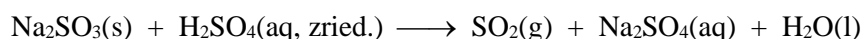
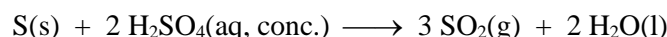
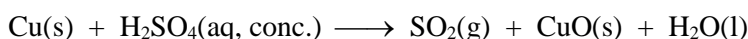
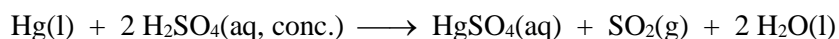


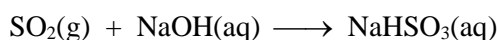
Preparation of sulphur dioxide – Procedure

Sulphur dioxide SO₂ is a colourless poisonous gas with a sharp irritating odour, heavier than air. It can easily be liquefied (boiling point –10.0 °C at pressure 101325 Pa, density 1.458 g cm⁻³). It is well soluble in water and its solubility decreases greatly with increasing temperature. An aqueous solution of SO₂ is called sulphurous acid. Sulphurous acid behaves as a weak and unstable acid that decomposes into SO₂ and water. In the solution, it is found mainly in the hydrated form of SO₂·H₂O. It has significant reducing, whitening and preservative effects.

In the laboratory, sulphur dioxide is prepared by reactions of concentrated sulphuric acid with some metals, with sulphur, or by reactions of sulphites with diluted strong acids, e.g. with hydrochloric acid or sulphuric acid.

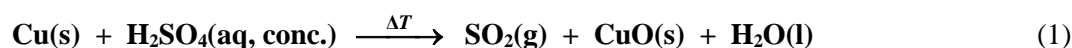


Unreacted sulphur dioxide is neutralized in an absorber with sodium hydroxide solution.



Work 1

Prepare sulphur dioxide by reacting copper with concentrated sulphuric acid.



Chemicals

- copper, Cu, swarf
- sulphuric acid, H₂SO₄, concentrated aqueous solution, $w(\text{H}_2\text{SO}_4) = 0,960$
- sodium hydroxide, NaOH, granulated

Procedure

Warning: We work in a fume hood and use perfectly tight equipment! We fasten the individual parts of the apparatus with appropriate brackets to an iron rod attached at the ends to two stands.

First, we assemble a gas generator (Fig. 1) from a fractional flask, a rubber stopper with two holes, through which the stem of the separating funnel and the safety valve (a glass tube with a pressure tube) pass. We put the calculated amount of copper in the fractional flask and close it with a rubber stopper, into which the separating funnel and the safety valve are inserted. We attach the fractional flask with the funnel to the stand with a suitable holder and connect it with a side pipe to the apparatus in which the sulphur dioxide will be prepared for further use. Then pour the required amount of concentrated sulphuric acid into the closed funnel. We guide the development of sulphur dioxide by gradually adding acid from the funnel to the fractionation flask. We speed up the reaction by heating it slightly. The content of the fractional flask gradually turns black from the copper oxide that is formed. The reaction mixture in the fractional flask must not be allowed to cool down, as an unwanted negative pressure may occur in the apparatus.

Stopping the evolution of sulphur dioxide

The evolution of sulphur dioxide can be stopped by adding distilled water to the fractionating flask through a separatory funnel. By diluting concentrated sulphuric acid, we stop reaction 1, because copper does not react with diluted sulphuric acid. Diluted sulphuric acid, however, will subsequently react with copper oxide in the fractional flask to form copper sulphate (equation 2).

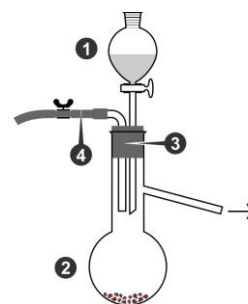


Fig. 1 Gas generator.

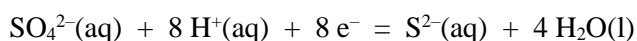
- 1 – separating funnel,
- 2 – fractional flask,
- 3 – stopper with two holes,
- 4 – safety valve.

By boiling the reaction mixture directly in the fractional flask, we achieve the reaction of copper oxide with diluted sulphuric acid. After slightly cooling, filter the contents of the fractional flask through a folded filter into an evaporating dish, which we place on a water bath to thicken the solution. We rinse the filtered copper into a larger beaker, where we wash it with distilled water, dry it, weigh it and return it to the teacher. The mass of unreacted copper is needed to calculate the yield of copper sulphate pentahydrate. Unreacted copper is collected for recycling.

Filtrate, i.e. copper sulphate solution, thicken on a water bath until a crystallization membrane forms. Then stop heating the solution and immediately measure its temperature. By cooling this saturated solution to laboratory temperature, we obtain crystals of copper sulphate pentahydrate, which we suck on a Büchner funnel, dry between filter papers, weigh and transfer.

Notes

- If a mixture of metallic copper and concentrated sulphuric acid is briefly boiled, a small amount of copper sulphide is also formed in the reaction mixture. It is a consequence of a redox half-reaction



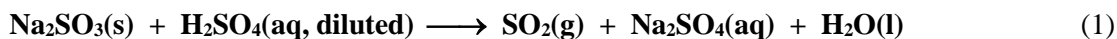
$$\Delta G = \Delta G^\ominus - RT \ln \frac{c_r(\text{SO}_4^{2-}) c_r(\text{H}^+)^8}{c_r(\text{S}^{2-})}$$

Since it is concentrated sulphuric acid, i.e. $c_r(\text{H}^+)$ and $c_r(\text{SO}_4^{2-})$ are large (\uparrow) and at the same time CuS is only slightly soluble, i.e. $c_r(\text{S}^{2-})$ is very small (\downarrow), the ΔG value of the mentioned half-reaction becomes more negative and the half-reaction proceeds more willingly: $c_r(\text{H}^+) \uparrow \wedge c_r(\text{SO}_4^{2-}) \uparrow \wedge c_r(\text{S}^{2-}) \downarrow \Leftrightarrow \Delta G \downarrow$. By diluting the sulphuric acid, however, the balance shifts back in the direction of the formation of sulphate anions, and the temporarily formed copper sulphide is “lost”.

- In reaction 1, the disappearance of one mole of sulphuric acid produces one mole of water. Thus, the acid is gradually diluted, so that in the end reaction 1 slowly stops and at the same time reaction 2 becomes more and more important. By adding water to the reaction mixture, we only speed up this process.

Work 2

Prepare sulphur dioxide by reacting sodium sulphite heptahydrate with dilute sulphuric acid.



Chemicals

- sodium sulphite heptahydrate, $\text{Na}_2\text{SO}_3 \cdot 7 \text{H}_2\text{O}$, white crystalline substance
- sulphuric acid, H_2SO_4 , dilute aqueous solution, $w(\text{H}_2\text{SO}_4) = 0,30$
- sodium hydroxide, NaOH, granulated

Procedure

Warning: We work in a fume hood and use perfectly tight equipment! We fasten the individual parts of the apparatus with appropriate brackets to an iron rod attached at the ends to two stands.

First, we assemble a gas generator (Fig. 1) from a fractional flask, a rubber stopper with two holes, through which the stem of the separating funnel and the safety valve (a glass tube with a pressure tube) pass. We put the calculated amount of sodium sulphite heptahydrate into the fractional flask and close it with a rubber stopper into which the separating funnel and the safety valve are inserted. We attach the fractional flask with the funnel to the stand with a suitable holder and connect it with a side pipe to the apparatus in which the sulphur dioxide will be prepared for further use. Then pour the required amount of diluted sulphuric acid into the closed funnel. We guide the development of sulphur dioxide by gradually adding acid from the funnel to the fractionation flask.

Sulphur dioxide drying

When preparing some compounds, it is necessary to use pure and dry sulphur dioxide. We clean it by bubbling through the filter (Fig. 2), i.e. a washer filled with distilled water, in which all impurities are captured. Dry sulphur dioxide is obtained by bubbling wet sulphur dioxide through a scrubber containing concentrated sulphuric acid. We can also use other dehydrating agents for drying. We fill the washers with liquids to about a quarter of their volume. We connect an empty (safety) washer in front of each washer with liquid. Sulphur dioxide, which will be used to prepare aqueous solutions of compounds, is not dried.

★ *Liquefaction of sulphur dioxide*

For some interesting experiments it is necessary to liquefy sulphur dioxide. Then we add a liquefier to the apparatus (Fig. 3), i.e. a dishwasher, whose ground glass lid will be replaced by a plug with two holes through which two short bent glass tubes pass. If we were to leave the original lid in this washing machine with one tube reaching to the bottom, the vacuum/overpressure in the apparatus could cause liquefied sulphur dioxide to move into the side (warmer) vessels of the apparatus, which could cause sudden changes in gas volume and therefore pressure in the apparatus.

Warning: We are working in a hood!

We introduce clean and dry sulphur dioxide into a smaller flask, which is filled in a beaker with a cooling mixture prepared from crushed ice and NaCl in a ratio of 1 : 1. Gaseous sulphur dioxide liquefies at a temperature of $-10\text{ }^{\circ}\text{C}$. Excess sulphur dioxide is absorbed in an absorber (Fig. 4) with sodium hydroxide solution. After obtaining $2 - 3\text{ cm}^3$ of liquid sulphur dioxide, we stop the experiment and observe its low boiling point, colour and odour. Finally, pour the liquid sulphur dioxide into the required amount of sodium hydroxide solution and dispose of it.

Disposal of unreacted sulphur dioxide (!)

Unreacted sulphur dioxide is introduced into the absorber (Fig. 4), which contains a sufficient amount of 15% sodium hydroxide solution. Add a few drops of ethanolic phenolphthalein solution to the hydroxide solution to see if the sodium hydroxide is not consumed. If we need to use a larger amount of sodium hydroxide solution, we can use a ground-glass washer or a suction flask instead of an ordinary washer.

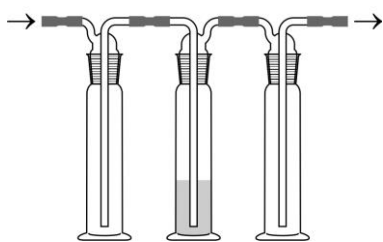


Fig. 2 Sulphur dioxide filter.
*distilled water,
respectively drying medium
(e.g. conc. sulphuric acid)*

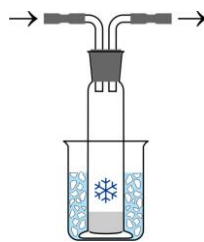


Fig. 3 Sulphur dioxide liquefier.
*cooling mixture
(e.g. a mixture of crushed ice
and sodium chloride)*

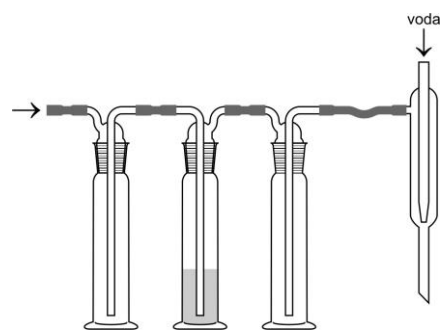


Fig. 4 Sulphur dioxide absorber
connected to a water pump.
aqueous solution of sodium hydroxide

Use of sulphur dioxide in the preparation of other substances

If we want to use the prepared sulphur dioxide in the laboratory preparation of other compounds, we must assemble the necessary equipment. The apparatus, including the gas generator (Fig. 1), must be tight so as not to leak gaseous and liquid substances. When assembling the apparatus, the glass parts must be attached to a piece of cloth to protect our hands from cuts. Empty washers serve as safety containers for catching water and relevant solutions in case of possible pressure changes in the apparatus.

★ Reducing properties of sulphur dioxide

Warning: We are working in a hood!

We will prepare four small test tubes and put 1 cm³ of distilled water in each.

- Add 2-3 drops of potassium permanganate solution with $c(\text{KMnO}_4) = 0.005 \text{ mol dm}^{-3}$ to the first and second test tubes, then add 3 drops of sulphuric acid solution with $c(\text{H}_2\text{SO}_4) = 2 \text{ mol dm}^{-3}$ to the first test tube and 3 drops to the second test tube of potassium hydroxide solution with $c(\text{KOH}) = 2 \text{ mol dm}^{-3}$.
- Into the third test tube, add 3-4 drops of dichromate solution with $c(\text{K}_2\text{Cr}_2\text{O}_7) = 0.1 \text{ mol dm}^{-3}$.
- Add 2 – 3 drops of potassium iodate solution with $w(\text{KIO}_3) = 0.005$ and 2 – 3 drops of starch oil to the fourth test tube.

Finally, a saturated aqueous solution of sulphur dioxide is dripped into each test tube until we observe a change in the colour of the solution or the formation of a precipitate. We write down the equations of the given reactions in the state form in the laboratory journal and write down the observed colour changes in the table.

★ Bleaching effects of sulphur dioxide

Warning: We are working in a hood!

Sulphur dioxide has bleaching effects, which are used to bleach wool, cotton, etc. We prepare two test tubes, which we fill with water in which we dissolve sulphur dioxide, i.e. j. they will contain sulphuric acid solution. We insert strips of filter paper into the first test tube, on which we drew different coloured lines with markers. Insert the petals of red or purple flowers into the second test tube. After a short exposure of the sulphur dioxide solution, we observe the whitening of the coloured lines on the paper and the change of colour of the flowers to pale pink or pale purple.

★ Preservative properties of sulphur dioxide

Warning: We are working in a hood!

Fill two test tubes with crushed raisins, to which we add a suspension of yeast in lukewarm water. Instead of raisins, we can eat a teaspoon of sugar. Fill one of the test tubes with sulphur dioxide. We close each test tube with a rubber stopper through which a glass tube passes. Dip the end of the tube coming out of the test tube into a beaker containing clear lime water (calcium hydroxide solution) or barium hydroxide solution. In a test tube whose contents were not preserved with sulphur dioxide, alcoholic fermentation will begin in a few minutes and carbon dioxide will be released. In the beaker, we observe the formation of turbidity or precipitation, which is proof of the presence of carbon dioxide. In the second test tube, into which we added sulphur dioxide, we do not observe any evolution of gas, nor the formation of turbidity in the beaker. In the laboratory journal, we will write down the observed events and equations of the reactions of carbon dioxide with the mentioned solutions of hydroxides in state form.

Preparation of sulfur dioxide – *Safety instructions*

Copper – Cu

- R36/37/38** Irritating to eyes, respiratory system and skin.
S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
S37/39 Wear suitable gloves and eye/face protection.

Sulfuric acid – H₂SO₄

- R23** Toxic by inhalation.
R34 Causes burns.
R49 May cause cancer by inhalation.
S23 Do not breathe gas/fumes/vapour/spray (appropriate wording to be specified by the manufacturer).
S45 In case of accident or if you feel unwell seek medical advice immediately (show the label where possible).
S36/37/39 Wear suitable protective clothing, gloves and eye/face protection.

Sulfur dioxide – SO₂

- R23** Toxic by inhalation.
R34 Causes burns.
R44 Risk of explosion if heated under confinement.
S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
S45 In case of accident or if you feel unwell seek medical advice immediately (show the label where possible).
S7/9 Keep container tightly closed and in a well-ventilated place.
S36/37/39 Wear suitable protective clothing, gloves and eye/face protection.

Copper(II) oxide – CuO

- R20/22** Harmful by inhalation and if swallowed.
R36/37/38 Irritating to eyes, respiratory system and skin.
S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
S36 Wear suitable protective clothing.

Copper(II) sulfate pentahydrate – CuSO₄ · 5H₂O

- R22** Harmful if swallowed.
R36/38 Irritating to eyes and skin.
S22 Do not breathe dust.

Sodium sulfite heptahydrate – Na₂SO₃ · 7H₂O

- R22** Harmful if swallowed.
R31 Contact with acids liberates toxic gas.
R36/38 Irritating to eyes and skin.
S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
S36/37 Wear suitable protective clothing and gloves.

Sodium sulfate heptahydrate – Na₂SO₄ · 10H₂O

- R36/37/38** Irritating to eyes, respiratory system and skin.
S36 Wear suitable protective clothing.
S37/39 Wear suitable gloves and eye/face protection.