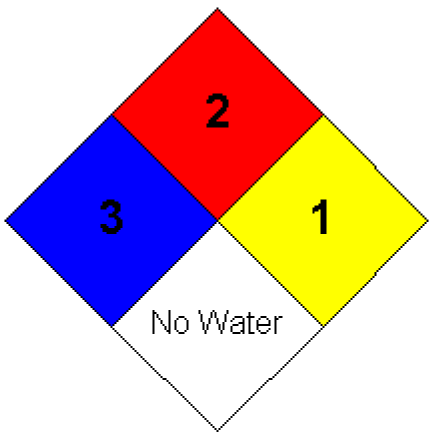
Technically Speaking
Reactivity
by John S. Nordin, Ph.D.

Chemical reactivity. What is it? Most responders are introduced to the subject of "reactivity" in the form of a National Fire Protection Association (NFPA) diamond. This is a label that accompanies hazardous chemicals that are used or stored. But the subject of reactivity is really much broader than the information conveyed in the label because many chemicals are reactive if they contact certain other chemicals. Let's first look at the NFPA diamond.

National Fire Protection Association diamond

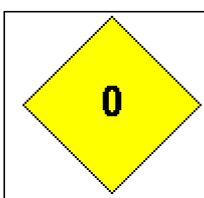
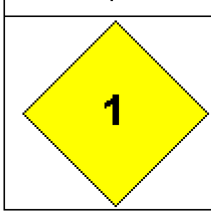
You have seen the NFPA diamond that should accompany hazardous chemicals that are stored or used.

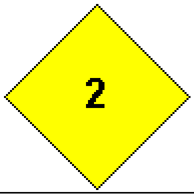
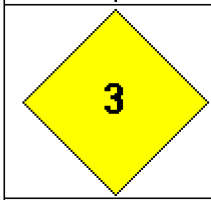
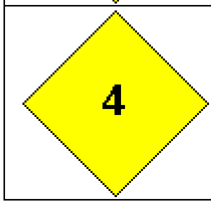


The blue diamond at the left represents health hazard ratings. The red diamond at the top represents flammability. The yellow diamond at the right represents reactivity. The white diamond at the bottom may convey additional information, but for many chemicals the white diamond is left blank. The colored diamonds each contain a hazard rating number from 0 to 4 with 4 being the most hazardous rating and 0 being the least hazardous.

Remember that we are talking about how the National Fire Protection Association considers hazard ratings and reactivity. The U.S. Environmental Protection Agency (EPA) may talk about hazardous waste, which is something different. The reactivity rating developed by the NFPA has nothing to do with mixing or storing incompatible chemicals. The NFPA reactivity rating has to do with susceptibility to release of energy because the material may detonate or react violently with water.

The NFPA rating system for reactivity is as follows:

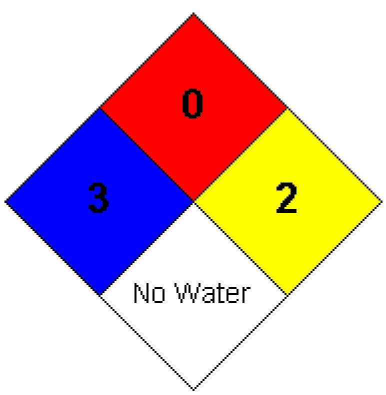
	Materials which in themselves are normally stable and do not detonate, even if exposed to fire, and which are not reactive with water.
	Materials which in themselves are normally stable, but which can become unstable at elevated temperatures and pressures, or which may react with water with some release of energy but not violently.

	Materials which in themselves are normally unstable and readily undergo violent chemical change but do not detonate. Also materials which may react violently with water or which may form potentially explosive mixtures with water fit into this category.
	Materials which in themselves are capable of detonation or can explode but which require a strong initiating source or which must be heated under confinement before initiation, or which reacts explosively with water.
	Materials which in themselves are readily capable of detonation or may explode at normal temperatures and pressures.

Only two situations are considered on the NFPA rating system for reactivity. One situation is the tendency to explode or detonate if stored or moved and the other situation is reactivity with water.

The white diamond at the bottom of the NFPA conveys additional information. "**No water**" or "**W**" means that the substance is water reactive. "**OX**" or "**Oxidizer"** means that the material is an oxidizer, that is, it carries its own oxygen or oxidizing part. Another message sometimes seen is "**air sensitive".**

Example: Sulfuric acid

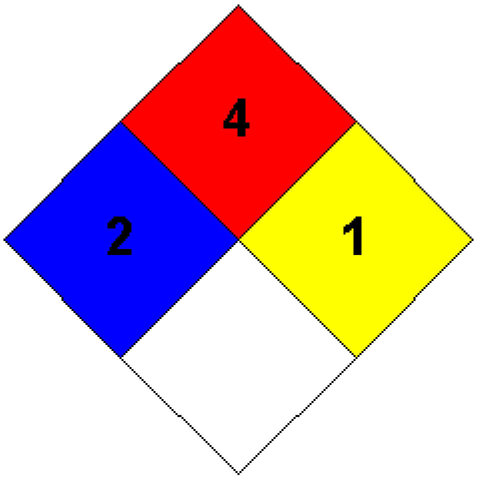


A common high school demonstration illustrating the reactivity of sulfuric acid is to pour some concentrated sulfuric acid onto one or two sugar cubes. After a minute or so, the sugar cubes will began to char with considerable release of heat. The sugar cubes may even catch fire. Why then, is sulfuric acid given a flammability rating of "0"? Because the NFPA flammability rating applies to sulfuric acid itself. Concentrated sulfuric acid reacts with many organic materials or with water releasing tremendous amounts of heat.

In the laboratory, the proper way of diluting sulfuric acid with water is to add the concentrated sulfuric acid slowly to the water under a fume hood. The person should wear protective goggles. The very large volume of water allows the heat to dissipate as the sulfuric acid is slowly added. Once the sulfuric acid is diluted with water, it is no longer reactive. The dilute sulfuric acid might still eat holes if spilled on clothing (depending upon its strength), but addition of more water does not generate any significant heat.

Should a fire fighter add water to sulfuric acid? If possible, the acid should be isolated and recovered. The addition of water to concentrated sulfuric acid will generate considerable heat and acid mists including poisonous sulfur trioxide into the air and compound cleanup. If water must be used as in a wash down of a spill, a very large volume should be added to the sulfuric acid to dissipate the heat followed by neutralization of the dilute sulfuric acid with lime or soda ash. Lime or soda ash should never be added to concentrated sulfuric acid.

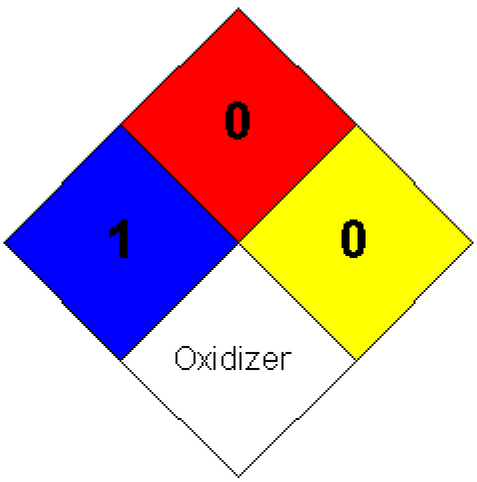
Example: Ethyl Ether



The 8-hour time-weighted-average exposure limit for ethyl ether is 400 parts per million (ppm) in air. The Immediately Dangerous to Life and Health limit (set by NIOSH) is at 1,900 ppm. The vapors if inhaled could cause temporary incapacitation (depending upon the concentration) and therefore a health rating of "2" is assigned. Under normal temperatures ethyl ether is stable, but could become unstable at elevated temperatures. Therefore a reactivity rating of "1" is assigned.

However, there is a hooker here that is <u>not</u> conveyed in the reactivity rating. Ethyl ether as well as many other types of ether can over time partly decompose forming dangerous explosive peroxides. Trace metal contaminates in the ether might accelerate the formation of the explosive chemicals. The peroxides might form under the cap. Old containers of ether can potentially detonate at normal temperatures at the slightest shock. This is of special concern to law enforcement officers who might raid an illegal drug lab where ether is used in the purification of the drug product, or in the discovery of old chemicals in some high school laboratory. Even though ethyl ether may have a "1" NFPA reactivity label, old stock should be treated as if it had a "4" rating. The NFPA ratings apply to the fresh chemical. Some chemicals will change over time because of exposure to moisture, trace metal contamination, dirt, ultraviolet light, or in some cases air.

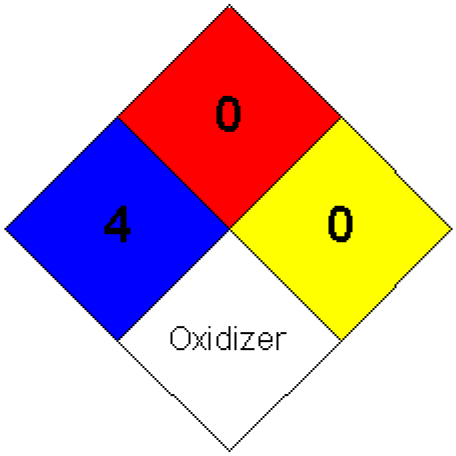
Example: Potassium Permanganate



However, potassium permanganate is an oxidizer. The chemical can supply oxygen in the case of a fire. If potassium permanganate is mixed with a combustible material, the combination will burn much more rapidly than if the combustible material is by itself. In fact, if potassium permanganate is mixed with a combustible material, some oxidation might take place over time generating enough heat to start a fire. Mixtures of potassium permanganate and flammable liquids may be explosive, that is, easily detonated. The individual chemicals by themselves may have a reactivity hazard rating of "1" or "0", but if mixed together the combination may have an effective rating of "4".

Oxidizers should be isolated from organic materials, flammables, toxicants, corrosives, heat, and strong sunlight.

Example: Chlorine



Water can be used to "knock down" the escaping gas from the boiling liquid. Water can also be used to keep fire-exposed containers cool. If water is directly sprayed on a boiling chlorine liquid, a chlorine-water ice will form. As the gas by itself is not explosive even if heated nor does it pose a special hazard when mixed with water, it is assigned a "0" reactivity hazard rating. Authorities differ whether chlorine should be assigned a "3" or "4" health hazard, but inhalation of the gas can cause serious injury or even death. The Immediately Dangerous to Life and Health concentration in air (established by NIOSH) is 10 parts per million (10 ppm). Breathing a 500 ppm concentration in air for even a few minutes may result in pulmonary edema and death or permanent lung damage if the person recovers.

Chlorine is an oxidizer. It reacts with many organic materials. Chlorine may react explosively with many metal powders or metal filings, for example, aluminum. A person might ask, "how can chlorine be an oxidizer if it contains no oxygen?" The answer is that chlorine easily pulls electrons off of many other chemicals in much the same way that oxygen does during burning. A lot of heat energy is released during the process. Sometimes the energy is released explosively.

Flame impingement upon steel containers containing chlorine can result in an iron-chlorine fire causing rupture of the container even though chlorine or iron by itself does not burn.

Chlorine can react violently with ammonia, acetylene, hydrogen, ether, turpentine, and finely divided metals.

In summary, chlorine by itself is stable and does not react violently with water. Therefore its reactivity rating assigned by the NFPA is "0". But chlorine can be very reactive, sometimes explosively, when mixed with metal powders and organic materials.