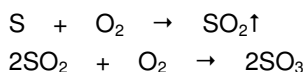


### Background

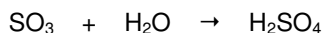
Sulphuric acid is the most widely used chemical in the world. It is cheap to manufacture, presents few storage problems, and because of its reactivity, has many possible applications.

### Manufacture & uses

Sulphuric acid is primarily produced by burning sulphur to form sulphur dioxide gas, which is then heated to 500 degrees C and passed over a vanadium pentoxide catalyst so it will react with oxygen to form sulphur trioxide.



The sulphur trioxide is dissolved in pure sulphuric acid to form fuming sulphuric acid or oleum, to which a precise quantity of water is added for the sulphur trioxide to react with it to give sulphuric acid.



Sulphur trioxide is not directly combined with water as would seem logical, because it creates a dense fog of sulphuric acid droplets which are not easily condensed back into the liquid form.

In WA, large quantities of sulphuric acid are produced as a by-product of the treatment of sulphide ores in which sulphur dioxide is formed. It is important this process is undertaken, since the only alternative option is to allow sulphur dioxide to be released into the atmosphere as a waste product.

Sulphuric acid is marketed with acid strengths, ranging from 33% to 98%, as well as in the form of fuming sulphuric acid containing 20 to 70% sulphur trioxide. About two thirds of all sulphuric acid is used to manufacture phosphate fertilizers, by chemically converting phosphate rock to superphosphate.

It is also used as the starting point for the manufacture of explosives, artificial fibres, dyes, pharmaceuticals, detergents, paint, paper and numerous other chemicals. Other applications include electrolytes in lead acid batteries, electroplating, etching, acid cleaning, mineral ore extraction, petroleum refining and as a laboratory reagent.

### Properties

Concentrated sulphuric acid that is pure is a clear, colourless oily liquid. If it contains impurities the colour can range from a pale yellow colour, to dark brown, even black. It has a specific gravity of 1.84, which makes it nearly twice as heavy to carry as water. For this reason road and rail tankers which transport

sulphuric acid have to be smaller than tankers which carry fuels.

### Dangerous Goods

Sulphuric acid is transported under a range of possible UN Numbers. The most common however is UN 1830 as:

**SULPHURIC ACID** with  
more than 51% acid

Class	8
Packing Group	II
Hazchem	2P



Other UN Numbers for sulphuric acid and its intermediates are:

UN 2796 as <b>SULPHURIC ACID</b> with not more than 51% acid	
Packing Group	III
Hazchem	2R
UN 1832 as <b>SULPHURIC ACID, SPENT</b>	
Class	8
Packing Group	III
Hazchem	2W
UN 1831 as <b>FUMING SULPHURIC ACID (OLEUM)</b>	
Class	8
Subsidiary Risk	6.1a
Packing Group	I
Hazchem	4WE
UN 1350 as <b>SULPHUR</b>	
Division	4.1
Packing Group	III
Hazchem	1Z
UN 1079 as <b>SULPHUR DIOXIDE</b>	
Division	2.3
Hazchem	2RE
UN 1829 as <b>SULPHUR TRIOXIDE, STABILIZED</b>	
Class	8
Packing Group	I
Hazchem	4WE

### Reaction with water

While sulphuric acid is non-volatile, there are definite vapour and mist hazards associated with its use. Depending on the degree of impurities, noxious vapours can be given off upon heating, even at temperatures as low as 30 degrees C. Above 200 degrees C, sulphur trioxide gas starts to come off, which in turn reacts with moisture in the air to form sulphuric acid mist.

Fuming sulphuric acid can be a colourless or cloudy to black liquid, and as its name implies, gives off continual choking fumes of sulphur trioxide. Sulphur trioxide itself is a volatile liquid at room temperature, with a boiling point of 45 degrees C, and a vapour density of 2.8 with respect to air. Vapours will tend to hug the ground, but will only exist as free sulphur trioxide until it comes into contact with moisture, where it reacts to form sulphuric acid.

Concentrated sulphuric acid reacts violently with water with evolution of considerable heat, spattering, steam and acid fumes. The spattering comes about as water droplets vaporize explosively from the localized heat released during the reaction. In concentrated form, the acid consists of discrete  $H_2SO_4$  molecules, but when water is added, the molecule is broken up with the release of energy into free positively charged hydrogen atoms ( $H^+$ ) known as hydrogen ions, and free sulphate ions ( $SO_4^{2-}$ ) which carry a double negative charge. It is still sulphuric acid and retains the properties of the diluted acid as long as free hydrogen ions are present.

The driving force behind this reaction with water is so strong that in contact with many types of organic materials including sugar, paper and wood, it will pull water out and leave behind a black carbon char. For example, sugar contains no free water, rather it is a molecule containing 12 carbon, 22 hydrogen and 11 oxygen atoms, however sulphuric acid is able to pull 11 molecules of water ( $H_2O$ ) out of sugar so that only carbon remains.



The concentrated acid is not as reactive towards metals, compared with dilute acids and for this reason they can be transported and stored in steel containers, whereas with dilute acids only lead, plastic or glass can be used. When it does react with metal, hydrogen gas is given off and the corresponding metal sulphate salt is formed.

### Health effects

In contact with the skin, sulphuric acid can cause first, second or third degree burns in three ways.

1. By drawing water out of skin tissue;
2. Thermal burns from the heat generated by reaction with water; and
3. Direct chemical reaction with skin tissue.

The contact zone first appears bleached, then turning brown, and leaves behind a slow healing ulcer. Extensive burns to the skin may prove fatal, and to the eyes permanent blindness may occur. Even dilute acids will make the skin feel very itchy quickly, and while it may take a little longer, they can also cause acid burns.

Inhalation of vapours from heated sulphuric acid will cause throat and eye irritation, runny nose and eyes, a burning feeling in the throat, cough and respiratory distress. Vapours of sulphur trioxide are extremely irritant, far more so than sulphur dioxide. Once again

the reason being, it reacts with body moisture to form sulphuric acid.

Sulphuric acid mists can be extremely fine and can lodge deep in the lungs when inhaled. Continual exposure to such mists can cause chronic conjunctivitis, teeth erosion and lung damage.

The International Agency for Research on Cancer (IARC) has classified "strong inorganic acid mists containing sulphuric acids" as a substance that will cause cancer in humans. It has been found that such mists have caused cancer of the larynx, however it has not been proven that sulphuric acid mist alone is the culprit. The reason is these findings have been made in industries where many other chemicals, including some known carcinogens, have been associated with such mists.

While sulphuric acid is not volatile an Exposure Standard has been allocated to mists.

Exposure Standard = 1 mg/m<sup>3</sup> TWA  
3 mg/m<sup>3</sup> STEL

### Environmental impact

Apart from immediate localized effects, sulphuric acid rapidly disappears from the environment once the acid component has been neutralized. However some incidents have had a major environmental impact such as massive spillages which have caused fish kills for many kilometres down stream.

The other major effect on the environment caused by sulphuric acid in association with nitric acid is acid rain. This does not come about from the manufacture or use of sulphuric acid itself, rather from the burning of massive quantities of coal containing small amounts of sulphur. The resultant sulphur dioxide forms part of the smoke stack emissions and in time various contaminants in the air catalytically convert it to sulphur trioxide, which in turn forms dilute sulphuric acid, and is caught up in the rain.

### Incidents

Incidents involving sulphuric acid can be roughly divided into 5 types:

**1. Environmental** - In Maryland, USA, on the 24th December, 1983, a storage tank ruptured spilling 1.5 million litres of acid over frozen ground into a nearby water-way. About 1.6 hectares of soil was contaminated 5 centimetres deep.

At another incident on the 9th June, 1984, Ontario, Canada, a train derailment involving 57 tanker cars spilt 1.5 million litres into a river.

**2. Water reaction** - A tank barge containing 1060 tonnes of fuming sulphuric acid capsized while being towed across Chesapeake Bay on the 18th August, 1976. All the cargo was lost over a 30 to 60 minute period, during which time a tremendously violent reaction producing vast amounts of steam and vapours took place underneath the barge, to the extent it was lifted 1.2 metres up in the water before it finally sank.

**3. Hydrogen formation** - Workmen at chemical storage tank facility in California, USA, began doing routine maintenance on a 300,000 litre tank containing a sludge mixture of sulphuric acid and volatile hydrocarbons. A valve ruptured and the contents ran into a sewer line that fed into a holding tank. The acid reacted with some metal fittings producing hydrogen which ignited, and in turn igniting the hydrocarbons. Fire fighters prevented other tanks from catching fire, however one workman died from acid burns.

Another report entitled, "Story of a Harmless Empty Sulphuric Acid Tank which Flew into the Air," says it all. This tank was emptied and washed out with water; however a residue of dilute acid was left on the bottom. The acid worked on the tank metal forming hydrogen gas, then after one week two welders started repairs on the top of the tank.

**4. Mixing with chemicals** - A 40,000 litre storage tank was wrongly labelled at chemical manufacturing plant in Castleford, England, and consequently methanol instead of xylene was added to a sulphuric/nitric acid mixture. The subsequent reaction launched about 2,700 litres of acid into the air.

Outside the factory a mother and baby were caught in the acid cloud. The baby was swabbed down with water in hospital and was alright; however the pram canopy was damaged beyond repair.

Frequent minor incidents have been reported, including some fatalities, where sulphuric acid has been mixed with other chemicals. The two most notable are with liquid hypochlorites which results in chlorine gas being given off, and that of pouring sulphuric acid down drains either to unblock or to clean them, this may result the release of hydrogen sulphide gas. Both these gases being extremely hazardous.

**5. Air-borne contamination.** A leak of sulphuric acid on the 4th December, 1985 at a dye works in Manchester, England, sent a gas cloud over 5 miles across a densely populated area. The cloud began to disperse after another 30 minutes, and people were told to stay indoors. Only 19 people were sent to hospital as a result.

A leak from an oleum tank on the 4th December, 1985, sent a gas cloud over New Delhi, India, killing one person and hospitalizing another 350.

### In conclusion

When sulphuric acid is involved emergency services must alert to the possible consequences, and not to be hesitant in obtaining specialist advice. There are many points to consider:

- Is it dilute or concentrated?
- Are the containers corroded?
- Is hydrogen likely to be present?
- Possible contact with other chemicals?
- Did it go down the drain?
- Likelihood of air-borne contamination?
- Environmental impact?

This is a very reactive chemical in which many things can happen.

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