



Accidents caused by blocked apparatus

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One of the commonest causes of accidents in school laboratories results from wholly or partially blocked apparatus: the resultant build-up of pressure has inevitable consequences. Sometimes the problem is caused by the use of tubing of too narrow a bore, but more frequently the tubing becomes blocked by a solid product of the reaction, or a powdered drying agent being blown through it. It is essential to:-

- Devised apparatus which allows a gas to be generated slowly under controlled conditions.
- Ensure that the dimensions of any tubing, etc. are such as to be able to cope with even an unexpectedly rapid flow of gas.
- Check the apparatus continually to ensure that blockages are not occurring.

The following accidents, from recent correspondence of the Laboratory Safeguards Sub-committee, will serve to illustrate the diverse ways in which the problem manifests itself, and possible strategies to minimize the risk. It is **not** intended to suggest that these experiments should not be carried out in school laboratories, but simply to emphasize that due care should be exercised with even the most commonplace procedures.

Preparation of oxygen [1]

Hydrogen peroxide solution was added, via a thistle funnel, to a catalyst of manganese(IV) oxide. Rather a large volume of solution was poured in all at once, and the delivery tube was too narrow to cope with the sudden release of a large volume of oxygen. In this case, a tap funnel would have allowed a more controlled addition of peroxide solution, and wider bore tubing should have been used.

Generating dry ammonia gas [1]

Aqueous ammonia solution was being warmed, and the vapours dried by passage over lumps of calcium oxide. The exit from the drying tube became blocked by calcium hydroxide powder, and the build-up of pressure resulted in hot ammonia solution, and calcium oxide particles being blown out with some force. Greater vigilance might have avoided this accident, and alternative drying agents could also be considered (see below). As this was a teacher demonstration the teacher had not thought it necessary to put on safety spectacles, nor insist that pupils put them on: two pupils ended up in hospital.

The reaction between sulphur dioxide and oxygen [2]

Sulphur(VI) oxide (sulphur trioxide) was being synthesized by passing sulphur dioxide and oxygen over a hot catalyst, and the product collected in a flask cooled in an ice/salt mixture. Crystals of sulphur(VI) oxide blocked the cooled tube, resulting in a pressure increase. When the oxygen delivery tube was disconnected concentrated sulphuric acid, used to dry the gas (see below), sprayed out of the apparatus. Again the problem was the use of tubing of too narrow a bore, together with a failure to check the condition of the apparatus at regular intervals.

Preparation of Ethene [1]

Ethene, prepared by the action of concentrated sulphuric acid on ethanol, was being bubbled through a wash bottle containing concentrated sodium hydroxide solution. The solution was so concentrated that crystals (probably of sodium sulphite) formed around the tip of the delivery tube, causing a build-up of pressure in the

reaction vessel. Use of less concentrated sodium hydroxide would have prevented the problem – 2 M NaOH is convenient—but continual vigilance would have prevented the accident.

In this preparation the amount of sulphur dioxide formed is usually small, although carbon dioxide also is formed. Where it is necessary to remove appreciable amounts of carbon dioxide from a gas stream potassium hydroxide is preferred to sodium hydroxide solution, since potassium hydrogencarbonate is about three times as soluble as sodium hydrogencarbonate. Moreover, since potassium carbonate is deliquescent, stoppers of bottles containing potassium hydroxide solution are much less likely to stick.

Thermal decomposition of lead(II) nitrate

Lead(II) nitrate crystals were being heated in a test tube. This was connected by a length of rubber tubing, to a cooled U-tube, to collect the nitrogen dioxide. However the hot nitrogen dioxide attacked the rubber, and the resulting sludge blocked the delivery tube although the problem was noticed before the blockage caused an accident. This could have been avoided by using an all-glass delivery tube. If a connection between two glass tubes is necessary, the tubes could be butted together inside a short piece of rubber tubing so that the area of rubber exposed to the gas is kept to the minimum.

Thermal decomposition of polyethene

Polyethene granules were being heated in a test tube, the vapour passed over hot porous pot further up the same test tube, and the gaseous products collected over water. Some liquid products condensed in the delivery tube, blocking it, with inevitable consequences. In this case the problem may have been caused by the use of too much polyethene, the probably unnecessary use of porous pot, tubing of too narrow a bore, or a rather sharp right angled bend in the tubing.

Silicon tetrachloride bottles

There have been numerous reports of bottles containing silicon tetrachloride exploding whilst being opened [3]. The compound hydrolyses readily, the neck then becomes blocked by hydrated silicon dioxide, and hydrogen chloride gas builds up under pressure. Frequently the silicon dioxide cements the bottle to its lid. At the very least there is a considerable release of hydrogen chloride gas when the crust of silicon dioxide is pierced, or when the neck is broken (a not infrequent occurrence). Ampoules of silicon tetrachloride are available [1], but care must be exercised in opening them. If bottles are used, they should be opened only in the fume cupboard, protective gloves and a face visor being worn. A dry duster placed over the entire bottle is an added precaution. Hydrolysis is less likely if the bottle is stored in a desiccator, or in a sealed plastic bag containing a desiccant.

Drying gases

When an explosion occurs in school laboratories - whether the result of a direct chemical reaction, or the result of blocked apparatus-the main damage is often caused not by broken glass, but by liquids spraying over the experimenter [2]. Concentrated sulphuric acid used to dry gases is a particular problem in this respect, and one which can be largely avoided by the use of alternative drying agents. It is perhaps also worth pointing out that gases taken from pressurised cylinders need no drying anyway.

For most of the gases commonly met in schools silica gel is a good drying agent [4] (and acceptable to examiners!) It has the advantage that it can be recycled. The presence of the self-indicating variety will show when regeneration is necessary. Silica gel is not suitable for ammonia, for which calcium oxide has traditionally been used. Calcium oxide, with its large lumps of low surface area, and a tendency to form a powder, is less than ideal. Soda lime has more to commend it. For hydrogen sulphide, anhydrous calcium chloride is suitable.

Fowles [5] recommends another solid drying agent: anhydrous calcium sulphate ('soluble anhydrite'). As the system $\text{CaSO}_4/2\text{CaSO}_4 \cdot \text{H}_2\text{O}$ has a vapour pressure of only 0.004 mm Hg at 20 °C it is superior to concentrated sulphuric acid. It is particularly suitable for use in desiccators, as well as being inert to acidic and alkaline gases. Fowles describes how the drying agent may be made from blackboard 'chalk' by roasting at 230-50 °C for 1–2 hours. ('Dustless' blackboard chalk is calcium carbonate, but the ordinary variety is calcium sulphate.) This drying agent, too, can be recycled.

There are occasions when a liquid drying agent is deliberately chosen so as to be able to monitor the gas flow as well as dry it. In such circumstances, it may well be best to use a solid drying agent, as above, and monitor the gas flow by the use of an inert liquid of low vapour pressure, e.g. di-(2-methylpropyl) benzene-1,2-carboxylate (isobutyl phthalate). Alternatively a saturated aqueous solution of calcium chloride (with excess solid to maintain saturation) may be used. This was the main method adopted by gas boards to lower the water content of town gas before leaving the works [6]. At 20 °C a saturated solution of calcium chloride has a vapour pressure of only 5.7 mm Hg, as compared with the svp of water of 17.6 mm Hg. This reduction in the moisture content may well be sufficient for some purposes.

If, however, there are good reasons to continue using concentrated sulphuric acid as a drying agent, consideration should be given to reducing the amount required, for example by the use of a wash bottle three-quarter packed with glass beads. This also reduces the 'dead space', and thus the volume of any possible explosive mixture. Finally, it may be of interest to note the conclusions of the Analytical Chemists Committee of ICI [7] who compared seven common desiccants on the following criteria:

- efficiency: power to remove water completely
- capacity: ability to absorb water without becoming saturated
- speed of drying
- safety, cost, regeneration, etc.

Their conclusions are shown in Table 1, where the numbers give an order of merit for each property.

Table 1	a Efficiency	b Capacity	c Speed	d Remarks
Phosphorus(V) oxide	1	2	1	Expensive
Sulphuric acid	2	1	2	Cheap, can be dangerous
Calcium chloride	7	3	3	Cheap, satisfactory for general use
Magnesium chlorate(VII)	3	4	7	May be hazardous with organics
Silica gel	4	5	6	Easily regenerated
Activated alumina	5	6	5	Easily regenerated
Calcium sulphate ('anhydrite')	6	7	4	Easily regenerated

References

- [1] Education in Science, June 1980.
- [2] Education in Science, June 1981.
- [3] Education in Science, November 1979.
- [4] CLEAPSE Hazcards, 1979.
- [5] Fowles, G., *Lecture Experiments in Chemistry*, 6th edn (Bell & Sons, 1963).
- [6] Priestley, I. J. (ed.) *King's Manual of Gas Manufacture* (London: Walter King Ltd, 1960)
- [7] Strauts, C.R.N., J. H. Gilfillan and N. H. Wilson (eds.), *Analytical Chemistry, The Working Tool* (Oxford: Clarendon Press, 1955), Vol. I, Chapter 2.