

Hydrogen

H. G. Andrew, formerly Chairman ASE Laboratory Safeguards Sub-committee

(The previous article in this series on Safety appeared in SSR 1978, 209, 59, 750.)

The unique properties of hydrogen render it both the cause of most of the explosions and some of the more serious accidents in schools, but also permit it to be used safely even if it is allowed to escape.

The dangers are that hydrogen-air mixtures are potentially explosive over the range of 4 to 74 percent of hydrogen; (c.f. 5 to 15 percent for CH₄). The ignition temperature of the mixtures is relatively low, about 500 °C, well below visible red heat; (c.f. about 750 °C for CH₄). Ignition can occur well below this temperature in the presence of many transition metals or their oxides. The very low density of hydrogen enables it to diffuse rapidly out of any leaks in an apparatus, the resulting fall of pressure inside causing air to be drawn in. On the other hand its extreme lightness and rapidity of diffusion mean that any that escapes into the air can scarcely form an explosive mixture with the air in a room. If the whole contents of a 20 cu ft (0.57 m³) cylinder are discharged into an average laboratory as quickly as possible it should be possible to strike a light quite safely ten seconds afterwards. (When I proposed to demonstrate this at a safety lecture, I did not conclude the experiment as my audience started to disperse almost as fast as the hydrogen!) If all this hydrogen mixed uniformly with the laboratory air the concentration would be only about 0.1 per cent. Its extreme lightness would prevent uniform mixing and cause it to rise rapidly to higher levels where it would quickly diffuse away through ceilings, walls and window cracks. There is therefore no danger of a major explosion from a leaking hydrogen cylinder.

The generation of hydrogen is traditionally from granulated zinc and dilute sulphuric acid. The acid can conveniently be about 3M. The final solution will then be warm enough and concentrated enough after filtering to give good crystals of zinc sulphate-7-water as it cools. If a more dilute acid is used the resulting solution requires concentrating to give crystals and if solid is deposited above 40 °C unsatisfactory basic salts and lower hydrates are produced.

Alternatively 3 M hydrochloric acid may be used. This is less corrosive than sulphuric acid but nice crystals of zinc chloride will not be obtained since these are deliquescent and very soluble.

A small quantity of copper(II) sulphate is usually added, preferably to the acid before it is run in, but the quantity should be very small. Too much defeats its object which is to form tiny sites of copper on the zinc so that the hydrogen bubbles form on these, leaving most of the zinc freely exposed to the acid. In

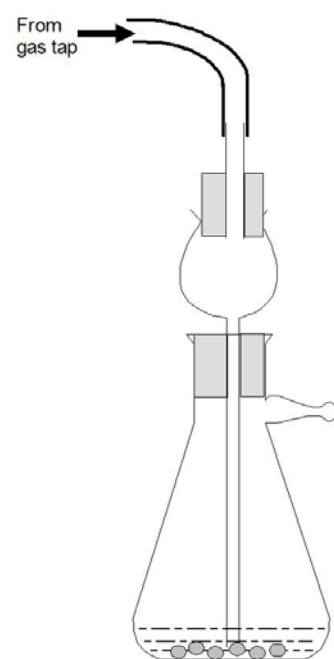


Figure 1

preparing hydrogen for reductions it is a good plan to place a few inches of magnesium ribbon under the zinc before starting. The initial vigorous action helps quickly to purge the apparatus of air.

It is when explosion occurs in a drying bottle containing concentrated sulphuric acid that most of the damage is done, both by flying glass splinters and dispersed acid. It is often convenient to have some kind of wash bottle containing liquid in a train of apparatus in order to monitor the rate of gas flow, but there are ways of doing this safely.

Concentrated calcium chloride solution will dry hydrogen sufficiently for most purposes and will also indicate flow rate. If sulphuric is needed for more complete drying, it should be soaked up in small lumps of pumice and used in a tower or U-tube. These could be followed by a small monitoring tube containing only a few cubic cm of acid. Or concentrated phosphoric(V) acid (H_3PO_4 S.G. 1.75) is a good desiccant and so is glycerol (propane-1,2,3-triol). Both these liquids have viscosities greater than sulphuric acid but this is no problem if they are dispersed on pumice. For monitoring, a low viscosity and low vapour pressure liquid such as dibutyl benzenedicarboxylate (phthalate) may be used with advantage. Hydrogen dried with sulphuric acid usually contains traces of hydrogen sulphide.

The safest way of showing that an apparatus through which hydrogen is passing is free from explosive mixture is to collect gas at the exit in a test-tube by upward delivery. If this burns quietly when ignited at a distant flame all is well.

If a thistle funnel is used in the generator a small quantity of air may be entrained when further acid is added but this does not involve additional risk since it would be necessary to entrain a volume of air equal to at least a quarter of the volume of the gas in the generator to obtain the minimum explosive concentration (24 percent of air). The back-pressure when a considerable train of apparatus is used makes the normal use of a funnel inconvenient. A good method is to have a tube from the laboratory gas supply connected to a cork which can be inserted into the top of the thistle funnel (Figure 1). The gas can then be used to flush air from the apparatus to start with, and if required, to act as a carrier gas at the end of a reduction experiment when hydrogen production is slowing down. The covered thistle funnel also overcomes back pressure.

Alternatively a tap funnel can be used and the pressure in the apparatus communicated to the top of the funnel (Figure 2). This device is useful in any apparatus in which gas is produced by dripping a liquid into a flask, as a very steady supply can be maintained.

Conical shaped pyrex flasks should be used. The dead space in these is much less than in the normal flasks used at one time. Plastic bottles are also suitable. Methods of preparing hydrogen other than the use of zinc and acid are not attractive. Dropping water onto calcium turnings or, better, technical grade calcium hydride, is expensive, but could be considered for special purposes. The hydrogen will be reasonably dry and the use of corrosive liquids is avoided.

Magnesium acts inconveniently fast with acids unless pieces of cut rod

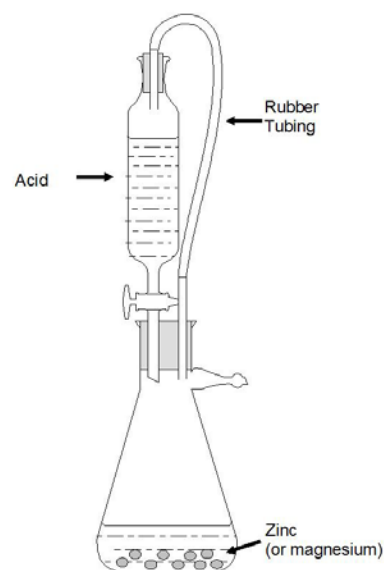


Figure 2

are used or the acid is dripped onto the turnings. Aluminium reacts too slowly with acids and froths unpleasantly with alkalis.

Approximate current costs for making a mole of hydrogen molecules using various substances are (in pence*): aluminium 15, zinc 15, magnesium turnings 25, calcium hydride 100, calcium 150. This excludes the cost of any acids used.

Some form of automatic generator, with a small dead space, such as can be made from an inverted long-bodied tap funnel, is convenient for providing occasional supplies of hydrogen (Figure 3).

Now that power packs and battery chargers are readily available the design of electrolytic generators for hydrogen or other gases is worth considering. For chlorine, titanium anodes have now replaced carbon in both mercury and diaphragm cells commercially.

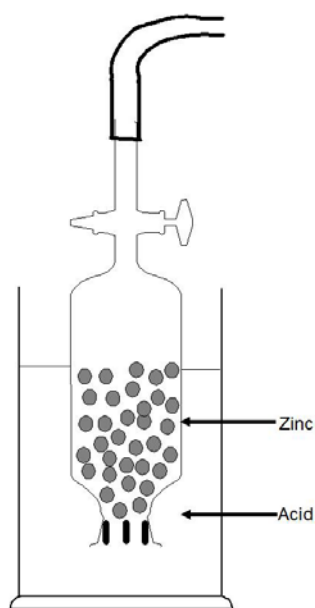


Figure 3

** The figures will now be inaccurate but the relative cost is still relevant.*