Preparing gases on microscale and demonstrating some exciting properties

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General: These experiments and procedures were developed following an inspirational lecture given at the 7th International Conference on Chemical Education held in Budapest in August 2000 by Viktor Obendrauf (Graz, Austria) and using the paper provided in the proceedings. Copies of the proceedings were also circulated to all members of the Chemical Education Research Group of the Royal Society of Chemistry. The most accessible summary, in English, of Obendrauf's procedures can be found in an electronic journal – although this focuses upon using the technique for showing the 'ammonia fountain experiment':
http://chem.sci.utsunomiya-u.ac.jp/v7n2/angela/angela_abstract.html

The examples developed in this section have been found to be particularly useful in demonstrating potentially **very** dangerous reactions relatively safely on a very small scale – albeit still with a spectacular result. These instructions allow the preparation of a wide variety of gases and their collection in plastic syringes. However the detail here is restricted to the demonstration of:

(a) The reaction between hydrogen and chlorine.
(b) The reaction between chlorine and ethyne.

Obendrorf's paper gives many other examples of reactions that can be followed through by these techniques – although to be really useful as demonstrations many of them require the use of a TV camera and a data projector (and considerable extra manipulative skill on the part of the demonstrator!)

It should also be noted that Obendrauf lays particular emphasis on the test-tubes, syringes and 'soft rubber' bungs to be used in these procedures. I have not been able to track these down and have used standard test-tubes, disposable syringes and normal 'red' rubber bungs as available in most science education suppliers' catalogues. This does not seem to have caused major problems. A description of the processes I have found to work is given below. If you feel the processes would benefit your teaching, *carefully* try them yourself, evaluate your results and develop a better way if possible!

Some general safety considerations:

1. Disposable needles and syringes are widely used in medical procedures – and it is important that NO ATTEMPT is made to recycle used syringes or needles that have been used for injections or taking blood samples from humans or other animals. Use only new stock initially, although with care it is possible to reuse apparatus a number of times for purely chemical purposes.

2. Syringes and needles are relatively inert chemically, but needles in particular are attacked slowly by reactive chemicals such as concentrated mineral acids and chlorine gas. The tubes should be

rinsed out with water and dried as soon as possible after use and before storage.

3. Disposable syringes and needles can be seriously misused for self administration of drugs and it is important that any stock maintained in school is kept secure such that it does not become a source of supply for illegal or harmful purposes.

4. Hypodermic needles are very sharp. Pressure should NOT be applied to a needle when the point is directed toward any part of a body. (Fig.1) They must be stored, handled and disposed of with care. However, once the point has been removed (Fig.2(c)) it is much less hazardous and need no longer be considered a needle. (A micro-tube?)

5. The main hazard inherent in these gas preparations is the inadvertent spraying of small amounts of reactants and/or products due to sudden increases of pressure – either because the reaction occurs too quickly or one of the micro-tubes becomes blocked. Safety spectacles should be worn at all times and gloves when appropriate.

6. The quantities of hazardous materials are minimised in these procedures – no more than 3-5cm^3 of any liquid reagent and the *total* volume of any gas liberated should be limited to a potential maximum of 100cm^3. If the room is large it may not be necessary to use a fume cupboard although one should be used if available. Excess of most hazardous gases can be absorbed by replacing the collection syringe by a syringe containing a suitable granular material such as ‘active’ charcoal or soda lime.

<u>Materials required:</u>

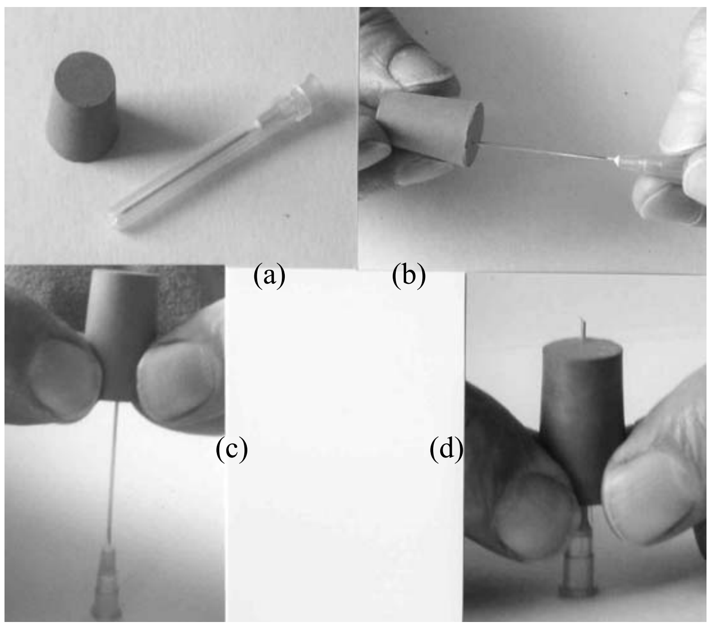
1. Disposable plastic syringes of 20cm^3, 10cm^3 and 5cm^3 capacity. I generally use the 20cm^3 size for collecting the gases (and for this purpose it is useful to smear the plunger – *very sparingly* – with silicone grease to ensure that it moves smoothly. The 5cm^3 size is appropriate for injecting the liquid reagent – and this should NOT be lubricated – since we do not want the gas liberated to enter this syringe. It is important that the nozzle, particularly of the larger syringe is off-set from the centre to allow two syringes to fit over the top of the small bung.

2. Syringe needles: They must be long enough to penetrate the bung. I prefer to use large gauge needles since these are less likely to buckle when being pushed through rubber bungs. It is useful to use two different gauges (e.g. 21G x 1.5inches = 0.8 x 40 mm. and 19G x 2inches = 1.1 x 50 mm.) since these also have different coloured plastic luer-fittings. It is convenient to be able to differentiate both ends of the micro-tubes since it is not always clear what path the tubes follow through the bungs.

3. Short borosilicate glass test tubes with rubber bungs to fit. (I use No13 bungs)

<u>Assembly of the gas generator:</u>

(A) Figure 1 shows a method of fitting a syringe needle through a bung. When pushing the needle through the bung ensure that your fingers are **behind** the tip of the needle and the plastic end rests on a firm surface. It is difficult to predict the direction the needle tip will take through the bung and it often emerges through the side of the bung. (If this happens simply pull the needle out and try again!) Try to use a gentle steady vertical pressure such that the needle keeps moving slowly into the bung.



<u>Fig.1:</u> (a) Needle and bung; (b) *Gently* push needle a few mm into bung to set the initial direction; (c) push the plastic fitting firmly on a flat surface keeping fingers **behind** the level of the tip; (d) tip emerging from base if bung.

(B) Fit a second needle through the bung adjacent to the first. Grind of the point of both needles. (Figure 2) (If the angle of the needle is too steep, grind off sufficient of the tube to prevent its touching the side of the test tube when the bung is inserted.) I find it most convenient use a cutting/grinding wheel on a high-speed mini-drill. N.B. It is not suitable to use pliers to cut the needle since these crush the tube and prevent free flow of fluid.

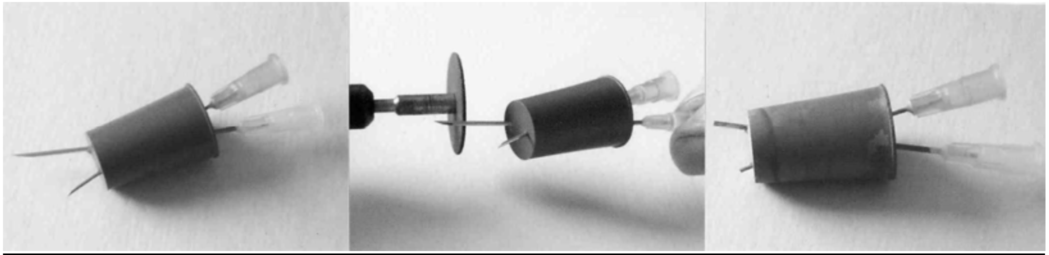


Fig.2:
Converting the needles into 'micro-tubes'.

(C) The Gas Generator: Figure 3 on next page.

The use of this apparatus is almost self evident. It is however important to check that fluids can pass freely through both micro-tubes before the apparatus is assembled (Blow air through from and 'empty' syringe.) and check that the collection syringe plunger moves smoothly. (It should have been lightly lubricated with silicone grease.) Place the solid reactant in the test tube – covering it with water if **dilute acid** is the other reagent – then **slowly** add the liquid reagent from the small syringe until the reaction proceeds at an appropriate speed.

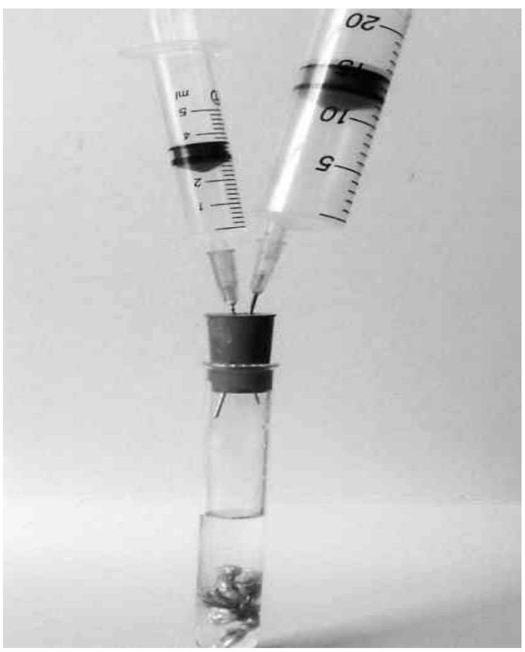


Fig.3:
In this set-up to produce hydrogen, zinc covered with water is in the test tube and conc. Hydrochloric acid is added from the 5cm^3 syringe. Hydrogen collects in the 20cm^3 syringe. (The first syringe full of gas is discarded since it is mainly air.)

If the plunger of the collection syringe does not move up the barrel it may be necessary to ease it by pulling on it gently and twisting it.

The first syringe full of gas contains air and is discarded.

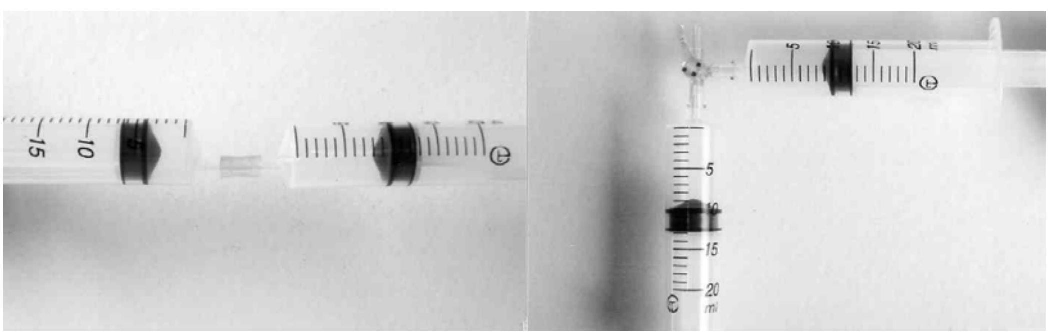
The following table gives possible reagents for the preparation of a range of gases. (If the gas needs to be dried or otherwise purified it may be possible to place a syringe, 5cm^3 or 10cm^3, containing a suitable granular drying agent (or even dry cotton wool if it does not react with the gas.) or other absorbent.

Target Gas	Solid Reagent	With Water (Yes/No)	Liquid Reagent
Hydrogen	Granulated zinc (contaminated with a trace of copper)	Yes	Concentrated hydrochloric acid
Oxygen	Manganese dioxide	Yes ?	20 vol. Hydrogen peroxide
Carbon dioxide	Calcium carbonate	Yes	Concentrated hydrochloric acid
Chlorine	Potassium permanganate	No	Concentrated hydrochloric acid
Ethyne	Calcium carbide	NO!	Water
Ammonia	Sodium hydroxide	NO!	Concentrated ammonia solution
Others include: CO; SO_2; HCl; H_2S; NO.			

Once a syringe of gas free from air has been filled it can be closed with an appropriate cap. (These are available commercially from some suppliers, but I make my own from the micro-tubes that have become blocked or needles that did not survive the process of being inserted through the bung. Simply pull off the metal tube from the plastic fitting and seal the 'thin' end of the plastic with one drop of quick setting adhesive such as Araldite.)

<u>To demonstrate the photolytic reaction between hydrogen and chlorine:</u>

Prepare and close 20cm^3 syringes full of hydrogen and chlorine. The chlorine does not store well (probably because I do not dry it) and thus it is better to prepare this within 5-20 minutes of its being used.



(a) **(b)**

Fig.4: syringes connected by (a) plastic tubing; (b) a 'three-way' tap.

Connect a dry empty syringe (20cm^3 or 10cm^3) – the reaction syringe – to the opened end of the hydrogen syringe using a short length of plastic tubing (Fig.4(a)) or using a commercially available 'three-way' tap (Fig.4(b)). Half fill the syringe with hydrogen, remove and cap the original hydrogen syringe and replace it with that full of chlorine. Whilst avoiding strong light on the syringes fill the other half of the reaction syringe with chlorine. Separate and cap both syringes and as quickly as possible clamp (or otherwise support) the reaction syringe vertically behind an explosion screen (a suitably supported sheet of Perspex is sufficient). Warn any onlookers that there may be an explosion, place a charged electronic flash gun directly against the side of the syringe and set off the flash. There is a loud explosion and the plunger from the syringe is ejected at high speed. (Clearly it is necessary to ensure that this does not hit anyone directly. You are the closest to it and also, normally the ‘wrong’ side of the explosion screen, unless you choose to use two screens! There is a possibility that the barrel of the syringe may shatter – any danger from plastic shards is minimised if you hold the flash gun very close to the syringe and stand behind it.) There almost always IS an explosion unless the chlorine had ‘gone off’ (see above) or unless you took too long before flashing the mixture – and then much of the reaction will have occurred quietly, initiated by the subdued light in the room. (I believe you really do need a fairly powerful flash – attempts using the built in flash of a ‘compact’ camera have so far failed.)

To demonstrate the reaction between ethyne and chlorine:
Contrary to the possible expectation of an addition reaction between ethyne (acetylene; HCCH) and chlorine, the two gases react violently on contact producing hydrogen chloride and carbon. IT IS IMPORTANT THAT YOU DO **NOT** ATTEMPT TO PUT A MIXTURE OF THESE TWO GASES IN THE SAME SYRINGE.

Carefully remove the copper wire from the centre of the insulation tube from single core electrical cabling to produce plastic tubes about 10-15cm long. Grind the points from two syringe needles whose tubes will then push into one end of each plastic tube to form a gas-tight seal. Fasten the free ends of the plastic tubes together ensuring that the tubes are not blocked and the holes in the end are as close together as possible.

Separately prepare and cap 20cm^3 syringes of each of the gases. (Considerable heat is generated when water reacts with calcium carbide and the second addition of water tends to react much more rapidly than the first. I have been surprised by the bung blowing off the test-tube instead of the gas collecting in the syringe!)

Attach one each of the chlorine and ethyne syringes to luer fittings on the plastic tubes prepared as above and dip the connected ends of the plastic tubes about 5cm below the surface of clean water in a 250cm^3 beaker. Gently expel the gases simultaneously through their respective tubes. As the bubbles come into contact the reaction produces explosive ‘crackles’ with bright white flashes under the water. Afterwards black particles of carbon can be seen on the surface of the water.

<u>Risk Assessment</u> (You MUST make your own):
Apart from the specific risks of particular chemicals (all of which are well documented e.g. by CLEAPSS) I have tried to mention most hazards at the appropriate point in the description.

I would stress again that the very small amounts of reactants and products make even these potentially hazardous reactions relatively safe. It is however important to wear effective eye protection and to practise your technique.

Educational Context

Hydrogen with chlorine is a clear example of a highly exothermic reaction – although energy (activation energy) is required to start it. A spark can be used, but the fact that it can be initiated by a flash of light is connected with the greenish colour of chlorine – which is caused by the fact that chlorine absorbs some visible light. (It may be useful to contrast this with the reaction of two volumes of hydrogen with one of oxygen – this mixture will explode violently when ignited with a spark or a flame but is unaffected by a flash of light.)

There is a link with both photography and photosynthesis but in these cases the reactions are endothermic so the light energy is required to drive the reaction not just to initiate it.

Chlorine and ethyne provide an example of a spontaneous exothermic reaction – this also demonstrates the high affinity chlorine has for hydrogen. (That chlorine is a very strong oxidising agent.)