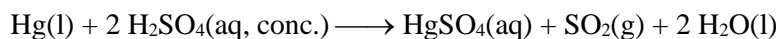


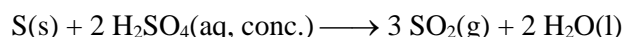
Preparation of sulphur dioxide

Sulphur dioxide is a colourless toxic gas with strong irritant odour. It may be easily liquified (b. p. = $-10,0\text{ }^{\circ}\text{C}$). It is well soluble in water, but its solubility rapidly decreases at higher temperature. Its aqueous solution is commonly called "sulphurous acid" H_2SO_3 , although the acid cannot be isolated as a pure substance. Therefore, some chemists prefer the formula $\text{SO}_2 \cdot \text{H}_2\text{O}$. Sulphur dioxide as well as sulphites have strong reductive properties.

In the laboratory, sulphur dioxide may be prepared by reaction of concentrated sulphuric acid with some metals,



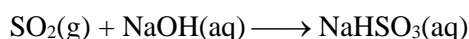
or with sulphur,



or by displacement of weak (sulphurous) acid by stronger (sulphuric) acid.

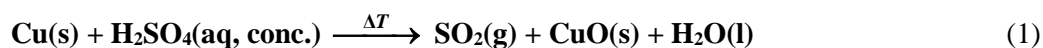


Being toxic and irritant, the unreacted sulphur dioxide must be eliminated in an absorber containing sodium hydroxide solution.



Work

Prepare sulphur dioxide by the reaction of copper with concentrated sulphuric acid.



Chemicals

- copper, freshly prepared by cementation,
- sulphuric acid, concentrated 96 wt% solution, oily colourless liquid,
- sodium hydroxide, white solid substance.

Procedure

At first, set up a gas generator according to the Fig. 1 and fix it to a stand. Put the calculated quantity of copper carefully into a fraction flask and connect an empty dropping funnel with rubber stopper. Pour the calculated volume of sulphuric acid to the funnel. A safety pressure valve must also be connected to the apparatus. The fraction flask set on a wire gauze must be heated by a burner, because the reaction 1 of copper with concentrated sulphuric acid occurs only at higher temperature. During the gas production the content of the flask changes to black by insoluble copper(II) oxide formed as a by-product.

Stopping the gas production

Stop heating and let cool down the gas generator. Adding water to the reaction mixture, the gas production stops. Diluted sulphuric acid doesn't react with copper but, on the other side, it reacts with copper(II) oxide formed. Exhaust gaseous sulphur dioxide using a water pump and boil the reaction mixture in the fraction flask to remove all dissolved sulphur dioxide. As copper(II) sulphate is formed by the reaction 2, the mixture slowly changes its colour to blue.



After stopping the boiling, filter the reaction mixture. Thicken the light blue filtrate on a water bath and then let it cool down to room temperature. Filter out, dry and weigh the crystals of copper(II) sulphate pentahydrate.

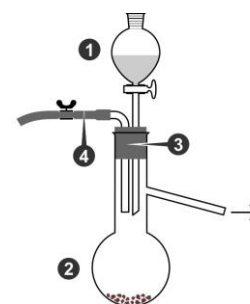


Fig. 1 The gas generator.

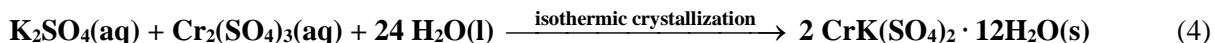
- 1 – dropping funnel,
- 2 – fraction flask,
- 3 – rubber stopper,
- 4 – safety pressure valve.

Preparation of chromium(III) potassium sulphate dodecahydrate

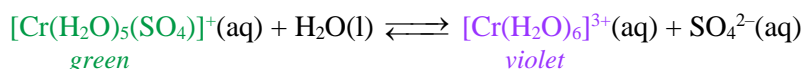
Chromium(III) potassium sulphate dodecahydrate is dark violet crystalline substance soluble in water. When heated loses its crystal water. Chromium(III) potassium sulphate dodecahydrate may be prepared the redox reaction of acidified potassium dichromate solution with gaseous sulphur dioxide.



From the dark green solution of potassium sulphate and chromium(III) sulphate in few days the dark violet chromium(III) potassium sulphate dodecahydrate crystallizes.



During the crystallization the colour of the solution changes from dark green to dark violet. It is caused by shifting the chemical equilibrium.



Work

Prepare dodecahydrate from 3,0 g of potassium dichromate.

Chemicals

- potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$, orange crystalline substance,
- sulphur dioxide, SO_2 , colourless irritant gas,
- sulphuric acid, concentrated 96 wt% solution, oily colourless liquid,

⚠ Potassium dichromate as well as all Cr(VI) compounds belong to potentially mutagenic compounds. Students must not manipulate with these solid substances. Therefore, their solutions must be prepared and poured to the reactor by an authorized person (teacher) only.

Important: How the unused dichromate solution may be safely eliminated?

Procedure

Build up an apparatus as depicted in the Fig. 2. Pour the calculated volume of 10,0 wt% potassium dichromate solution to the reactor. Using a dropping funnel add slowly concentrated sulphuric acid in a 50 % excess according to the equation 3. Heat the fraction flask moderately. As sulphur dioxide reaches the orange reaction mixture, it turns gradually to dark green.

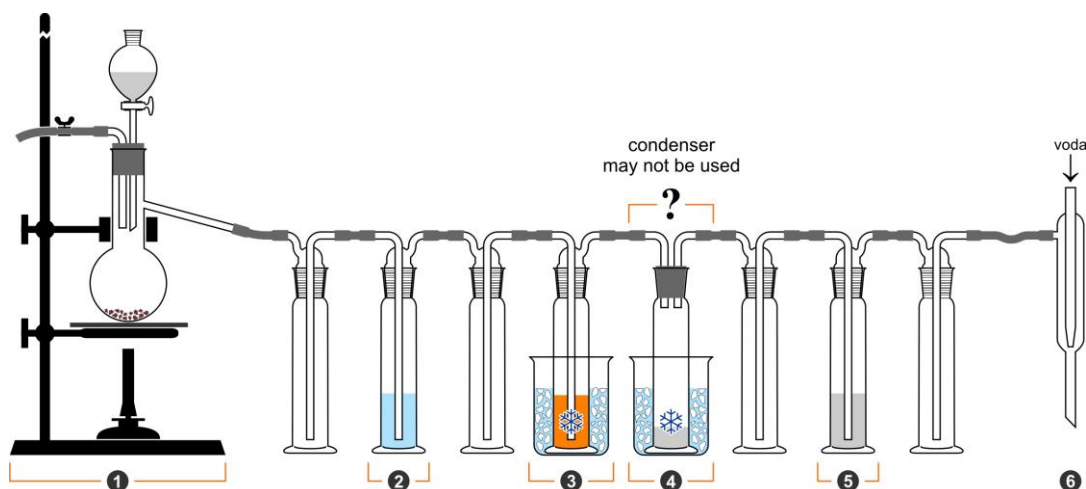


Fig. 2 Apparatus for preparation of chromium(III) potassium sulphate.

- 1 – gas generator (Fig. 1), 2 – filter = a gas-washing bottle with water,
 3 – reactor = a gas-washing bottle with acidified reaction mixture,
 4 – condenser = a gas-washing bottle in an ice bath, absorber (15% NaOH solution), water pump.

At this moment the reactor must be cooled by ice bath. There are two reasons why to do it:

- The reaction is strongly exothermic. Therefore, the reaction equilibrium should be shifted to the products by intensive cooling.
- Solubility of sulphur dioxide in the reaction mixture rapidly decreases at higher temperature, what subsequently decreases the yield of the reaction.

Depending on the reaction conditions, only around 40 % of generated sulphur dioxide reacts in the reactor. Unreacted toxic sulphur dioxide must be eliminated in an absorber containing 15 wt% sodium hydroxide solution, enough to eliminate all generated sulphur dioxide.



Fig. 3 The reactor before the reaction.



Fig. 4 The reactor after the reaction.

The reaction is finished when the reaction mixture has dark green colour. No orange shade should be visible, even in thin layers on the glass of the reactor. Then stop the production of sulphur dioxide as described above. When the apparatus contains no sulphur dioxide and it is cooled, detach the reactor, pour the reaction mixture to a bigger beaker, and boil it few minutes to exclude last traces of sulphur dioxide. Then pour the hot dark green solution to a crystallizing dish and let it crystallize for two weeks.

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.

Potassium dichromate – K₂Cr₂O₇

- R8** Contact with combustible material may cause fire.
- R21** Harmful in contact with skin.
- R25** Toxic if swallowed.
- R26** Very toxic by inhalation.
- R34** Causes burns.
- R45** May cause cancer.
- R46** May cause heritable genetic damage.
- R60** May impair fertility.
- R61** May cause harm to the unborn child.
- R42/43** May cause sensitization by inhalation and skin contact.
- R48/23** Toxic: danger of serious damage to health by prolonged exposure through inhalation.
- R50/53** Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.
- S45** In case of accident or if you feel unwell seek medical advice immediately (show the label where possible).
- S53** Avoid exposure – Obtain special instructions before use.
- S60** This material and its container must be disposed of as hazardous waste.
- S61** Avoid release to the environment. Refer to special instructions/safety data sheet.

Sodium hydroxide – NaOH

- R34** Causes burns.
- S26** In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
- S28** After contact with skin, wash immediately with plenty of (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.

Chromium(III) potassium sulphate dodecahydrate – CrK(SO₄)₂ · 12H₂O

- 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.