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# LABORATORY NOTES:

## Generation and collection of nitrogen dioxide ($NO_2$) gas for equilibrium demonstration

Nitrogen dioxide gas is used to demonstrate Le Chatelier's principle of equilibrium. The gaseous equilibrium is a mixture of nitrogen dioxide, a brown to reddish brown gas, and dinitrogen tetroxide, a colourless gas, and is represented by the chemical equation

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

(colourless) (brown)

Two main effects are demonstrated:

1. The effect of temperature, where a fixed volume of gas is observed at different temperatures.
2. The effect of pressure, where gas is collected in a syringe and compressed.

The effects can be observed in the change in the colour of the gas.

## Safety and technical notes:

**The preparation and handling of nitrogen dioxide should only be conducted in an operating fume cupboard by trained staff, wearing appropriate PPE.**

**PPE:** safety glasses, closed shoes, laboratory coat, nitrile gloves. (Note: Viton®, butyl, neoprene provides protection for prolonged direct exposure to nitric acid. Nitrile is acceptable for splash contact with nitric acid. Gloves should be removed, hands washed and new gloves put on in the event of splash contact).[1,2]

**Nitrogen dioxide** is a brown gas with a pungent, acrid odour. It is a toxic, corrosive gas and a strong oxidising agent, which supports combustion. Exposure may cause severe irritation to the skin, eyes and respiratory tract. Inhalation of low concentrations can cause lung damage. Inhalation of high concentrations can lead to pulmonary oedema, which can be fatal; the effects can be delayed. Inhalation of $NO_2$ can aggravate respiratory conditions such as asthma.[3]

Preparation involves the use of concentrated 70% (not fuming) nitric acid.

**Concentrated (70%) nitric acid** is highly corrosive and a powerful oxidant and should be handled with care. Exposure may cause severe irritation and burns to the skin, eyes and respiratory tract and on ingestion. Eye contact may result in severe eye damage and permanent injury. Handle only in an operating fume cupboard, do not breathe vapour or mist, avoid contact with skin, eyes and clothing and avoid any prolonged or repeated exposure. Handle away from heat and sources of ignition.[1]

**Handling nitric acid:** It is best practice to use a spill tray under your work and to use a glass pipette, although a polyethylene pipette is acceptable for limited use when the acid is cold. Pour a small quantity into a small beaker. Use a glass pipette (Pasteur or graduated) to deliver the nitric acid into the flasks. Do not remove open vessels containing concentrated acid from the fume cupboard into the open lab. Any glassware or other equipment, which is contaminated with concentrated acid, should be rinsed with water before removal from the fume cupboard. Any unused concentrated acid should be diluted by addition to water before being removed from the fume cupboard.


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**Stoppers and flexible tubing:** Silicone is preferred over rubber, which is adversely affected by $NO_2$

**Syringes:** It is essential that syringes are of good quality and have a Luer lock tip. The Luer lock tip enables a cap to be fitted to prevent the gas from escaping.

- Glass syringes are preferred because they are transparent and it is easier to see the colour of the gas. A small amount of vacuum grease can be applied to the plunger to minimise the potential loss of $NO_2$ gas.
- If using plastic disposable syringes, these MUST be new to ensure that the rubber tips on the plungers have not been degraded.

## Generation of $NO_2$ gas directly in a flask for a demonstration to observe the effect of temperature

The generation of nitrogen dioxide gas occurs as a result of the reaction of nitric acid on copper metal, usually in the form of small pieces of copper turnings or copper foil.

We can estimate the volume of gas we require and use a limited quantity of nitric acid given that '8 ml of concentrated nitric acid produces 1000 $cm^3$ of nitrogen dioxide at room temperature and pressure'.[4]

To make three flasks of $NO_2$ gas:

**Materials:**

- 3 x 250mL round bottom flasks with well-fitting stoppers, preferably Quickfit® style (alternatively a flat bottom flask could be used, again with well-fitting stoppers)
- For each flask, about 0.5 gram of copper turnings or 3 small pieces of copper foil about $5mm^2$
- For each flask, about 2mL of concentrated (70%) nitric acid
- Glass Pasteur or graduated 2–3mL pipette
- Ice water bath
- Warm water bath (60–70°C)

**Procedure:**

In a fume cupboard place the copper foil/turnings into each of 3 flasks; using a pipette, add the nitric acid to the flask and then stopper the flasks.

Once stoppered the flasks can be taken out of the fume cupboard and used in the classroom as a demonstration.

The three flasks should then be put into three different temperatures and any colour changes observed. The use of a white background enhances the visibility of the colour changes.

- Ice water bath: The gas contracts and becomes paler in colour as the equilibrium shifts to the left adjusting to the decrease in temperature.
- Room temperature: This is the control; there should be no colour change.
- Warm water bath, approximately 60–70ºC: The gas expands and becomes darker as the equilibrium moves to the right adjusting to the high temperature.[6]

When the demonstration has finished, simply return the flasks to the fume cupboard, then either unstopper the flasks, allowing the gas to dissipate, or simply dilute the residual mixture with water. Decant the solution from any residual copper metal, neutralise the solution to within pH 6–8 and wash to waste. The copper metal can be rinsed and recycled or disposed of with general waste.


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# Generation and collection of $NO_2$ gas into test tubes and syringes

**Materials:**

- 1 x 250mL Büchner flask with a side arm with a short length of flexible tubing, or 1 x 250mL round or flat bottom flask with a one-hole stopper with a glass delivery tube with flexible tubing
- The tubing connection between the flask and the syringe should be gas-tight. This can be achieved by using two lengths of tubing, one with an internal diameter that fits onto the connection at the flask and one that fits onto the tip of the syringe. A reducing tubing connector[5] can be used to connect the two lengths. The tubing may need to be softened by briefly placing in boiling water before attaching.
- About 1 gram of copper turnings or 6 small pieces of copper foil about $5mm^2$
- About 4mL of concentrated (70%) nitric acid (to produce about 500mL $NO_2$)
- Glass syringe with small amount of vacuum grease applied to the plunger

Or **NEW** 60 mL plastic disposable syringes with a Luer lock tip. Lubricate the plunger with a small amount of vacuum grease or sewing machine oil to improve their 'gastightness' under pressure.

- Luer lock caps
- Glass Pasteur or 2–3mL graduated pipette
- 3 large test tubes plus stoppers
- Ice water bath
- Warm water bath (60–70ºC)

**Note: Hoffman tubing clamps are not required for the tubing, as they will create an additional hazard.**

## Collection in test tubes

**Procedure** (See Figures 1a,b):

1. Attach the flexible tubing to the side arm of the Büchner flask or delivery tube and set up the equipment in the fume cupboard with the flask clamped securely to a retort stand so that it doesn't tip over.
2. Have the test tubes ready to be filled via the length of tubing. Have the stoppers nearby.
3. Place the copper foil/turnings into the flask; add the nitric acid and then stopper the Büchner flask with the solid stopper (or round bottom/flat bottom flask with the delivery tube stopper assembly).
4. As the gas is produced, collect it in each test tube by downward delivery (the more dense nitrogen dioxide gas will sink down into the test tube resulting in the upward displacement of the less dense air).[6]
5. When the test tubes are filled with gas, insert the stopper.
6. The test tubes should then be put into three different temperatures and any colour changes observed, as in the above demonstration to observe the effect of temperature.
7. When sufficient gas has been collected, water should be added to the reaction vessel to quench the reaction.
8. After the test tubes have been observed for any colour change, return the test tubes to the fume cupboard, then unstopper the test tubes and either allow the gas to dissipate or immerse the test tubes in water.


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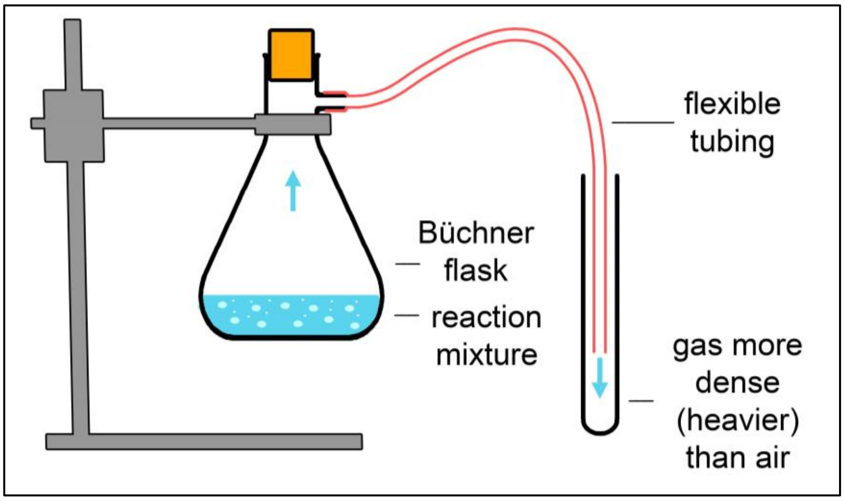
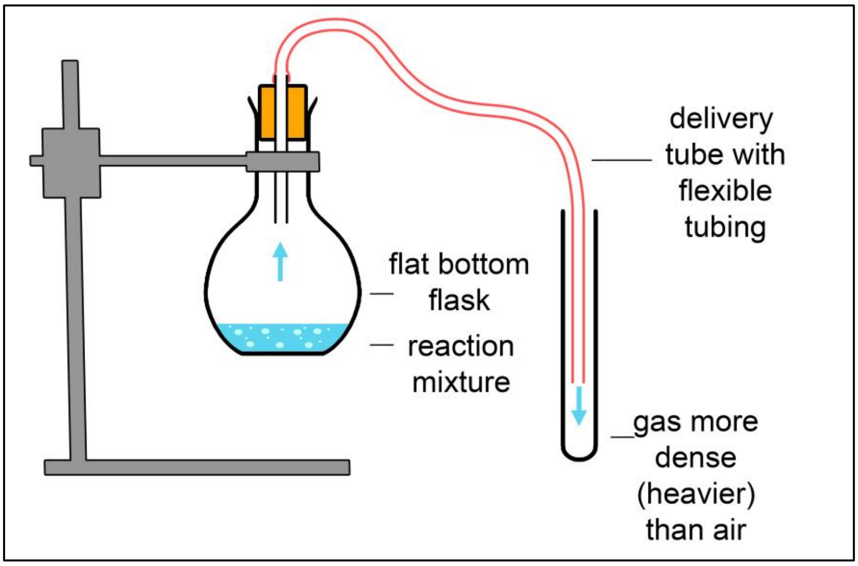
**Figures 1a, b:** Gas collection system for preparing and collecting a gas in a test tube. The $NO_2$ gas which is more dense than air sinks down into the test tube, and displaces, the less dense air upwards. This is called downward delivery of gas.

1a) Using a Büchner flask




1b) Using a flat bottom or round bottom flask



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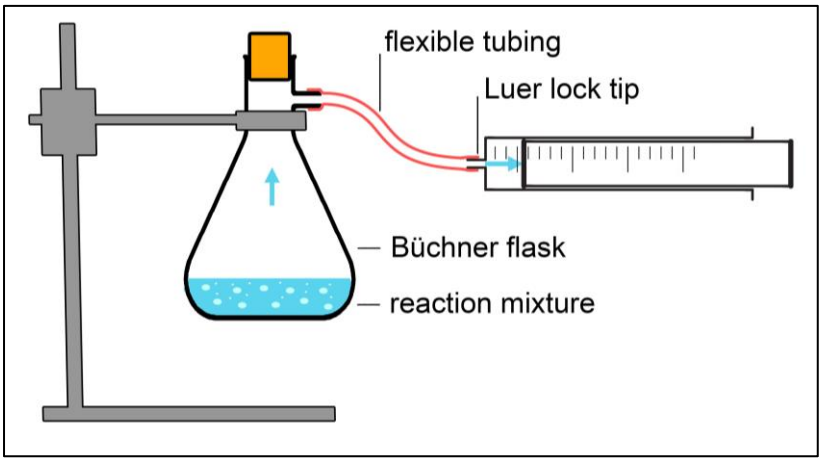
## Collection in syringes

**Procedure (**see Figures 2a, b**):**

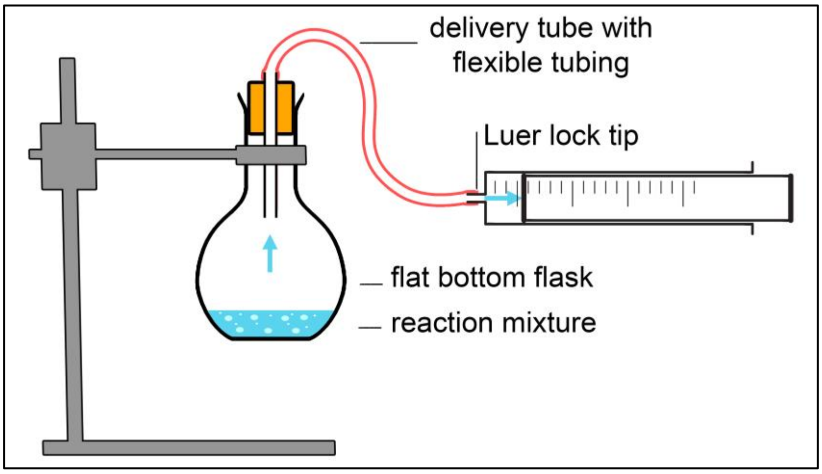
1. Attach the flexible tubing to the side arm of the Büchner flask or delivery tube and set up the equipment in the fume cupboard with the flask clamped securely to a retort stand so that it doesn't tip over.
2. Have the syringes ready to be filled via the length of tubing. The plunger must be depressed all the way in and the Luer lock cap available nearby.[7]
3. Place the copper foil/turnings into the flask, add the nitric acid and then stopper the Büchner flask with the solid stopper (or round or flat bottom flask with the delivery tube stopper assembly).
4. As the gas is produced, connect the flexible tubing to each syringe in turn. Observe the syringe being filled with brown gas and the movement of the plunger. When filled to a sufficient level, remove the tubing and close the tip of the syringe using the Luer lock cap.
5. Take care to stop the gas collection before the end of the graduations is reached, to avoid the plunger being forced from the syringe
6. When sufficient gas has been collected, water should be added to the reaction vessel to quench the reaction.

Figures 2a, b: Gas collection system for preparing and collecting a gas in a syringe.

2a) Using a Büchner flask




2b) Using a flat bottom or round bottom flask





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**When the syringes have been sealed to prevent the loss of gas, they can be taken out of the fume cupboard into a well-ventilated room and the effect of pressure on the equilibrium demonstrated as below:**

Rapidly depress the plunger of the syringe as far as it can go. The colour should become darker initially as the gas concentration increases due to a decrease in volume. It then becomes paler in colour as the equilibrium adjusts, converting the brown nitrogen dioxide to colourless dinitrogen tetroxide.

When the plunger is pulled back decreasing the pressure the colour changes in reverse to above.

**Once they are finished with, the syringes should not be opened and the gas should not be released into the classroom but returned to the fume cupboard. Here the syringes can have their stopper or cap removed to allow the gas to dissipate, or can simply be rinsed with water.**

**The prepared gases should last as long as they are contained in the syringes without leaks. Nitrogen dioxide weakens rubber, so this does not provide a long-term seal. Ideally, they should be made up as close as possible to the time required and disposed of as soon as practicable when finished.**

## Alternative methods

### In-Syringe Method for microscale gas using solid sodium nitrite and acidified iron sulfate solution

The In-Syringe Method is described in detail by Bruce Mattson and Michael P. Anderson and 'features the generation of gases by reacting two chemicals, typically one solid and one aqueous liquid, inside a plastic syringe.'[8] Prior to manufacturing toxic $NO_2$ gas, it is recommended that users practice (and are competent in using) the in-syringe method with gases such as $CO_2$, $H_2$ and $O_2$.[9]

### The heating and decomposition of lead nitrate[5]

This method has different hazards and results in the production of heavy metal waste. Therefore, this is not the preferred method of production of $NO_2$ gas.

### References and further reading


1. Science ASSIST. 2018. *Chemical Management Handbook for Australian Schools – Edition 3*, Science ASSIST website, https://assist.asta.edu.au/resource/4193/chemical-management-handbook-australian-schools-edition-3. See nitric acid.
2. Chem-Supply. 2017. *Nitric acid*, Safety Data Sheet, Chem-supply website, https://www.chemsupply.com.au/documents/RP1137M.pdf
3. Science ASSIST. 2018. *Chemical Management Handbook for Australian Schools – Edition 3*, Science ASSIST website, https://assist.asta.edu.au/resource/4193/chemical-management-handbook-australian-schools-edition-3. See nitrogen dioxide, generated from a reaction.
4. 'Diffusion of gases – a safer alternative to bromine', Royal Society of Chemistry website, http://www.rsc.org/learn-chemistry/resource/res00000684/diffusion-of-gases-a-safer-alternative-to-bromine (March 2018)
5. 'Le Chatelier's principle: the equilibrium between nitrogen dioxide and dinitrogen tetroxide', Royal Society of Chemistry website, http://www.rsc.org/learn-chemistry/resource/res00001739/le-chateliers-principle-the-equilibrium-between-nitrogen-dioxide-and-dinitrogen-tetroxide?cmpid=CMP00005253 (October 2015)



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6. ‘Reducing hose connectors’, Burkle website, https://www.buerkle.de/en/reducing-hose-connectors#similar (Accessed May 2019)
7. ‘Gas preparation and collection methods revision notes’, Doc Brown’s chemistry website, http://www.docbrown.info/page13/ChemicalTests/GasPreparation.htm#Ex%203 (Accessed May 2019)
8. Mattson, Bruce and Michael P. Anderson. 2017. *Microscale Gas Chemistry*, 2017 Web Version, p.6, Creighton University website, http://mattson.creighton.edu/Nitrogen_Oxides.html
9. ‘Three Easy Gases: Carbon Dioxide, Hydrogen and Oxygen’, Creighton University website, http://mattson.creighton.edu/ThreeEasyGases.html (9 March 2010)


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