An investigative approach into some factors effecting intact crystal growth of Copper (II) sulfate pentahydrate ($CuSO_4 \bullet 5H_2O$) under room conditions and searching of suitable medium circumstances and alternative method favoring this type of growth.

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2004.

Contents

Abstract

In most laboratories, crystal growth of soluble salts in water is made with classical methods: obtaining a supersaturated or saturated solution at a higher temperature, slowly cooling or evaporating the solution. A chosen crystal nucleus is then used as a “seed crystal”, and the largest crystal formed is re-put into a saturated solution of itself while filtering other precipitates being formed. However, this methodical approach needs intensive and continuous care on crystal, consumes both time and solute. ***This study is therefore aimed to find such stable circumstances that will supply intact crystal growth of an ionic crystal under room conditions grown by this method, with an alternative method not requiring the prerequisite of periodical care.***

The researches stated that one-piece crystal growth required a reversible, kinetically limited reaction pathway. Second task was to find an easily obtainable and soluble salt used commonly and could easily form intact crystals, resistant to possible random changes in the determined constants during time that may erroneously happen during experimentation in a school laboratory. It was copper (II) sulfate pentahydrate.

A series of experiments are then conducted including attempts to change the vapor pressure and phase of the solution, changing the supersaturation temperature, cooling rate, cleanliness and the evaporation rate of the system in basis of a controlled experiment. The experimentation lead itself to the conclusion that:

Combination of decreased vapor pressure in a constant room temperature; clean system in the most soluble phase let through continuous evaporation can produce intact crystals of Copper (II) sulfate with an alternative method that is requiring only initial care.

Although the experimentation was successful, I was unable to find a quantitative optimum of the mentioned variables due to the time constraint. At least, I think I prepared a basis of alternative approach on a simple growth method.

Word Count: 299

Keywords: Intact crystal, seed crystal, copper (II) sulfate, copper (II) sulfate pentahydrate, crystal growth

Title

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Introduction

The Concept: Intact Crystal

Intact crystals are defined as crystals that are originating from a unified center that consists of either a symmetrical or asymmetrical arrangement of particles, having the same repeating pattern in any place of the crystal, pure and uniformly refracting, reflecting or absorbing light due to the wavelength of light used. The shape of the crystal is the one theoretically assumed to be, dismissing some uncommon exceptions.

The Case – Copper (II) sulfate

Grown crystals of Copper (II) sulfate is commonly used in protection of and as a solid additive in agriculture, in breeding cattles as a feed additive, in manufacture of batteries and in mines as an electrorefining material and in desalination and distillation plants. The intact crystals evaluated in laboratories are used in UV-visible light spectroscopy as a standard reference material and in optical devices as a filter and an irregular lens. They are also used in jewelry, after hydrophobic layer coating.

Commercial, and the aqueous form of Copper (II) sulfate crystals are in dark blue pentahydrate form, which also occurs naturally. The natural form is mostly found in South America, named as “Blue vitriol”. Gray monohydrate form is available at 110°C, while the white anhydrous form can be isolated near 250°C.

Copper (II) sulfate is highly soluble both in water and highly polar aprotic organic solvents such as methanol. It is commercially prepared in 97-99% purity by the reaction of copper metal and sulfuric acid under catalyzation of lead, including the removal of sulfur dioxide gas formed:

$$Cu(s) + 2\,H_2SO_4\,(aq) \rightarrow CuSO_4\,(aq) + SO_2\,(g) + 2\,H_2O\,(l)$$

The solution formed is slightly acidic ($pH \approx 3.5$ in $1.0M$ solution) when commercial copper (II) sulfate in norm I (with more acidic precipitate than more purified but expensive norm II) is dissolved. Although the sulfate ion is the conjugate base of a strong acid, the presence of unrefined sulfuric acid and the ability of the cation, Cu^{+2}, to form hydrated acidic octahedral complexes, as hexaaquacopper (II) in aqueous phase leads to the acidity of copper (II) sulfate solutions.

The Crystal Quality

Copper (II) sulfate crystals, as a non-volatile ionic solute highly soluble in water and some other highly polar solvents, are usually grown by seed crystal method: A small nuclei is put under a supersaturated solution and let to cool, or it is put into a saturated solution and let to evaporate. Between chosen periods, the biggest grown mononucleated crystal is re-used as the seed crystal. This method (Appendix 1), still lacks in quality of crystals produced other than the seed material, consumes time, care and solute, especially during the transfer processes. Copper (II) sulfate pentahydrate has more chance to give out intact crystals with guidance of purity and cleanliness of material; while rate of dissolving during preparation of saturated solutions is smaller and crystallization of copper (II) sulfate pentahydrate is slightly higher than some other common ionic salts due to thermodynamic factors that will be mentioned in the following part.

Thermodynamics and Kinetics of Crystal Formation

The crystal quality of a non-volatile soluble ionic salt like copper (II) sulfate is determined by the thermodynamics of its summarized characteristic formation:

The ions more than the solubility of the desired salt in a determined phase, at first desolvates: “survives” from the solvent molecules that surround the ion. Then, it rejoins with its desolvatized anion or cation and forms a crystal.

In a system of supersaturated ionic solute solution, there are possibilities of the future of it, and their energetic and entropic states:

- The solution may stay in this meta-stable form and not give a precipitate (high energetic and low entropic state due to the presence of arranged solvated pairs with electrostatic tension: the state is likely to destroy.)
- The solution may give scattered mass of crystals (high energetic due to irregular formation and increased bond tensions, with irregular shape but relatively high entropic state due to multinucleation)
- The solution may give intact crystal or crystals (low energetic due to regular formation and less bond tension, but relatively low entropic state due to arranged repeating patterns)

The kinetics of ionic crystallization originates from the energy exchanges during the process. The desolvation of ions in soluble phase and crystallization of them are the two spontaneously following processes of crystal formation. In the case of dissolving, destroying of crystals acts as an activation energy in order to minimize electrostatic attractions between ion pairs. The kinetic energy of solvent molecules then determines the rate of solvation as a secondary factor, which is thermodynamically favorable even in room conditions in case of copper (II) cation and sulfate anion in aqueous and methanoated phase, therefore displaying high standard solubility values. However, dissolving needs some extra energy in the case of copper (II) sulfate pentahydrate; the asymmetrical triclinic pentahydrate crystal system is in a higher entropic state than other types of crystalline structures with its relative randomness, therefore having less free energy. The form to be dissolved is more stable, thus dissolving has higher activation energy, and the rate of dissolving is lower compared to some other ionic solids. As the crystals are asymmetrical and the crystals are in a high entropy state, the entropy of an intact asymmetrical crystal is now more comparable to the entropy of multinucleation. Hence, the system is now less likely to form scattering results during crystallization. The crystallization rate is higher, but with more chance to be intact, and the dissolving rate is slightly lower than other common ionic solids.

To make the system do the most work and lose the most energy, the system must be made as reversible as possible. Then, this reversibility in exothermic and entropy increasing reactions will allow low entropy but low energy states to occur. Maximum energy flow and obtaining of lowest entropy phase can take place in infinitely reversible systems. Most of the arts requiring processing of fragile raw materials such as glass require excess reversibility and great care. The enzymatic reaction pathways in our body, supercooling of liquid water to -15°C are just some other examples to this. Though, a high reaction rate comes along with decrease in reversibility of processes.

Using either the process of evaporation or cooling of supersaturated solutions, initial temperature of the supersaturated solution and the speed of cooling, the vapor pressure of the solution, the phase of system will be the variables to be investigated during the experimental phase, under this section.

Event of Multinucleation

Nature always has a tendency to give scattered results. Sprinkled crystal growth originates from continuous growth from many centers, or disorders in centers, or a disorder in any point in the crystal. Both of them may be caused by the tendency of leaning towards high entropy states due to high reaction rates and low work output by system caused by this irreversibility, but also may be caused because of the purity of samples, cleanliness of environment and the properties of crystal growing surface. Especially amorphous surfaces with scratches promote as sites of multinucleation, while they decrease the desolvation enthalpy while crystallization. Also, other ions or impurities that may act as native growth centers because of their similar ionic radius to the selected anion or cation pair. A crystal is perfectly intact, if it gives the same X-ray reflection value and parallax in every point of the crystal structure; which is merely impossible. Only the shape of the result crystals will be the only visible factor that will help to determine the intactness of a crystalline structure under the limitations of time and material.

The effect of purifying material by means of strong oxidizing agents and level of purification of materials used will be the variables to be experimented with respect to the discussed aspects under this section.

Main Body

The Experiment Phase of The Investigation

Research Question:

Is it possible to find such stable circumstances and methodical approach that will result with intact crystal growth of an ionic salt, copper (II) sulfate pentahydrate, leading through an alternative method not requiring the prerequisite of periodical care, and if possible, exhibiting a desirable growth rate?

Aim:

To induce an alternative methodical approach that will efficiently favor intact crystal growth of copper (II) sulfate pentahydrate under room conditions with only the requirement of initial care and stability of the supplied outside factors. To find out the stable medium circumstances that will make such induction valid.

Hypothesis:

A copper (II) sulfate solution supplied with continuous evaporation, let through a low vapor pressure solution system, purified with strong oxidizing agents and in most soluble phase can produce intact Copper (II) sulfate pentahydrate crystals at a citable rate at room temperature.

The Experimentative Procedure

The experimentation phase of the investigation are broken down into four different stages. Complete procedures and apparatus including required safety precautions are provided in Appendix 4. The experiment system is identified by their associated methods and results as follows:

- **Experiment A:**

Obtained adequate information about the crystallization process and copper (II) sulfate, I decided first to apply my findings and observe the outcome of the primitive seed crystal systems made from supersaturated solutions of copper (II) sulfate pentahydrate cooled at different rates and let to evaporate if let with no additional care then preparation. I named the control group of all of the experimentation phase as “1”. It was a system prepared as a saturated solution under room temperature. System “2” was made as a supersaturated solution at 40.0°C and let to cool in room. Systems “3” and “4” were both set at 70.0°C as supersaturated solutions but their cooling places were different. “4” was let to cool in a 0.0°C refrigerator, while “3” was let to cool in the same room. This arrangement of groups gave me the opportunity to test the variables of cooling rate and initial temperature of supersaturation onto the intactness of crystals of copper (II) sulfate pentahydrate and efficiency of this type of growth in the same time, including a control group.

Groups “1”, “2” and “3” were parts of a controlled system experimenting the effect of initial temperature of supersaturation, while groups “1”,”2” and “4” were purely showing the effect of rate of cooling correspondingly. (Assuming that the room temperature is constant, thermal equilibrium situations can also be considered as cooling, but with a net rate of “0”).
Overall, the results in this set were not surprising, although they prepared me a basis to continue with a focused optimum set of experiments and reduce the number of groups to be tested, to save time.

Group “4” produced a thick layer of randomly scattered tiny crystals, near to an amorphous structure. The layer produced was opaque. The result was almost opposite of the desired one. The amount of precipitate produced was at maximum. Unexpectedly, a layer showing the melting of ice could be observed; the system had drawn ice from the refrigerator.

Group 3 crystals were a bit “proper”, with a scattered combination of layers of larger crystals and containing some translucency. One thing to be considered in this experimentation was that, the last grown crystals (crystals on the top layer) were larger and more orderly than the ones on the bottom layers (first grown crystals). The bottom layer was similar to the surface of group “4”, while the top layer was like the result of group “2”. The amount of precipitate produced was less than group “4”.

Group “2” crystals, with a thinner layer of precipitate, were completely translucent. The system produced interconnected, but distinguishable layer of crystals, with larger and more discrete ones on the top. Scattering was less observed than the other mentioned systems. Group “1” crystals, summed up as a layer as thick as group “2” results. Completely translucent precipitate contained four distinguishable large crystals, intact in shape.

Nevertheless, they were partially immersed in a layer of smaller interconnected crystals, which were more discernible than the ones of group “2”.

The results were obvious: Saturated systems let through constant temperature produced much more wanted results then the supersaturated systems, if no periodical care was applied to any “seed-crystal system”. If the process is aimed to produce intact crystals, then a produced mass of scattered crystals will be of no use. So, other system applications producing scattered tiny mass of crystals can be easily classified as processes continuously producing unwanted form of precipitate solute.

In the light of these statements and results, I will continue my experiments in constancy of the process of constant temperature evaporation, like in group “1”, more likely to result with intact crystals of copper (II) sulfate pentahydrate.

- **Experiment B:**

The second variable to be investigated was the effect of rate of evaporation of a saturated solution of copper (II) sulfate pentahydrate in room temperature on intact crystal growth of the mentioned ionic, soluble salt hydrate.

Observation of a closed system in presence of a hygroscopic material, which would increase the rate of evaporation, was the first experiment in this set. Actually, I was planning to use sodium hydroxide and I conducted an experiment in presence of it, because it was a strong hygroscopic material. It drew water at a tremendous rate. However, it did not act as an efficient hygroscopic material, as it almost completely converted to a solution in two days, with its low capacity of water drying (1 water molecule per 1 formula). Sodium hydroxide monohydrate made the system very difficult to clean up. Any small contact with the solution easily caused hydrolysis of fats (esters) under the skin caused pain and itching.

After some additional research (Appendix 5), I found a more suitable material: Calcium chloride. It was non-poisonous and non-hazardous, and the drying was just happening by the method of hydration; causing neither formation of solution, nor a chemical reaction like sodium hydroxide, had a much higher capacity of water intake (6 water molecule per formula), and used commonly for this purpose. It was also cheap and easily obtainable. Anhydrous copper (II) sulfate could be another alternative, however I did not have enough copper (II) sulfate to supply a drying system with it, and it would be waste of solute if used in this purpose. Anhydrous calcium sulfate would be a better alternative in drawing water, but the hydrate form of calcium sulfate would be so hard after absorbing water that, removal of the system from the gypsum (calcium sulfate dihydrate) layer would be impossible without heating, which meant loss of the crystal due to the increased temperature, or loss of the container.

Preparing a saturated system at room temperature, I placed the saturated solution into a closed system containing calcium chloride. The result, labeled as “5” showed crystals, which are scattered than the results found of group “1”, formed with a faster rate of crystal growth and with a thicker translucent layer.

Group “6”, the one treated with tap water, therefore supplying a lower vapor pressure system gave a slightly wanted result than the group “1”. Similar to the results of group “1”, there were 4 distinguishable intact crystals in shape, but the layer they were immersed was thinner compared to group “1”.

By adding scarce amounts of other solutes with foreign ions that may hardly cause multinucleation due to ionic radii, like sodium nitrate, I tried to test the effect of native impurities and effect of vapor pressure on intact crystal formation of copper (II) sulfate with a much more decreased vapor pressure of the system (the concentration was 1g/30ml). I named it as group “7”. However, I was mistaken by assuming that the ions were native. The solution went instantly green, as colorless gas of metallic odor produced. The green-white precipitate formed was not copper (II) sulfate, dissolving much less in water.

- **<u>Experiment C:</u>**

During my researches I had found that, copper (II) sulfate was soluble in one more material: methanol. I used pure methanol and commercial methanol solutions as solvents in the system in order to test the effect of other phases made. Copper (II) sulfate pentahydrate would form in any presence of water in room temperature (water is a much more stronger ligand, and is more basic than methanol). So, I dissolved anhydrous copper (II) sulfate inside pure and commercial methanol. The solution treated with pure methanol, “9”, gave out no crystals at all, but a white precipitate that turned to blue forming copper (II) sulfate pentahydrate crystals in presence of humidity of air. “8”, the system treated with commercial methanol ended up with very tiny but completely intact crystals in shape, apart from each other, completely distinguishable.

- **Experiment D:**

For the final trial, I tried to combine all the favoring factors I have found from the set of variables tested in the previous set of experiments. I designed the last group, group “10” as a saturated system in room temperature and treated in tap water. Difference of this group from group “6” was that, the container to build the crystals was initially treated with a strong oxidizing agent, 98% pure sulfuric acid, which cleaned up many impurities in the system and smoothed the glass surface. The result was very surprising. Different from all the results got, nearly 50 tiny and 2 large intact in shape were obtained (Appendix 6; large crystals lost their intactness after drying and with humidity of air, intact crystals combined), without the formation of a bottom layer of connected crystals. The obtained crystals were purely translucent.

Conclusion

1. **Higher initial temperature favors scattered crystal growth:**

Experiment A clearly showed that the statement was valid. It can be said that this is caused because of the increasing free energy difference between a scattered crystal state and an intact state. $\Delta G = \Delta H - T\Delta S$; therefore increase in T will increase the $-T\Delta S$ term for processes where the enthalpy term for crystallization is not so considerable in most transition metal salts. This increase will also increase the difference between two reaction pathways having similar enthalpy, but different entropies (scattered and intact crystal growth). The system will now thermodynamically tend to create the result with higher entropy, a sprinkled set of tiny crystals making up an opaque layer. The opacity originates from absorption and destructively superposition of light of binding and overlapping crystal layers.

Cooling in a tightly closed system in the same refrigerator could have prevented the ice intake problem of group “4”. Deionised water, if there were a practical process available to obtain it in the conditions of a high school laboratory, could have been used instead of samples of distilled water in the whole process.

2. **Lower cooling rate allows intact crystal growth:**

Observations in experiment A also stated that lower cooling rates of supersaturated solutions made a positive effect over intact crystal growth. Researches had stated that reversibility was required to do the most work and therefore decrease the entropy of the system. Systems cooled at a higher rate easily showed more unwanted results. However, here, concentration of the reactant, copper (II) sulfate was another important factor effecting the kinetics of crystal formation in case of saturated systems. So a group prepared with same concentration of copper (II) sulfate and fixed to different initial temperatures would test this effect much more better than performing the experiment with two supersaturated solutions at different temperatures, as the solubility changes with temperature in the case of Copper (II) sulfate pentahydrate.

3. Low vapor pressure systems favor intact crystal growth:

Experiment B supplied the statement that reversibility was required to do the most work and therefore decrease the entropy of the system. Low vapor pressure meant a lower rate of evaporation, and it meant a lower rate of crystal formation. Group “6” was closer to the preferred than group “5”. I could not find a reason of the unexpected result in “7”, after any research but I predict that this is caused because of the decomposition of copper (II) sulfate into copper (II) oxide, while copper (II) oxide is also green-white, and much less soluble than copper sulfate in pure water, as far as I know. The colorless gas exiting may be sulfur dioxide. But it is not nitrogen dioxide, as it is brown. I could not solve this “mystery”.

If not limited in time and space, a series of experiments could be conducted on the effect of poor drying agents on crystal growing of Copper (II) sulfate in room temperature. Maybe, a weak drying agent would still produce intact crystals although the increase in crystal formation speed and increased irreversibility of the process. The results would be very useful, while a faster intact crystal growth would meet practical needs more handily.

4. Most soluble phase produces intact crystals of Copper (II) sulfate pentahydrate:

Experiment C made it clear that, Copper (II) sulfate in the pentahydrate phase could not be obtained in methanoated phases. In presence of methanol, although the salt is soluble, the solubility decreased so much that, formation of triclinic or rhombic pentahydrate crystals were impossible. This is caused because of high energetic state of copper-methanol complexes. Copper (II) sulfate was crystallizing at a so fast rate that (note that methanol has also a very high vapor pressure in room temperature) a powdery white precipitate, copper (II) sulfate anhydrous was reformed.

Although group “8” ended up with intact crystals, the crystals were still very tiny and most of the residue was still in the white form. The reason behind this can be said as the increased presence of water. This increased presence started a competition between the hydrate crystals and the white precipitate. In the first case, there was too much methanol, with the ability to immediately convert any crystal formation to an amorphous structure. The second case contained the presence of water molecules, which could crystallize the structures in the pentahydrate form. The process wasted solvent instead of solute this time, as the solubility was drastically decreased in this phase. The wasted up solvent, methanol is a very toxic and irritant material, which can cause blindness in small doses. So, choosing a methodical approach with methanol seems impractical.

5. <u>An alternative method rather than the "seed crystal method" for growth of intact Copper (II) sulfate pentahydrate crystals can be offered:</u>

Including the knowledge that strong oxidizing agents dissolve impurities and destroy rough solid surfaces in the system that can more speedily produce crystals, with the help of them in cleaning the system, intact crystals of copper (II) sulfate pentahydrate can be obtained. Intact crystals were grown in one week, with no care than the preparation procedure. However, the result was not so efficient: Even the largest crystal formed was very tiny compared to the theoretical one-piece crystal the system can make (An intact crystal gravimetrically correspondent to the mass of formed precipitate). A widespread design of more groups of initial temperatures between 0.0 and 40.0°C, drying material and level of native impurities on size of intact crystal production (using mineral water instead of tap water) would contribute to find an analytical efficiency optimum for Copper (II) sulfate pentahydrate, over the experimented variables.

Of course, a crystal cannot be identified as intact or scattered if not analyzed in X-ray diffraction. All of the classifications of crystals in the essay as intact, scattered or sprinkled were just done by identifying the shape. Actually, when zoomed, even crystals of group 10 after 8 months were showing many visible disorders. If there was enough time and material, I could check the absolute intactness of the resultant crystals under X-ray.

To sum up, I think that the alternative methodical approach I proposed for Copper (II) sulfate pentahydrate can be applied to other soluble salts in different optimums of the variables tested, due to their thermodynamic constants. This essay, in my opinion, covers nothing but an experimental approach on the basis of variables of the intact crystal growth puzzle.

Word Count: 3999

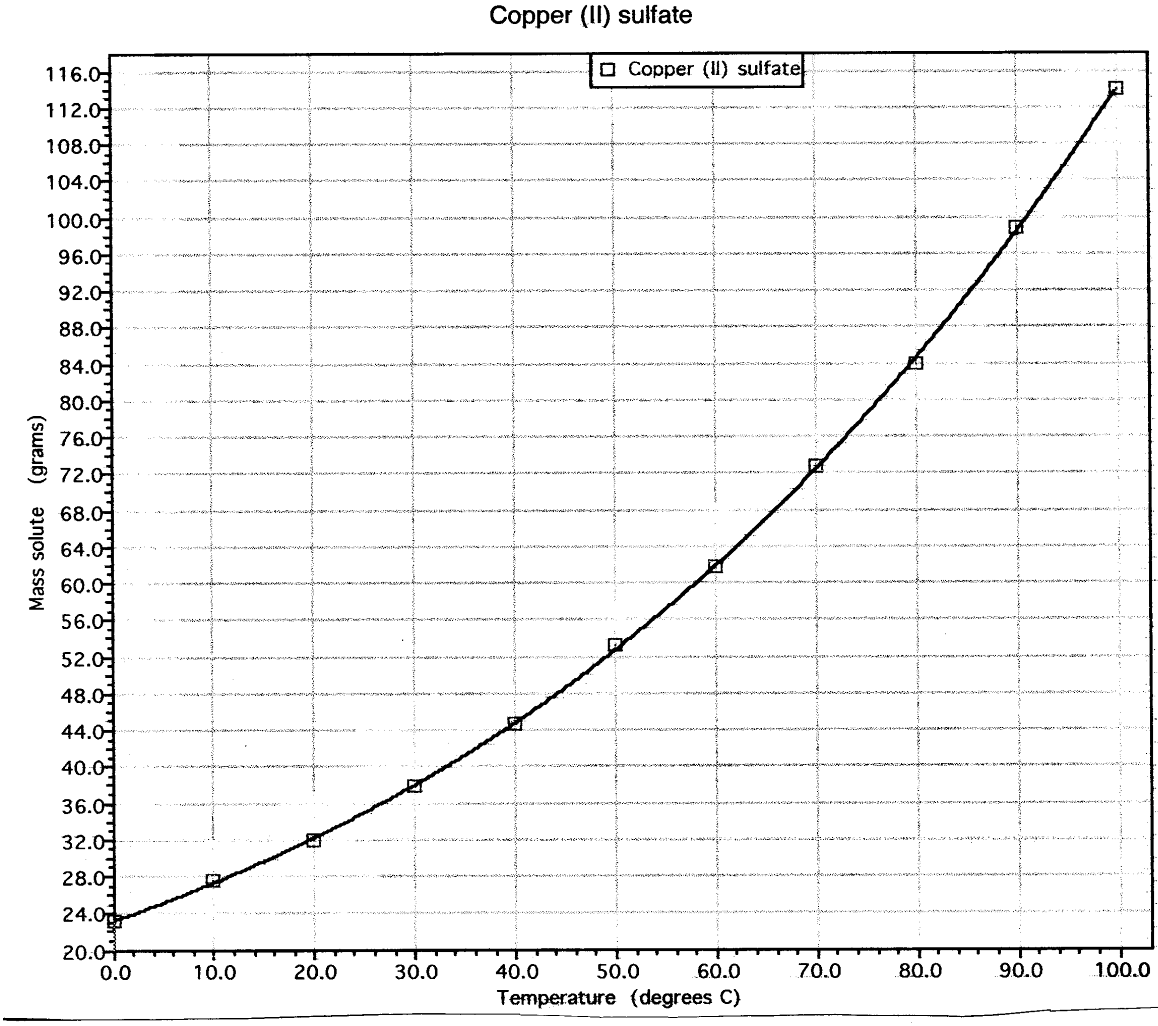
Appendix 1

A typical “seed-crystal” methodical approach for crystal growth of ionic soluble salts, under room conditions.

Buraya “Crystal Growth” deneyinin föyü yapıştırılacak

Appendix 2

The mass solubility of Copper (II) sulfate in 100cc of liquid water



(The solubility of Copper (II) sulfate, experimental results. Information taken from

“Crystals and Crystal Growing” by Alan Hollen and Phylis Morrison, 1982)

Appendix 3

The properties of the tap water used in the place of experimentation. (Average values taken from the supplier company's analysis laboratory, November 2003. Based upon the information taken from www.aski.gov.tr/laboratuvarlar/sukalitesi.doc)

AVERAGE ANALYSIS RESULTS OF TAP WATER OF URBAN REGION OF ANKARA

(NOVEMBER 2003)

Parameter	**Result**
Trihalomethane	48 µg/l
Aluminum	<0.03 mg/l
Arsenic	<0.001mg/l
Antimony	<0.01 mg/l
Barium	0.026 mg/l
Mercury	<0.001mg/l
Fluoride	0.14 mg/l
Silver	<0.01 mg/l
Cadmium	<0.005 mg/l
Chromine (of all oxidation states)	<0.01mg/l
Lead	<0.01mg/l
Selenium	<0.001mg/l
Nitrate	0.21mg/l
Copper	<0.01mg/l
Zinc	0.099 mg/l
Iron	<0.005 mg/l
Detergents	<0.1mg/l
Chlorine	9.45 mg/l
Manganese	<0.005 mg/l
pH	7.21
Sulfate	31.84 mg/l
Total dissolved material	173 mg/l
Ammonium	<0.05 mg/l
Calcium	25.28 mg/l
Magnesium	6.27 mg/l
Hardness / ppm $CaCO_3$	89.00 mg/l
Sodium	9.20 mg/l
Potassium	3.70 mg/l

Appendix 4

The complete apparatus and method of all experimentations carried on during the investigative process.

The Apparatus of Experimentations

The apparatus set were consisting of material easily obtainable commercially or from any high school lab rather than the apparatus used in specialized industrial methods or in laboratories, chosen especially for the ease and efficiency of the experimentation:

- 1 x 99% commercial (norm 2 preferred in order to decrease the level of impurity) 500 g. package of copper (II) sulfate pentahydrate
- Evaporating dish
- 11 x 100 ml. beakers
- Distilled Water
- Tap Water (Appendix 2)
- 1 x Stirring Rod
- 1 x Plastic dropper
- 50 x package of filter paper
- Plastic gloves
- 2 x 250 ml. Erlenmeyer flasks
- Stretch film
- 20 ml %98 refined commercial sulfuric acid or commercial nitric acid. (%52-68)
- 100g calcium chloride
- 1 x Mercury thermometer
- 1 x Bunsen burner
- 1 x Tripod
- Refrigerator with a two-star freezer (to obtain nearly 0°C in the top shelf of the refrigerator)
- 2.0g sodium nitrate
- Absolute methanol
- Commercial methanol (%33)
- 1 x Electronic balance
- Plastic bucket of 9.0-12.0cm.depth
- Safety goggles

Procedure of Experimentations

General Precaution:

Copper (II) sulfate is listed as hazardous according to the criteria of National Occupational Health and Safety Commission of Australia (NOHSC). Read carefully through a conventional Material Safety Data Sheet associated with Copper (II) sulfate before experimenting.

Experiment A

- Take three 100ml. beakers; clean them with distilled water and filter papers as much as possible.
- To filter the impurities in the crystals, place the hydrated crystals into a clean and dry evaporating dish and let the system evaporate its crystalline water in presence of a Bunsen burner, until the sample gets powdery and grayish white (Note that the system will form pentahydrate crystals in presence of excess water. Do not put excess copper (II) sulfate pentahydrate into the dish, while the boiling water may spill hot solid onto your body.)
- During the purifying process, record the temperature of the experiment location.
- Put the desired amounts of copper (II) sulfate into the beakers in order to make 4 saturated solutions of 60ml at 27.0°C, 40.0°C and 2 for 70.0°C, with the help of the electronic balance and according to the table in Appendix 3.
- Label the beaker to be treated under room temperature as “1”, 40.0°C as “2”, and 70.0°C as “3” and “4” respectively.
- For beaker “1”, slowly add distilled water by the help of the dropper to the beaker to be completed at 60 ml of total volume (being sure that the walls of the beaker is also washed) and mix the beaker constantly with the other hand. If some precipitate remains, add water drop by drop and mix until the solution is again at equilibrium.
- Filter the solution in beaker “1” by pouring the solution into another rinsed and cleaned beaker and repouring it into the rinsed and cleaned beaker “1” through filter papers. (Pour one or two drops of distilled water on the filter paper before use.)
- Leave the beaker under the protection of a blank filter paper.

- For beaker “2”, place the beaker with the mercury thermometer inside, on a tripod over a Bunsen burner.
- Fill the beaker up to 60 ml and heat the beaker with the Bunsen burner until it is 40.0°C. Mix the solution until this temperature.
- When the solution gets to 40.0°C, fix the intensity of the flame to a degree that will maintain the temperature. Replace the volume lost due to dissolving of salt with distilled water in the dropper.
- If some precipitate remains, ensuring that the temperature is fixed at 40.0°C, continue adding water drop by drop and mix until no precipitate remains. Inject the excess volume with the dropper and maintain the volume as 60ml.
- As soon as the process is completed, immediately take the beaker off the tripod and put somewhere in the room, under the protection of a blank filter paper.
- For beakers “3” and “4”, repeat the process for preparation of beaker “2” for 70.0°C, but use your gloves when carrying the solutions not to burn your hands.
- Leave beaker “3” in room, while carrying “4” inside the freezer. Protect the beakers by laying blank filter papers onto them.
- Wait for one week, decant any remaining solution on the precipitates formed and collect the beakers as data.

Experiment B

- Prepare excess of (200-250 ml.) tap water and 1g/30ml. sodium nitrate solutions into the Erlenmeyer flasks.
- Simply pour 100g of calcium chloride into the plastic bucket.
- Prepare a saturated solution by means of the exact process of preparation of beaker 1, and label it as “5”. Set beaker 5” into the plastic bucket under protection of a filter paper, tightly over the plastic bucket with a sheet of stretch film.
- Repeat the procedure for beaker “1” two times with the sodium nitrate solution and tap water instead of distilled water.
- Label the beaker treated with tap water as “6”. Label the beaker treated with sodium nitrate solution as “7” respectively.

- Protect the beakers under room temperature and under blank filter papers. Sodium nitrate must be handled carefully while it may be harmful to the skin.
- Wait for one week, pour any remaining solution on the precipitates formed and collect the beakers as data.

Experiment C

- During the preparation of those experimental groups under the heading, safety goggles and plastic gloves must be worn in order to protect from any probable hazardous effect of methanol on the experimenter.
- Pour commercial methanol into one of the Erlenmeyer flasks and pure methanol to the other. Tightly close the ends of the flasks with the stretch film when not in use.
- Fill one of the beakers with commercial methanol up to a volume of nearly 60ml and sprinkle some copper (II) sulfate into the system. Label the beaker as “8”.
- Mix the solution until the solute is completely dissolved. If the addition is completely dissolved, sprinkle some more solute and mix until a precipitate is formed. Complete the volume some more than 60ml and continue to mix it. Filter the solution twice like the procedure in Experiment A. Be careful not to pour methanol on your skin.
- Leave the solution under the protection of a filter paper and place the system in a well-ventilated place.
- Repeat this procedure for pure methanol instead of commercial methanol. Caution is the key. Label the saturated, filtered and cleaned solution as “9”. Place the system in a well-ventilated place.
- Wait for one week, decant any remaining solution on the precipitates formed and collect the beakers as data.

Experiment D

- During the preparation of this experimental group under the heading, safety goggles and plastic gloves must be worn in order to protect from any probable hazardous effect of the strong oxidizing agent, nitric or sulfuric acid on the experimenter. If encountered with any amount of nitric or sulfuric acid, halting the process and rinsing of the site immediately with excess and streaming water is required.
- Clean two remaining beakers by rinsing the beaker either with commercial nitric or sulfuric acid. Use the plastic dropper for the process.
- Now, rinse the beakers with distilled water and clean the beakers with filter papers that are made humid with distilled water also.
- Repeat the procedure for preparation of beaker “1” using tap water instead of distilled water and label the system as “10”.
- Leave the system under protection of a filter paper and in constant room temperature.
- Wait for one week, pour any remaining solution on the precipitates formed and collect the beakers as data.

Appendix 5

Data for some industrial drying chemical agents based upon information from (http://www.rhodium.ws/chemistry/equipment/dryingagent.html)

Drying Agent	**Suitable for Drying**	**Residual Water mg H_2O/L Dried Air**	**g H_2O/g Desiccant**	**Regeneration**	**Reaction Mechanism**
Calcium Chloride (<20 Mesh)	Alkyl and Aryl Halides, most esters, saturated and aromatic hydrocarbons, ethers	0.14-0.25	0.2 (1H_2O) 0.3 (2H_2O)	250ºC	Hydration
Calcium Oxide	Alcohols, amines and ammonia gas	0.007	0.3	1000ºC	Chemisorption
Calcium Sulfate	Most organic compounds	0.005	0.066	235ºC	Absorption
Cupric Sulfate	Esters, alcohols (excellent for benzene and toluene)	1.4	0.6	200ºC	
Magnesium Oxide	Hydrocarbons, aldehydes, alcohols, basic gases, amines	0.008	0.5	800ºC	Hydration
Phosphoric Acid		0.003		Not recommended	Absorption and Solution
Phosphorous Pentoxide	Saturated hydrocarbons, aromatic hydrocarbons, ethers, alkyl halides, aryl halides, nitriles, anhydrides, nitrites, esters	$3x10^{-5}$	0.5	No	Chemisorption leading to H_3PO_4
Potassium Carbonate	Alcohols, nitriles, ketones, esters, amines		0.2	300º C	Hydrate Formation
Silica Gel 6-16 Mesh	Most organics	0.03	0.2	200-350ºC	Adsorption
Sodium Hydroxide Pellets	Amines	0.16	Indefinite	Not Recommended	Absorption and Solution Formation
Sulfuric Acid	Inert gases, HCl, Cl_2, CO, SO_2, air used in desiccators	0.003	Indefinite	No	Hydration
Zinc Chloride	Hydrocarbons	0.9	0.2	110ºC	Hydration

Appendix 6

A large and a tiny intact crystal from group "10, eight months after the experimentation.

16x view

Original size

Bibliography

- Dana's New Mineralogy, 8th Ed., Gaines. pg. 605, 1997.

- What is “Blue Vitriol”? Copyright © 1997-2004, Fred Senese. [cited 23 June 2003]
<http://antoine.frostburg.edu/chem/senese/101/inorganic/faq/blue-vitriol.shtml>

- Wulfsberg, Gary. Principles of Inorganic Chemistry. California: University Science Books, 1991.

- Shriver, D.F. and Atkins, P. W. Inorganic Chemistry. Third edition. ed Özkâr, Saim. Oxford University Press, 1999.

- Drying Agent Selection Guide. [cited 2 July 2003.]
< http://www.rhodium.ws/chemistry/equipment/dryingagent.html>

- Water and Canalization Works of Ankara (ASKI). Average analysis results of tap water of urban region of Ankara. Translated from Turkish. [cited 1 January 2004.]
<http://www.aski.gov.tr/laboratuvarlar/sukalitesi.doc>

- Crystal Growth föyü ☺

- Hollen, Allan and Morrison, Phylis. Crystals and Crystal Growing, p. 25-43, 83-87, 120-129, 1982

- Markov, J. Crystal Growing and Epitaxy for Beginners, Bulgarian Academy of Chemistry-Sofia, 1987

- Smart, Lesley and Moore, Elaine. Solid State Chemistry: An introduction, p. 1-20, 149-187, 1992.

- Burgess, John. Ions in solution, p. 32-36, 40-56, 1988.