling.

Figure-7: Aqua regia

Due to the reaction between its components resulting in its decomposition, aqua regia quickly loses its effectiveness (yet remains a strong acid), so its components are usually only mixed immediately before use. While local regulations may vary, aqua regia may be disposed of by careful neutralization, before being poured down the sink. If there is contamination by dissolved metals, the neutralized solution should be collected for disposal.[9]

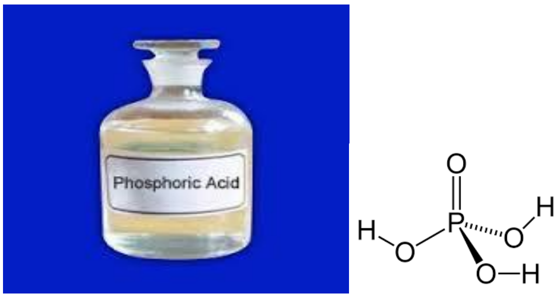


Figure-8: Phosphoric acid

Phosphoric acid (also known as **orthophosphoric acid** or **phosphoric(V) acid**) is a mineral (inorganic) acid having the chemical formula H_3PO_4. Orthophosphoric acid refers to *phosphoric acid*, which is the IUPAC name for this compound. The prefix ortho is used to distinguish the acid from related phosphoric acids, called polyphosphoric acids. Orthophosphoric acid is a non-toxic acid, which, when pure, is a solid at room temperature and pressure. The conjugate of phosphoric acid is the dihydrogen phosphate ion, $H_2PO_4^-$, which in turn has a conjugate base of hydrogen phosphate, HPO_4^{2-}, which has a conjugate base of phosphate, PO_4^{3-}. Phosphates are nutritious for all forms of life.

In addition to being a chemical reagent, phosphoric acid has a wide variety of uses, including as a rust inhibitor, food additive, dental and orthopedic etchant, electrolyte, flux, dispersing agent, industrial etchant, fertilizer feedstock, and component of home cleaning products. Phosphoric acids and phosphates are also important in biology. The most common source of phosphoric acid is an 85% aqueous solution; such solutions are colourless, odourless and non-volatile. The 85% solution is a syrupy liquid, but still pourable. Although phosphoric acid does not meet the strict definition of a strong acid, the 85% solution is acidic enough to be corrosive. Because of the high percentage of phosphoric acid in this reagent, at least some of the orthophosphoric acid is condensed into polyphosphoric acids. For the sake of labeling and simplicity, the 85% represents H_3PO_4 as if it were all orthophosphoric acid. Dilute aqueous solutions of phosphoric acid exist in the ortho- form.[10]

Figure-9: Phosphoric acid as corrosive

R-phrases: R34=Causes burns.

S-phrases: S1/S2=Keep locked up, Keep out of the reach of children, S26=In case of contact with eyes, rinse immediately with plenty of water and seek medical advice, S45=In case of accident or if you feel unwell seek medical advice immediately).

Food additive

Phosphoric acid used to make Pepsi. Food-grade phosphoric acid (additive E338) is used to acidify foods and beverages such as various colas and jams. It provides a tangy or sour taste. Various salts of phosphoric acid, such as monocalcium phosphate, are used as leavening agents.

Rust removal

Phosphoric acid may be used to remove rust by direct application to rusted iron, steel tools, or other surfaces. The phosphoric acid changes the reddish-brown iron(III) oxide, Fe_2O_3 (rust) to ferric phosphate, $FePO_4$. An empirical formula for this reaction is: $2H_3PO_4+Fe_2O_3\rightarrow 2FePO_4+3H_2O$. Liquid phosphoric acid may be used for dipping, but phosphoric acid for rust removal is more often formulated as a gel. As a thick gel, it may be applied to sloping, vertical, or even overhead surfaces. Different phosphoric acid gel formulations are sold as "rust removers" or "rust killers". Multiple applications of phosphoric acid may be required to remove all rust. Rust may also be removed via phosphate conversion coating. This process can leave a black phosphate coating that provides moderate corrosion resistance (such protection is also provided by the superficially similar Parkerizing and blue electrochemical conversion processes).

In medicine

Phosphoric acid is used in dentistry and orthodontics as an etching solution, to clean and roughen the surfaces of teeth where dental appliances or fillings will be placed. Phosphoric acid is also an ingredient in over-the-counter anti-nausea medications that also contain high levels of sugar (glucose and fructose). This acid is also used in many teeth whiteners to eliminate plaque that may be on the teeth before application.

Other applications

Among many applications, phosphoric acid is used: As a solution for anodizing, As an external standard for phosphorus-31 NMR, As a buffer agent in biology and chemistry; For example, a buffer for HPLC, As a chemical oxidizing agent for activated carbon production, as used in the Wentworth Process, As the electrolytes in phosphoric acid fuel cells, With distilled water (2–3 drops per gallon) as an electrolyte in oxyhydrogen generators, As a catalyst in the hydration of alkenes to produce alcohols, predominantly ethanol, As an electrolyte in copper electro polishing for burr removal and circuit board planarization, As a flux by hobbyists (such as model railroaders) as an aid to soldering, In compound semiconductor processing, phosphoric acid is a common wet etching agent: for example, in combination with hydrogen peroxide and water it is used to etch InGaAs selective to InP, Heated in microfabrication to etch silicon nitride (Si_3N_4). It is highly selective in etching Si_3N_4 instead of SiO_2, silicon dioxide, As a cleaner by construction trades to remove mineral deposits, cementitious smears, and hard water stains, As a chelant in some household cleaners aimed at similar cleaning tasks, In hydroponics pH solutions to lower the pH of nutrient solutions. While other types of acids can be used, phosphorus is a nutrient used by plants, especially during flowering, making phosphoric acid particularly desirable, As a pH adjuster in cosmetics and skin-care products, As a dispersing agent in detergents and leather treatment, As an additive to stabilize acidic aqueous solutions within a wanted and specified pH range, As a sanitizing agent in the dairy, food, and brewing industries.

Hazards: Exposure

The exact dangers of phosphoric acid, H_3PO_4 depend on the concentration strength of the solution, with higher concentrations presenting greater hazards. Phosphoric acid, 85 wt.% is considered a corrosive chemical solution that can cause severe skin burns and permanent eye damage. Inhalation and ingestion can also have serious effects. Eye exposure symptoms include: pain, redness, swelling, and blurred vision. Permanent eye damage including blindness can occur. Skin exposure symptoms include: pain, redness, burns, blisters, and scarring of tissue. A serious skin exposure to high-strength phosphoric acid can even cause death. Inhalation exposure symptoms include: cough, burning sensation, sore throat, and shortness of breath. Ingestion exposure symptoms include: burning of lips, tongue, throat, and stomach, abdominal pain, shock or collapse.

Toxicology

Phosphoric acid is not a known carcinogen, mutagen, nor is it known to exhibit toxicity towards a growing embryo or the reproductive systems.

Incompatibilities

Strong bases (e.g. sodium hydroxide), strong oxidizers (e.g. perchloric acid) and certain metals (e.g. aluminium). Violent reactions and splattering of dangerous chemicals can occur upon mixing H_3PO_4 with a strong base. There is an increased risk of fire or causing an explosion from adding strong oxidizers to phosphoric acid. Phosphoric acid will attack many metals and drive the formation of highly flammable and potentially explosive hydrogen gas. If flammable combustion occurs, toxic fumes of phosphorous oxides will form.

In the Household

1Examples of household products that contain or can contain H_3PO_4 are: cleaners for toilet bowls, grout, tile, automobile rims, some general purpose cleaners/degreasers; some hair/beauty products; and some toothpastes and mouth rinses may contain phosphoric acid. These examples, while the amount of H_3PO_4 may be dilute, still present potential health hazards and should always be handled safely. Additionally, never mix chemicals at home unless fully aware of the occurring chemical reaction, hazards, and safe-handling precautions necessary to remain safe. In example, the mixing of household bleach and phosphoric acid from a toilet bowl cleaner can cause the release of highly toxic chlorine gas.

Other Considerations

Phosphoric acid is not combustible, nor flammable, and will not burn in itself. Flammability of the chemical exists only from incompatible reactions with other compounds/materials. Decomposition of H_3PO_4 to toxic fumes readily occurs upon mixing with: alcohols, aldehydes, cyanides, ketones, phenols, est ers, sulfides, and halogenated organics.

Handling

Personal protective equipment recommended for handling of H_3PO_4 85 wt.%: Eye/Face Protection: wear tight-fitting government approved safety goggles (NIOSH or EN 166). Skin Protection: Nitrile rubber gloves are recommended for all handling conditions. Inspect gloves prior to usage for tears, holes, weak spots. Contaminated gloves should be disposed of according to all laws and regulations. Body Protection: complete chemical-protective suit recommendation is dependent upon concentration and amount of phosphoric acid to be handled. Respiratory Protection: use full-face air-purifying respirators with multi-purpose or type ABEK respirator cartridges as a backup to the engineering controls and when proper risk assessment recommends its usage.

To prevent exposure, the CDC recommends taking serious precautions to prevent the generation of mists, avoiding potentially hazardous exposure to eyes, skin, and nasal passageways. The CDC also recommends no eating, drinking, or smoking when handling phosphoric acid to avoid the possibility of ingestion.

Storage

Store H_3PO_4 in containers made of corrosion-resistant materials. Sigma-Aldrich recommends storing phosphoric acid in a stainless steel container with a resistant inner lining. Containers should always be stored upright to avoid leaks. Do not store in incompatible metals such as aluminum, the alloys of aluminum, and carbon steel. Store away from all incompatible chemicals and compounds. Keep away from food and feedstuffs. Ensure any solid material is kept dry. Do not reuse containers, even if they appear clean and empty.[11]

Figure-10: Boric acid

Boric acid (H_3BO_3) also called hydrogen borate, boracic acid, orthoboric acid and acidum boricum, is a weak, monobasic Lewis acid of boron often used as an antiseptic, insecticide, flame retardant, neutron absorber, or precursor to other chemical compounds. It has the chemical formula H_3BO_3 (sometimes written $B(OH)_3$), and exists in the form of colorless crystals or a white powder that dissolves in water. When occurring as a mineral, it is called sassolite.

R-phrases: R60=May impair fertility, R61=May cause harm to the unborn child.

S-phrases: S53=Avoid exposure - obtain special instructions before use, S45=In case of accident or if you feel unwell seek medical advice immediately.[12]

Industrial

The primary industrial use of boric acid is in the manufacture of monofilament fiberglass usually referred to as textile fiberglass. Textile fiberglass is used to reinforce plastics in applications that range from boats, to industrial piping to computer circuit boards. In the jewelry industry, boric acid is often used in combination with denatured alcohol to reduce surface oxidation and fire scale from forming on metals during annealing and soldering operations.

Boric acid is used in the production of the glass in LCD flat panel displays. In electroplating, boric acid is used as part of some proprietary formulas. One such known formula calls for about a 1 to 10 ratio of H_3BO_3 to $NiSO_4$, a very small portion of sodium lauryl sulfate and a small portion of H_2SO_4. Boric acid, mixed with borax (sodium tetraborate decahydrate) at the weight ratio of 4:5, is highly soluble in water, though they are not so soluble separately. The solution is used for fire retarding agent of wood by impregnation. It is also used in the manufacturing of ramming mass, a fine silica-containing powder used for producing induction furnace linings and ceramics. Boric acid is one of the most commonly used substances that can neutralize active hydrofluoric acid (HF). It works by forcing the free F^- anions into complex salts. This process defeats the extreme toxicity of hydrofluoric acid, particularly its ability to sequester ionic calcium from blood serum which can lead to cardiac arrest and bone decomposition; such an event can occur from just minor skin contact with HF. Boric acid is added to borax for use as welding flux by blacksmiths. Boric acid, in combination with silicone oil, is used to manufacture Silly Putty. Boric acid may be used in Marcellus Shale hydraulic fracturing in Pennsylvania.

Medical

Boric acid can be used as an antiseptic for minor burns or cuts and is sometimes used in dressings or salves. Boric acid is applied in a very dilute solution as an eye wash. Dilute boric acid can be used as a vaginal douche to treat bacterial vaginosis due to excessive alkalinity, as well as candidiasis due to non-albicans candida. As an antibacterial compound, boric acid can also be used as an acne treatment. It is also used as prevention of athlete's foot, by inserting powder in the socks or stockings and in alcohol solution can be used to treat some kinds of *otitis externa* (ear infection) in both humans and animals. The preservative in urine sample bottles in the UK is boric acid. Boric acid solutions used as an eye wash or on abraded skin are known to be toxic, particularly to infants, especially after repeated use; this is because of its slow elimination rate.

Insecticidal

Boric acid was first registered in the US as an insecticide in 1948 for control of cockroaches, termites, fire ants, fleas, silverfish, and many other insects. The product is generally considered to be safe to use in household kitchens to control cockroaches and ants. It acts as a stomach poison affecting the insects' metabolism, and the dry powder is abrasive to the insects' exoskeletons.

Preservation

In combination with its use as an insecticide, boric acid also prevents and destroys existing wet and dry rot in timbers. It can be used in combination with an ethylene glycol carrier to treat external wood against fungal and insect attack. It is possible to buy borate-impregnated rods for insertion into wood via drill holes where dampness and moisture is known to collect and sit. It is available in a gel form and injectable paste form for treating rot affected wood without the need to replace the timber. Concentrates of borate-based treatments can be used to prevent slime, mycelium and algae growth, even in marine environments. Boric acid is added to salt in the curing of cattle hides, calfskins and sheepskins. This helps to control bacteria development and helps to control insects.

pH buffer

Boric acid in equilibrium with its conjugate base the borate ion is widely used (in the concentration range 50 - 100 ppm boron equivalents) as a primary or adjunct pH buffer system in swimming pools. Boric acid is a weak acid, with pKa (the pH at which buffering is strongest because the free acid and borate ion are in equal concentrations) of 9.24 in pure water at 25°C. But apparent pKa is substantially lower in swimming pool or ocean waters because of interactions with various other molecules in solution. It will be around 9.0 in a salt-water pool. No matter which form of soluble boron is added, within the acceptable range of pH and boron concentration for swimming pools, boric acid is the predominant form in aqueous solution, as shown in the accompanying figure. The boric acid - borate system can be useful as a primary buffer system (substituting for the bicarbonate system with pKa1=6.0 and pKa2=9.4 under typical salt-water pool conditions) in pools with salt-water chlorine generators that tend to show upward drift in pH from a working range of pH 7.5 - 8.2. Buffer capacity is greater against rising pH (towards the pKa around 9.0), as illustrated in the accompanying graph. The use of boric acid in this concentration range does not allow any reduction in free HOCl concentration needed for pool sanitation, but it may add marginally to the photo-protective effects of cyanuric acid and confer other benefits through anti-corrosive activity or perceived water softness, depending on overall pool solute composition.

Lubrication
Colloidal suspensions of nanoparticles of boric acid dissolved in petroleum or vegetable oil can form a remarkable lubricant on ceramic or metal surfaces with a coefficient of sliding friction that decreases with increasing pressure to a value ranging from 0.10 to 0.02. Self-lubricating H_3BO_3 films result from a spontaneous chemical reaction between water molecules and B_2O_3 coatings in a humid environment. In bulk-scale, an inverse relationship exists between friction coefficient and Hertzian contact pressure induced by applied load. Boric acid is used to lubricate carom and novuss boards, allowing for faster play.

Nuclear power: Boric acid is used in some nuclear power plants as a neutron poison. The boron in boric acid reduces the probability of thermal fission by absorbing some thermal neutrons. Fission chain reactions are generally driven by the probability that free neutrons will result in fission and is determined by the material and geometric properties of the reactor. Natural boron consists of approximately 20% boron-10 and 80% boron-11 isotopes. Boron-10 has a high cross-section for absorption of low energy (thermal) neutrons. By increasing boric acid concentration in the reactor coolant, the probability that a neutron will cause fission is reduced. Changes in boric acid concentration can effectively regulate the rate of fission taking place in the reactor. Boric acid is used only in pressurized water reactors (PWRs) whereas boiling water reactors (BWRs) employ control rod pattern and coolant flow for power control. BWRs use an aqueous solution of boric acid and borax or Sodium Pentaborate for an emergency shut down system. Boric acid may be dissolved in spent fuel pools used to store spent fuel elements. The concentration is high enough to keep neutron multiplication at a minimum. Boric acid was dumped over Reactor 4 of the Chernobyl Nuclear Power Plant after its meltdown to prevent another reaction from occurring.

Pyrotechnics
Boron is used in pyrotechnics to prevent the amide-forming reaction between aluminium and nitrates. A small amount of boric acid is added to the composition to neutralize alkaline amides that can react with the aluminum.

Boric acid can be used as a colorant to make fire green. For example, when dissolved in methanol it is popularly used by fire jugglers and fire spinners to create a deep green flame.

Agriculture
Boric acid is used to treat or prevent boron deficiencies in plants.

Recreational
For the game of carom, boric acid is sprinkled onto the board of play to act as a dry lubricant to increase the speed of the pieces when struck.[13]

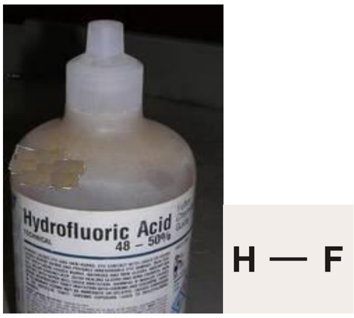


Figure-11: Hydrofluoric acid

Hydrofluoric acid is a solution of hydrogen fluoride (HF) in water. It is a precursor to almost all fluorine compounds, including pharmaceuticals such as fluoxetine (Prozac), diverse materials such as PTFE (Teflon) and elemental fluorine itself. It is a colourless solution that is highly corrosive, capable of dissolving many materials, especially oxides. Its ability to dissolve glass has been known since the 17th century, even before Carl Wilhelm Scheele prepared it in large quantities in 1771. Because of its high reactivity toward glass and moderate reactivity toward many metals, hydrofluoric acid is usually stored in plastic containers (although PTFE is slightly permeable to it). Hydrogen fluoride gas is an acute poison that may immediately and permanently damage lungs and the corneas of the eyes. Aqueous hydrofluoric acid is a contact-poison with the potential for deep, initially painless burns and ensuing tissue death. By interfering with body calcium metabolism, the concentrated acid may also cause systemic toxicity and eventual cardiac arrest and fatality, after contact with as little as 160 cm^2 (25 square inches) of skin.[14]

R-phrases: R26/R27R/28=Very toxic by inhalation and in contact with skin and if swallowed, R35=Causes severe burns.

S-phrases: S1/S2= Keep locked up and out of the reach of children), S7/S9=Keep container tightly closed and in a well-ventilated place, S26=In case of contact with eyes, rinse immediately with plenty of water and seek medical advice, S36/S37=Wear suitable protective clothing and gloves, S45=In case of accident or if you feel unwell seek medical advice immediately.

Uses
Hydrofluoric acid has a variety of uses in industry and research. It is used as a starting material or intermediate

in industrial chemistry, mining, refining, glass finishing, silicon chip manufacturing, and in cleaning.

Oil refining

In a standard oil refinery process known as alkylation, isobutene is alkylated with low-molecular-weigh alkenes (primarily a mixture of propylene and butylene) in the presence of the strong acid catalyst derived from hydrofluoric acid. The catalyst protonates the alkenes (propylene, butylene) to produce reactive carbonations, which alkylate isobutane. The reaction is carried out at mild temperatures (0 and 30°C) in a two-phase reaction.

Production of organofluorine compounds

The principal use of hydrofluoric acid is in organo fluorine chemistry. Many organo fluorine compounds are prepared using HF as the fluorine source, including Teflon, fluoropolymers, fluoro carbons, and refrigerants such as Freon.

Production of fluorides

Most high-volume inorganic fluoride compounds are prepared from hydrofluoric acid. Foremost are Na_3AlF_6, cryolite and AlF_3, aluminium trifluoride. A molten mixture of these solids serves as a high-temperature solvent for the production of metallic aluminium. Given concerns about fluorides in the environment, alternative technologies are being sought. Other inorganic fluorides prepared from hydrofluoric acid include sodium fluoride and uranium hexafluoride.

Etchant and cleaning agent

In metalworking, hydrofluoric acid is used as a pickling agent to remove oxides and other impurities from stainless and carbon steels because of its limited ability to dissolve steel. It is used in the semiconductor industry as a major component of Wright Etch and buffered oxide etch, which are used to clean silicon wafers. In a similar manner it is also used to etch glass by reacting with silicon dioxide to form gaseous or water-soluble silicon fluorides. It can also be used to polish and frost glass. $SiO_2+4HF \rightarrow SiF_4(g)+2H_2O$; $SiO_2+6HF \rightarrow H_2SiF_6+2H_2O$.

A 5% to 9% hydrofluoric acid gel is also commonly used to etch all ceramic dental restorations to improve bonding. For similar reasons, dilute hydrofluoric acid is a component of household rust stain remover, in car washes in "wheel cleaner" compounds, in ceramic and fabric rust inhibitors and in water spot removers. Because of its ability to dissolve iron oxides as well as silica-based contaminants, hydrofluoric acid is used in pre-commissioning boilers that produce high-pressure steam.

Niche applications

Because of its ability to dissolve (most) oxides and silicates, hydrofluoric acid is useful for dissolving rock samples (usually powdered) prior to analysis. In similar manner, this acid is used in acid macerations to extract organic fossils from silicate rocks. Fossiliferous rock may be immersed directly into the acid, or a cellulose nitrate film may be applied (dissolved in amyl acetate), which adheres to the organic component and allows the rock to be dissolved around it. Diluted hydrofluoric acid (1 to 3%wt.) is used in the petroleum industry in a mixture with other acids (HCl or organic acids) in order to stimulate the production of water, oil and gas wells specifically where sandstone is involved. Hydrofluoric acid is also used by some collectors of antique glass bottles to remove so-called 'sickness' from the glass, caused by acids (usually in the soil the bottle was buried in) attacking the soda content of the glass. Offset printing companies use hydrofluoric acid to remove unwanted images from printing plates. Felt-tip markers called "deletion pens" are available to make the process safer for the worker.

Safety

In addition to being a highly corrosive liquid, hydrofluoric acid is also a powerful contact poison. Because of the ability of hydrofluoric acid to penetrate tissue, poisoning can occur readily through exposure of skin or eyes, or when inhaled or swallowed. Symptoms of exposure to hydrofluoric acid may not be immediately evident, and this can provide false reassurance to victims, causing them to delay medical treatment. Despite having an irritating odor, HF may reach dangerous levels without an obvious odor. HF interferes with nerve function, meaning that burns may not initially be painful. Accidental exposures can go unnoticed, delaying treatment and increasing the extent and seriousness of the injury. Symptoms of HF exposure include irritation of the eyes, skin, nose, and throat, eye and skin burns, rhinitis, bronchitis, pulmonary edema (fluid buildup in the lungs) and bone damage. Once absorbed into blood through the skin, it reacts with blood calcium and may cause cardiac arrest. Burns with areas larger than 160 cm^2 (25 square inches) have the potential to cause serious systemic toxicity from interference with blood and tissue calcium levels. In the body, hydrofluoric acid reacts with the ubiquitous biologically important ions Ca^{2+} and Mg^{2+}. Formation of insoluble calcium fluoride is proposed as the etiology for both precipitous fall in serum calcium and the severe pain associated with tissue toxicity. In some cases, exposures can lead to hypocalcaemia. Thus, hydrofluoric acid exposure is often treated with calcium gluconate, a source of Ca^{2+} that sequesters the fluoride ions. HF chemical burns can be treated with a water wash and 2.5% calcium gluconate gel or special rinsing solutions. However, because it is absorbed, medical treatment is necessary; rinsing off is not enough. Intra-arterial infusions of calcium chloride have also shown great effectiveness in treating burns. Hydrogen fluoride is generated upon combustion of many fluorine-containing compounds such as products containing Viton and polytetrafluoroethylene (Teflon) parts. Hydrofluorocarbons in automatic fire supression systems can release hydrogen fluoride at high temperatures, and this has led to deaths from acute respiratory failure in military personnel when a rocket-propelled grenade hit the fire suppression system in their vehicle. Hydrofluoric acid can be released from volcanoes, sea salt aerosol and from welding or manufacturing processes.[15]

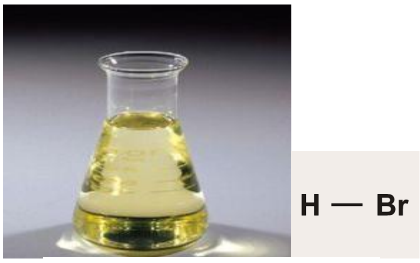


Figure-12: Hydrobromic acid

Hydrobromic acid is a strong acid formed by dissolving the diatomic molecule hydrogen bromide (HBr) in water. "Constant boiling" hydrobromic acid is an aqueous solution that distills at 124.3°C and contains 47.6% HBr by weight, which is 8.89 mol/L. Hydrobromic acid has a pKa of −9, making it a stronger acid than hydrochloric acid, but not as strong as hydroiodic acid. Hydrobromic acid is one of the strongest mineral acids known. Hydrobromic acid is mainly used for the production of inorganic bromides, especially the bromides of zinc, calcium, and sodium. It is a useful reagent for generating organobromine compounds. Certain ethers are cleaved with HBr. It also catalyzes alkylation reactions and the extraction of certain ores. Industrially significant organic compounds prepared from hydrobromic acid include allyl bromide, tetrabromobis(phenol), and bromoacetic acid.[16]

R-phrases: R34=Causes burns, R37=Irritating to respiratory system.

S-phrases: S1/S2=Keep locked up and out of reach of children, S7/S9=Keep container tightly closed and in a well ventilated place, S26=In case of contact with eyes, rinse immediately with plenty of water and seek medical advice, S45=In case of accident or if you feel unwell seek medical advice immediately.[17]

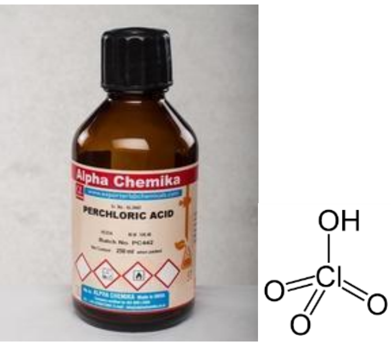


Figure: 13 Perchloric acid

Perchloric acid is a mineral acid with the formula $HClO_4$. Usually found as an aqueous solution, this colorless compound is a stronger acid than sulfuric and nitric acid. It is a powerful oxidizer when hot, but its aqueous solutions up to approximately 70% by weight at room temperature are generally safe, only showing strong acid features and no oxidizing properties. Perchloric acid is useful for preparing perchlorate salts, especially ammonium perchlorate, an important rocket fuel component. Perchloric acid is dangerously corrosive and readily forms potentially explosive mixtures.

Use

Perchloric acid is mainly produced as a precursor to ammonium perchlorate, which is used in rocket fuel. The growth in rocketry has led to increased production of perchloric acid. Several million kilograms are produced annually. Perchloric acid is one of the most proven materials for etching of liquid crystal displays and critical electronics applications as well as ore extraction and has unique properties in analytical chemistry. Additionally it is a useful component in etching of chrome.[18]

As an acid: Perchloric acid, a superacid, is one of the strongest Brønsted–Lowry acids. Its pKa is −10, −15.2 (±2.0). It provides strong acidity with minimal interference because perchlorate is weakly nucleophilic (explaining the high acidity of $HClO_4$). Other acids of noncoordinating anions, such as fluoroboric acid and hexafluorophosphoric acid are susceptible to hydrolysis, whereas perchloric acid is not. Despite hazards associated with the explosiveness of its salts, the acid is often preferred in certain syntheses. For similar reasons, it is a useful eluent in ion-exchange chromatography. It is also used for electropolishing/etching of aluminium, molybdenum, and other metals.

Safety

Given its strong oxidizing properties, perchloric acid is subject to extensive regulations. It is highly reactive with metals (e.g., aluminium) and organic matter (wood, plastics). On February 20, 1947, in Los Angeles California, 17 people were killed and 150 injured when a bath, consisting of over 1000 litres of 75% perchloric acid and 25% acetic anhydride by volume, exploded. The plant, 25 other buildings and 40 automobiles were obliterated and 250 nearby homes were damaged. The bath was being used to electro-polish aluminium furniture. In addition, organic compounds were added to the overheating bath when an iron rack was replaced with one coated with cellulose acetobutyrate (Tenit-2 plastic). A few minutes later the bath exploded. Work conducted with perchloric acid must be conducted in fume hoods with a wash-down capability to prevent accumulation of oxidisers in the ductwork.

R-phrases

R5=Heating may cause an explosion, R8=Contact with combustible material may cause fire, R35=Causes severe burns.

S-phrases: S1/S2=Keep locked up and out of the reach of children, S23=Do not breathe gas/fumes/vapour/spray, S26=In case of contact with eyes, rinse immediately with plenty of water and seek medical advice, S36=Wear suitable protective clothing, S45=In case of accident or if you feel unwell seek medical advice immediately.[19]

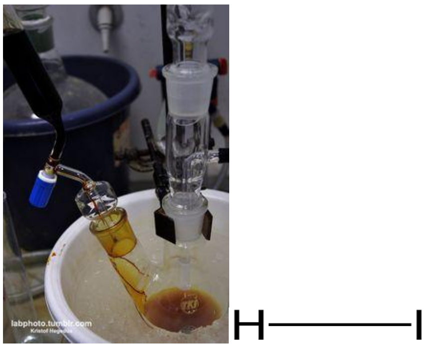


Figure-14: Hydroiodic acid

Hydroiodic acid (or hydriodic acid) is a highly acidic aqueous solution of hydrogen iodide (HI) (concentrated solution usually 48 - 57% HI). It is the strongest hydrohalic acid. Hydroiodic acid is a commonly used chemical reagent and is one of the strong acids that ionize completely in an aqueous solution. Concentrated hydroiodic acid has a pH of less than 0. Hydroiodic acid is currently listed as a Federal DEA List I Chemical. Owing to its usefulness as a reducing agent, reduction with HI and red phosphorus has become the most popular method to produce methamphetamine in the United States. Clandestine chemists react pseudoephedrine (recovered from nasal decongestant pills) with hydroiodic acid and red phosphorus under heat. HI reacts with pseudoephedrine to form iodoephedrine, an intermediate which is reduced primarily to methamphetamine. This reaction is stereospecific, producing only (d)-methamphetamine. Due to its listed status and closely monitored sales, clandestine chemists now use red phosphorus and iodine to generate hydroiodic acid *in situ*.[20]

R-phrases: R34=Causes burns.
S-phrases: S1/S2=Keep locked up and out of the reach of children, S26=In case of contact with eyes, rinse immediately with plenty of water and seek medical advice, S45=In case of accident or if you feel unwell seek medical advice immediately.

CONCLUSION

An acid is a substance that can donate a hydrogen ion (H^+) (generally speaking, this will be a proton) to another substance. Acids have a pH less than 7.0. A chemical can donate a proton if the hydrogen atom is attached to an electronegative atom like oxygen, nitrogen, or chlorine. Some acids are strong and others are weak. The weak acids hold on to some of their protons, while the strong acids let go of all of them. All acids will release hydrogen ions into solutions. The amount of ions that get released per molecule will determine if the acid is weak or strong. Weak acids are acids that partially release the hydrogen atoms that are attached. These acids, then, may lower pH by dissociation of hydrogen ions, but not completely. Weak acids generally have a pH value of 4-6 while strong acids have a pH value of 1 to 3. A base is an acid's "chemical opposite." A base is a substance that will accept the acid's hydrogen atom. Bases are molecules that can split apart in water and release hydroxide ions. Acids and bases typically exist together in equilibrium. This means that within a sample of an acid, some molecules will give up their protons and others will accept them. Even water is a mixture of an acidic ion, H_3O^+ (called a hydronium ion) and a basic ion, OH^- (called a hydroxide ion). A hydronium ion will give up its proton to a hydroxide ion, forming two molecules of H_2O, which is neutral. This reaction happens continuously in a sample of water, but overall the sample is neutral because there are equal amounts of hydronium and hydroxide in the sample. For most reactions, however, the acids and bases are not present in equal amounts, and this imbalance is what allows a chemical reaction to occur. Every acid has a conjugate base formed by removing the acid's proton. Hydrochloric acid (HCl), for example, is an acid and its conjugate base is a chlorine anion, or Cl^-. An acid and its conjugate base are opposite in strength. Since HCl is a strong acid, Cl^- is a weak base. Acids can have different strengths, some are more reactive than others. More reactive acids are often more dangerous. Acids can have a lot of different properties depending on their molecular structure. Most acids have the following properties: taste sour when they are eaten, can sting the skin when they are touched, can corrode (or eat away at) metals and skin, can be used as a reactant during electrolysis due to the presence of mobile ions, turn blue litmus paper red, turn red or orange on universal indicator conduct electricity. Acids can burn the skin, the severity of the burn depending on the type and concentration of the acid. Chemical burns such as these require immediate medical attention. Because acids donate hydrogen ions, all acids must have hydrogen in them.

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