Preparation of calcium sulphate hemihydrate and magnesium sulphate heptahydrate

Calcium sulphate hemihydrate $CaSO_4 \cdot 0{,}5H_2O$ can be obtained by heating of calcium sulphate dihydrate $CaSO_4 \cdot 2\,H_2O$ (gypsum) over 150 °C. Gypsum has layer-like structure. Layers of cations and anions are connected by the molecules of water with relatively weak hydrogen bonds. Therefore the crystals of gypsum are easily fissile. Mohs scale of mineral hardness defines hardness value 2 as gypsum. After the reaction with water calcium sulphate hemihydrate hardens to solid substance formed of fibrous crystals of dihydrate.
Magnesium sulphate heptahydrate $MgSO_4 \cdot 7H_2O$ is white crystalline well soluble in water. It is usually used in medicine as a laxative, as a source of magnesium, or as a bath salt. Commonly it is a component of mineral waters. Heating $MgSO_4 \cdot 7H_2O$ the lower hydrates are stepwise obtained. Over 238 °C anhydrous magnesium sulphate is formed. Depending of temperature various hydrates $MgSO_4 \cdot xH_2O$, (x = 1, 2, 4, 5, 6, 7 and 10) crystallize from the aquatic solution.
Both calcium and magnesium sulphates are commonly prepared from calcium-magnesium carbonate $CaCO_3 \cdot MgCO_3$ (dolomite) by the reaction with HCl a H_2SO_4.

$$CaCO_3 \cdot MgCO_3(s) + 4\,HCl(aq) \longrightarrow CaCl_2(aq) + MgCl_2(aq) + 2\,H_2O(l) + 2\,CO_2(g)$$

$$CaCl_2(aq) + H_2SO_4(aq) + 2\,H_2O(l) \longrightarrow CaSO_4 \cdot 2\,H_2O(s) + 2\,HCl(aq)$$

$$MgCl_2(aq) + H_2SO_4(aq) \longrightarrow MgSO_4(aq) + 2\,HCl(aq)$$

Attention! Because of unavailability of chemically pure dolomite, a mixture of calcium carbonate and magnesium oxide must be used instead. Mix both chemicals in molar ratio Ca : Mg = 1 : 1 like in dolomite.

$$CaCO_3(s) + MgO(s) + 4\,HCl(aq) \longrightarrow CaCl_2(aq) + MgCl_2(aq) + 2\,H_2O(l) + CO_2(g)$$

Magnesium oxide should be prepared by thermal decomposition of basic magnesium carbonate $MgCO_3 \cdot Mg(OH)_2$ at higher temperature (annealing), according to the reaction

$$MgCO_3 \cdot Mg(OH)_2 \xrightarrow{\Delta T} 2\,MgO(s) + H_2O(g) + CO_2(g)$$

Work

Prepare calcium sulphate hemihydrate and magnesium sulphate heptahydrate from 4,0 g of mixture of calcium carbonate and magnesium oxide with molar ratio Ca : Mg = 1 : 1.

Chemicals

- calcium carbonate, $CaCO_3$, white crystalline
- magnesium carbonate basic, $MgCO_3 \cdot Mg(OH)_2$, white crystalline
- hydrochloric acid, HCl, concentrated, w(HCl) = 0,36
- sulphuric acid, H_2SO_4, concentrated water solution, w = 0,96

Procedure

In a clean iron crucible anneal enough basic magnesium carbonate. Let cool down the obtained magnesium oxide powder. Mix the calculated amount of magnesium oxide with the calculated amount of calcium carbonate. If necessary, spread the mixture in a mortar. Put the powdered mixture to a beaker and add stoichiometric volume of 20,0 % hydrochloric acid. If some unreacted solid is still present in the beaker, add another portion of hydrochloric acid remove all traces of a white solid. After the reaction heat the solution and filter it through a fluted filter paper.
Add calculated volume of 20,0 % solution of sulphuric acid in small excess to the filtrate containing $CaCl_2$ and $MgCl_2$. White $CaSO_4 \cdot 2\,H_2O$ precipitates while $MgSO_4$ remains dissolved in the solution. Filter out the precipitated $CaSO_4 \cdot 2\,H_2O$ on a Büchner funnel and wash the filter cake with water. After drying over 120 °C in an oven we obtain $CaSO_4 \cdot 0{,}5H_2O$.
Evaporate the filtrate containing magnesium sulphate in an evaporation dish until dry to eliminate the unreacted excess of hydrogen chloride. Weigh the dried $MgSO_4 \cdot H_2O$ and dissolve it in the calculated amount of water to obtain the solution saturated at 45 °C. Cool down the mixture in an ice bath. Under 48 °C heptahydrate $MgSO_4 \cdot 7H_2O$ crystallizes. Over this temperature hexahydrate is formed.

Safety instructions

***Calcium carbonate* – $CaCO_3$**

R37/38 Irritating to 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

***Magnesium carbonate* – $MgCO_3$**

–

***Magnesium hydroxide* – $Mg(OH)_2$**

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

***Magnesium oxide* – MgO**

–

***Hydrochloric acid* – HCl**

R34 Causes burns.
R37 Irritating to respiratory system.
S2 Keep out of the reach of children
S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice

***Sulfuric acid* – H_2SO_4**

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.

***Calcium sulfate hemihydrate* – $CaSO_4 \cdot 0{,}5H_2O$**

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.

***Magnesium sulfate heptahydrate* – $MgSO_4 \cdot 7H_2O$**

–