

## Session 1

# SYNTHESIS OF $\text{NaHCO}_3$ AND $\text{Na}_2\text{CO}_3$ BY MEANS OF THE SOLVAY PROCESS

### INTRODUCTION

Sodium bicarbonate and sodium carbonate are two very important chemicals. Sodium bicarbonate is the major component of sodas and baking powders, which act as a source of carbon dioxide to make dough rise. In medicine it is used as anti-acid. Some fire extinguishers even contain sodium bicarbonate powder. Most of the sodium bicarbonate produced industrially is used to generate sodium carbonate by heating, according to the following reaction:



Anhydrous sodium carbonate is commonly known as soda Solvay. It has also received other names such as laundry soda, soda salt, or soda ash. It is used in large amounts in the industrial manufacturing of glass, soap, paper, varnishes and other chemicals, and for softening in water treatment.

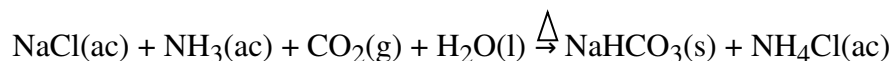
Both sodium carbonate and sodium bicarbonate are currently manufactured by means of the Solvay process, which was discovered in 1861 by Belgian chemist and industrialist Ernest Solvay. In the Solvay process (ammonia-soda), sodium bicarbonate precipitates in a sodium chloride saturated solution through the combined action of ammonia and carbon dioxide; next, it is heated in order to obtain carbonate, and the carbon dioxide is regenerated. The starting materials are common salt ( $\text{NaCl}$ ) and limestone (of which  $\text{CaCO}_3$  is the major component) which are plentiful and cheap. Ammonia, on the other hand, is more expensive, but it is regenerated from  $\text{NH}_4\text{Cl}$  in the process and recirculated. This procedure is considered an example of good industrial workflow.

The process could be described as a series of chemical reactions which are described in turn.

Limestone, which is fundamentally made up of  $\text{CaCO}_3$ , is heated to produce  $\text{CO}_2$ :

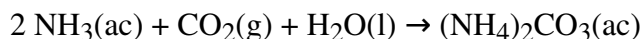


$\text{CO}_2$  passes through a saturated solution of common salt and  $\text{NH}_3$  (ac) at  $0^\circ\text{C}$ . In these conditions, sodium bicarbonate precipitates in the form of finely divided crystals which can be filtered out from the  $\text{NH}_4\text{Cl}$  solution. The overall reaction is:

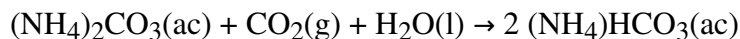


This reaction could be considered the result of the following three reactions combined:

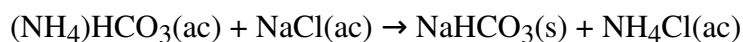
a) reaction of  $\text{CO}_2$  with the dissolved ammonia yielding ammonium carbonate:



b) with  $\text{CO}_2$  in excess, ammonium bicarbonate is generated:



c) finally, sodium carbonate (the least soluble salt) precipitates in the saturated  $\text{NaCl}$  solution, while  $\text{NH}_4\text{Cl}$  stays in solution:



Sodium bicarbonate can be filtered out and further purified by recrystallisation, although its solubility in water can be an issue.  $\text{NH}_3$  can be recovered from the  $\text{NH}_4\text{Cl}$  solution, by reaction with  $\text{CaO}$  from the thermal decomposition of limestone:



$\text{CaCl}_2$  is the only by-product.

In this lab session, given that carrying out the whole industrial process would be difficult, only steps (b) and (c) will be carried out.

### PRELIMINARY QUESTIONS

1. Draw a flow diagram of the experimental procedure.
2. Draw Lewis structures of the  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  ions, and indicate their geometry.
3. How can  $\text{CO}_2$  be generated easily in the lab without heating limestone ( $\text{CaCO}_3$ )? Write and balance the corresponding chemical reaction.
4. From the reactions for the synthesis of  $\text{NaHCO}_3$  in the Solvay process, pick and highlight those which are going to be used in this lab session.
5. Write and balance the reaction which corresponds to the synthesis of anhydrous  $\text{Na}_2\text{CO}_3$ .
6. The aqueous solution of which salt is expected to be more alkaline:  $\text{Na}_2\text{CO}_3$  or  $\text{NaHCO}_3$ ? Why is that? Justify your answer based on the acidic constants of  $\text{H}_2\text{CO}_3$ :  $K_{a1} = 4.4 \times 10^{-7}$ ;  $K_{a2} = 5.6 \times 10^{-11}$ .

### EXPERIMENTAL PROCEDURE

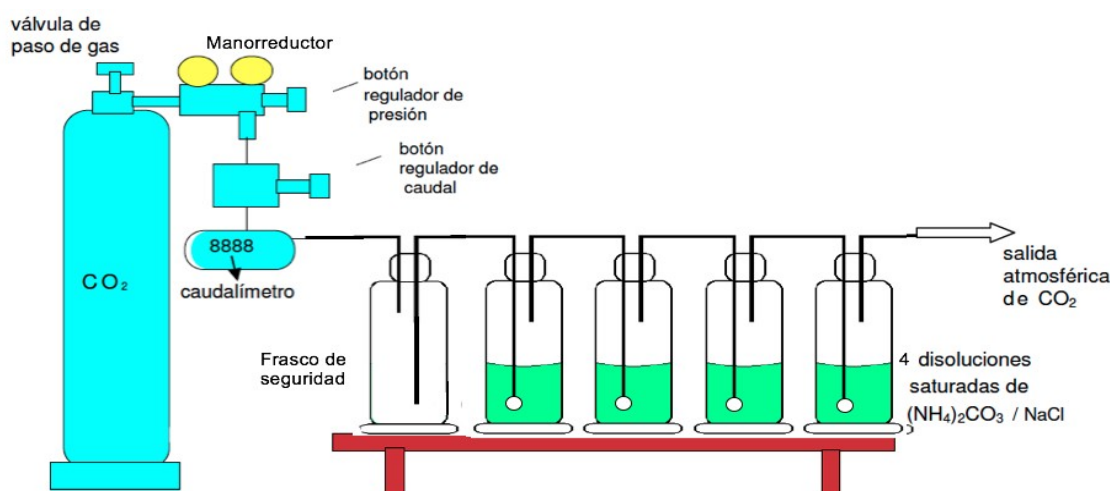
Material	Reagents
200 mL bubblers	1M $(\text{NH}_4)_2\text{CO}_3$ , saturated NaCl solution
Small buchner flask and funnel	HCl 6 M
250 mL erlenmeyer flask	Calcium dihydrogen phosphate
100 mL and 200 mL beakers	Ethanol
Crucible	
100 mL graduated cylinders	
Watch glass	
Stand and clamps	
Flow meter	
$\text{CO}_2$ bottle	
pH indicator paper	

#### **A) Synthesis of $\text{NaHCO}_3$ .**

Set up the reaction system as described in the figure below (check that the  $\text{CO}_2$  cylinder outlet is closed), with the bubblers connected in series with each one containing 50 mL of the

$(\text{NH}_4)_2\text{CO}_3$  (1M) / NaCl solution. Check that the joints are properly sealed with grease to prevent gas leaks. Secure the bubblers with holders and clamps.

Open the tap of the  $\text{CO}_2$  bottle and adjust the gauge to 0.5–1 atm pressure. Next, slowly open the flow meter until the digital display indicates 0.8 a.u. (arbitrary units). After several minutes, the formation of  $\text{NaHCO}_3$  will cause turbidity and precipitation inside the bubblers. The reaction should be complete in roughly 30 minutes. Filter the  $\text{NaHCO}_3$  obtained in the Buchner funnel and wash carefully with portions of 10 mL of very cold water. Repeat the washing three times with 2mL portions of very cold  $\text{H}_2\text{O}$ : EtOH (1:1), and let it dry in the air current. Dry up the filter paper with the product and keep for the next session for weighing. It is very difficult to completely remove all the chloride without losing most of the product.



### B) Reactivity Assays with $\text{NaHCO}_3$

1. Dissolve a small portion of  $\text{NaHCO}_3$  in 2 mL of water and check the pH with indicator paper. Write the equilibria taking place in solution.
2. Put a small sample of  $\text{NaHCO}_3$  on a watch glass and add 2 or 3 drops of HCl 6M. A gas release should be observed. Write down the reaction.

### C) Use of $\text{NaHCO}_3$

The use of fermenting agents, such as yeasts, in order to raise bakery products and make them spongy, dates back to ancient Egypt. In the reactions taking place during fermentation, simple sugars generate alcohol and  $\text{CO}_2$  gas which raises the dough and gives the spongy texture.

Baking powder is a mixture of  $\text{NaHCO}_3$  and acidic substances such as  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  or  $\text{KHC}_4\text{H}_4\text{O}_6$ , which generate  $\text{CO}_2$  upon addition of water. An inert additional third component such as starch is commonly added as an anti-caking and drying agent.

Mixtures of  $\text{NaHCO}_3$ - $\text{Ca}(\text{H}_2\text{PO}_4)_2$  are also ingredients in effervescent tablets commonly used in pharmaceutical products. Such tablets disintegrate in water releasing  $\text{CO}_2$  gas and facilitating the dissolution of the medicine.

Mix 0.75 g of  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  and 0.25 g of dry  **$\text{NaHCO}_3$**  in a 50 mL beaker. Add 3 mL of water to the mix. Observe what happens.

#### ***D) Synthesis of anhydrous $\text{Na}_2\text{CO}_3$ .***

Weigh 1g of  **$\text{NaHCO}_3$**  and place it on a crucible. Cover it with a watch glass and heat it until all the  $\text{CO}_2$  generated from carbonate transformation is released. Check that the transformation took place by comparing the sample weight before and after the thermal decomposition. Weigh the sample when it reaches room temperature.

Pick a small sample of the  $\text{Na}_2\text{CO}_3$  obtained and dissolve it in 2 mL of  $\text{H}_2\text{O}$ . Check the pH and compare the result with that of the  $\text{NaHCO}_3$  solution.

### **ADDITIONAL QUESTIONS**

1. Which gas is released from the addition of  $\text{HCl}$  to  $\text{NaHCO}_3$ ?
2. Write and balance the reaction that takes place between  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  and  $\text{NaHCO}_3$ .
3. Compare the pH values of aqueous solutions of  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  with those you would expect from the acidity constants values.

Note: In some fume hoods there is a set up for  $\text{CO}_2$  generation from marble and concentrated  $\text{HCl}$ . A package of baking powder can also be found in order to determine its composition.

*Traducido por Salvador Blasco*

## Session 2

# OBTAINING BORIC ACID

### INTRODUCTION

Boron is the first element in group 13. In Nature, it is commonly found in mineral form as borax,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ , and kernite,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$ . It can be considered a scarce element since its natural abundance is *ca.* 0.0003%. Elemental boron can be obtained by reduction of  $\text{B}_2\text{O}_3$  with magnesium, with a final purity around 95 to 98%.

In elemental form, it has properties that lie in between a metal and non-metal. It is a semiconductor (unlike the other elements in its group, which are conductors), and is hard with a high melting point (2352.2 K). From a chemical point of view, it has to be classified as a metal.

In general, the chemistry of boron is more similar to that of silicon than the elements of its group. For example, boron forms oxyanions that tend to condense as discreet anionic polymers, chains, sheets, and 3D structures.

The range of applications of boron, both in household or industrial uses, is very wide. About 30 to 35% is used in the form of borosilicate (solid containing boron, silicon and oxygen), for the manufacture of heat-resistant glass and glass fibre. Around 15 to 20% is used in detergents, soaps, and water softening agents. Boric acid is used as fire retardant. Some boron derivatives are used as herbicides and synthetic fertilisers. Tiny amounts of boron are required for plant growth, although it can be hazardous in larger quantities. More recent applications involve its extreme hardness, chemical inertness and the heat-resistance of titanium, zirconium and chromium borides.

### OBJECTIVES

- 1.- Study of some boron derivatives: borates, boric acid, boron ethoxides.
- 2.- Synthesis of boric acid, acid-base properties and acid-base titration.

### PRELIMINARY QUESTIONS

1. Draw a flow chart or scheme of the operations to carry out during the experimental procedure.
2. Write down the formula of boric acid and its Lewis structure. Write a chemical reaction that explains its acidity. Look up its acidity constant.
3. Describe the structure of borax. Write down and balance the reaction of borax with water to give boric acid (alkaline hydrolysis).
4. The synthesis of boric acid is carried out by adding acid to borax. Justify the addition of acid with the Le Châtelier principle and the reaction from question 3. Write and balance the reaction between borax and HCl.
5. Calculate the number of moles of borax and hydrochloric acid used in the synthesis. Which reagent is in excess?
6. Look up what happens to boric acid upon heating in the bibliography. From there, explain why boric acid cannot be dried in an oven.
7. What amount of boric acid would you obtain if the yield of the reaction was 100%?
8. Indicate one assay that could be used for the detection of chloride anions in solution.
9. Look up the formula of mannitol and its reaction with boric acid.
10. Look up information regarding boron trialkoxydes (alkyl borates) in the bibliography.

## EXPERIMENTAL PROCEDURE

Material	Reagents
100 mL beaker	Borax
Graduated cylinders	HCl 6 M
Buchner funnel	Ice
Vacuum filtration device	AgNO <sub>3</sub> solution
250 mL Buchner flask	Mannitol
50 mL volumetric flask	Ethanol
5 mL pipette	Phenolphthalein
10 mL graduated cylinder	pH indicator paper
Crucible	H <sub>2</sub> SO <sub>4</sub> conc.
100 mL conical flask	NaOH 0.05M
Lighter, tripod and grid	Filter paper

**A) Synthesis of boric acid**

Weigh 8g of borax and put it into a clean, dry, 100mL beaker. Add 20 mL of distilled water and gently heat it up until complete dissolution.

Check the pH with pH indicator paper. Continue heating and stirring the solution without reaching the boiling point, then slowly add 12 mL of HCl 6 M.

Let the bulk cool down to room temperature and then put it into the ice bath. Filter out the precipitate under vacuum, let it dry and wash it with a small amount of cold water (0 °C) until there are no more chloride anions in the rinse water. Let the resulting crystals dry up in air and weigh them. Calculate the yield.

Waste management: put all  $\text{Ag}^+$  containing solutions into the corresponding waste bottle.

**B) Assays and characterisation**

1. Weigh 0.15-0.20 g of boric acid (with precision of 0.0001g), dissolve it in water and dilute to 50 mL in a volumetric flask. Take two portions of 2 mL (with graduated cylinder) and introduce them into two test tubes. To one of the tubes add 0.2 g of mannitol. Measure the pH of both tubes with pH indicator paper.

2.- Take 5 mL from the solution in the volumetric flask with a pipette, and add it to a 100 mL conical flask, then dilute it with distilled water (approx. 20-30 mL). Add 0.5 g of mannitol and a few drops of phenolphthalein, and then proceed with an acid-base titration with a 0.05M NaOH solution. A pale pink colour shift signals the end point. Repeat the titration in order to accurately determine the boric acid concentration and its purity.

3. Take 5 mL from the volumetric flask with a pipette and put it into a 100 mL conical flask, then dilute with distilled water (approx. 20-30 mL). Add a few drops of phenolphthalein and proceed with an acid-base titration with a 0.05M NaOH solution. A pale pink colour shift signals the end point.

Waste management: put all the waste generated in the titrations into the bottle labelled "titration waste".



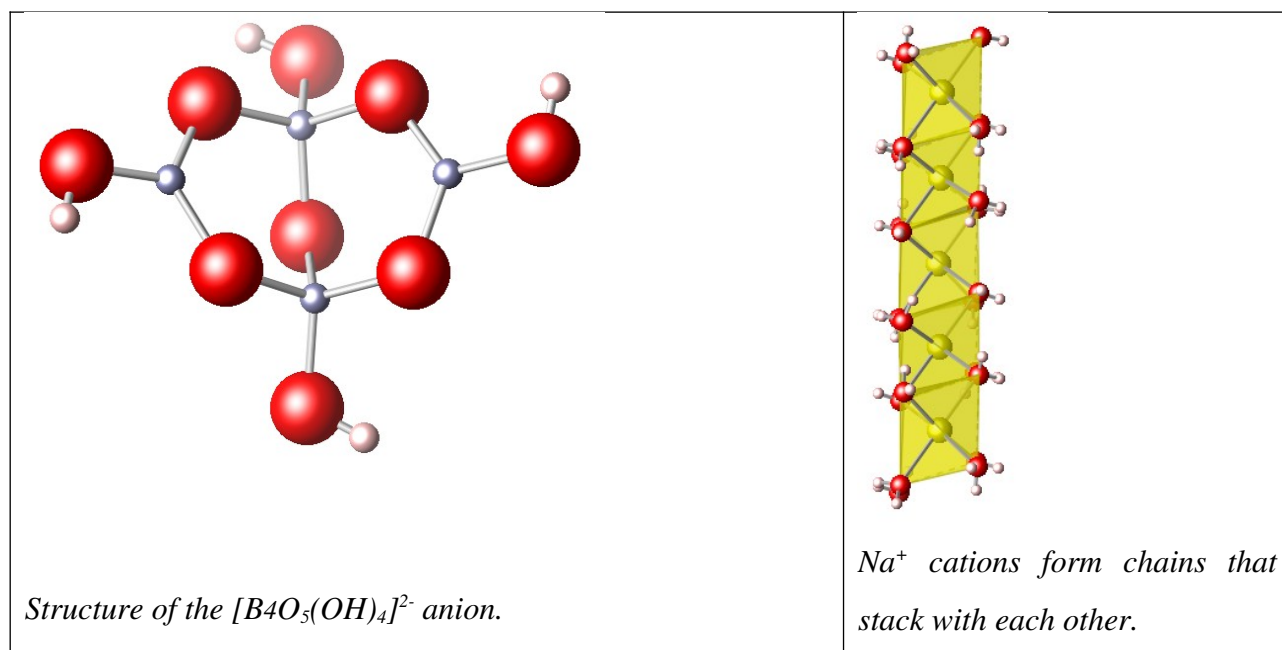
4. Weigh 0.5 g of boric acid put it in a crucible, and add 2 mL of concentrated sulphuric acid. When the mixture is homogenised, add 3 mL of ethanol. Gently heat up the crucible inside the fume hood until the vapours ignite (if this doesn't happen, ignite it with the lighter)

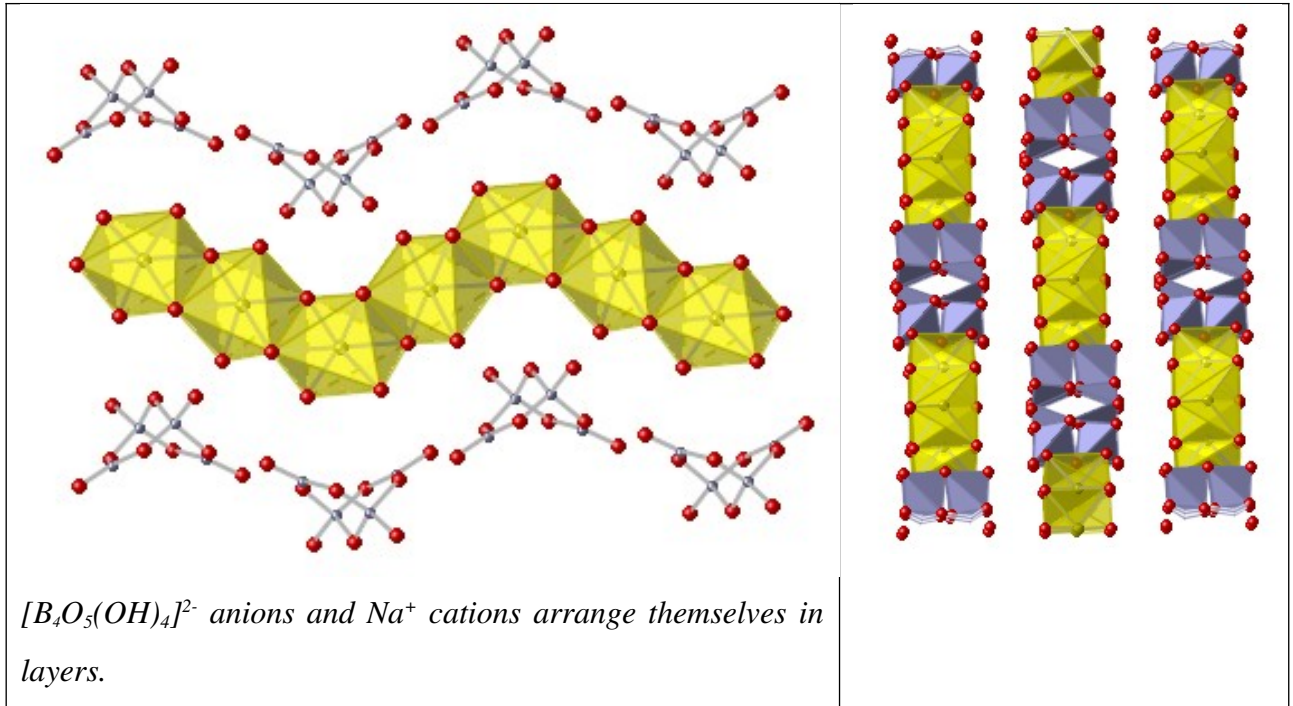
Waste management: put the waste in the crucible into the bottle labelled "boric/sulphuric acid"

### ADDITIONAL QUESTIONS

1. In the synthesis of boric acid, why is it necessary to cool the mixture down with ice and wash with cold water at 0 °C?
2. Explain the difference in the pH values in the two test tubes from section B-1, and why mannitol is added in order to titrate the solution of boric acid.
3. Calculate the degree of purity of the boric acid obtained from the result of the titration with mannitol. Justify the different amounts of NaOH consumed in the titrations with and without mannitol.
4. Calculate the yield for the synthesis of boric acid and apply a suitable correction taking into account the purity. Discuss the result and justify the possible reasons why the yield is low.
5. Interpret the results from assay B-4.

Structure of Borax:  $[B_4O_5(OH)_4]^{2-}$





*Traducido por Salvador Blasco*

## Session 3

# PROPERTIES AND REACTIVITY OF ALUMINIUM

### INTRODUCTION

Aluminium belongs to group 13 (B, Al, Ga, In and Tl), which has a ground state electronic configuration of  $ns^2np^1$ . Therefore, the elements in this group form compounds in the +3 oxidation state, although the monovalent oxidation state grows in importance down in the group. When in oxidation state +3, the compounds are covalent for boron and mostly covalent in aluminium.

Aluminium is the third most abundant element in the Earth's crust, after oxygen and silicon (8.1% in weight). It can replace silicon in silicates giving aluminosilicates as a result (e.g. mica and feldspar). Aluminium is obtained from bauxite ( $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ), by dissolving it in NaOH in order to remove insoluble iron impurities and then precipitating the aluminium again as  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  (hydrated alumina). The metal form is obtained from the electrolysis of alumina dissolved in molten cryolite ( $\text{Na}_3\text{AlF}_6$ ).

*Physical properties:* Aluminium is a grey, silvery metal, and is corrosion-resistant, a good heat and electricity conductor, and the lightest of industrial metals. (density:  $2.7 \text{ g cm}^{-3}$ ).

*Chemical properties:* It exhibits an electropositive and reducing character, given its tendency to give three valence electrons away to form  $\text{Al}^{3+}$ . Its high charge and small size causes its salts to have a certain covalent character. The metal can be dissolved in either diluted mineral acids or bases, releasing hydrogen gas. Despite being a very reactive metal, it appears to be inert. This apparent contradiction is due to the formation of a surface oxide layer which prevents deeper metal layers to be oxidised. If the outer protecting oxide layer is removed, i.e. by scratching or amalgamation, it readily reacts with oxygen or water.

### OBJECTIVES

- To study the behaviour of metallic aluminium against common reagents such as air, water, acids and bases.
- To observe the behaviour of metallic aluminium as an oxide reducing agent.
- To study the acid-base behaviour of Al(III) salts.

- To determine the pH range of formation of aluminium hydroxide and to observe its amphoteric behaviour.

### PRELIMINARY QUESTIONS

1. Taking into account the redox potentials given below, write down the thermodynamically spontaneous reaction of aluminium with protons in water. Is the metal oxidised?

Data:  $E^\circ(\text{Al}^{3+}(\text{aq})/\text{Al}) = -1.67 \text{ V}$ ;  $E^\circ(\text{H}_3\text{O}^+/\text{H}_2) = 0.0 \text{ V}$ .

2. From the thermodynamic data given below, calculate  $\Delta_r G^\circ$  for the reaction between aluminium and oxygen in the air to give aluminium(III) oxide. Is the metal oxidation thermodynamically spontaneous at 25°C?

Data:  $\Delta_f H^\circ(\text{Al}_2\text{O}_3) = -1669 \text{ kJ mol}^{-1}$ ;  $S^\circ(\text{Al}_2\text{O}_3) = 51.0 \text{ J K}^{-1} \text{ mol}^{-1}$ ;  $S^\circ(\text{Al}) = 28.3 \text{ J K}^{-1} \text{ mol}^{-1}$ ;  $S^\circ(\text{O}_2) = 205 \text{ J K}^{-1} \text{ mol}^{-1}$ .

3. Look up an explanation in the bibliography for the fact that aluminium is resistant to air and water corrosion in its uses in everyday life. What is this phenomenon called?

4. What is an alloy? An "amalgam" is an alloy where one of the components is a peculiar metal. Which metal is it?

5. Look up information about  $\text{HgCl}_2$  toxicity.

6. From bibliographical data, write down the hydrolysis reaction of the cation  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ . Will the resulting solution be acidic, alkaline or neutral? What are the effects of a cation undergoing a hydrolysis reaction? How can the hydrolysis of an  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  solution be minimised?

7. What are the grounds of aluminothermic reactions (thermite welding) from a thermodynamic point of view? What temperature values can be reached in such a reaction?

8. Why are aluminothermics not used for the industrial manufacturing of iron? How much aluminium would be needed to reduce 10g of iron(III) oxide?

9. a) Calculate the amount of aluminium sulfate octadecahydrate,  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ , required to prepare 5 mL of an aqueous solution containing 0.5M of  $\text{Al}^{3+}$ . What if you start from  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ?

b) If 2 mL from the previous solution are reacted with  $\text{NH}_3(\text{aq})$  4M in order to obtain  $\text{Al}(\text{OH})_3$ , what volume of ammonia should be added to consume all the  $\text{Al}^{3+}$ ?

10. Look up information about the properties of aluminium(III) hydroxide. Write down the corresponding reactions with acids and with bases.

### EXPERIMENTAL PROCEDURE

Material	Reagents
Heat-resistant surface	Aluminium foil
Centrifuge tubes	Aluminium powder
Beakers	$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$
Assay tubes	Magnesium fuse
Centrifuge	Ferric oxide
Tweezers	$\text{NaHCO}_3$
Mortar and pestle	$\text{NaHCO}_3$ saturated solution
Watch glass	$\text{HCl}$ 6 M solution
pH indicator paper	$\text{HNO}_3$ 6 M solution
Magnet stirrer	$\text{NaOH}$ 6 M solution
	$\text{NH}_3$ 4 M solution
	$\text{HgCl}_2$ 0.1 M solution
	$\text{NH}_4\text{Cl}$ 2 M solution

## A) ALUMINIUM REACTIVITY

### I) Action of moist air and water on aluminium amalgam.

Introduce two strips of aluminium foil (*ca.* 3x1 cm) in a 50 mL beaker, cover them with 3 mL of 0.1 M  $\text{HgCl}_2$  and let them react for a couple of minutes. Next, remove the aluminium strips from the solution with tweezers and wearing gloves, rinse them carefully with distilled water, and dry them on filter paper on a watch glass.

**WARNING:** the  $\text{HgCl}_2$  waste must be deposited into the bottle labelled "Hg/Al waste".


I.1) Quickly introduce one of the aluminium strips into a test tube with 3 mL of deionised water and let it react for 10 min. During the reaction time, take note of any observable change and read the pH with indicator paper. When the test is over, dispose of the waste in the bottle labelled "Hg/Al".

I.2) Leave the other aluminium strip onto the filter paper in contact with air. Observe the appearance of the strip after 15 min.

After these assays, dispose of all waste into the bottle labelled "Hg/Al".

Demonstrative assay for the whole group, to be carried out by the professor. (optional).

**Reactivity of an anodised (passivated) aluminium foil.**

- a) If the previous assay is repeated with a 3cmx2mm aluminium strip, its passivation can be confirmed. It will only react on the edges. When the cut is carried out, a bare (non-passivated) aluminium surface is exposed and that is why it can react with  $\text{HgCl}_2$ .
- b) If a scratch is made with scissors on the aluminium foil surface before introducing it into the  $\text{HgCl}_2$  solution, it can be observed through a magnifier  metallic mercury is generated from the reaction.

See attachment.

When the assay is finished, dispose of the waste in the bottle labelled "Hg/Al".

**All waste from the aforementioned experiments contain mercury or mercury salts which are highly toxic. They must never be disposed into the sink.**

**II) Effect of acids and bases on aluminium.**

Into three labelled test tubes introduce one aluminium strip (ca. 3x1 cm) and add to each of them:

II.1) 5 mL of HCl 6 M.

II.2) 5 mL of  $\text{HNO}_3$  6 M.

II.3) 5 mL of NaOH 6 M.

Observe whether a reaction happens in each case.

Waste management: dispose of the resulting solutions, once the assay is over, into the bottle labelled "Al/solutions".

**III) Action of oxygen in hot air.**

III.1) With tweezers, hold a small piece of aluminium foil in the hottest area of the burner flame. Observe whether any change happens.

III.2) In a fume hood, sprinkle some aluminium powder onto the burner flame with a spatula (with the flame aimed horizontally), collecting the burned powder onto a ceramic plate placed below. Compare the observations in this experiment with the previous one with aluminium foil.

**IV) Reducing properties of aluminium. Aluminothermic processes.**

Aluminium is a strong reducing agent. This property is useful to obtain metals which cannot be easily obtained by other procedures (Cr, Mn, etc.), from their oxides, according to the reaction known as *aluminothermics*:



Aluminothermic methods are very exothermic and the resulting metals are obtained in molten form. In the case of iron, the aluminothermic reaction is not used for the industrial production of iron, but rather for in-place welding of iron or steel pieces that cannot be easily welded together by other methods (such as train rails).

**Procedure:** Mix well 0.3 g of aluminium powder and 0.9 g of ferric oxide in a dry mortar. Put the sample onto a heat-resistant surface in a pile that is as compact as possible. **In a fume hood and with safety goggles**, ignite the sample with a clean magnesium fuse (*danger of ejections: close fume hood*).

Once the strongly exothermic reaction is over, small iron nuggets can be collected with a magnet.

Waste management: once the assay is over, dispose of the waste into the bottle labelled "Al/Fe".

**V) Hydrolysis of aluminium(III) salts.**

In a test tube, dissolve 0.1g of  $AlCl_3 \cdot 6H_2O$  in 2 mL of water. Check pH with pH indicator paper.

Waste management: dispose of the generated waste into the bottle labelled "Al/solutions".

**B) ALUMINIUM HYDROXIDE****I) Synthesis of aluminium hydroxide.**

Aluminium hydroxide is a white gelatinous solid. It can be obtained by precipitation of an aluminium(III) salt with a base, such as ammonia.

**Procedure:** Prepare 5 mL of a 0.5 M  $Al^{3+}$  aqueous solution using  $AlCl_3 \cdot 6H_2O$ . Take two centrifuge tubes (**b1 y b2**) and add to each of them 2 mL of the freshly prepared solution. Next, add dropwise a solution of  $NH_3$  4M for a final stoichiometric ratio of around 10% in excess (calculate the required volume in advance). Centrifuge it, pour the supernatant out and wash the

resulting solid with distilled water (centrifuge twice, at 2000 rpm for 3 minutes). Write down its visual appearance.

## II) Amphoteric behaviour of aluminium hydroxide

To each one of the tubes from the previous experiment (**b1** y **b2**) in which aluminium hydroxide has been obtained:

**b1)** Add dropwise a solution of HCl 6 M until the solid **completely** dissolves.

**b2)** Add dropwise a 6 M NaOH solution until the solid almost completely dissolves, then centrifuge it and split the supernatant liquid between two test tubes (**b2.1** y **b2.2**). Slowly add the following reagents, mixing well between additions, until the  $\text{Al}(\text{OH})_3$  precipitates again.

**b2.1** -  $\text{NH}_4\text{Cl}$  2 M

**b2.2** - Saturated  $\text{NaHCO}_3$  solution

Write down what you observe.

Waste management: dispose of the resulting solutions from the experiment into the bottle labelled "Al/solutions".

## ADDITIONAL QUESTIONS

1. Explain all the experimental observations in section A). For each experiment, write down the properly balanced chemical reaction that explains what has been observed.
2. What is *slag* in a metallurgic process? What is the major component in an aluminothermic process?
3. What is the use of the magnesium fuse in the aluminothermic reaction?
4. What is the use of  $\text{NH}_4\text{Cl}$  and  $\text{NaHCO}_3$  in experiment b2?
5. When *hard water* is boiled many times in a vessel, a solid sediment appears on the bottom which is basically composed of calcium and magnesium carbonates. This deposit can be removed with acid which transforms the carbonate into  $\text{CO}_2$ . Which acid would be suitable for this cleaning operation if the recipient was made of aluminium?
6. Are aqueous solutions of Al(III) salts acidic or alkaline? Write the corresponding hydrolysis reaction.
7. What does *amphoteric* mean? Summarise this behaviour in a small scheme of the amphoteric reactions carried out with aluminium hydroxide.
8. In what pH interval does aluminium hydroxide precipitate? Which is the major aluminium species at acidic pH? Which is the major species in alkaline pH?



## ADDITIONAL BIBLIOGRAPHY

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## Attachments



Effect of mercury(II) chloride on aluminium foil.

*Traducido por Salvador Blasco*

## Session 4

# SILICON COMPOUNDS

Silicon is the second most abundant element in the Earth crust, after oxygen. Silicon and oxygen compounds constitute the major part of sand, rocks and soil. Among the silicon-containing minerals are quartz, feldspar, mica, amphibole and pyroxenes.

The most important silicon compound is silica, silicon dioxide. In Nature, it is found in two forms: a crystalline form named quartz, and a non-crystalline form named silex. The structure of quartz is based on the tetrahedral structural unit of  $\text{SiO}_4$ . These units are interconnected through the oxygen atoms to form 3D structures.

Silica gel is amorphous silicon dioxide which is obtained when an aqueous solution of sodium silicate is treated with an acid. After careful dehydration the silica gel can be used as a drying agent. It has an open structure which water can penetrate and become trapped in. Silica gel is also used as a stationary phase in chromatography and as a heterogeneous catalyst.

The silicates constitute a large family of compounds with varied structural forms. The basic structural unit is the tetrahedral  $\text{SiO}_4$ . These units can be isolated (olivine,  $(\text{Mg}, \text{Fe})_2\text{SiO}_4$ ) or form cycles (beryl,  $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ ), chains (diopside,  $\text{CaMgSi}_2\text{O}_6$ ) or sheets (talc,  $\text{Mg}_3(\text{OH})_2\text{Si}_4\text{O}_{10}$ ). 95% of the Earth's crust and the upper part of the mantle are silicates; they are the major components of igneous rocks, and are also important constituents of sedimentary and metamorphic rocks, as well as moon rocks, meteorites and the solid surfaces of Mercury, Venus and Mars.

Aluminosilicates are compounds which contain both  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedrons. Among them we can mention zeolites, a large group of porous compounds that can be either synthetic or natural. Different zeolites present different pore sizes, meaning molecules of different sizes can enter them or not. This fact is the basis for the use of zeolites as catalysts in many industrial processes. For example, ZSM-5 zeolite is used as a catalyst for benzene alkylation or xylene isomerisation. Another interesting property of zeolites is related to OH groups next to an aluminium centre. They are strongly acidic and the protons can be exchanged with other cations. This is why zeolites can be used in ionic exchange processes, and as such they have been used extensively in applications for water purification and detergent formulation. In the laboratory, zeolites are used as sieves to retain water molecules.

Furthermore, silica is a key ingredient in one of the most useful products on Earth is produced. When silica, in the form of sand, is melted together with sodium carbonate and calcium carbonate, glass is produced. There are thousands of different types of glass, with many different compositions for many different purposes. Glass is transparent, which makes it suitable for windows, glasses, optical lenses for telescopes or microscopes, etc. Glass is rather inert and resistant to many chemicals, making it ideal for food or beverage storage. Pyrex is a special kind of glass made by adding boron to the silica, sodium carbonate and calcium carbonate mixture. It does not expand or contract much with temperature, unlike common glass. It is ideal for the manufacturing of laboratory glassware.

Ceramics are another important type of silicon-based compound. Just like glass, they have been manufactured and used for food and water containers since ancient times. Ceramics are commonly made of clay. Clays are silicates produced during the weathering of granite and other rocks. They have a layered structure which can absorb large amounts of water. When they are heated in an oven they lose the water and become rigid.

Silicon has the same crystal structure as diamond. Silicon is prepared by heating quartz sand with coke at a temperature near 3000°C. Diamond is an insulator while silicon is a semi-conductor. This conducting property is strengthened by doping the silicon with tiny amounts of other elements such as arsenic and boron. In 1947 the first transistor was built in Bell labs. Transistors have completely replaced vacuum tubes in modern electronic devices, such as computers and televisions. Thanks to integrated circuits based on silicon, we have gone from room-sized computers to small laptops or netbook computers. Solar panels are also based on silicon. Electronic grade silicon must be extremely pure.

Another interesting class of silicon compound is the silicones. They are polymers made up of silicon atoms linked together with oxygen atoms. Each silicon atom is also bonded to two organic groups which, along with the length of silicon and oxygen chains, determine the physical properties of the silicones. Some silicones are specifically designed for use as a lubricant, whilst others are used for implants. The chains are stable and they can move smoothly between each other, which is why silicones are good lubricants. Depending on the length of the chains, the fluid can be less viscous (shorter chains) or more viscous (longer chains). By interconnecting these chains we can obtain resins or rubber which repel water and are resistant to chemical attack. Another remarkable application for silicones is the formulation of hygiene products such as shampoos and conditioners which modify hair texture, allowing it to be combed and shaped more easily. Since silicones are thick, water-immiscible oils, they can be shipped as emulsions to the hygiene product manufacturers.

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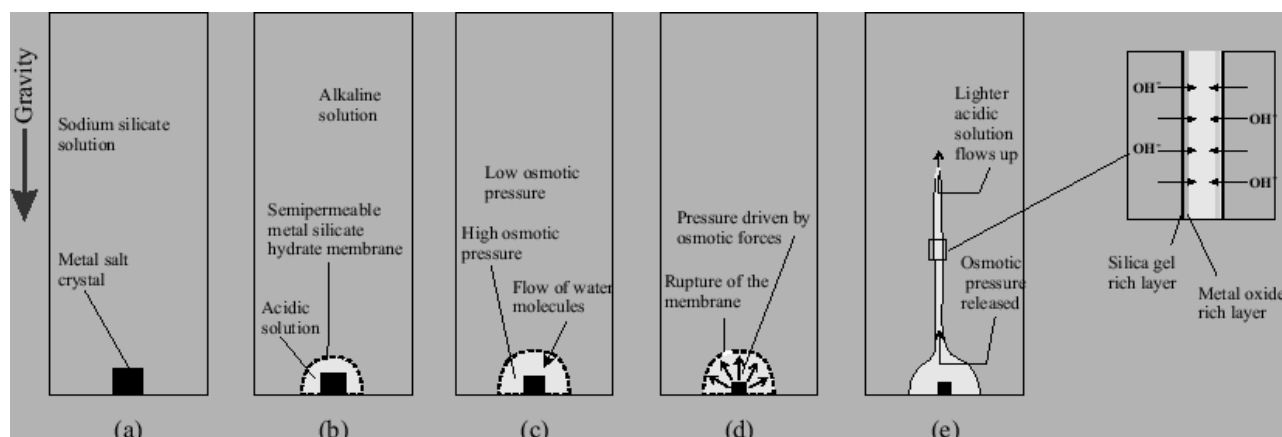
## A. THE CHEMICAL GARDEN

Chemical gardens are obtained by addition of crystals of water-soluble metal salts to aqueous solutions containing anions such as aluminates, borates, carbonates, chromates, cyanoferrates, phosphates, or silicates. A growth similar to that of trees or plants is observed and the final result recalls a garden. Despite their chemical diversity, a trait common to all is the precipitation around the crystals of a semi-permeable colloidal membrane, towards which osmosis phenomena can occur.

Among all reactions that produce chemical gardens, the most widely studied are those that happen in sodium silicate solutions. The addition of a crystal of a water-soluble metal salt to the sodium silicate solution starts the formation of a gel of "hydrated silicate" around the crystal. This gel acts as a semi-permeable membrane: the solution on the inside of the membrane is much more concentrated than that on the exterior, in such a way that there is an osmotic pressure gradient that causes water to flow from the silicate solution to the interior. As the crystal dissolves, water flows into the interior of the membrane and puts it under increasing tension until it breaks. At that precise moment, the release of the metal salt solution towards the silicate solution takes place. Upon contact between these two solutions, the gel formation happens. Thus, hollow tubular structures grow and, depending on the conditions, they can reach up to several centimetres long.

Chemical gardens were first observed in the 17<sup>th</sup> century and, in the 19<sup>th</sup> century, they called attention of chemists interested in the origin of life. Before the modern chemo-phobic age, chemical gardens were regarded as chemistry experiments for children. Today, many students know nothing about them. Additionally, apart from being an amazing experiment, the scientific interest in chemical gardens experienced a great comeback when the addition of aluminium nitrate crystals to sodium silicate solutions was studied. Transmission electron microscope images highlight the hierarchical structure of the walls in the tubes that form. Moreover, this material behaves as a good acidic catalyst.

In this experiment, the formation of hollow tubes is to be observed by reaction between some salts of metal ions with a sodium silicate solution.



## EXPERIMENTAL PROCEDURE

**Safety and caution:** safety goggles and gloves must be worn at all times.

**Material:** Glass flask or beaker, glass rod, tweezers or small spatula, safety goggles, gloves.

**Reagents:** deionised water, sodium silicate solution, cobalt chloride hexahydrate crystals, nickel sulphate hexahydrate, iron(III) chloride, calcium chloride.

Sodium silicate is dissolved in deionised water in a 1:2 volume ratio. The resulting solution is added to a long vial up to 1 cm from the top. When the solution settles, add a few crystals with tweezers or a spatula; try several products ensuring the crystals do not fall on top of one another. Cover the vial and leave for several hours.

See attachment.

**Waste management:** dispose of the waste into the bottle labelled "Silica/metal".

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## **B and C. SOL-GEL PROCESSES**

Sol-gel processes are processes in which a solution undergoes a transition towards a solid gel. The sol-gel process has many technological applications such as linings with specific optical properties, synthesis of hybrid organic-inorganic materials, or preparation of cell culture support in biology.

The principle of sol-gel processes is simple: we start from molecular precursors that are hydrolysed, followed by a progressive, room-temperature (or near), inorganic reaction which results in the formation of gel. The molecular precursors commonly used are organometallic chemicals such as alkoxides. Tetraethylsilicate is commonly used for the synthesis of silica-based sol-gels, although a sodium silicate solution can also be used.

The first step, when using an alkoxide, is the hydrolysis. Next, the condensation reaction occurs with the formation of oxo bridges. Initially a sol is obtained, which is a colloidal dispersion of small-sized particles inside the liquid. As polymerisation reactions take place, the particles grow and bind with each other until, finally, a 3D network of oxide particles linked together is formed, which contains space inside which the solvent can become trapped. Nevertheless, under certain conditions it is possible to stabilise a sol, a colloidal dispersion of small-sized particles with sizes ranging from a few nanometres and a few hundred nanometres.

## **B. SYNTHESIS OF SILICA MICROSPHERES**

Stöber's method allows for the synthesis of silica microspheres of varied sizes, from less than 100 nm to more than 1  $\mu\text{m}$ . TEOS (tetraethylorthosilicate) is dissolved in a water-ethanol mixture and the reaction is triggered by the addition of ammonia. The subsequent supersaturation conditions determine the number of nuclei that are formed, and the amount of TEOS controls the final size of the spherical particles. Once the mechanism has been understood, it's possible to work in conditions of undersaturation, by introducing the seeds over which the growth of the silica takes place. If the seeds are silica, the growth of the particles is produced. However, if gold or magnetite nanoparticles are used, the result is nanoparticles at the core covered with a silica coating. Also, these microspheres

can orderly sediment on a substrate, generating an artificial opal and, from there, inverse opals can be obtained by filling the space between the microspheres with a suitable material and later on, removing the microspheres. The avenues that this chemistry makes possible, as well as micro-sphere assembly, are among the most important fields in nanochemistry.

In this experiment, silica microspheres are prepared by Stöber's method. With the help of a laser we will assess the colloidal nature of the resulting suspension (Tyndall effect).

## EXPERIMENTAL PROCEDURE

**Material:** 150 mL beaker, magnetic stirrer, magnet stirrer or polypropylene rod.

**Reagents:** TEOS, ethanol, water, ammonia.

To a polypropylene recipient with a lid, add 2.5 mL of 25%  $\text{NH}_3$ , 1 mL of water and 8 mL of ethanol. Stir and then add 2-3 drops of TEOS. Within several minutes turbidity should be observed. The reaction takes around 2h to complete. The size of the microspheres depends on the ammonia concentration, water, TEOS, and the work temperature. Dilute a small sample of the suspension in ethanol in a glass beaker and then shine a laser beam into this diluted solution and observe the Tyndall effect.

See attachment.

Waste management: dispose of the waste of this experiment into the bottle labelled "silica".

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## C. SYNTHESIS OF SILICA GEL



Alkaline silicates have the composition  $M_2O \cdot nSiO_2$  ( $M=Na, K$ ). Commercial sodium silicate has a composition close to  $Na_2Si_3O_7$ . These solids are insoluble in water and, in particular, a concentrated sodium silicate solution is sold as "soluble glass" or "water glass". The acidification of these solutions results in the formation of silicic acids ( $H_2Si_3O_7$ , for the case of the sodium compound) which, by water removal, form polysilicic acids which condensate to form a rigid mass or a jelly precipitate. They are then washed to remove sodium and sulphates and the solid is dried by heating.

Silica gel is a very porous, non crystalline form of silica. In fact, silica density is  $2.2 \text{ g}\cdot\text{cm}^{-3}$ , whereas commercial silica gels commonly have density of  $0.7 \text{ g}\cdot\text{cm}^{-3}$  and specific surfaces of  $750 \text{ m}^2 \text{ g}^{-1}$ . It has a strong affinity for water and that is why it is used to dry liquids and gases. In everyday life we can find it as packed beads in moisture-permeable plastic bags. This is used to control local moisture in packaging preventing moisture condensation ruining the contents. In the laboratory, silica gel is used as desiccant and, normally, a gel is used to which ammonium tetrachlorocobaltate has been added in order to have a visible indicator for the moisture level: when hydrated the colour shifts from pale pink to deep blue.

In this experiment, silica gel is prepared by acidic hydrolysis of a concentrated solution of sodium silicate.

## EXPERIMENTAL PROCEDURE

**Safety and Caution:** safety goggles and gloves must be worn at all times.

**Material:** a 150 mL beaker and glass rod

**Reagents:** sodium silicate solution and sulphuric acid 1M.

In a 150 mL beaker, dilute 10 mL of a sodium silicate solution with 2-3mL of distilled water. Add 10 mL of 1M sulphuric acid and stir with the glass rod, after that, the precipitation of the gel happens. Sometimes the gel can be removed from the beaker as a solid block.

**Waste management:** dispose of the generated waste into the bottle labelled "silica".

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#### D. ION EXCHANGE PROPERTIES OF A ZEOLITE

The term 'zeolite' is derived from the Greek words meaning 'to boil' and 'stone'. It was coined in 1756 by the Swedish mineralogist Cronstedt to describe minerals that release water upon heating. There are natural zeolites, of sedimentary origins, in many parts of the world, which are commercially exploited. Synthetic zeolites are prepared by hydrothermal crystallisation of alkaline aluminosilicate amorphous gels at temperatures between 80 and 220°C.

The remarkable versatility of these materials is due to their unusual crystal structures made up of  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedrons which share vertices resulting in microporous 3D networks. There are channels with diameters 300-800 pm which connect cavities up to 1300 pm wide. The lattice is anionic, since each unit of  $\text{AlO}_4$  contributes one negative charge. In order to balance the negative charge, the lattice voids are occupied by cations, along with a large number of water molecules. The empirical formula of zeolites can be described as  $\text{M}^+[(\text{AlO}_2)(\text{SiO}_2)_x] \cdot n\text{H}_2\text{O}$ . The value of  $x$  cannot be smaller than 1, since there are no Al-O-Al bonds in zeolites; on the other hand, there is no upper limit for  $x$ .

One of the applications of zeolites is their capacity to adsorb molecules. For this use, the embedded water is removed by heating under vacuum, allowing other molecules to occupy the voids. The pore size determines which molecules can be adsorbed by a particular zeolite type. This property can be used to selectively adsorb molecules, unlike other adsorbing substances. The adsorptive properties also depend on the value of  $x$ . Aluminous zeolites are hydrophilic with a preference for polar molecules, while zeolites with high silica contents adsorb organophilic, hydrophobic molecules. Aluminous zeolites are potent water removing agents and they are used in industry and in the laboratory to dry gases and organic liquids. Zeolites with high silica contents are very effective for the removal of organic molecules in diluted water solutions, which is why they are used for water purification.

Another feature of zeolites is their ability to exchange ions in solution. Alkaline cations are found in the openings and they can move freely through the structure. When in contact with a solution containing another type of cation, the alkaline metals can go from the zeolite to the solution and the cations from solution can enter the zeolite. This makes zeolites suitable for detergents as water softeners. The zeolite used, with ion exchange capacity, would exchange sodium for calcium.

Zeolites are commonly used as catalysts in their acidic forms, which are prepared by calcination of the ammonia forms. In particular, they are used for cracking in the petroleum industry to produce useful lighter hydrocarbons in order to increase the octane content of gasoline. One of the most interesting outcomes of this application is that, since the reactions take place in the interior of the zeolite pores, there is a restriction on the size of the molecules involved in the reaction (reagents, products and transition states). That is, only the products from reagents able to enter the pore can be produced, only the transition states that fit in the cavity can be formed and lead to product formation, and only the products able to escape the pore will be released.

In this experiment, the ionic exchange between a zeolite in its sodium form and a solution of cobalt(II) ions is observed. The colour of the cobalt(II) ions facilitates the observation of the ionic exchange.

### PRELIMINARY QUESTIONS

1. Why do zeolites exhibit ionic exchange properties?

### EXPERIMENTAL PROCEDURE

#### Safety and Caution:

**Material:** 1 × 250 mL Erlenmeyer flask, 1 porcelain capsule

**Reagents:**  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , zeolite, 0.1 M  $\text{AgNO}_3$  water solution

Dissolve 0.1 g of cobalt(II) chloride hexahydrate in 100 mL of water in a 250 mL Erlenmeyer flask. Add 1 g of zeolite and stir while gently heating until the colour is gone. Filter and rinse. Check the presence of chloride anions in the supernatant solution. Dry with air. Put the product in the capsule and carefully heat it while observing any change. Weigh it and let it cool down in air. Weigh it again when the original colour returns.

**Waste management:** dispose of the waste from the experiment into the bottle labelled "zeolites/Co".

### ADDITIONAL QUESTIONS

1. What changes are observed when the zeolite is mixed with the cobalt(II) chloride solution? What is the reason for these changes?
2. What changes are observed, firstly, when the zeolite sample is heated, and then, when it cools down to room temperature? What are the reasons for these changes?

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## E. SILANES

The great development of synthetic inorganic chemistry from 1830 onwards led to the idea that Si chemistry could exist similar to C chemistry. During the second half of the 20th century certain silanes were obtained but not much further development happened due to their thermal instability and elevated reactivity. It was A. Stock who initiated the systematic study of boron and silicon hydrates which he named boranes and silanes respectively.

Both linear and branched silanes are known, with general formula  $\text{Si}_n\text{H}_{2n+2}$ , and with values of  $n$  between 1 and 10. Cyclic compounds with formulas  $\text{Si}_5\text{H}_{10}$  y  $\text{Si}_6\text{H}_{12}$  are also known.

Only  $\text{SiH}_4$  and  $\text{Si}_2\text{H}_6$  have long term stability at 25°C. At room temperature, heavier silanes decay yielding hydrogen, monosilane and disilane. All silanes decompose at  $T > 500\text{ }^\circ\text{C}$  resulting in silicon and hydrogen.

The original method for the synthesis of silanes by Stock consisted in treating magnesium silicide with dilute hydrochloric acid in the absence of air. This reaction produces a mixture of silanes with  $n = 1-4$ , with traces of silanes of higher  $n$ . This silane mixture can be separated by chromatography.

A compound related to silanes is the trichlorosilane,  $\text{SiHCl}_3$ , which is obtained when Si is treated with HCl. This compound can be purified by distillation and, by means of chemical vapour deposition it is deposited on the surface of a high purity, polycrystalline silicon substrate. This is how Si is purified for the production of integrated circuits.

In this experiment, magnesium silicide will be prepared and its reactivity with diluted acid will be observed. Therein, a mixture of silanes will be produced, compounds which burn spontaneously in contact with air.

## PRELIMINARY QUESTIONS

1. Explain why silanes are much more reactive than alkanes.
2. Explain the reactivity of silanes against diluted mineral acids and bases.
3. What happens when silanes are exposed to air? Write down the corresponding reaction.

## EXPERIMENTAL PROCEDURE

**Safety and Caution:** The whole procedure must be carried out inside a fume hood.

**Material:** Porcelain mortar and pestle, iron crucible with lid.

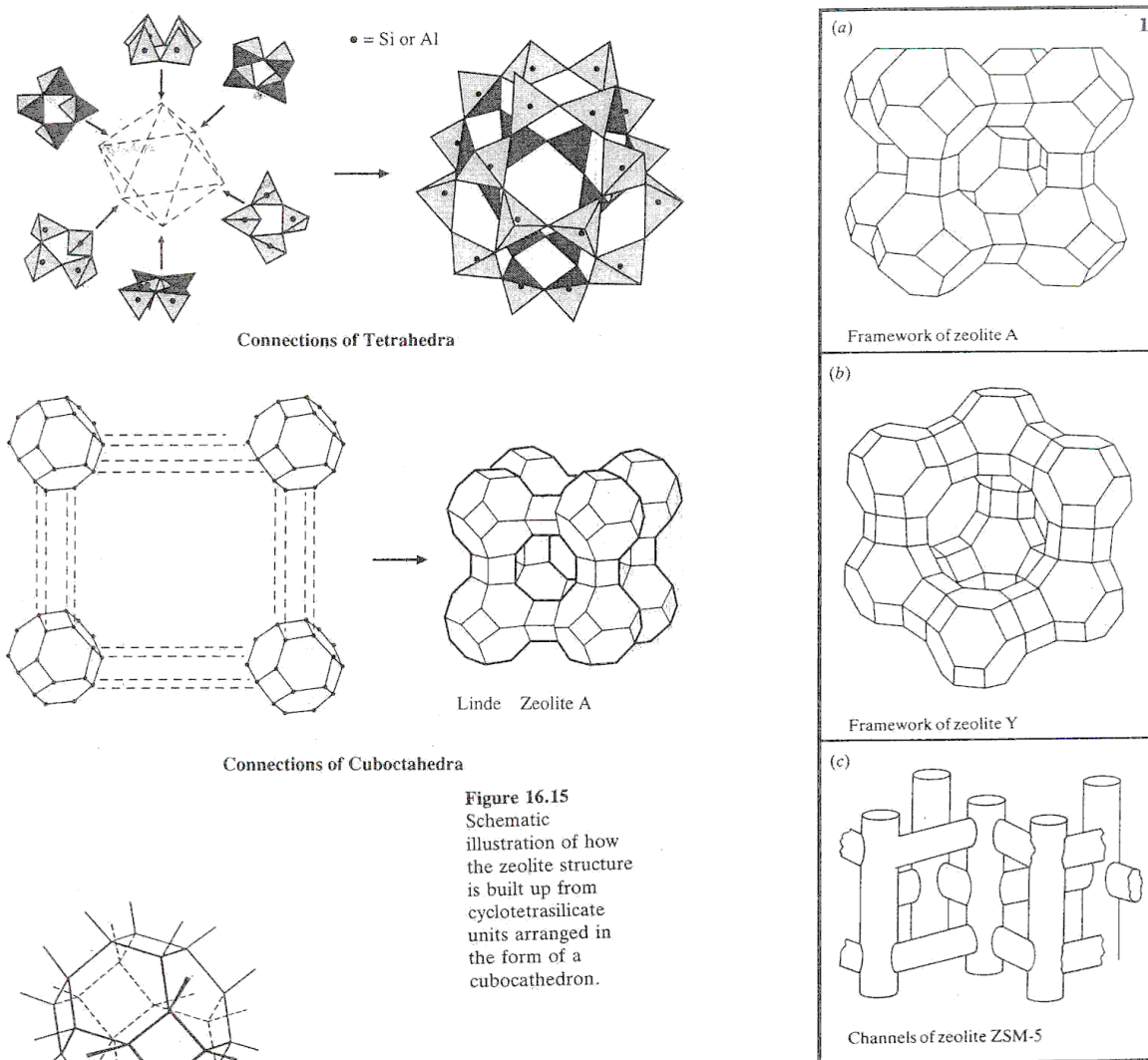
**Reagents:** 0.5 g of silicon dioxide, 1 g of magnesium powder, hydrochloric acid 2M, magnesium ribbon.

Thoroughly mix 0.5g of  $\text{SiO}_2$  and 1g of magnesium powder in the porcelain mortar. Put the mixture into a very dry iron crucible. The reaction is initiated by igniting the mixture with the magnesium fuse, and it quickly propagates to the bulk which turns white red. Immediately after the ignition, cover the crucible with the lid. Let it cool down, the product forms a coherent mass, which will have the appearance of a bluish grey powder. Next, very carefully, add to the same crucible 2M HCl dropwise, giving rise to the formation of silanes which spontaneously ignite in contact with air. Continue adding HCl to the crucible until no more silanes are formed and the reaction stops.

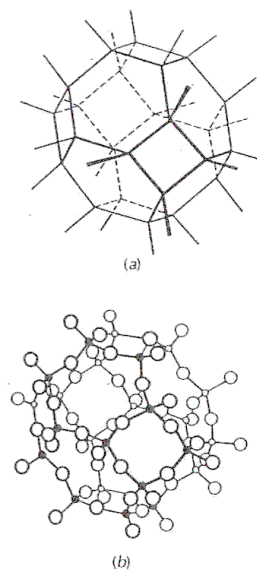
Waste management: ensure that silanes are no longer generated before you dispose of the waste into the bottle labelled "silicon dioxide/Mg/HCl".

### ADDITIONAL QUESTIONS

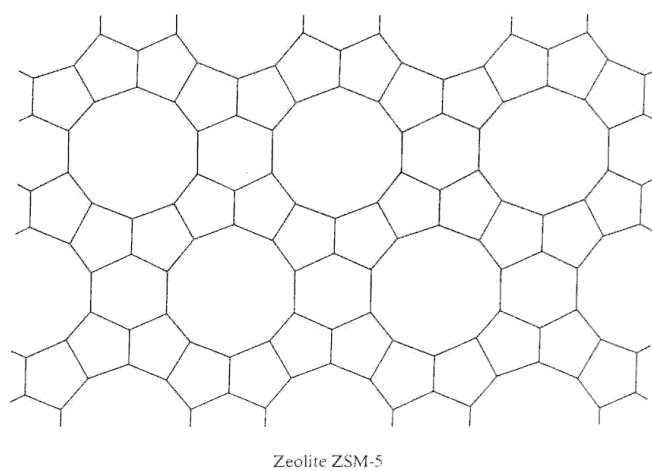
1. Write all the reactions taking place in this process.
2. What would happen if the mixture of  $\text{SiO}_2$  and Mg were equimolar?



**Figure 16.15**  
Schematic illustration of how the zeolite structure is built up from cyclotetrasilicate units arranged in the form of a cubocathedron.



**FIGURA 11.32** (a) Representación del armazón de un octaedro truncado (truncado según la dirección perpendicular al eje cuaternario del octaedro). (b) Posiciones de los átomos de Si y O relativas al armazón. Obsérvese que el átomo de Si está en cada uno de los vértices del octaedro truncado y un átomo de oxígeno se dispone aproximadamente en cada una de las aristas.



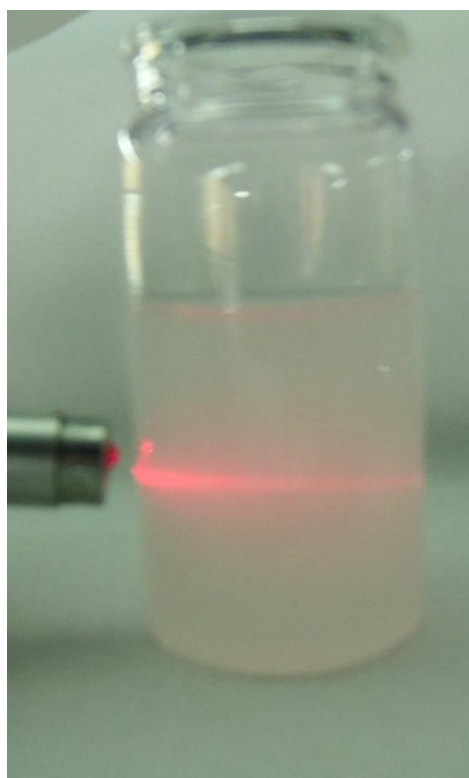
**Fig. 2.** Sheet projections for ZSM-5. Each vertex represents a tetrahedral site, the fourth bonds (not shown) connect the layer to the rest of the framework.

## ATTACHMENT

### CHEMICAL GARDEN



### TYNDALL EFFECT



*Traducido por Salvador Blasco*

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## Session 5

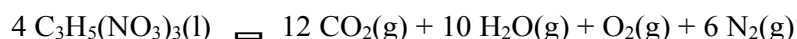
# NITROGEN COMPOUNDS

### INTRODUCTION

Nitrogen is the most abundant among the non-combined elements accessible to man. It makes up around 78.1% of the atmospheric volume. In combination with other elements it is an essential element for life, constituting around 15% of the proteins. The fixation of nitrogen at industrial scale, for use as fertilisers in agriculture and other chemicals, is one of the top industrial activities in many countries. Ammonia is, after sulphuric acid, the second most important industrial product in the world by volume of production.

Despite being very abundant in the atmosphere, nitrogen is relatively scarce in the Lithosphere. As a matter of fact, its average concentration is comparable to that of Ga or Li. The larger deposits of  $\text{KNO}_3$  are located in India, and those of  $\text{NaNO}_3$  in Chile. In any case, current industrial processes for the production of ammonia do not depend on the existence of these mineral resources.

Nitrogen, like oxygen, is a gas because of the ability of its atoms to bind to one another with multiple bonds. Since it has three unpaired electrons in its electronic configuration, its molecules are diatomic, bound together by a very strong triple bond. The dissociation energy is 226 kcal/mol, much higher than that of hydrogen (104 kcal/mol) or fluoride (37 kcal/mol). Such a high value explains the explosive nature of many nitrogen compounds when they transform to nitrogen, e.g. the decomposition of nitro-glycerine.



Nitrogen forms compounds in all oxidation states between  $-3$  and  $+5$ . The most important oxides are the oxidation states (II) and (IV) in which the monomeric forms have one unpaired electron. NO is an oxide that is very versatile in its reactions and it can give rise to several compounds. Halogens oxidise it to nitrosyl halides which are covalent compounds that hydrolyse easily. Additionally, in some coordination compounds it can act as a coordinating ligand. Nitrogen (IV) oxide may exist in monomeric ( $\text{NO}_2$ ) or dimeric form ( $\text{N}_2\text{O}_4$ ). It is a very strong oxidant, comparable to  $\text{Br}_2$ .

The most important oxoacids are nitrous and nitric acids. The first is obtained when a strong acid is reacted with a nitrite solution. The free acid cannot be isolated due to its instability; it readily decomposes. Since nitrogen is in an intermediate oxidation state, (III), it can be expected to exhibit either oxidising or reducing properties. Nitric acid is of great industrial importance for the manufacture of fertilisers and nitrogenated organic compounds. The most important method for its industrial production is the catalytic oxidation of ammonia.

Despite being a colourless compound, it often exhibits a yellowish appearance due to partial decomposition to nitrogen oxides. Metals react with nitric acid in diverse ways. Thus, noble metals such as Au or Pt are not attacked by  $\text{HNO}_3$ , but they are by *aqua regia* (a mixture of concentrated HCl and  $\text{HNO}_3$  in 3:1 ratio). Other metals, such as copper, are oxidised easily by nitric acid. On the other hand, more reducing metals such as Fe, Al or Cr are passivated and cease to exhibit reducing properties.

## OBJECTIVES

- 1 Synthesis and study of the chemical properties of nitrogen monoxide and nitrogen dioxide.
- 2 To study the oxidative character of nitric acid.
- 3 To carry out qualitative characterisation tests for nitrites and nitrates.

## PRELIMINARY QUESTIONS

1  $\text{N}_2$  is much less reactive than  $\text{O}_2$  or Fe. As a matter of fact, it is commonly used to create an "inert" atmosphere. Explain and reason the chemical inertness of nitrogen compared to  $\text{O}_2$  or  $\text{F}_2$ .

2 In general, the chemistry of the elements in the same group is similar, but the first element in the group presents different traits to the others. Name some differences (and explain their causes) between the chemistry of nitrogen and that of phosphorous.

3 Nitrogen is very prolific in the formation of molecular oxides. Study the synthesis and properties of NO and  $\text{NO}_2$ . Explain why some of them are paramagnetic.

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4 In this session, NO and  $\text{NO}_2$  oxides are obtained by reaction of nitric acid with copper or iron respectively. Write and balance the corresponding chemical reactions.



- 5 Explain how  $\text{N}_2\text{O}_3$  could be obtained from the two aforementioned oxides.
- 6 Explain how the so-called Griess test for the identification of nitrites works.

## EXPERIMENTAL PROCEDURE

Material	Reagents
100 and 500 mL beakers	Copper metal
Watch glass	Iron metal
Drop test plate	Zinc metal
Assay tubes and grid	Aluminium foil
Rubber lids	0.1 M $\text{NaNO}_3$ aqueous solution
Graduated cylinder	0.1 M $\text{NaNO}_2$ aqueous solution
Gas generation set-up	4 M $\text{NaOH}$ aqueous solution
Lighter, tripod and grid	0.01 M $\text{KMnO}_4$ aqueous solution
KI starch paper	2 M $\text{CH}_3\text{COOH}$ aqueous solution
pH indicator paper	5% urea solution
	6M $\text{HCl}$
	0.1 M potassium iodide
	Chloroform
	Methyl red and bromophenol blue
	16, 6 and 4 M $\text{HNO}_3$ solution
	Griess' reagent A and B
	$\text{FeSO}_4$

*IMPORTANT NOTE: Nitrogen oxides are toxic. Therefore, all experiments involving gas generation must be carried out in FUME HOOD.*

### Qualitative preliminary tests for nitrite and nitrate recognition:

#### **Nitrites**

On a drop test plate, successively add one drop of 0.1 M sodium nitrite, one drop of Griess' reagent A and another drop of Griess' reagent B. The apparition of a red colour indicates the presence of nitrites.

#### **Nitrates**

On a drop test plate, add two drops of 0.1 M sodium nitrate and then acidify with two drops of 2 M acetic acid. Then add one drop of Griess' reagent A and another drop of Griess' reagent B and a little bit of zinc powder. A red colour next to the zinc indicates nitrate.

**Identification of nitrites in presence of nitrates**

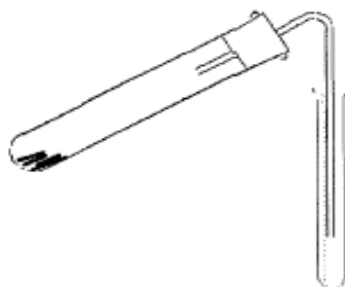
In a test tube, add 0.5 mL of a 0.1 M sodium nitrite solution and 0.5 mL of a 0.1M sodium nitrate solution. Then, add a few drops of 2 M acetic acid and 3-4 drops of 5% urea. Warm the tube up in a water bath for 10 min and then let it cool down. By doing this, the nitrites are removed and we can proceed with the identification of nitrates like in the previous experiment.

Waste management: dispose of the resulting solutions in the corresponding bottles.

**I Synthesis of nitrogen dioxide. Tests.**

*Generation of nitrogen dioxide. NOTE: Carry out in FUME HOOD*

Prepare set-up as depicted in **Figure 1** to collect the gas generated (use dry test tubes).



**Figure 1**

To the bottom of a test tube, add 1 g of copper wire, and then add 5 mL of concentrated nitric acid (14 M). Wait a moment until a gas starts being released. Collect it in a test tube by water displacement, until the tube appears to be full of a brown gas. Once the gas has been collected, close the tube with a rubber lid and keep it for later. Repeat this with four additional tubes (one of them is kept in reserve in case an experiment fails).

Waste management: dispose of the solution in the tube where the gas is generated when the reaction is over into the bottle labelled “Cu/HNO<sub>3</sub>”.

*Characterisation tests.*

*I-1. Dimerisation reactions ( $2\text{NO}_2 \leftrightarrow \text{N}_2\text{O}_4$ ).* One of the tubes in which the gas is stored is introduced into a crushed ice bath. After a few minutes, gently heat the upper third of the tube, constantly moving the burner in order to prevent localised overheating. Observe the colour of the gas against a white background, and note where its colour is most intense: the cold or the warm end of the tube. Interpret this colour change on the grounds of the dimerisation equilibrium.

*I-2. Oxidant character of NO<sub>2</sub>.* Place a wet KI-starch strip in the mouth of the test tube containing NO<sub>2</sub>. Observe what happens to the strip. Interpret this result and write the possible reactions taking place. Explain the redox character of NO<sub>2</sub>.

*I-3. NO<sub>2</sub> solubility in water.* In order to qualitatively assess the solubility of NO<sub>2</sub>, take the third tube containing this gas and introduce it upside down into a recipient with water containing two or three drops of methyl red or bromophenol blue, noting the rise in the water level. An identical tube full of air (not very soluble) can be used for comparative purposes.. Comment on the colour change of the indicator.

*I-4. Disproportionation of NO<sub>2</sub> in water.* Quickly introduce 2 mL of water into one of the test tubes containing NO<sub>2</sub> and immediately close it. Vigorously shake the tube for a few minutes for the gas to dissolve. Actually, nitrogen dioxide disproportionates in the presence of water, resulting in nitrates and nitrites. Write down the reaction. Next, carry out the assays described above in order to confirm the presence of both ions.

### *Recognition of nitrite ions*

On a drop test plate, place a drop from the  $\text{NO}_2$  solubility test. Add a drop of Griess reagent A and another drop of Griess reagent B. A red colour indicates the presence of nitrites.

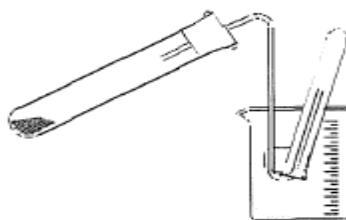
### *Recognition of nitrate ions*

In order to avoid the possible interference of nitrite ions present in the solution, it is necessary to first eliminate them. With this aim, add a few drops of 2 M acetic acid and 4-5 drops of 5% urea to 1 mL of the solution coming from the  $\text{NO}_2$  solubility test. Next, warm it up in a water bath for 10 minutes. Wait for it to cool down, and then assess the presence of nitrates by adding, on a drop test plate, two drops of the previous solution, one drop of Griess A and another of Griess B and a little bit of zinc powder. A red colour next to the zinc powder indicates the presence of nitrates.

## **II Synthesis of nitrogen monoxide. Tests.**

### *Generation of nitrogen monoxide. NOTE: Carry out in the FUME HOOD*

In this part, the set-up depicted in Figure 2 will be used. Place 1 g of iron nuggets, 1 mL of distilled water and 6 mL of nitric acid 6M into the test tube where the gas will be generated. The gas released is collected by displacement into an upside down test tube full of water inside a beaker, also full of water (**Figure 2**).



**Figure 2**

What is the colour of this gas? The gas will displace the water inside the tube. Once it is full, close it with a rubber lid and keep it for later. Repeat this to fill another tube in order to have a total of two tubes for the following tests.

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### Characterisation assays

II-1. Open the first test tube containing the gas collected previously, and let it slowly mix with the oxygen in the air. Watch for the colour change and then interpret the process happening there.

II-2. Into the second test tube, add a solution of 50 mg of  $\text{FeSO}_4$  in 3 mL water, quickly close it again and shake. The complex  $[\text{Fe}(\text{H}_2\text{O})_5(\text{NO})]^{2+}$  is brown, therefore indicating the presence of NO.

Waste management: introduce the solution from the tube where the gas was generated into the bottle labelled "Fe/HNO<sub>3</sub>".

### III Nitric acid as an oxidising agent towards reducing metals.

Place a small zinc nugget and a piece of clean aluminium foil into two test tubes. Add 3 mL of 4 M nitric acid into both tubes, and observe what happens in them. When all the zinc is dissolved, we must identify one of the reaction products of this metal with dilute nitric acid. We proceed by pouring the resulting solution into a 100 mL beaker, and covering it with a watch glass which has a wet strip of pH indicator paper (with water). Remove the watch glass and add 5 mL of 4 M NaOH solution, then close it again and gently warm up the mixture. Note any change in the colour of the pH indicator paper, and then explain any chemical process that might have taken place.

On the bottom of the beaker in the previous experiment, a white precipitate will be observed. Transfer a small amount of this white precipitate to a test tube and add NaOH 4M drop wise. Observe the result. Write down the reaction.

Waste management: when the experiment is over, dispose of the solution into the bottle labelled "Zn/NaOH".

### IV Qualitative assays to test the redox properties of nitrites and nitrates.

*Note. The following reactions will be carried out in a test tube.*

## Nitrites

IV-1. 8 drops of 2M acetic acid are added to 1 mL of a 0.1 M sodium nitrite solution, followed by 2-3 drops of 0.1M potassium iodide and 1 mL of chloroform. Stir the solution and interpret the results.

Waste management: dispose of the solution in the bottle labelled "Chloroform/I<sub>2</sub>".

IV-2. 16 drops of 2M acetic acid and two drops of 0.01M KMnO<sub>4</sub> are added to 1 mL of a 0.1 M sodium nitrite solution. If the permanganate colour does not disappear, gently heat the tube up.

Waste management: dispose of the solution into the bottle labelled "Mn".

## Nitrates

IV-3. In a test tube, introduce a small amount of solid sodium nitrate and add 1 mL of water. Add 4-5 drops of potassium iodide and 1mL of chloroform. Observe the colour of both phases. Add 10 drops of hydrochloric acid 12 M. Mix the solution and note any change that might occur.

Waste management: dispose of the solution into the bottle labelled "Chloroform/I<sub>2</sub>".

## ADDITIONAL QUESTIONS

IV.1 In experiment I-1 the dimerisation of NO<sub>2</sub> is observed. Comment on the effect of temperature on the dimerisation equilibrium. Explain why NO<sub>2</sub> has a greater tendency than NO to dimerise.

IV.2 In experiment I-3, NO<sub>2</sub> reacts with water by disproportionating. Write down the reaction that happens and explain it with the reduction potentials of the species involved.

IV.3 In experiment III-1 the phenomenon called *passivation* was highlighted. Explain what this is and name other metals that undergo the same process.

IV.4 Write balanced equations for the reactions that take place in section IV.

*Traducido por Salvador Blasco*

## Session 6

# PHOSPHORIC ACID AND PHOSPHATES

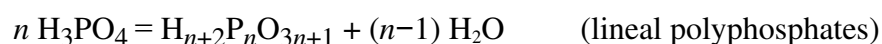
### INTRODUCTION

Phosphorous forms oxoacids more than any other element, and the number of oxoanions it forms is exceeded only by silicon. Many of them are of great technological importance, and also perform a relevant role in biological processes. Therefore, the knowledge of the chemistry of these systems it is of great interest.

Despite the large number of phosphorous oxoacids, they all share common traits which facilitate their study and systematization. Basically, these structural traits are:

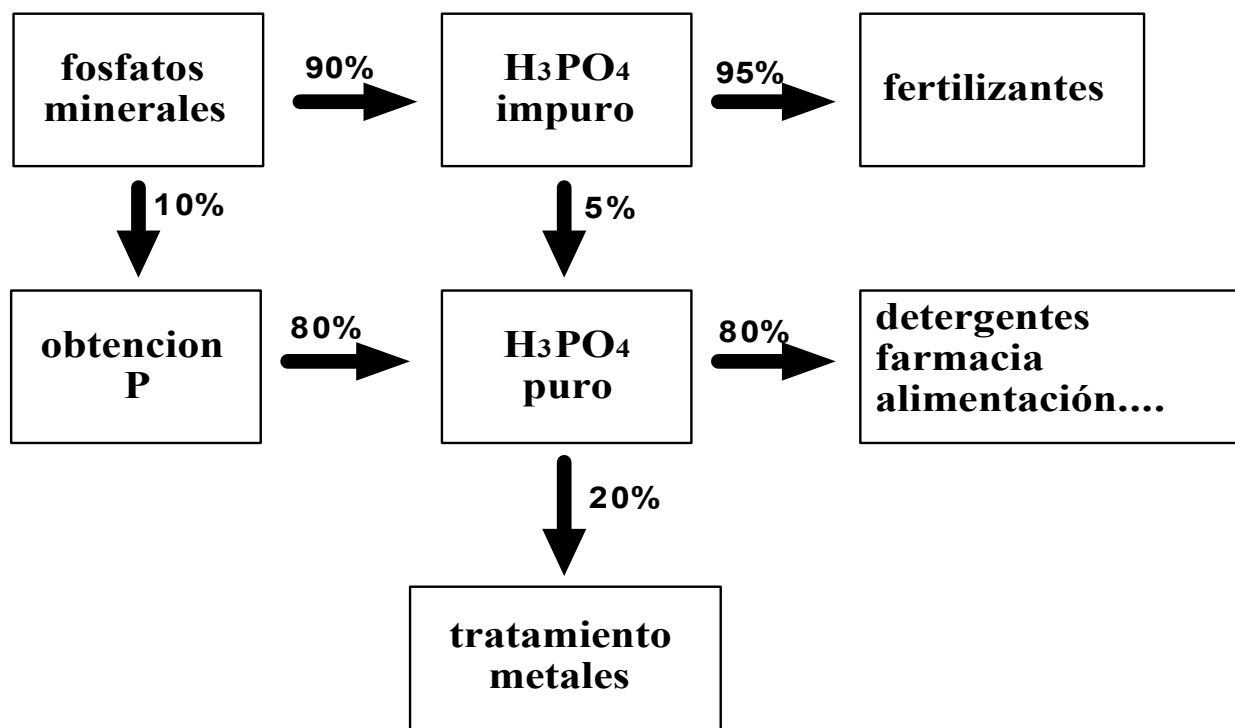
- a) In all oxoacids, the phosphorous atoms are tetra-coordinated and they contain at least one P = O bond.
- b) All P atoms contain at least one P-OH unit; this group is ionisable and a proton donor.
- c) Some species contain one or more P-H groups; hydrogen atoms directly bonded to phosphorous are not ionisable.
- d) Concatenation may occur either through P-O-P links or direct P-P bonding. In the first case, either open (linear) or closed (cyclic) tetrahedral chains are obtained by sharing the tetrahedron vertices, never the sides or faces.

Phosphoric acid forms a series of salts in which one, two, or three hydrogen atoms have been replaced. By condensation of the simple phosphates, polyphosphates can be obtained, which feature the concatenation of "PO<sub>4</sub>" units in linear chains (chain polyphosphates) or cyclic units (metaphosphates or cyclophosphates, the latter being the recommended denomination). The condensation process (referred to as the condensation of orthophosphoric acid) can be described with the following reactions:



Linear polyphosphates chains of up to 200 "PO<sub>4</sub>" units have been obtained. As the chain length increases, the ratio O/P = (3n+1)/n approaches 3, which is why such compounds were wrongly denominated metaphosphates.

Applications of phosphoric acid and phosphates are numerous and diverse. The most representative ones are displayed in the scheme below.



## OBJECTIVES

- 1.- To examine some of the most relevant aspects of the equilibria of phosphoric acid and its salts in solution by carrying out a potentiometric titration of a diluted solution of phosphoric acid and the preparation of a buffer solution.
- 2.- To obtain polyphosphates (either linear or cyclic) by heat dehydration of simple phosphates (optional).

## PRELIMINARY QUESTIONS

- 1.- Orthophosphoric acid is industrially obtained by treating mineral phosphates with sulphuric acid.
  - a) Look up a scheme for this process in the bibliography.
  - b) Calculate the mass of orthophosphoric acid that can be obtained from 1 ton of 80% pure apatite\* if the yield is 60%

\* Chemical formula:  $\text{Ca}_5(\text{PO}_4)_3(\text{OH}, \text{F}, \text{Cl})$  Contents in P 18.25%.



- 2.- Considering the values for the acidity constants of orthophosphoric acid at 25°C ( $pK_{a1} = 2.1$ ;  $pK_{a2} = 7.2$ ;  $pK_{a3} = 12.4$ ), calculate the pH of a 0.1 M solution of sodium dihydrogen phosphate as well as that of a solution of sodium monohydrogen phosphate at the same concentration.
- 3.- Describe the different phosphate oxoacids ( $H_3PO_4$ ,  $H_3PO_3$ ,  $H_3PO_2$ ) including their Lewis structures and their acid-base character.
- 4.- Look up the structures of the following anions in the bibliography: pyrophosphate ( $P_2O_7^{4-}$ ), tetrapolyphosphate ( $P_4O_{13}^{6-}$ ) and cyclotetraphosphate ( $P_4O_{12}^{4-}$ ).
- 5.- Explain the selection of the acid-base indicators used in the titration of this experiment based on the  $pK_a$  values (see experimental procedure).
- 6.- Calculate the volume of concentrated phosphoric acid needed to prepare 100 mL of a 1M solution. Concentrated acid properties:  $R=85\%$  and  $d=1.7g/mL$ .

## EXPERIMENTAL PROCEDURE

Material	Reagents
50 mL beaker	Concentrated $H_3PO_4$ acid
250 mL beaker	0.1 M NaOH solution (standardised)
pH-meter	0.1 M hydrochloric acid
25 mL burette	Phenolphthalein
10 mL pipette (graduated and volumetric)	Methyl orange
100 mL volumetric flask	Sodium dihydrogen phosphate ( $NaH_2PO_4$ )
Graph paper	Sodium monohydrogen phosphate ( $Na_2HPO_4$ )
Pasteur pipette	
Graduated cylinder	
Funnel	
Porcelain capsule	

### A) Titration of 0.1M $H_3PO_4$ with 0.1M NaOH and elaboration of the titration curve

- 1) Prepare 100 mL of 1M  $H_3PO_4$  from concentrated  $H_3PO_4$ . Consider the information on the label: density and purity. Calculate the required volume.

Place exactly the calculated volume into a 100 mL volumetric flask, fill it with water and mix well.

2) Prepare 100 mL of  $\text{H}_3\text{PO}_4$  0.1 M from the 1M  $\text{H}_3\text{PO}_4$  solution.

Calculate the volume required to prepare this solution and then proceed as in the previous step.

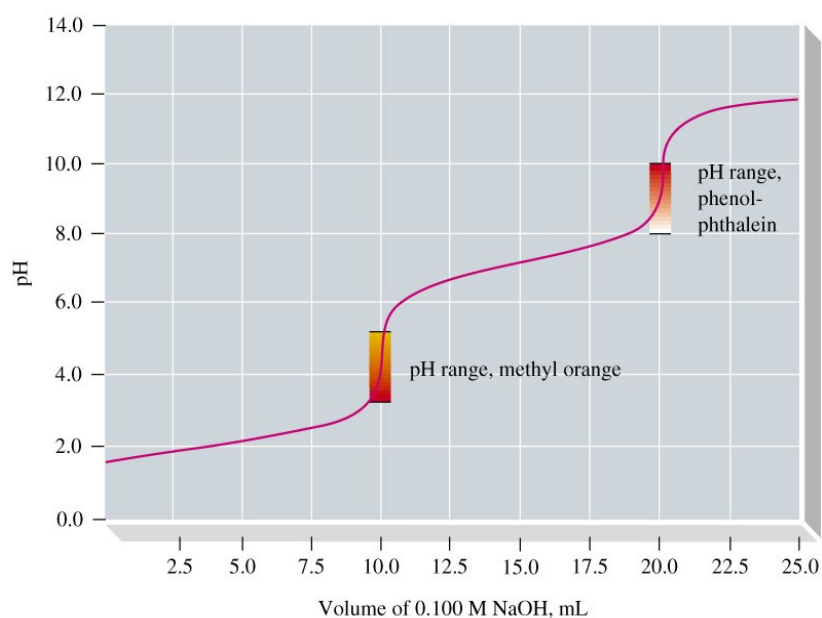
3) Titrate the 0.1  $\text{H}_3\text{PO}_4$  with 0.1M NaOH and draw the titration curve.

Measure exactly 10 mL of 0.1M  $\text{H}_3\text{PO}_4$  with a pipette, add it to a 250 mL beaker, and then add *ca.* 100 mL of distilled water (so that the volume is enough for the electrode to be properly immersed). Add a few drops of methyl orange and phenolphthalein.

In a 25 mL burette, introduce the 0.1M NaOH solution and zero it.

Place the beaker with the acid solution onto the stirrer plate, immerse the electrode and begin the titration. Proceed by adding the sodium hydroxide solution under constant stirring and measuring the pH after each addition.

Draw the pH values against the titre volume, in mL. A curve similar to that shown in the figure below should be obtained where the x-axis will coincide if the NaOH concentration used is the same than that in the figure. The pH jumps are, however, independent of both acid and base concentrations.



**Recommendations:**

Add the NaOH solution in 1 mL intervals until the pH is close to 2.5, and then continue adding NaOH at 0.5 mL intervals. If you observe that the pH change is much greater than the previous step, further reduce the increment. If the pH increment is too small, increase the volume added.

Waste management: dispose of the solutions into the bottle labelled "phosphoric solutions".

## B) Buffer solution

In many chemical processes it is necessary to keep the pH of a solution constant, e.g. in the treatment of industrial waste water, in electrodeposition processes, and in the manufacturing of photographic materials. It is also important to keep the pH constant for the reactions taking place in living beings, since in many metabolic processes the function of the proteins depend on their structure, which in turn depends on the pH. For example, in the blood, the pH has to be around 7.4, in the saliva it should be around 6.8, and the enzymes in the stomach only work at *ca.* 1.5.

A solution that has the ability to maintain its pH constant upon addition of moderate amounts of acids or bases is called a *buffer* solution. These buffer solutions contain either a weak acid with a salt of the weak acid, or a weak base and a salt of the weak base; both components must be present in approximately the same ratio.

1) Preparation of a buffer solution at pH=7.

Method A: Using the titration curve obtained.

Determine the amount of sodium hydroxide necessary to reach this pH value by mixing it with the phosphoric acid solution. Check it by measuring the pH. Proceed to prepare a total of approximately 25 mL.

Method B: Using a salt of the acid.

The monohydrogen phosphate required is produced *in situ* according to the following reaction:



In order to do this, mix precise volumes of sodium hydroxide and sodium or potassium dihydrogen phosphate.

Weigh 0.7 g of sodium dihydrogen phosphate and dissolve it in 20 mL distilled water. Calculate the amount of 0.1 M NaOH necessary to reach a pH=7 solution. Check the pH.

2) Assessment of the buffering capacity.

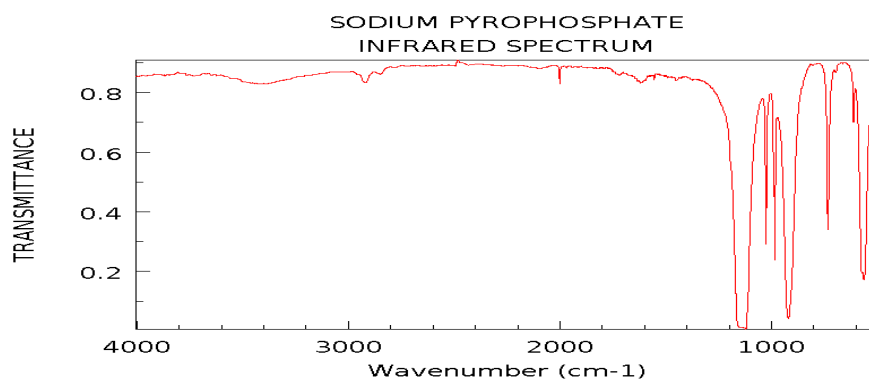
Place 20 mL of each of the two previously prepared buffer solutions in two 25 mL beakers. To the first, add 1 mL of 0.1 M HCl; to the second, add 1 mL of 0.1M NaOH. Repeat the experiment but replacing the buffer solution with 20mL of distilled water. Measure the pH of each solution.

Waste management: dispose of the buffer solutions into the bottle labelled “buffer pH=7”

### C) Preparation of tetrasodium pyrophosphate. (Optional)

Place 1.5g of sodium monohydrogen phosphate in a porcelain capsule and heat it up until complete removal of water. Remove the product from the capsule and weigh it when it is cold.

Register an IR and compare it with the pure sample.



Waste management: Dispose of the solid into the bottle labelled “pyrophosphate”

### ADDITIONAL QUESTIONS

1. From the titration curve, recalculate the titre concentration. Compare this value with the theoretical one.

2. If experiment C was carried out, calculate the mass of pyrophosphate that should be obtained if the yield were 100%. Compare this value with the experimental one and calculate the yield of the synthesis.
3. Plot the titration curve with Excel or other software.

*Traducido por Salvador Blasco*

## Session 7

# SULPHUR AND ITS COMPOUNDS

### INTRODUCTION

**(a) Presence in Nature.** Elemental sulphur is a yellow, insipid and odourless solid. It is soluble in water and in  $\text{CS}_2$ . It is widespread in the world. The most important sources of elemental S are native S deposits of volcanic origin. It also exists in the form of metallic sulphides ( $\text{ZnS}$ ,  $\text{FeS}$ ,  $\text{PbS}$ , ...) and earth-alkaline sulfates ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , ...). Additionally, sulphur is present in certain amino acids and is therefore an essential element for life.

**(b) Position in the Periodic System.** Sulphur is a non-metal which belongs to the same group as oxygen. These two elements, however, exhibit very different chemical and physical properties. These differences are due to several reasons:

- » The size of sulphur is about 60% bigger than oxygen; and as a consequence it is much more difficult for S to form strong double bonds like O.
- » S is less electronegative (2.5) than O (3.5).
- » S has vacant low-energy  $3d$  orbitals that can be used to complete the octet.

On the other hand, the S-S single bond is extraordinarily strong ( $270 \text{ kJ mol}^{-1}$ ) compared to O-O ( $145 \text{ kJ mol}^{-1}$ ). This entails a great tendency to *catenation*, or formation of compounds with chains of S-S bonds. In this sense, sulphur is the element second to carbon in terms of its capacity to form extended X-X-X single bonds.

**(c) Allotropy and Polymorphism.** The structure of elemental sulphur has been the theme of many studies. A considerable number of **allotropes** and **polymorphs** exist.

The best-known allotrope of sulphur is the  $\text{S}_8$  ring. This is the predominant form of sulphur vapour, and the constituent of the two common solid forms (polymorphs), **rhombic S** ( $\alpha\text{-S}_8$ ,  $d = 2.069 \text{ g cm}^{-3}$ ) and **monoclinic S** ( $\beta\text{-S}_8$ ,  $d = 1.94 \text{ g cm}^{-3}$ ) (see schemes in Fig. 2).



Rhombic S is the most stable form at low temperature, but is transformed into monoclinic S at  $95^\circ\text{C}$ , which in turn melts at  $120^\circ\text{C}$ . The molecular unit in both polymorphous cases is an 8-member  $\text{S}_8$  ring, which has a boat conformation. The rhombic  $\leftrightarrow$  monoclinic transformation consists, therefore, in a crystal structure change with no modification in the molecular constitution. This small transformation justifies the small transformation energy.

If heating is quick this transition does not take place, and the rhombic S instead melts at 113°C resulting in a shiny, fluid, yellow liquid. This liquid sulphur is also obtained from the melting of monoclinic S at 120°C.

Liquid sulphur has low viscosity due to the mobility of the S<sub>8</sub> rings. As the temperature rises the rings break to form radical chains of S<sub>8</sub> which then combine with each other to yield longer chains. The progressive increment in the chain size in liquid sulphur results in an increase in viscosity. Above 190°C its viscosity reaches its maximum. It is estimated that when these chains have the maximum size and contain about ~10<sup>5</sup> S atoms the sulphur turns dark. As the temperature increases, the liquid shows low viscosity again. The chains shorten (S<sub>8</sub>, S<sub>6</sub>, S<sub>4</sub>, S<sub>2</sub>) and there may even be free atoms which can move freely. Above 600°C, the species S<sub>2</sub> and S<sub>3</sub> predominate (analogue to O<sub>2</sub> and O<sub>3</sub>).

If a sudden cooling of boiling sulphur occurs (i.e. pouring it onto cold water) elastic fibres of reddish brown colour form. A new allotrope is generated, the amorphous or plastic S, composed of helicoidal linear chain -S<sub>n</sub>- of variable length. Its polymeric structure gives it mechanical properties similar to those of amorphous plastics. After enough time, the plastic S becomes brittle and finally reverts to the most stable form, rhombic S. Figure 1 summarizes these changes.

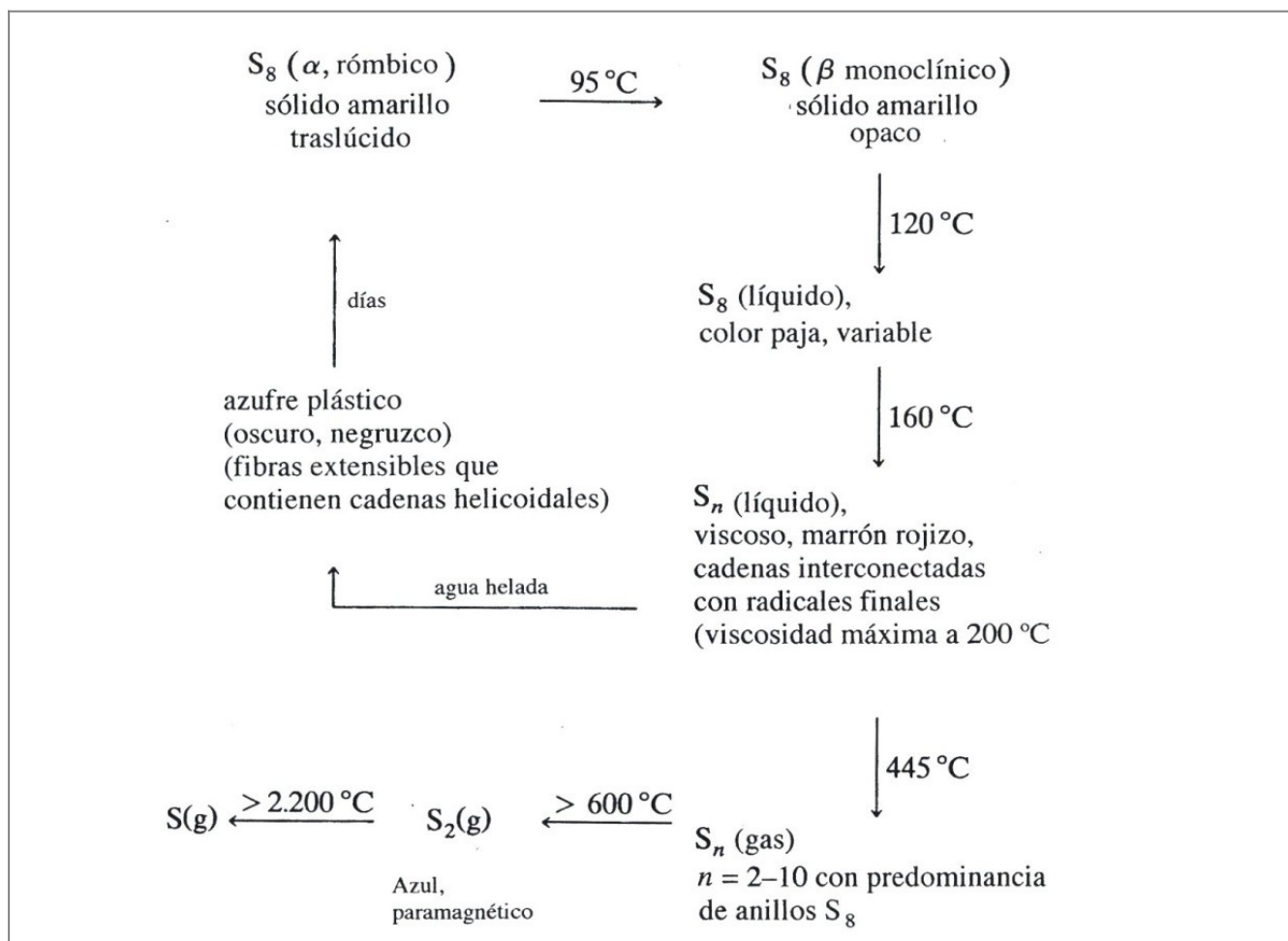
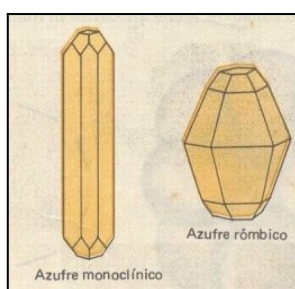
Furthermore, at least one additional allotropic form exists called colloidal S, which is obtained by thiosulfite disproportionation in acidic medium (HCl) which consists of 6-membered rings of S atoms.

**(d) Chemical properties.** Despite being in its native state, sulphur is moderately reactive. Every reaction requires an initial attack that opens the S<sub>8</sub> ring which entails an initial energetic cost.

Since sulphur is less electronegative than oxygen it can form compounds in which it is in a positive oxidation state. Sulphur can present oxidation states ranging from -2 to +6, including several "fractionary" or "mixed" states such as +2.5 in the tetrathionate ion (see Frost and Latimer diagrams in Figs. 3 and 4).

A great number of S compounds are known, although the most representative ones by importance and abundance are **sulphides**, **oxides** and **oxoacids** (among the latter, sulphuric acid stands out as the most important industrial inorganic chemical).

**Figure 1.** Most relevant allotropy/polymorphism in S with temperature.

Figure 2. Polymorphs of S<sub>8</sub>

## OBJECTIVES

1. To get familiar with elemental sulphur and its allotropic forms.
2. To observe the phase transitions that sulphur undergoes with temperature changes and the different properties of the obtained allotropic forms.
3. To synthesise a sulphur oxosalt with an unusual oxidation state.
4. To crystallise a product that is very soluble and thermally very unstable.


## PRELIMINARY QUESTIONS

1. Define the terms *allotrope* and *polymorph*.



2. True or False?: “Monoclinic S is an allotropic variant of rhombic S”
3. True or False?: “Colloidal S and plastic S are two polymorphs of S”
4. Draw the structure of S<sub>8</sub> and that of S<sub>6</sub>.
5. Write the most likely Lewis structure for thiosulfate and tetrathionate anions.
6. Calculate the oxidation state of S in thiosulfate and tetrathionate anions.
7. Look up information about the properties of tetrathionate.

## EXPERIMENTAL PROCEDURE

Material	Reagents
Grid of test tubes	Sulphur
Pyrex test tube	Carbon disulphide
Glass funnel	HCl 4M
Watch glass	0,1 M Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> solution
25 mL beaker	Concentrated solution NaOH
25 mL buret	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ·5H <sub>2</sub> O (s)
Large crystalliser	Iodine
Eppendorf tubes	NaCl (s)
Magnifier 	Ethanol
Pipette Pasteur	Ether
Cotton	

### I. ALLOTROPY/POLYMORPHISM OF SULPHUR

#### *Precautions and Safety*

The test tubes have to be perfectly dry.

CS<sub>2</sub> must be handled inside the fume hood: it is very volatile and it is toxic. Do not handle CS<sub>2</sub> in the proximity of a flame: it is highly flammable and forms explosive mixtures with air.

Sulphur heating must be carried out in a fume hood. It must be done slowly and aiming the tube away from any person. Brown stains indicate that it has been overheated.

#### *Experimental*

*Rhombic sulphur: crystallisation from S powder*

Weigh 0.01g of S powder and introduce it into an eppendorf tube. Add 0.5 mL of CS<sub>2</sub> (FLAMMABLE), close the eppendorf tube and shake the mixture. Next, pour it into a Pasteur pipette with a little piece of cotton inside so that the undissolved sulphur is filtered out. The filtrate is put onto a watch glass and the CS<sub>2</sub> is allowed to evaporate in a fume hood set aside for that purpose (it is convenient to put the watch glass inside an inverted glass funnel so that the evaporation is slower). Observe the crystals obtained with a magnifying glass. Describe its shape and name it. Compare with Fig 2. SEE ATTACHMENT I

Waste management: dispose of the eppendorf tubes closed into the bottle labelled "CS<sub>2</sub>".

*Monoclinic sulphur: preparation with temperature changes*

Prepare a piece of filter paper over a conical funnel, and a beaker with cold water. On a porcelain crucible, introduce 2.5g of sulphur and heat them with a Bunsen burner until the solid melts and a shiny, yellow fluid is formed. Quickly pour half of that fluid onto a previously prepared filter paper, and pour the other half onto the beaker containing water. The sulphur will be retained in the paper and crystallise onto it. Observe the formation of a crust by solidification of the liquid; the moment the liquid solidifies, the crust breaks opening the filter. The formation of crystals has to be observed. Note their shape and colour. Note also the shape and colour of the solid formed in the beaker containing water. SEE ATTACHMENT II

Waste management: dispose of the sulphur into the bottle labelled "S".

*Plastic sulphur (amorphous): obtained with temperature changes.*

Prepare a beaker with water. In a Pyrex tube introduce 2.5g of sulphur and slowly heat it with a Bunsen burner. During the heating, changes in fluidity and colour should take place. Write down the observations. Keep heating until the dark product (almost black) generated in the process becomes more fluid (this change coincides with the appearance of vapours). The dark liquid is poured onto the beaker with water. Write down the shape, colour and hardness of the product formed in the water.

Waste management: dispose of the sulphur into the bottle labelled "S".

Cleaning the Pyrex tube: The Pyrex tube with remainders of sulphur is put into a recipient set apart for that purpose which contains a concentrated solution of NaOH.

*Colloidal sulphur: obtained from a chemical process*

Introduce 2 mL of a 0.1 M sodium thiosulfate solution into a test tube. Next, add 1 mL of a 4 M HCl solution and mix. Note the colour and appearance of the product formed. Leave the solution for 30 minutes and observe any change after this time.

Waste management: dispose of the solution into the bottle labelled "thiosulfate/HCl".

## II. PREPARATION OF SODIUM TETRATHIONATE MONO-HYDRATE.

### *Safety*

The S-S bond in tetrathionate is very unstable towards a rise in temperature. In order to avoid decomposition, all the procedure must be carried out at a low temperature.

### *Experimental*

(a) *Preparation of solutions:* Prepare a saturated aqueous solution of sodium thiosulfate (11.5 g of thiosulfate in 10 mL of water) and another solution of iodine (3.00 g in 20 mL of ethanol). Introduce the thiosulfate solution into the burette. The ethanolic iodine solution is cooled down by putting the beaker into a larger vessel with ice (add some salt to the ice in order to decrease the melting point to less than 0°C).

(b) *Synthesis:* Next, add the thiosulfate solution dropwise onto the iodine whilst stirring until the iodine solution colour becomes a very pale yellow. If it goes colourless, add one or two extra crystals of iodine. Keep the resulting solution very cold in order to facilitate the crystallisation of the sodium tetrathionate while avoiding the decomposition.

Waste management: dispose of the remaining thiosulfate solution from the burette into the bottle labelled "thiosulfate waste".

The solid (powder) formed is filtered in a conical funnel with simple paper filter. Discard the filtrate. Rinse the solid with **cold** ethanol added very slowly with a **Pasteur pipette** until all the excess iodine has been removed (the yellow colour disappears).

Waste management: dispose of the rinse water into the bottle labelled "iodine/ethanol".

(c) *Recrystallisation (purification):* Redissolve the solid in the same funnel (it is advisable to hold the funnel with a ring or tripod), with the minimum amount of water (added dropwise; no more than 12 mL in total should be needed). The resulting solution is collected in a 100 mL

beaker and put onto ice (to which sodium chloride has been added). Add 25 mL of ethanol to the solution in order to facilitate the crystallisation of the product.

(d) *Filtration and drying*: When half an hour has elapsed, filter the crystalline product obtained with Buchner funnel, maintaining everything cold. DO NOT WASH WITH WATER. Rinse with small amounts of cold ethanol (*ca.* 5 mL) and ether. DO NOT DRY IN THE OVEN. Dry on filter paper and then weigh it.

Waste management: dispose of the solid into the flask labelled "tetrathionate".

### ADDITIONAL QUESTIONS

- Which allotropic/polymorphic varieties are obtained from the experiences in part I? (Build a TABLE that summarises the observations).
- Explain the changes in viscosity observed during the formation of the plastic S.
- Why are the remainders of S washed away with concentrated NaOH?
- Write and balance the reaction of formation of the colloidal S.
- Write and balance the reaction for the synthesis of tetrathionate synthesis.
- Calculate the  $\Delta E^\circ$  of the previous reaction and check that it is spontaneous in standard conditions.
- Calculate the yield of the synthesis. Discuss the result. How could the yield be improved?

Figure 3. Latimer diagrams of S.

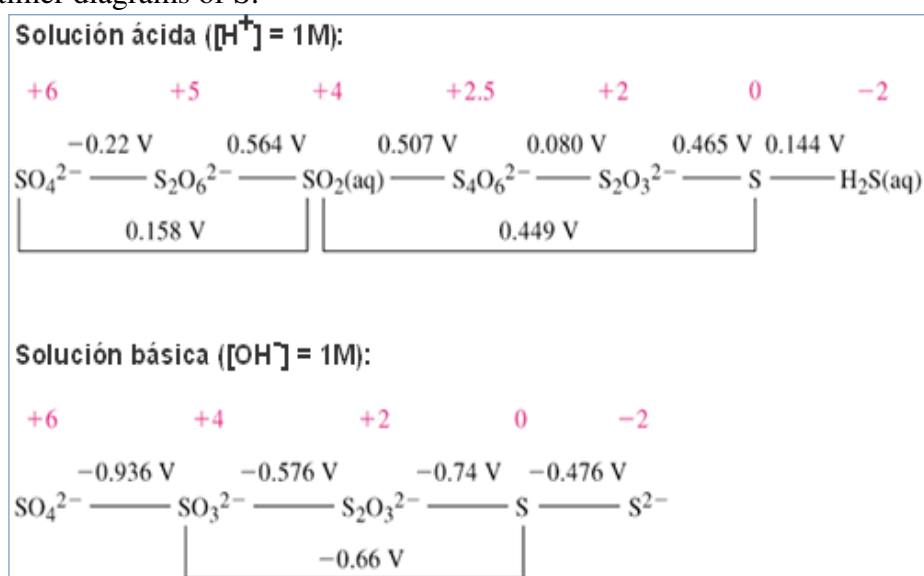
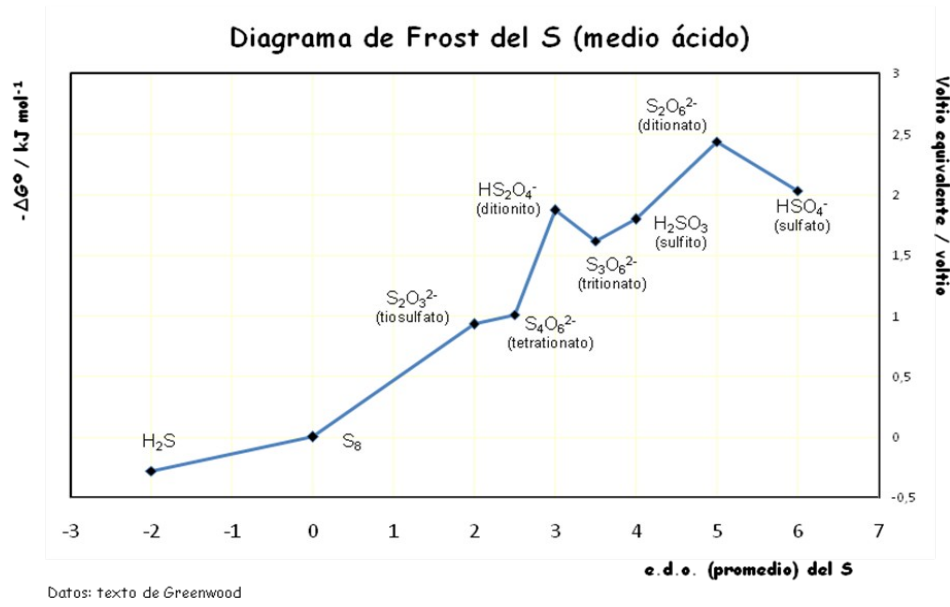


Figure 4. Frost diagram of S (acidic conditions).



### Attachment I



### Attachment II



Traducido por Salvador Blasco

## Session 8

# SYNTHESIS OF H<sub>2</sub>SO<sub>4</sub> USING THE CONTACT METHOD: CATALYTIC OXIDATION OF SO<sub>2</sub> to SO<sub>3</sub>

### INTRODUCTION

Catalytic oxidation of SO<sub>2</sub> to SO<sub>3</sub> is the most important reaction in the manufacturing process of sulphuric acid. Pure sulphuric acid is a thick, oily, liquid which boils at 290 °C and then decomposes releasing SO<sub>3</sub> gas and water. After this point, when a composition of 98.3% and a boiling point of 317 °C is reached, the composition remains constant, yielding the familiar sulphuric acid used in the laboratory (18 M), which is extremely corrosive and must be handled with care. When water is added to the concentrated acid, a great amount of heat is generated due to the formation of hydrates. For this reason, when diluting concentrated sulphuric acid, the acid is slowly added to cold water with constant stirring (*water should never be added to the concentrated sulphuric acid*). Sulphuric acid is a good oxidant, a diprotic acid and a good dehydrating agent.

At an industrial level, it is the most manufactured chemical (e.g. in the USA, in 2000, 44×10<sup>6</sup> tons were manufactured). The quantity of sulphuric acid consumed by one country's industry used to be taken as a direct indicator of the level of industrialisation of that country. Among its many applications, the manufacturing of fertilisers (superphosphate and ammonium sulphate) deserves mentioning, also the leather, tin, pigments, detergents, explosives, plastics, herbicides, oil refining, and textile industries, as well as many industrial organic chemistry applications that are also very important.

### OBJECTIVES

In this session we aim to reproduce the industrial process for the manufacturing of sulphuric acid, but at a laboratory scale. In addition to illustrating the reactions of sulphur with oxygen and the use of catalysts, this experiment will highlight the need for a thermochemical study of the process in order to select the optimal working conditions.

The process can be broken down into three stages:

1<sup>a</sup>. - Oxidation of S to SO<sub>2</sub>, simply by combustion of sulphur in air.

2<sup>a</sup>. - Catalytic oxidation of SO<sub>2</sub> to SO<sub>3</sub>.

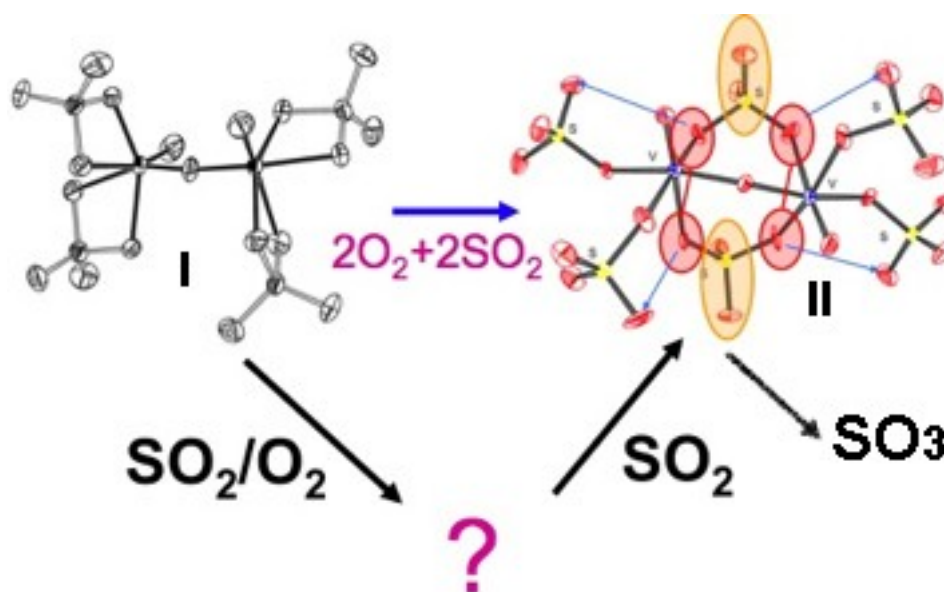
3<sup>a</sup>. - Formation of H<sub>2</sub>SO<sub>4</sub> by reaction of SO<sub>3</sub> with water (since the reaction of SO<sub>3</sub> with water is slow, in practice it is more convenient to fixate SO<sub>3</sub> as Na<sub>2</sub>SO<sub>4</sub> by reaction with an aqueous solution of NaOH)

For the second stage, a vanadium catalyst will be used.

*The catalytic process.*

The catalyst is composed of  $V_2O_5$  and  $K_2S_2O_7$  scattered onto an inert support. The active phase is melted over  $400^\circ\text{C}$ . For the catalyst to be active, it has to be pre-heated to  $400^\circ\text{C}$  for several hours, and then saturated with a  $\text{SO}_2$  current.

Two species that are assumed to participate in the process have been characterised. These are the salts of the anions  $[(VO)_2O(SO_4)_4]^{4-}$  (I) and  $[(VO)_2O(SO_4)_6]^{8-}$  (II).



Although several mechanisms have been proposed, the specific details are still unclear. It is well established that the first stage in the process is that species I is saturated with  $\text{SO}_2$  and  $\text{O}_2$  to form species II. Both species have been confirmed by X-ray diffraction. It follows, then, that when using a new batch of catalyst, larger amounts of sulphur have to be used. The professor will discuss the appropriateness of using more than 2g of sulphur.

This is not the only catalytic process whose specific mechanism is not clearly established. The synthesis of ammonia is another example.

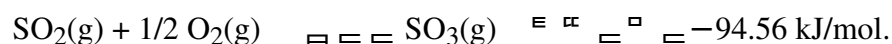
### PRELIMINARY QUESTIONS

1. - Discuss the most adequate conditions of  $P$  and  $T$  in order to carry out the following reaction:



Why is pre-heating is required to initiate the reaction?

2. - The synthesis of  $\text{SO}_3$  is carried out according to the following reaction:



This reaction is slow. Comment on the most favourable  $P$  and  $T$  conditions to carry out the aforementioned reaction.



3. - Every catalyst is most efficient at a particular temperature. For the conversion of  $\text{SO}_2$  to  $\text{SO}_3$ , the most convenient catalysts and their optimal working temperature are:

Catal.	Pt	$\text{Fe}_2\text{O}_3$	$\text{V}_2\text{O}_5$
T/°C	400 $\approx$ C	600 $\approx$ C	400 $\approx$ C

Which is the most appropriate?

4. - What is the problem with direct  $\text{SO}_3$  absorption into pure water?

5. - What safety measures should be in place for this experiment?

### EXPERIMENTAL PROCEDURE

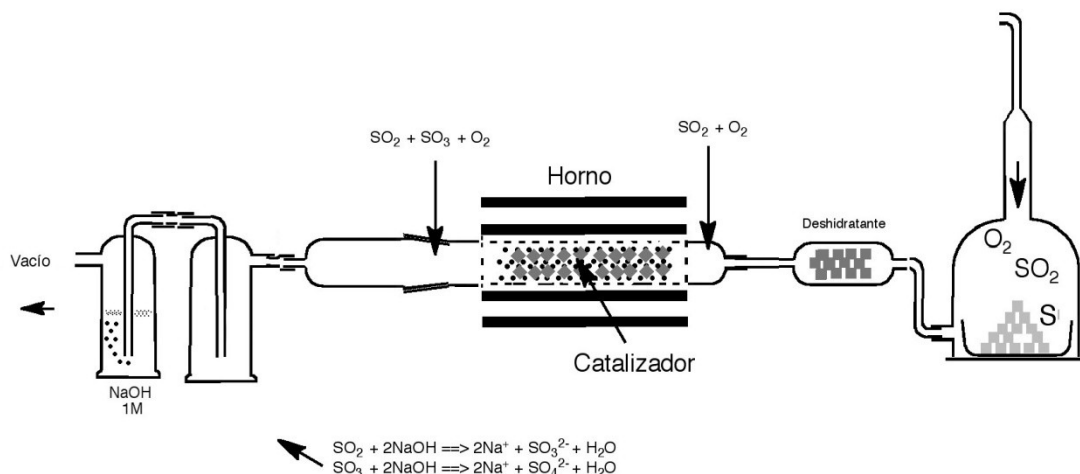
Material	Reagents
Tubular oven	Drying agent
Rubber tubes	Potassium Iodide
Rubber lids	0.5M and 6M hydrochloric acid
Tube for drying	Sugar
Refractory glass tube for combustion (T ~ 500 °C)	Coal
Bubblers	Catalyst $\text{V}_2\text{O}_5$ and $\text{K}_2\text{S}_2\text{O}_7$
Vacuum and compressed air system	0.05M potassium triiodide
Porcelain capsule	Sulphur
Burner, tripod and grid	1 M NaOH solution
Test tubes	Starch indicator solution
50 and 25 mL burettes	Concentrated and diluted sulphuric acid
250 mL conical flask	Phenolphthalein indicator solution
Glass wool	$\text{Ca}(\text{OH})_2$ saturated solution
	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

### Synthesis of $\text{H}_2\text{SO}_4$

#### Set up:

The catalyst has to be pre-heated prior to the start of the reaction. Therefore, place it in the oven at 490°C.





The sulphur combustion chamber has an air inlet on top. Inside the chamber, the porcelain capsule containing a weighed amount of sulphur powder is placed. The outlet at the bottom is directly connected to the tube with the drying agent, which is subsequently connected to the tubular oven that contains the catalyst.

The oven outlet is connected to a bubbler containing 75 mL of 1M NaOH. In this bubbler the sulphur oxides are collected as sodium salts.

#### *Procedure.*

1. Prepare the set-up and introduce the drying agent into the corresponding tube.
2. In the porcelain capsule, weigh *ca.* 2.0g of sulphur. Write down the weight of the capsule containing the sulphur.
3. Raise the burning chamber and introduce the capsule. Close the chamber, making sure that the contact of the glass with the rubber bottom is properly sealed in order to avoid SO<sub>2</sub> leaks.
4. Introduce 75 mL of NaOH 1M into the bubbler.
5. Light the top of the sulphur with a lighter until a blue flame is observed. That indicates that the sulphur has been ignited and the combustion has begun. Then, close the burning chamber to avoid SO<sub>2</sub> leaks.
6. Connect the vacuum system to the last bubbler.
7. If the flame fades before most of the sulphur is consumed, light it again with the lighter.
8. After 15-20 minutes, when most of the S is consumed, quench the combustion and to conclude the reaction. Then unplug the NaOH bubbler and turn off the vacuum.
9. Proceed with:
  - a) Weigh the capsule once it reaches room temperature, in order to evaluate the amount of sulphur that reacted.

- b) Analyse the contents of the 1 M NaOH solution in the intermediate bubbler.

### DETERMINATION OF THE H<sub>2</sub>SO<sub>4</sub> OBTAINED

The reactions that took place are written in the set-up scheme. The remaining NaOH in the bubbler is determined by titration with 0.5M HCl solution. This information will allow us to calculate the total amount of SO<sub>2</sub> and SO<sub>3</sub> that the NaOH solution has captured. The titration of the same solution with 0.05M iodine will enable us to calculate the amount of Na<sub>2</sub>SO<sub>3</sub> retained in the flask.

1. *Determination of the total number of moles of SO<sub>2</sub> y SO<sub>3</sub> retained.* Introduce 10 mL of the NaOH solution into a 250 mL conical flask and then add two drops of phenolphthalein. Titrate it with a 0.5M HCl solution using the 25 mL burette.

By calculating the moles of NaOH consumed, we can calculate the moles of SO<sub>2</sub> + SO<sub>3</sub> obtained from the combustion of S that reacted with the NaOH.

2. *Determination of the SO<sub>2</sub> with iodimetric titration.* When the previous titration is finished, add some drops of 6 M HCl in order to ensure an acidic environment. Add the indicator (between 1 and 2 mL of the starch solution) to the solution and titrate it with the 0.05M potassium triiodide solution using the 25 mL burette.

- i) Write and balance the redox reaction that is taking place.
- ii) Calculate the total amount of SO<sub>2</sub> retained.

Waste management: introduce the solutions resulting from the titration into the bottle labelled "iodide/sulphate".

3. With the result of both titrations:

- i) Calculate the amount of SO<sub>3</sub> formed.
- ii) Calculate the conversion % from S to SO<sub>3</sub>.

### ADDITIONAL ASSAYS

1. - Place some crystals of copper(II) sulphate pentahydrate into a test tube and then cover it with concentrated sulphuric acid. Gently heat the mixture and note any change in the visual appearance of the salt.

**Waste management: introduce the solution into the bottle labelled "CuSO<sub>4</sub>/sulphuric acid".**

2. - Place 0.5 g of sugar into a test tube and then add concentrated sulphuric acid dropwise until the sugar turns black. Note any transformation that might occur.

**Waste management: introduce the solution into the bottle labelled "C/sulphuric acid".**

3. - Place a small amount of potassium iodide into a test tube and add two drops of concentrated sulphuric acid. If no changes are observed, heat the tube gently and add some distilled water. Write any change you observe.

**Waste management: introduce the solution into the bottle labelled “I/sulphuric acid”.**

4. - Heat in a tube, 1.0g of coal with 3 mL of concentrated sulphuric acid and collect the gas released into a second test tube containing a 0.05 M potassium permanganate solution previously acidified with a few drops of diluted sulphuric acid. The gas released from this tube is passed through a third tube containing a calcium hydroxide solution (see figure). Note any changes.

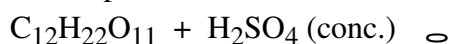
**Waste management: introduce the solutions, when the experiment is finished, into the bottles labelled “Mn” y “Ca(OH)<sub>2</sub>”**

5. - Which properties of sulphuric acid do the previous tests demonstrate?

### ADDITIONAL QUESTIONS

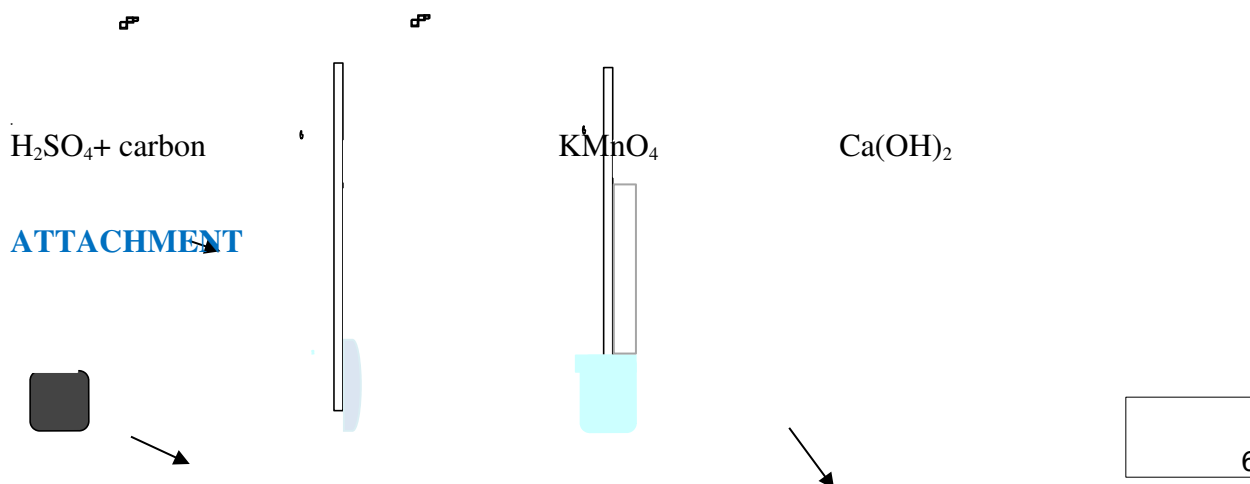
1. - In the contact process for the synthesis of sulphuric acid, what are the roles of the calcium chloride, the vacuum system, and the soda solution?

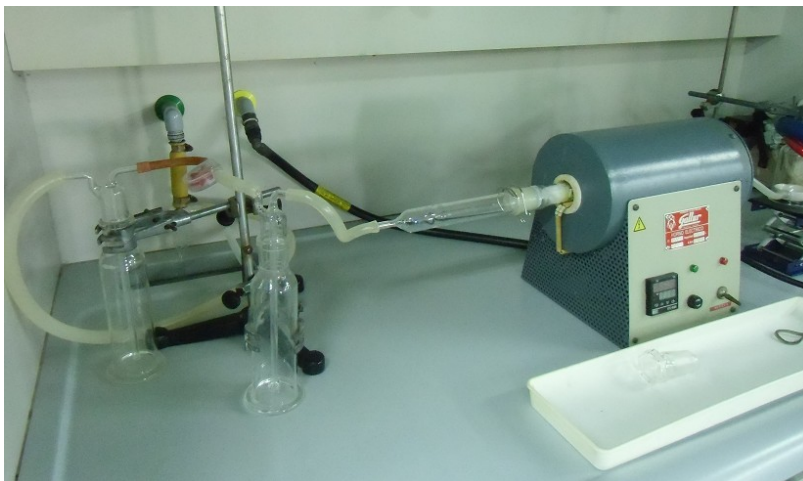
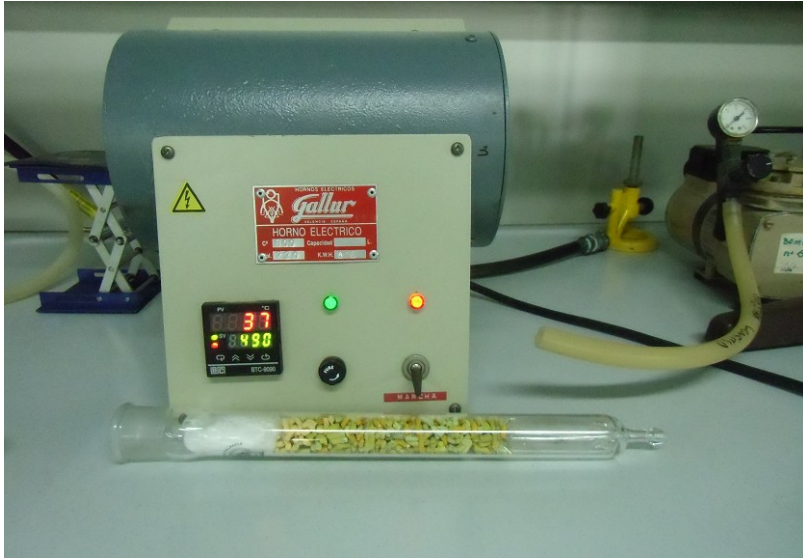
2. - Complete and balance the following reactions:



### ADDITIONAL BIBLIOGRAPHY

J. A. Martin et al.; *J. Chem. Educ.*, **1975**, 52,188.





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## Session 9

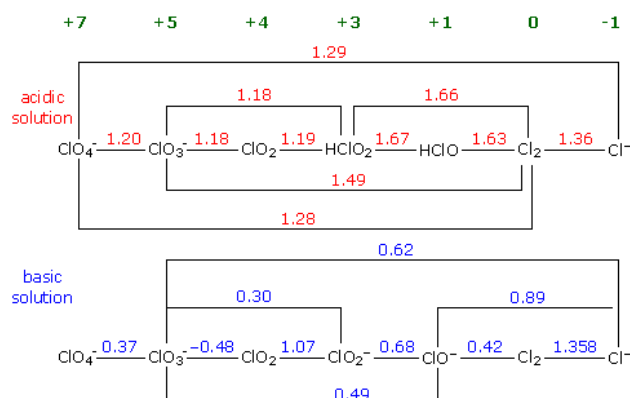
# HALOGENS: REACTIVITY AND PROPERTIES

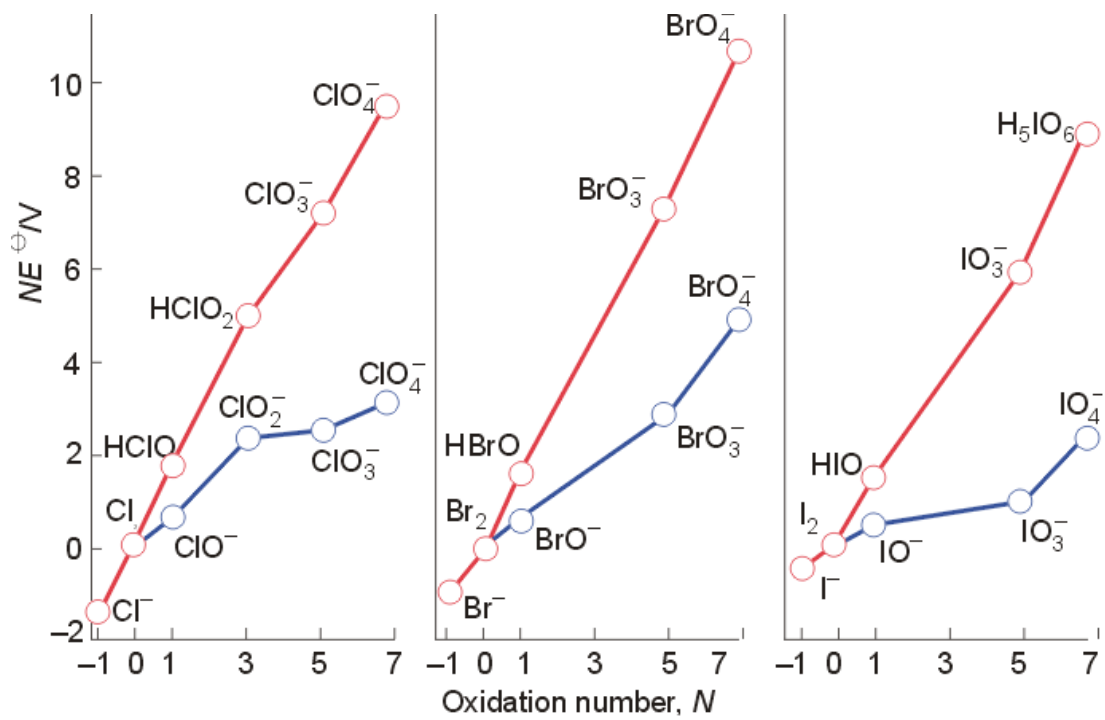
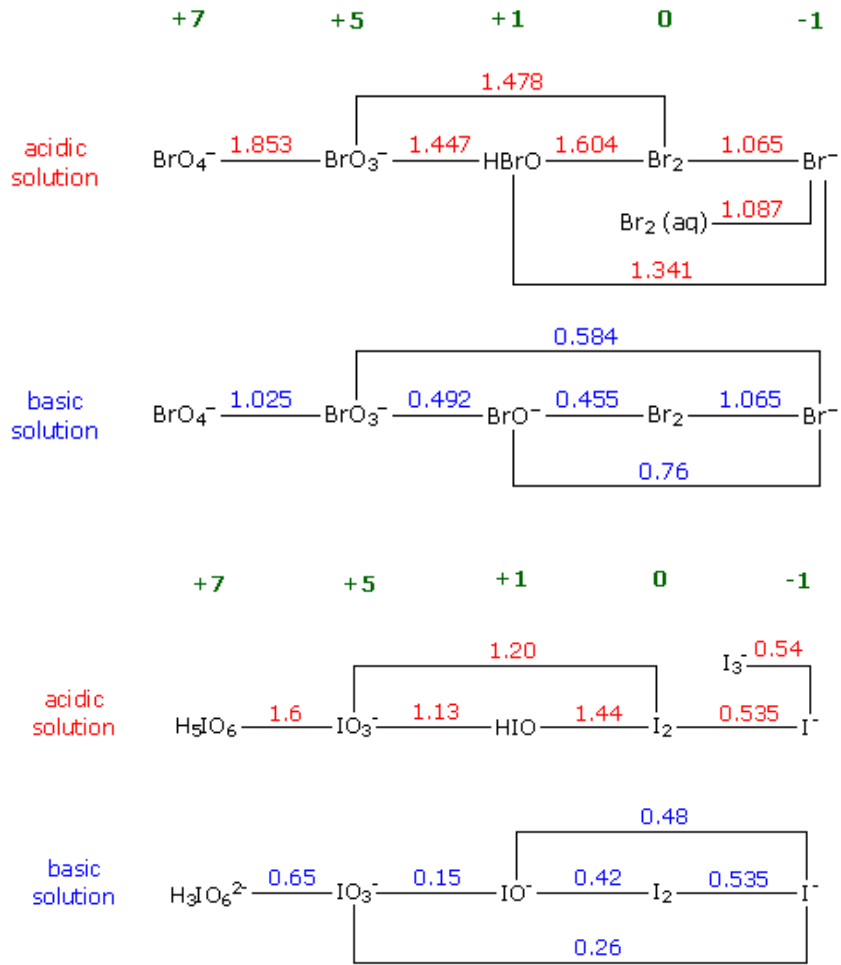
### INTRODUCTION

**Halogens** (from Greek *hals*, 'salt' and *genes*, 'generator', *salt generator*) constitute **group 17** in the periodic table. This is the one and only group in the periodic table that contains elements in all three states of matter at standard pressure and temperature; gas (fluorine, chlorine), liquid (bromine) and solid (iodine, astatine). They are very electronegative ( $\chi_{\text{Pauling}} \geq 2.5$ , according to the Pauling scale), in fact fluorine is the most electronegative element in the periodic system. In elemental state they are powerful oxidants (in particular,  $\text{F}_2$ ,  $\text{Cl}_2$  and  $\text{Br}_2$ ). It is worth remarking that fluorine is able to oxidise most of the elements to their highest oxidation state. In short, the strong reactivity is associated to its electronic configuration ( $ns^2 np^5$ ) and its marked tendency to form mononegative anions  $\text{X}^-$  (*halides*).

	F	Cl	Br	I
$\chi(\text{Pauling})$	3.98	3.16	2.96	2.66
$\Delta H_{\text{at}}(\text{X}_2)$	79	122	96	76
AE (X)	333	348	351	305
$E^\circ(\text{X}_2/\text{X}^-_{(\text{aq})}, \text{V})$	3.05	1.36	1.10	0.54

The diagrams of oxidation states (Latimer and Frost) contain all the information summarised for the corresponding redox pairs that a particular element can present, and therefore allow us to make predictions about the stability and reactivity of each of the species. These diagrams are very useful for halogens which present many possible oxidation states.





One very interesting and remarkable aspect about halogens is their different colours. Fluorine is colourless, chlorine is a yellowish-green gas, bromine is a red liquid, and iodine is a violet solid (which sublimates releasing violet vapours). The colour in the gas phase can be interpreted from the MO diagram of the  $X_2$  molecules with a transition from the  $\sigma_g^*$  level (occupied) to the  $\sigma_u^*$  level (empty). The interpretation of the colour in solution is more complex. It is experimentally verified that the colour of the halogen strongly depends on the donor properties of the solvent. Those with little donor capacity give solutions with a colour similar to that of the gas because the energy of the molecular orbitals is not significantly altered. In solvents with a greater donor capacity, the LUMO  $\sigma_u^*$  of the halogen acts as electron acceptor, producing a weakening of the X-X bond and modifying the energy of the electronic transitions. The  $\sigma_g^* \rightarrow \sigma_u^*$  transition generally takes place in the visible range of the spectrum (between 400 and 550 nm approximately, depending on the solvent). On the other hand, in the range between 200-300 nm a much more intense band appears associated to charge transfer.

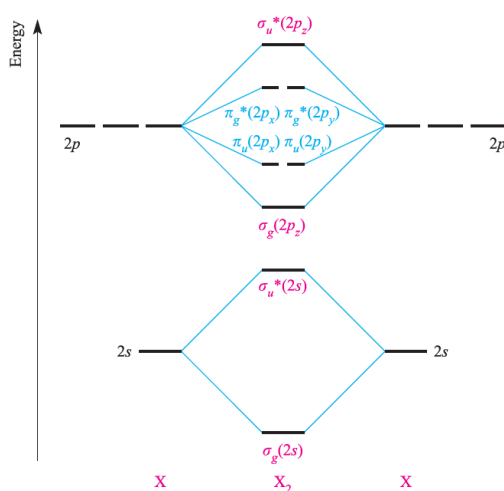


Diagram of energy of molecular orbitals for the molecules  $X_2$  ( $X = F, Cl, Br$  and  $I$ ) with electronic configuration  $2s^2 2p^5$ .

(Source: Inorganic Chemistry. Housecroft and Sharpe (second edition) Fig.1. 21. Chapter 1, page 34)

## OBJECTIVES

- 1.- To study the colour of iodine in different solvents spectroscopically.
- 2.- To study redox reactions of certain compounds with halogens.

## PRELIMINARY QUESTIONS

1. Indicate and justify which of the following species will spontaneously disproportionate in basic media: dichlorine, chlorite, bromate, hypiodite. Write down the corresponding chemical reactions for each case.

2. The study of the reactivity of  $F_2$  has been deliberately omitted in this session. Give a reason for this.
3. Calculate the reduction potential of the  $BrO_3^-/Br^-$  couple in acidic medium.
4. Solid iodine is not very soluble in water (0.029 g in 100 mL at 20 °C). However, its water solubility increases considerably in the presence of iodide ions. Give an explanation for this phenomenon.
5. Describe briefly the starch test for the presence of iodine.

## EXPERIMENTAL PROCEDURE

Material	Reagents
Spectrophotometer	Iodine
100 mL conical flask	Ethanol, hexane, toluene, $CCl_4$
100, 150 and 250 mL beakers	$KBrO_3$ (s)
Chlorine generator device	$H_2SO_4$ 1M
Test tubes	KI(s) and solution 0,1 M
Pipette Pasteur	Cr(III) solution
	Starch
	Concentrated HCl
	NaOH (s)
	Acetone
	$KMnO_4$ (s)

### 4.1. Measuring Iodine UV-visible spectra in several solvents

- a) Take a small portion of each of the prepared iodine solutions in  $H_2O$ , ethanol, hexane, carbon tetrachloride and toluene, and introduce them with a Pasteur pipette into the UV-visible cuvette.
- b) Register the UV-visible spectrum for each one in the range 400-700 nm (it is necessary to correct the baseline by measuring a blank with solvent prior to that).
- c) Determine the values of  $\epsilon_{max}$  for the different peaks in the spectrum.
- d) Classify the solvents according to their donor ability.

### 4.2. Experiments to illustrate the oxidative capacity of the bromate ions.

#### 4.2.1. Preparation of the solution.

- Dissolve 0.1 g of starch in 10 mL boiling water.



- Dissolve 1g of  $\text{KBrO}_3$  in a 100 mL mixture of 94 mL distilled water and 6 mL 1 M  $\text{H}_2\text{SO}_4$ .
- Dissolve 0.1 g of KI in 10 mL distilled water.

4.2.2. In a 150 mL beaker introduce 25 mL of distilled water, 2 mL of the previously prepared starch solution and 1 mL of 1M  $\text{H}_2\text{SO}_4$ , two drops of the bromate solution and 1 mL of the KI solution. Observe and note any change. Use the oxidation states diagrams to indicate all the reactions that might have taken place, and what the final reaction products are.

4.2.3. Add the rest of the bromate solution to the solution resulting from the previous reaction. Observe and note any change for approximately 10 minutes. Use the oxidation states diagrams to indicate all the reactions that might have taken place and what the final reaction products are.

Waste management: introduce the solutions into the bottle labelled "halogen waste"

#### 4.3. Experiments to illustrate the oxidative ability of elemental chlorine.

***(Warning: this experiment must be carried in the fume hood under the professor's supervision).***

Use the set-up prepared in the fume hood to generate a chlorine gas stream. Then carry out the following experiments:

4.3.1. Pass a chlorine stream through a test tube containing 2 mL of a 0.1M KI solution.

Waste management: dispose of the waste into the bottle labelled "iodine waste".

4.3.2. Pass a chlorine stream through 1 mL of a 0.1 M of a Cr(III) salt solution to which one tenth of NaOH has been added. After that, heat up the tube.

Waste management: dispose of the waste into the bottle labelled "Cr(VI) waste".

4.3.2. Pass a chlorine stream through a dry test tube containing 0.05g of solid iodine.

Waste management: dispose of the waste into the bottle labelled "I/Cl waste".

#### ADDITIONAL QUESTIONS

Write down and balance all reactions taking place in the experiments carried out which justify the results observed.

### **ADDITIONAL BIBLIOGRAPHY**

C.E. Ophardt, *J. Chem. Educ.* 1987, 64, 807-808.

*Traducido por Salvador Blasco*

## Session 10

# SYNTHESIS OF SODIUM METAPERIODATE NaIO<sub>4</sub>

### INTRODUCTION

At least four periodic acids are known, related to each other by complex solution equilibria involving deprotonation, dehydration and aggregation processes. In the table below is a summary of these processes:

Formul	Name	Formal relation to H <sub>5</sub> IO <sub>6</sub>
<b>a</b>		
H <sub>5</sub> IO <sub>6</sub>	orthoperiodic	
HIO <sub>4</sub>	metaperiodic	<i>Elimination of two water molecules from H<sub>5</sub>IO<sub>6</sub></i>
H <sub>6</sub> I <sub>2</sub> O <sub>10</sub>	mesoperiodic (diperiodic)	<i>Condensation of two H<sub>5</sub>IO<sub>6</sub> molecules with H<sub>2</sub>O elimination.</i>
H <sub>7</sub> I <sub>3</sub> O <sub>14</sub>	triperiodic	<i>Condensation of three H<sub>5</sub>IO<sub>6</sub> molecules with H<sub>2</sub>O elimination.</i>

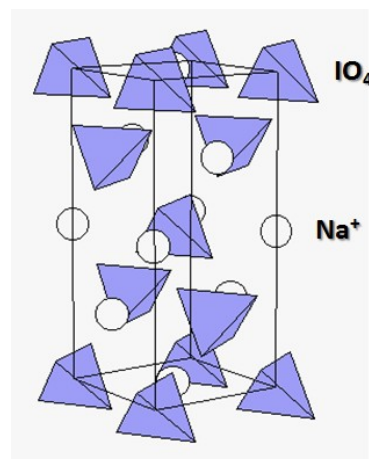
Periodates can be obtained by oxidation of I<sub>2</sub> or IO<sub>3</sub><sup>-</sup> by chemical (such as the one to be carried out in this session) or electrochemical methods. In general, the species obtained is the [(OH)<sub>3</sub>IO<sub>3</sub>]<sup>2-</sup> anion which can be converted to other periodate oxoanions by modifying pH and temperature in a controlled manner.

The aim of this session is the synthesis of sodium metaperiodate in three stages:

a) synthesis of IO<sub>3</sub><sup>-</sup> ions by iodine oxidation with chlorate ions;

b) oxidation of the iodate ions to [(OH)<sub>3</sub>IO<sub>3</sub>]<sup>2-</sup> by oxidation with peroxodisulfate.

c) transformation of [(OH)<sub>3</sub>IO<sub>3</sub>]<sup>2-</sup> ions into metaperiodate ions by acidifying the solution and subsequently crystallising the NaIO<sub>4</sub>.

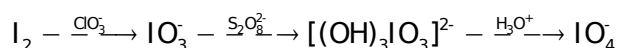


Sodium metaperiodate is a colourless, water soluble, crystalline solid ( $\rho = 3.9 \text{ g cm}^{-3}$ ), which decomposes at over  $300 \text{ }^\circ\text{C}$  with oxygen release to form sodium iodate. It crystallises in a tetragonal system and its crystal structure can be described as the periodate anion packing ( $d_{100} = 178 \text{ pm}$ ) with sodium cations.

The applications are based in its oxidative power. For example, it is used to oxidise cellulose and create a biocompatible, biodegradable compound which has surgical or drug dosing applications.

### PRELIMINARY QUESTIONS

1. Read the experimental section carefully and draw a flow chart for the synthesis of NaIO<sub>4</sub>.
2. Write and balance the chemical equations for all the processes involved in the transformation of elemental iodine into metaperiodate ions:



3. Look up for the redox potentials for the pairs IO<sub>3</sub><sup>-</sup>/I<sub>2</sub> and ClO<sub>3</sub><sup>-</sup>/Cl<sub>2</sub>. From these data, justify the spontaneity of the reaction between them.
4. Look up the formula of sodium peroxodisulfate in the bibliography. Draw its Lewis structure and highlight the *peroxo* group. Write down the corresponding semi-reaction for the reduction to sulphate.

### EXPERIMENTAL PROCEDURE

Material	Reagents
100 mL erlenmeyer flask	Sodium chlorate(s)
250 mL beaker	Iodine(s)
100 mL beaker	HNO <sub>3</sub> concentrated
Small Buchner and filtration flask	NaOH(s)
Graduated cylinder	Sodium peroxodisulfate(s) Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub>
Hot plate	0.1 M Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> solution
Watch glass	Borax. Na <sub>4</sub> B <sub>2</sub> O <sub>7</sub> ·10H <sub>2</sub> O
Grid	KI
Mortar and pestle	Boric acid H <sub>3</sub> BO <sub>3</sub>
10 mL burette	Starch solution 1%

### 3.1 Synthesis of sodium metaperiodate

In a 100 mL conical flask introduce 3.13g of  $\text{NaClO}_3$  and dissolve it in 12.5 mL of water. After acidifying the solution with 4-5 drops of concentrated  $\text{HNO}_3$ , add 2.5 g of crushed  $\text{I}_2$  and stir. The oxidation of  $\text{I}_2$  by chlorate ions is produced upon gently heating the flask ( $50\text{ }^\circ\text{C}$ ) on the hot plate in the **fume hood**. It is advisable not to heat the mixture too much since iodine sublimation may occur. In order to avoid losses, close the mouth of the flask with an inverted small beaker or a cold finger that fits properly. The reaction is complete in around 30-45 minutes (the end point corresponds with the loss of colour in the solution).

Pour the contents of the flask into a 100 mL beaker and add 20 mL of distilled water which is used to wash the conical flask. While the solution is still hot, add 1g of  $\text{NaOH}$ . Heat the mixture to near boiling point and add 5.5g of sodium peroxodisulfate. Once everything is dissolved, slowly add another 4.25g of  $\text{NaOH}$ . Heat the solution for 30 min in a boiling water bath. Let it cool down to room temperature and filter in a Buchner funnel and wash with cold water. Transfer the precipitate to a 100 mL beaker and add 7.5mL of distilled water. Heat the mixture to boiling point and slowly add 6 mL of a solution 1:1v/v of  $\text{HNO}_3$  and distilled water. When the solid is dissolved, concentrate in a boiling water bath (Bunsen burner and grid) until small crystals appear. Let the mixture cool down to room temperature and vacuum filter it, rinsing twice with cold water. Dry the product in an oven at  $110\text{ }^\circ\text{C}$  and weigh it. The yield will be calculated once the purity is known (see next section).

### 3.2. Volumetric determination of periodate

The procedure for the analysis of the periodate content of a solution is based on the fact that, in alkaline medium, periodate oxidises iodide to iodine whilst reducing itself to iodate, and the iodine generated can be titrated with thiosulfate.

Weigh approximately 0.100g (with 0.001g precision) of sodium periodate (prepared in the previous section) and dissolve it in 100 mL of water. Add 2g of borax and saturate the solution with 4.5g of boric acid. Add 3.0g of  $\text{KI}$  to the resulting solution and let it settle for 3 minutes. Next, titrate the iodine liberated with a 0.1M sodium thiosulfate solution, stopping at the point where the solution becomes pale yellow. At this point, add 2 mL of freshly prepared starch water and the solution will become blue, from the starch-iodine complex. Resume the titration

until the blue colour is gone for about 30 seconds. Write the volume  $V_1$  of the thiosulfate solution used.

Waste management: introduce the waste from the titration into the bottle labelled "metaperiodate titration waste".

Introduce the remaining metaperiodate solution into the bottle labelled "synthesised metaperiodate".

### ADDITIONAL QUESTIONS

1. Calculate the maximum amount of product that can be obtained assuming that all the initial iodine is converted to periodate. Next, calculate the yield assuming that the obtained periodate is 100% pure.
2. Write and balance all the reactions taking place during the periodate titration.
3. Why is an excess of potassium iodide used in the periodate titration?
4. Justify the effect of pH in the periodate titration.
5. With the result of the titration, calculate the purity of the sodium periodate synthesised and correct the yield.

## Session 11

# COMPARATIVE STUDY OF THE CHEMICAL BEHAVIOUR OF THE METAL IONS OF THE 'S' BLOCK

### INTRODUCTION

The *s* block is composed of two groups of elements: the alkalines and earth-alkalines, and their chemistry is one of the simplest in the whole periodic system. The alkalines give univalent cations and the earth-alkalines, divalent cations. In the latter case, the solvation energy of the dissolved  $M^{2+}$  salts, or the lattice energy of the ionic solids, compensates for the high ionisation energy. All the *s*-block elements are strongly electropositive. The alkaline elements are more reactive than the earth-alkaline elements, and the reactivity increases down the group. Although most of the compounds are ionic, beryllium compounds show some covalent character due to the high charge/radius ratio for Be(II). This covalent character is also highlighted in the chemistry of Mg(II), although not so markedly, and the rest of the elements in the group display ionic character in all of their compounds. When the alkaline metals are heated in air, the major products are the corresponding metal oxides (Li), peroxides (Na) and superoxides (K, Rb and Cs). The oxides of those other than Li can be obtained by thermal decomposition of the peroxides (Na) and superoxides (K, Rb and Cs). Regarding the earth-alkaline metals, Be yields the oxide while Mg, Ca, Sr and Ba give either the oxide or the peroxide. The tendency to form complexes is poor for both groups compared to transition metals. Nevertheless, earth-alkaline metals can form more, and more stable, coordination compounds than alkaline metals. The physical and chemical properties of both the elements and the compounds vary smoothly along the group, simplifying the study of their properties.

### OBJECTIVES

- 1) To prepare and characterise barium peroxide.
- 2) To comparatively study the solubility of some earth-alkaline salts, stressing how concepts such as lattice energy, solvation energy, and charge/radius ratio of the ions in question can qualitatively explain the observed variations.
- 3) To study the colour of certain *s*-block elements in a flame.

## PRELIMINARY QUESTIONS

- 1 Draw a flow chart for the synthesis of barium peroxide.
- 2 What is the concentration in mol/L of 20 volume hydrogen peroxide?
- 3 In the experiments to be carried out, the salts of beryllium, radium and francium have been disregarded. Give some reasons for these omissions.
- 4 What is the "flame test" of alkaline elements based on? Why is it especially useful for these elements?
- 5 Indicate how, in the group of earth-alkaline elements, the solubility should vary for hydroxides, carbonates, fluorides and sulphates, according to the rule that states "*small cation precipitates with small anion and large cation precipitates with large anion*".

## EXPERIMENTAL PROCEDURE

Material	Reagents
Test tubes and grid	Saturated solutions of: Li, Na, K, Rb salts
Centrifuge tubes	0.1M solns. of Mg, Ca, Sr, Ba chlorides
Buchner funnel	Chromium(III) chloride 0.1 M
Watch glass	Carbonate-free 3 M NaOH
100 mL beaker	Ammonium chloride
50 mL graduated cylinder	Sodium carbonate (s)
10 mL graduated cylinder	BaCl <sub>2</sub> ·2H <sub>2</sub> O
Kolle handle	EDTA 0.1 M
	Concentrated and 3M ammonia
	0.1 M sodium sulphate
	3 M hydrochloric acid
	2 M ammonium fluoride
	20 vol. hydrogen peroxide
	0.005M potassium permanganate
	Acetone

### (A) Synthesis of barium peroxide. Characterisation assays.

1) In a 100 mL beaker and in a fume hood, dilute 5 mL of the concentrated ammonia in 10 mL of distilled water. Next, carefully add 30 mL of 20 vol. hydrogen peroxide. The resulting solution is cooled down in an ice bath and then added drop wise to another aqueous solution (also cooled



down in an ice bath) which contains: 10.5 g of barium chloride dihydrate dissolved in a minimal volume of water (25-30 mL). The precipitate formed is left to settle for half an hour in an ice bath and then it is vacuum-filtered in a Buchner funnel. The solid is rinsed with small portions of very cold water and acetone. The product is then dried by vacuum and put onto filter paper. Calculate the yield.

Waste management: dispose of the solid when the experiment is over into the bottle labelled "barium peroxide"

## 2) Characterisation assays:

**a.-** Dissolve a small amount of barium peroxide in water in a test tube. Read the pH of the solution with pH indicator paper and add a few drops of an aqueous solution of sodium sulphate.

Waste management: dispose of the solutions when the session is over in the bottle labelled "Ba/sulphate waste".

**b.-** Dissolve a small amount of peroxide in water and add a few drops of a diluted and acidified solution of potassium permanganate.

Waste management: dispose of the solutions when the session is over in the bottle labelled "Ba/permanganate waste"

**c.-** Dissolve a small amount of peroxide in water and add a few drops of 0.1 M chromium(III) chloride solution. Then, heat the mixture until a colour change is observed.

Waste management: dispose of the solutions when the session is over in the bottle labelled "Residues Ba/Cr"

Write down the reactions taking place in each one of the sections.

## (B) Reactions in solution.

**1)** Introduce 1 mL of each one of the 0.1M  $MCl_2$  solutions ( $M = Mg, Ca, Sr$  y  $Ba$ ) in different test tubes and add the following reagents successively to each tube (tabulate the changes that are produced between additions for each tube).

**(a)** 1 mL of 3 M NaOH (carbonate free).

**(b)** 0.2 g of  $NH_4Cl$ .

**(c)** 0.1 g of  $Na_2CO_3$  and heat the mixtures up to  $50\text{ }^\circ\text{C}$  for several minutes.

- (d) 3 mL of EDTA 0.1 M.  
(e) 1 mL of  $\text{Na}_2\text{SO}_4$  0.1 M.  
(f) 2.5 mL of HCl 3 M (drop wise).  
(g) 1 mL of  $\text{NH}_3$  3 M.

**Note:** The reactions taking place in experiments 1d and 1f may be slow.

2) Introduce 1 mL of 0.1M  $\text{Na}_2\text{SO}_4$  into a centrifuge tube and add 1 mL of the 0.1M  $\text{CaCl}_2$  solution, mix well, centrifuge, then add 1mL of the 0.1M  $\text{SrCl}_2$  solution to the resulting mixture, and then centrifuge again. Repeat this operation but adding 1 mL of the 0.1M  $\text{BaCl}_2$  solution instead. If a precipitate does not appear for any mixture, heat it up.

3) Repeat with 1 mL of  $\text{NH}_4\text{F}$  0.2 M but reversing the order of addition of the metal ions.

Draw conclusions from these tests.

Waste management: dispose of the solutions when the session is over in the bottle labelled "Earth-alkaline metals waste".

4) Introduce a Kofle handle into a series of saturated aqueous solutions of s-block metal salts and observe the colour of the flame.

### ADDITIONAL QUESTIONS

1. Annotate all the observations for the assay **B-1** in a table, such as precipitation, redissolution, colour changes, or no change. To construct the table, make a column for the reagents added, and a row for the metal ions. Interpret the observations.

2. Interpret the results of the assays **B-2** and **B-3** by writing the corresponding chemical reactions.

3. Why is ammonia used for the preparation of barium peroxide?

4. Propose other methods for synthesising barium peroxide.

### ADDITIONAL BIBLIOGRAPHY

M. A. Malati, *Experimental Inorganic Chemistry*, Horwood Publ., Chichester, 1999.

*Traducido por Salvador Blasco*