

6. NITROGEN OXIDES & THEIR FORMATION IN FLAMES

INTRODUCTION

The elements oxygen (O₂) and nitrogen (N₂) are *the* major components of the atmosphere, being present in approximately 20% and 80% abundance respectively. These elements are also present in compounds contained in the earth's crust, although their abundance is very different; oxygen is about 50% abundant while nitrogen is present only in trace amounts.

Both elements are, in very different ways, essential to life. Oxygen is used in the oxidation of sugars in our bodies, which produces the energy that keeps us alive. Nitrogen is not directly essential for human life, but nitrogen atoms are widely used as components of bio-molecules such as nucleic acids and proteins (as of course are oxygen atoms), and the ultimate source of these atoms is atmospheric N₂. Humans, like other animals, cannot convert atmospheric N₂ into biologically useful molecules; plants, however, contain enzymes that convert elemental N₂ from the air into more useful compounds of nitrogen. This process is called *nitrogen fixation*. Once the nitrogen has been fixed we can take in essential nitrogen-containing nutrients by eating plants (or eating animals which have eaten plants). So far, no-one has come close to matching the efficiency of nitrogen fixation by these naturally occurring enzymes. Industrially produced ammonia (NH₃) is made from N₂ and H₂ by a much less energy efficient process which involves high temperatures and pressures.

In this experiment you will examine the efficiency with which atmospheric N₂ can be 'fixed' in a flame by reacting with oxygen.

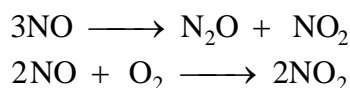
Fixation of Nitrogen in Flames

Nitrogen is far more stable, and hence less reactive, than oxygen due to its extremely strong triple bond (bond energy = 944 kJ mol⁻¹), in contrast with double bonded O₂ (bond energy = 496 kJ mol⁻¹). Thus, O₂ reacts readily with many metals whereas N₂ does not. However at very high temperatures N₂ will react with O₂ to a very slight extent according to the following chemical equation:

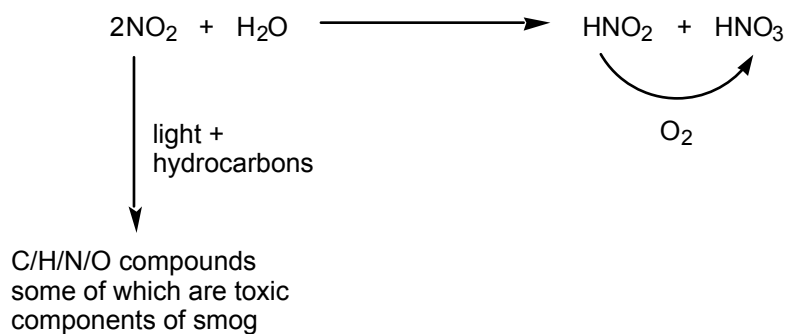


Note the arrows in the above equation, they show that this is an *equilibrium reaction*. This means that the reactants (N₂ and O₂) do not fully undergo reaction to form the product (NO). At room temperature the reaction is insignificant and equilibrium is said to lie completely to the left hand side of the equation; no NO is formed. However at high temperatures some NO can be formed, so that at 1800°C, in the hottest part of a Bunsen flame, there is about 1% conversion of atmospheric N₂ and O₂ to NO. Some of the NO formed decomposes in the cooler parts of the flame, but enough NO escapes from flames (*e.g.* in internal combustion engines) to contribute to acid rain and the formation of smog in sunshine via aerial oxidation to NO₂. Small amounts of NO are also formed in lightning discharges.

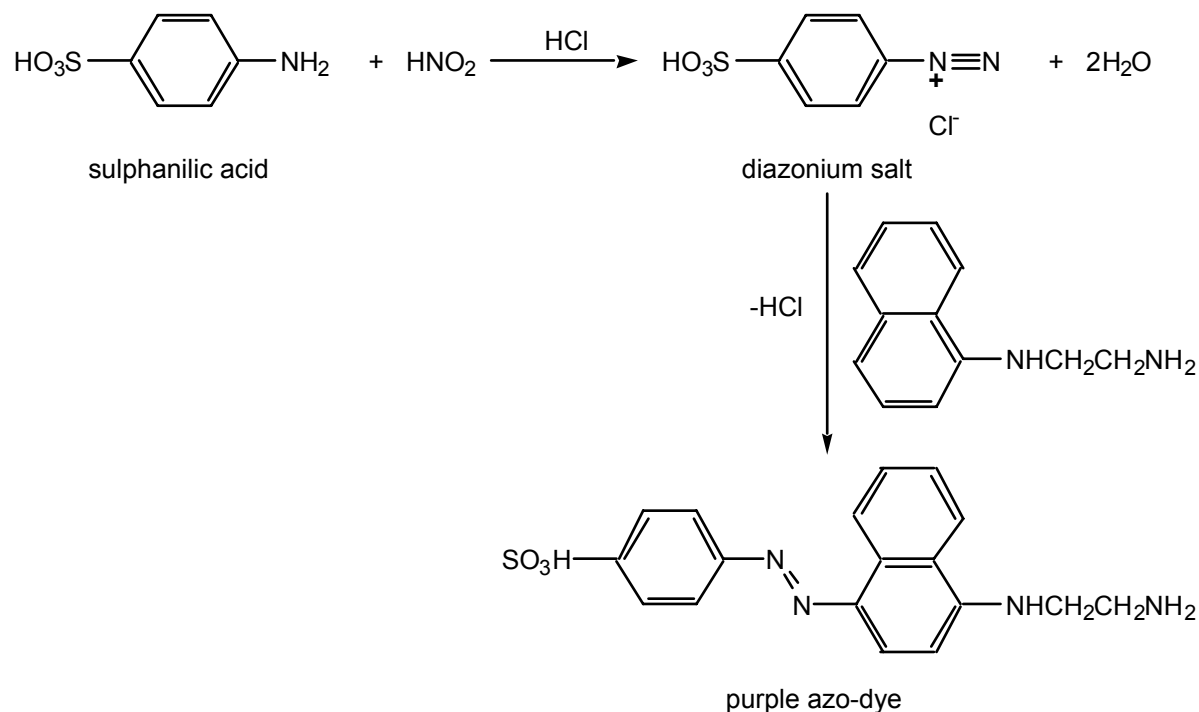
The main reactions of NO in the tail of the flame and the atmosphere at large are shown below:



Of these, the second reaction is dominant over the first. Nitrous oxide (N_2O) is essentially unreactive although it is found to be useful as an anaesthetic: its common name is laughing gas. On the other hand, nitrogen dioxide (NO_2), once formed, reacts with moisture in the air to produce nitrous and nitric acid which contribute to the formation of acid rain. The action of sunlight on NO_2 in the presence of unburnt hydrocarbons from car exhausts produces a toxic smog which is responsible for the pollution of many cities:



The presence of oxides of nitrogen in a flame can be detected by allowing the flame to impinge on a cold, wet surface. This traps some of the NO_2 as nitrous acid, HNO_2 , which we can use to form an intensely-coloured azo-dye. The intensity of the dye colour in the solution is then directly proportional to the amount of HNO_2 originally present and we can use a machine called a spectrophotometer to measure this intensity. The chemical reactions leading to the purple colour are shown below:



In this experiment you will initially prepare three solutions of varying concentrations of sodium nitrite (NaNO_2) and use these to prepare different concentrations of the purple azo-dye shown in the diagram above. By measuring the absorbance of these solutions on a spectrophotometer you will be able to plot a calibration graph of

absorbance against concentration of nitrite anion (NO_2^-) which you can use to determine the concentration of nitrite produced by different flames in the second part of the experiment.

Preparation of Initial Calibration Standard

WORK IN PAIRS FOR THIS EXPERIMENT, EACH PERSON MUST DO THEIR OWN WRITE-UP

Prepare a roughly 1.6×10^{-4} M solution of sodium nitrite as follows. Weigh accurately (using a four decimal-place analytical balance in the balance room) about 0.69 g (0.01 moles) of sodium nitrite, NaNO_2 . Dissolve it in distilled water and make up the solution to 250 ml in a volumetric flask, ensuring that all traces of NaNO_2 are transferred to the flask. Carefully mix the solution by stoppering the flask and inverting it several times.

Take exactly 1 ml of this solution (graduated pipette and bulb) and dilute it to 250 ml in another volumetric flask, and again mix well. Calculate the exact concentration of NaNO_2 in this standard solution. Write the details for this solution below. Call this *Solution A*.

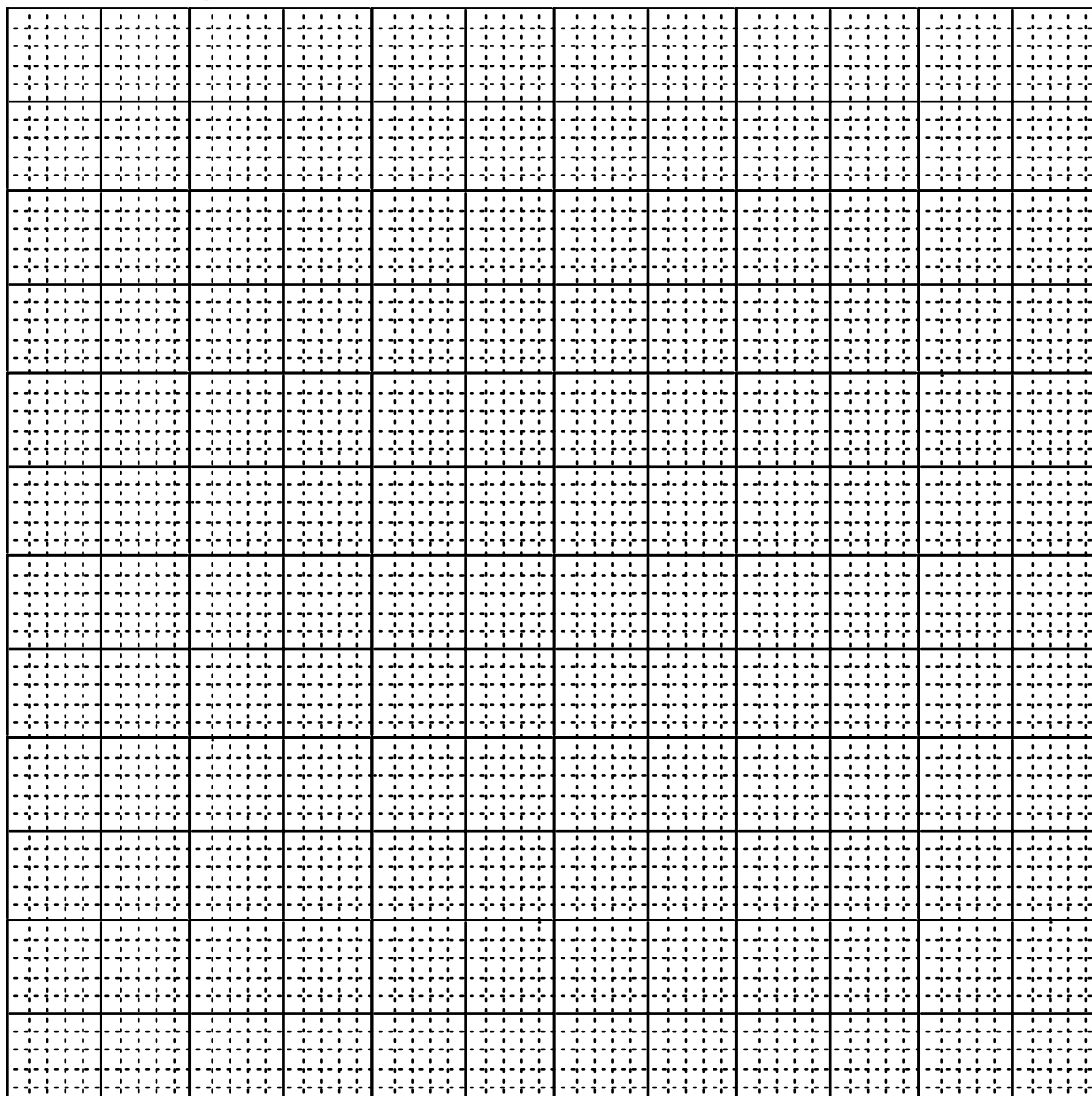
Weighings

Calculation of Standard *Solution A* Strength

Calibration Graph

You now use *Solution A* to prepare a calibration graph for the spectrophotometer. Take 5 ml of *Solution A* (graduated pipette) and dilute it to roughly 50 ml in a beaker. Mix it with 1 ml of the sulphanic acid solution, allow it to stand for about 5 minutes and then add 1 ml of the naphthylethylenediamine solution. Dilute the solution to 100 ml in a volumetric flask and mix it carefully; after five to ten minutes a purple colour will have developed corresponding to an initial concentration of about 8×10^{-6} M nitrous acid; it should be stable for some hours. Determine the absorbance of this solution on a spectrophotometer set at 543 nm (instructions are provided by the machines); remember to use distilled water for the reference. The reading should be about 0.75, depending on the exact weight of NaNO_2 you used. If your reading differs from this by more than 20% you have probably made a mistake and should start again. Repeat this process using 2.5 ml and 7.5 ml portions of *Solution A*; plot a graph of absorbance against concentration; it should be a straight line running through the origin.

Calibration Graph



Calculations

Comparison of NO₂ Formation in Different Flames.

Clamp the stainless-steel sieve above a large glass dish. Weigh out roughly 70 g of ice in a beaker and put it in the sieve; all of the drips should collect in the glass dish below. The ice is made from tap water which does not contain enough nitrite to cause errors in this experiment. Next, light a large Bunsen burner and adjust the gas flow so that with the air hole fully opened the length of the flame is about 7 cm. DO NOT

ADJUST THE GAS FLOW AFTER THIS, as you need to compare air-rich and air-poor flames with the same flow of gas each time.

Fully open the air-hole and, holding the Bunsen, allow the TIP of the flame – about the last 1 cm at most - to impinge on the ice through the bottom of the sieve. MOVE THE FLAME AROUND RAPIDLY AND DO NOT LET IT PLAY ON ONE PART OF THE SIEVE FOR ANY LENGTH OF TIME OR THE SIEVE WILL MELT! This will trap any NO_2 in the flame in the water which runs off into the glass dish. Do not hold the flame very close to the bottom of the sieve as this will alter the burning characteristics of the flame (and melt the sieve). After 30 seconds, move the Bunsen away and tip any remaining ice from the sieve into the glass dish; try to ensure that all of the ice and melted water is transferred to the dish. Tip the ice/water into a beaker.

Add 1 ml of the solution of sulphanilic acid, stir for 3 minutes, and then add 1 ml of the naphthyl-ethylenediamine solution. Warm the solution just enough to melt any residual ice, dilute it to 100 ml with more water (the graduated mark on the beaker is sufficiently accurate for this), and leave it to stand for at least five minutes for the purple colour to develop.

Repeat the process using the Bunsen flame with the air-hole closed. This is a little trickier as the flame flickers about a lot and it is difficult to keep it impinging on the ice; also a certain amount of soot collects on the ice and you may have to filter the solution before adding the sulphanilic acid/naphthyl-ethylenediamine to develop the colour.

For each solution, determine its absorbance at 543 nm against water as a reference, and hence calculate (from your calibration graph) the concentration of NO_2^- in each solution. You should find that it is higher for the hotter flame, indicating that more NO_2 was formed in the oxygen-rich flame than in the cooler, fuel-rich flame, although some people see the opposite trend (this is not a quantitatively accurate experiment!).

Notes on the experimental procedure and any difficulties you encountered.

Use your graph to determine the amount of HNO_2 formed from trapping the gases in each type of flame.

What do you think are the main sources of error in this experiment?

