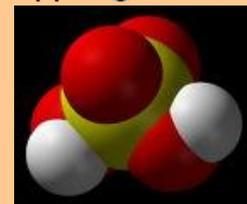
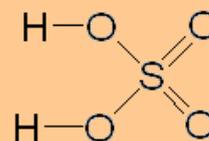




SULFURIC ACID



Mike Thompson
Winchester College, UK



Molecule of the Month - May 2008

Also available: [Chime Enhanced](#), [JMol](#), and [VRML](#) versions.

Spelling

If you wish this molecule of the month was on sulphuric acid rather than sulfuric acid then please click on the danger sign (right). It used to be known as 'oil of vitriol'. In fact it might be even better to call it sulfur(VI) acid.



Contact Process

Sulfuric acid is produced in larger quantities than any other acid. Almost every manufactured item in the modern world comes into contact with H₂SO₄ at some stage in its history. It is so important, that at one time the annual production of sulfuric acid was taken as a measure of the degree of industrialisation of a country, and earned it its nickname of the 'king of chemicals'.

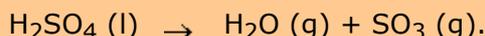
Sulfuric acid (H₂SO₄) is still an extremely important chemical used in the manufacture of fertilisers and explosives. It is made nowadays from sulfur dioxide by the [Contact Process](#). This process reacts together oxygen, O₂ and sulfur dioxide, SO₂ at 450°C and 2 atmospheres pressure, with the help of vanadium(V) oxide, to make sulfur trioxide, SO₃ gas in a 98% yield. This is then dissolved in water to make H₂SO₄. [Note that



directly dissolving SO₃ in water is not practical due to the highly exothermic nature of the reaction, forming a corrosive mist instead of a liquid. Instead, SO₃ can be absorbed into existing H₂SO₄ to produce *oleum* (H₂S₂O₇), which may then be mixed with water to form sulfuric acid]. The original reaction to make SO₃ has a high activation energy and without the catalyst is therefore very slow. It only became economically viable when in 1746, John Roebuck developed the [lead chamber process](#), which catalysed the reaction using oxides of nitrogen through the intermediate formation of HOSO₂ONO. It could be argued that the discovery of this process catalysed the Industrial Revolution (as well as the reaction!) in the UK, and as a result even helped to forge the British Empire!

Properties of sulfuric acid

At room temperature pure sulfuric acid (100%) is a covalent liquid. Concentrated sulfuric acid is 98% (18.7M) and is an oily liquid with a density of 1.83 g/cm³. It decomposes at its b.p. (330°C) and forms white fumes.



The reverse reaction is how to make sulfuric acid.

For safety data, [click here](#).

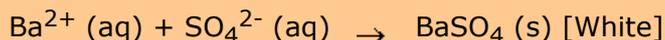
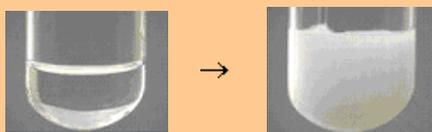
It has several important properties when concentrated; acid, oxidizing agent and dehydrating agent which makes it a very versatile reagent. It tastes sour not that you would taste it in a laboratory! It turns blue litmus red except when it is the covalent molecule, *i.e.* 100% H₂SO₄.

Concentrated sulfuric acid is very [hygroscopic](#). Its affinity for water is so great that if you left a beaker half full with conc. H₂SO₄ for three weeks, its volume would greatly increase and it would become more dilute because it would have absorbed so much water vapour out of the air.

Test for sulfuric acid (and soluble sulfates)

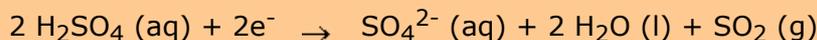
Firstly, add dilute HNO₃. This is to prevent precipitation of other insoluble barium compounds such as BaCO₃ or BaSO₃. Secondly, add Ba(NO₃)₂ (aq). If sulfuric acid or a sulfate is present a white precipitate will be immediately

observed.

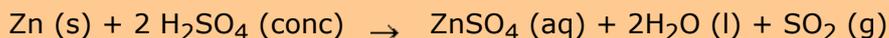


As an oxidising agent

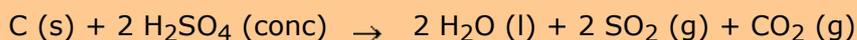
Hot concentrated sulfuric acid is an oxidising agent when it accepts electrons. The electrons are supplied by the reducing agent in the reaction:



Reactions with metals



Reactions with non-metals



Sulfur dioxide can be detected with a strip of filter paper moistened with potassium dichromate which turns from orange to green.

Halide salts with conc. sulfuric acid

Chlorides

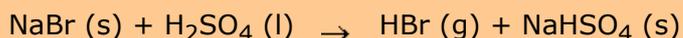
Chlorides only react in one way, no matter what the temperature.



The misty fumes of hydrogen chloride gas are seen. The reason chlorine gas is not formed is because sulfuric acid is not powerful enough to oxidise chloride ions.

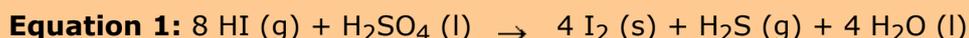
Bromides

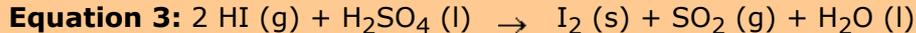
Bromide ions are a stronger reducing agent than chloride ions. As bromide ions are larger than chloride ions their electrons are easier to remove. Bromide ions reduce sulfuric acid into sulfur dioxide in two steps.



Iodides

Iodide ions are even larger than bromide ions and iodides electrons are even easier to remove. Iodide ions will reduce concentrated sulfuric acid into hydrogen iodide gas, which will further reduce sulfuric acid in three ways at room temperature.



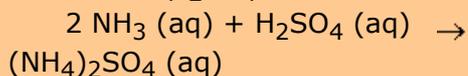


What might you expect to observe if conc. sulfuric acid was added to solid sodium iodide?

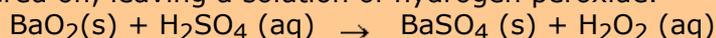
- Smell of bad eggs due to toxic H_2S (equation 1)
- purple iodine vapour (equations 1-3)
- brown due to triiodide formation ($\text{I}_2 + \text{I}^- \rightarrow \text{I}_3^-$)
- dark grey iodine solid condensing on cold glassware

Uses of Sulfuric acid

- nitrogenous fertilizers such as ammonium sulfate ($\text{NH}_4)_2\text{SO}_4$



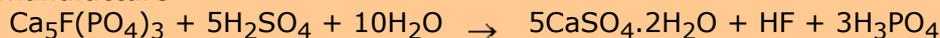
- making **hydrogen peroxide** (H_2O_2) by reacting barium peroxide with sulfuric acid. The insoluble barium sulfate can be filtered off, leaving a solution of hydrogen peroxide.



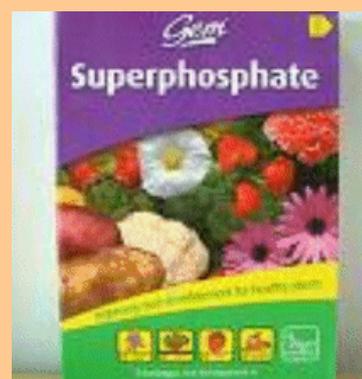
- 'pickling' to clean metal surfaces (see photos, right)
- extraction of metals
- HCl via the Mannheim process



- detergents and soaps
- **drain cleaner**
- drying gases (but not ammonia)
- paints and pigments
- natural and man-made fibre manufacture
- **superphosphate** manufacture
- HF manufacture

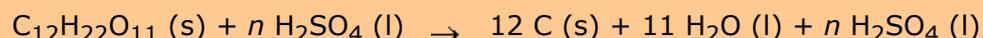


- the electrolyte (33% H_2SO_4) in the **lead-acid storage battery** used in motor vehicles.

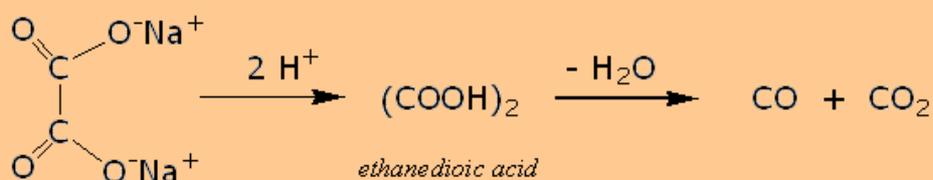


As a dehydrating agent

Concentrated sulfuric acid is very good at removing the water from sugars. When the elements of water are removed from sucrose it leads to a black mass of carbon (see photo, left and the Molecule of the Month page on [glucose](#)).



Sulfuric acid can also be used to dehydrate sodium salts of some carboxylic acids. This use of sulfuric acid has already been mentioned in the [Molecule of the Month](#) page on [Carbon monoxide](#). The reactions involve protonation by the acid followed by subsequent dehydration.



Reactions of sulfuric acid

With bases

Dilute sulfuric acid neutralises basic oxides or hydroxides to form sulfate salts and water. Don't forget sulfuric acid is a strong acid (completely ionizes in water).



As sulfuric acid is dibasic (ionizes in two stages) when it reacts with sodium hydroxide it can form two possible sodium salts. To see which one is favoured you need to consider the stoichiometry (number of moles in the balanced equation) for the following two reactions.



With carbonates

Dilute sulfuric acid neutralises basic carbonates to form sulfate salts, water and carbon dioxide, resulting in effervescence (as shown in the photo, right).



The rate of reaction not only depends on the surface area of the carbonate and the concentration and temperature of the acid, but also on the solubility of the sulfate. When marble (CaCO_3) reacts with dilute H_2SO_4 it initially effervesces but because calcium sulfate is only sparingly soluble in water, once it forms as a deposit on the marble surface, the reaction soon slows.

With metals

Dilute sulfuric acid reacts with metals higher than hydrogen in the reactivity series to form sulfate salts and hydrogen gas. Note the metal reactions are different with concentrated sulfuric acid.

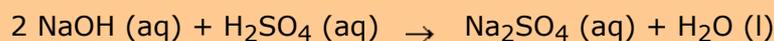


Iron is cleaned free from rust prior to coating with tin to form tinplate and with zinc to form galvanized iron.

Sulfates

The biggest (80%) use of sulfuric acid in the manufacture of sulfates.

Gypsum is $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and is used to make plaster board as well as plaster casts (see photo, right). The laxative '*epsom salt*' is $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, and *green vitriol* is $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. In 1648, Glauber made sulfuric acid by distilling crystals of this salt. Potassium sulfate is unusual in that it crystallizes without water of crystallization and has the formula K_2SO_4 . As sulfuric acid is dibasic, (diprotic) it is capable of forming two salts depending on the amount of alkali present in the reaction mixture;



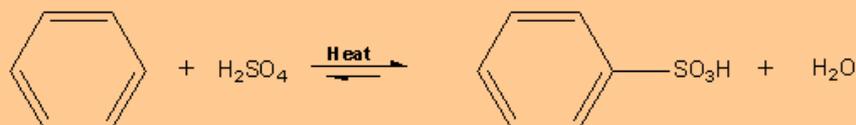
Sulfuric acid in Space

In 1999, solid (frozen) sulfuric acid was discovered on Jupiter's moon, [Europa](#). Scientists have even identified solid sulfuric acid [hydrates](#) such as hemitriskaidecahydrate ($\text{H}_2\text{SO}_4 \cdot 6\frac{1}{2}\text{H}_2\text{O}$).



Sulfonation

Aromatic sulfonation is when an H is replaced by SO_3H (a sulfonic acid group). In the case of benzene, it needs to be heated with conc. H_2SO_4 for 8 h to produce benzenesulfonic acid. This reaction is too slow and not to be attempted as benzene is implicated in childhood leukemia.



Instead, it's better (faster and safer) to use toluene (methylbenzene), as the methyl (CH_3) group is electron releasing and speeds up the reaction. The procedure is: Add 30 drops of conc. H_2SO_4 to 12 drops of (toluene) in a test-tube. Warm until the methylbenzene has dissolved into the acid layer. Pour the mixture into 30 cm^3 of a cold saturated solution of sodium chloride. White crystals of sodium methylbenzene sulfonates are formed. The methyl group is *ortho-para* directing.

and finally...

Even Bart Simpson can spell sulfuric acid

