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METHODS IN GROWING MICROCRYSTALS OF CALCIUM SULFATE

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ABSTRACT

Some of the chemical properties of calcium sulfate as well as isothermal and non-isothermals methods in growing crystals of CaSO_4 are discussed. Special emphasis are placed on the crystal growth in gel.

I. THE CHEMISTRY OF CALCIUM SULPHATE

The main point of interest in the chemistry of gypsum concerns the products of its dehydration.

Four principal phases have been reported in the system calcium sulphate-water

| | |
|--|-----------------------------------|
| $\text{CaSO}_4, 2\text{H}_2\text{O}$ | mineral form \rightarrow gypsum |
| $\text{CaSO}_4, 1/2\text{H}_2\text{O}$ | \rightarrow bassanite |
| γCaSO_4 | soluble anhydrite |
| βCaSO_4 | anhydrite |

The transformations of one phase into another are very slow; because of that it is very difficult for a solution to reach its equilibrium, and very often solubility data differ from one author to another because of the tendency of the product to form supersaturated solutions.

Fig. 1 gives the solubilities of gypsum, anhydrite and the hemihydrate in pure water according to POSNJAK⁽¹⁾. The temperature of transition of gypsum to anhydrite in pure water is 42°C . According to HULETT and ALLEN⁽²⁾ the temperature of transition is 60°C . The general conclusion from the work of J. H. Van't HOFF⁽³⁾ is that gypsum and natural anhydrite are the only forms of calcium sulfate which are stable in the presence of any solution. In water gypsum is stable up to about 66°C when it passes into natural anhydrite, while in presence of others salts the transformation temperature is lowered; for a saturated solution of sodium chloride $T_{\text{tr}} = 30^\circ\text{C}$.

In the presence of concentrated sulphuric acid, the stable phase is anhydrite.

II. CRYSTAL GROWTH

A. Isothermal methods

1. Evaporation Methods

Sulphuric acid reacts with calcium salts to give calcium sulphate partially dissolved in the excess of solvent.

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STRUVE⁽⁴⁾ found that 100 parts of sulphuric acid, of specific gravity 1,82, dissolved 2 parts of calcium sulphate.

A mixture of calcium carbonate and dilute sulphuric acid is evaporated under reduced pressure until dryness (Fig. 2). We first collect in a container the distilled water, the product is subsequently solved in sulphuric acid, then we raise the temperature and collect concentrated sulphuric acid.

Since there is a circulation of sulphuric acid, not all the products have to be in solution.

If the same evaporation is to be done at normal pressure, the concentrated sulphuric acid must be used and whole of calcium sulphate produced must be in solution.

Since the solubility of calcium sulphate in sulphuric acid is very low, we must use sulphuric acid about 10 times more concentrated than in the previous method, furthermore we have to work at high temperature, (under normal pressure the boiling point of concentrated sulphuric acid is 315°C). The experiment should only be done in a fume hood because of the toxicity of sulphuric anhydride SO_3 produced, and great care must be taken in handling hot, concentrated, sulphuric acid.

In order to produce dosimeters, known amount of a chosen impurity will be introduced in the solutions. The calcium sulphate doped with thulium or dysprosium have excellent thermoluminescent properties.

The product obtained under reduced pressure is a fine grain powder. When evaporation is done at normal pressure bigger crystals are obtained. The sensibility of the later is about twice that of the former.

2. Temperature differential-method

a) Principle

For several substances the diagram of solubility versus temperature is of the type represented in fig. 3. In such a case, the differential method can be used to grow single crystals (Fig. 4).

First, the whole system is kept at the same temperature and is left to reach equilibrium; then, gradually the temperature is lowered until the desired value of temperature is reached. The solution is circulated between the vessel for solution and the vessel for growth by convection. The solution flowing into the growth vessel is supersaturated. A crystal germ placed in the low temperature vessel will grow.

b) Application

Since we know that the stable phase of calcium sulphate in the presence of concentrated sulphuric acid is anhydrite, we intend to use this method. Actually the diagram of solubility of CaSO_4 in sulphuric acid versus temperature is not simple, the curve presents a maximum at 25°C for a solution containing 75g of H_2SO_4 per liter⁽⁵⁾.

We intended to work at higher temperature, but, we never observed the solute transported from the high temperature vessel to the low temperature vessel, probably because of the existence of other compounds such as $\text{Ca}(\text{HSO}_4)_2$, $\text{CaSO}_4 \cdot 3\text{H}_2\text{SO}_4$, $2\text{CaSO}_4 \cdot \text{H}_2\text{SO}_4$, which have been reported by some authors.

The solubility curve of calcium sulphate in the presence of hydrochloric acid is simpler, hence, we did an experiment using differential method with diluted hydrochloric acid as solvent. In this case, using as germs the powder obtained after evaporation, we did grow needle shape crystals. The temperature of the cold region was $\lesssim 60^\circ\text{C}$, but even in this case, the analysis showed the crystals to be in the dihydrated form. Therefore in this case the mixture still was below the transition temperature. This method could be tried at higher temperature using natural anhydrite as germ.

Crystals of anhydrite can be obtained by slow cooling of melts of CaSO_4 with CaCl_2 (or BaCl_2 , or NaCl) plus K_2SO_4 . This method seems to produce rather large single crystals, but, they are often of poor quality, and some authors reported that their TL sensitivity is lower than those grown by evaporation.

III. CRYSTAL GROWTH IN GELS

It has long been noted that advances in solid state sciences depend on the availability of single crystals specimens.

In spite of an enormous amount of works, there are still many substances for which never was obtained single crystal, or never was obtained in the required size or degree of perfection. Therefore, new or unusual methods of growing crystals are of wide interest.

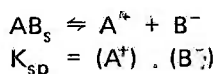
The gel growth method in the early period mainly developed because of the interests of geologists who believes that all quartz on earth was, at one time, a silica hydrogel, which later hardened through dehydration. Quite plausible is then that inclusions found in quartz may be examples of crystal growth in gel.

Presently the method is used for substances which have very slight solubility in water, or which have low dissociation temperature or else substances which would present structural changes when grown at high temperature and cooled.

A. Basic growth procedure

The gel method itself is exceedingly simple, but the physical and chemical process involved are not.

If we consider an almost insoluble substance, the solubility K_{sp} of the product is very small. This solubility can be considered to be caused mainly by ionic components, thus



Most mixing schemes will result in local $(\text{A}^{+}) (\text{B}^{-})$ products that exceed K_{sp} by such an

amount to cause spontaneous nucleation and crystalline powder will be produced. However, techniques that bring solutions of AC and DB together slowly enough will give larger crystals. This slow mixing may be readily accomplished utilizing the natural process of diffusion.

A simple way of growing $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is to use diffusion of reagents through water. In Fig. 5 a small beaker is filled with a solution of saturated calcium chloride, a second one is filled in the same way with a saturated solution of sodium sulphate. The two beakers are placed in a large beaker, 10 cm apart. Without stirring, the large vessel is filled with distilled water to a height of at least 4 cm above the tops of the small beakers; then a layer of melted paraffin is poured over the surface of the water to prevent evaporation and avoid any disturbance that might accelerate the process of mixing of the two products.

Crystals grow very slowly as diffusion brings the reagents into contact. In this way, we did grow crystals of LiF . The process is the same in the gel method. The gel structure provides an ideal medium for the diffusion of ions to take place. In general, two geometries have been used as shown in Fig 6. In Fig 6A a gel containing A^+ (or B^-) ion is placed in a test tube and then on top of it, a solution containing B^- (or A^+). In Fig. 6B the gels is formed in a U tube, in one branch is deposited a solution of A^+ , in the other one a solution containing B^- . The ions diffuse across the gel and crystals are formed in due course.

Great care must be taken to place the solution on top of the gel without damaging its surface: with a pipet drops of the solution are introduced into the tube.

The gel must be kept under well controlled temperature.

We have grown in our laboratory: calcium tartrate, copper tartrate, calcium sulphate and copper sulphate.

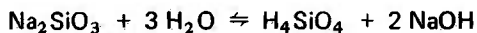
It can also be grown by this method; crystals of BaCO_3 , silver dichromate (sulphate), lead sulphate, lead chromate, lead chloride, lead iodide, lead sulphate, mercuric chloride HgCl_2 , 2HgO , silver sulphate, Ni-Co-phosphate, CaCO_3 calcite (laser technology), Au, Cu and Pb.

The crystals are ordinarily grown from the melt, but, undesirable thermal strain arise as a consequence of cooling from the melting point to RT.

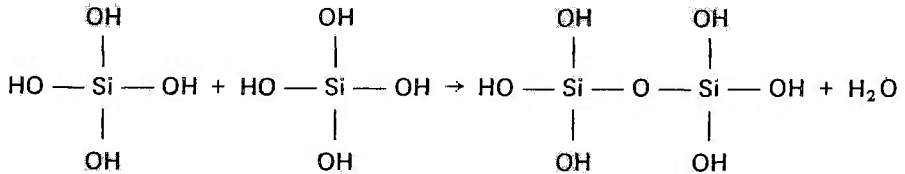
In addition, there is a phase change at 407°C , hence, there are obvious advantages in using the gel method.

B. Gel structure and properties

A great variety of materials are used as gels such as agar and gelatin. We used silica gel. When sodium metasilicate goes into solution, it may be considered that monosilicic acid is produced, in accordance with the dynamical equilibrium:



monosilicic acid can be polymerized with the liberation of water



This can happen again and again until a three dimensional network of (Si - O) - links is established. As the polymerization process continues, water accumulates on top of the gel surface, a phenomenon known as syneresis. The phase of gelatination is fast and generally is preceded by an "incubation time", the importance of which is dependent on and sensitive to pH.

A complicated interplay of reaction does that, in the absence of other reagents the minimum incubation time occurs somewhere near a pH of 8 (Fig. 7). This minimum time is temperature dependent.

In order to produce a good quality gel, this minimum time can only be approached from the low value-side of pH; otherwise we will obtain particules in suspension in the gel.

We first prepare a molar stock solution of sodium metasilicate in water. The gels are then prepared when mixing this stock solution with the required acid and water modify the gel density.

The curve of neutralization of a strong acid by a strong base is shown in Fig. 8A. Curves type B in Fig. 8 are obtained when neutralizing a strong base with a weak acid solution.

Since the minimum incubation time is obtained for pH close to 8, and since clear gel can only be obtained when approaching this point from the low pH value, we proceed as following. The sodium metasilicate stock solution is added drop wise to the solution of acid and water. The solution is thoroughly mixed in order to avoid local rise of pH, the addition of sodium metasilicate is stopped just before the neutralizing point depending on how long incubation time we want to get. An incubation time between hour and 24 hours seems to be desirable. In this way we can get a good uniformity of the gel. Also if the test tube is kept at constant temperature before gelling, this will avoid the formation of bubbles later on.

C. Crystal formation

The speed of crystal formation depends on

- the gel density which affects ionic diffusion constant
- the concentration of reagents diffused into the gel
- the temperature
- the length of diffusion path

The crystals can be doped with desired element for instance Mn. Calcium tartrate crystals have been grown and doped with Mn. When a crystal does not grow anymore in the gel, it may be reimplemented in another gel.

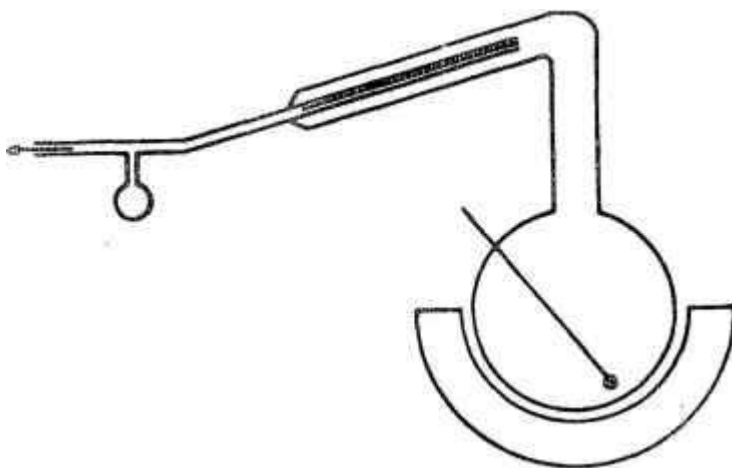


Fig. 1 - Solubility of gypsum, anhydrite and hemihydrate in pure water according to Ponsjak⁽¹⁾.

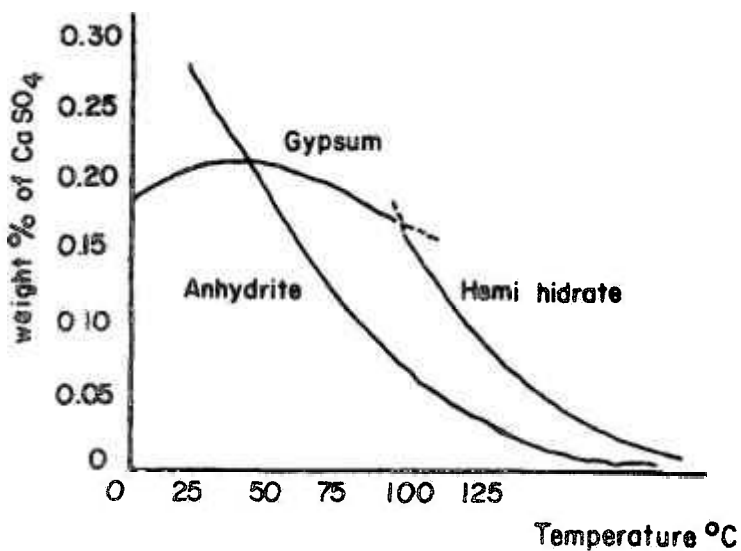


Fig. 2 - Device for evaporation method.

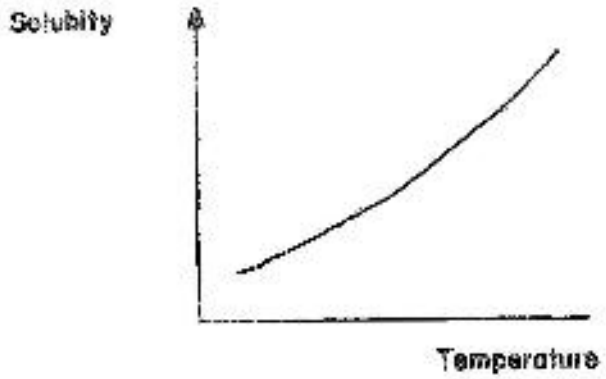


Fig. 3 - Diagram of solubility vs. temperature for several substances.

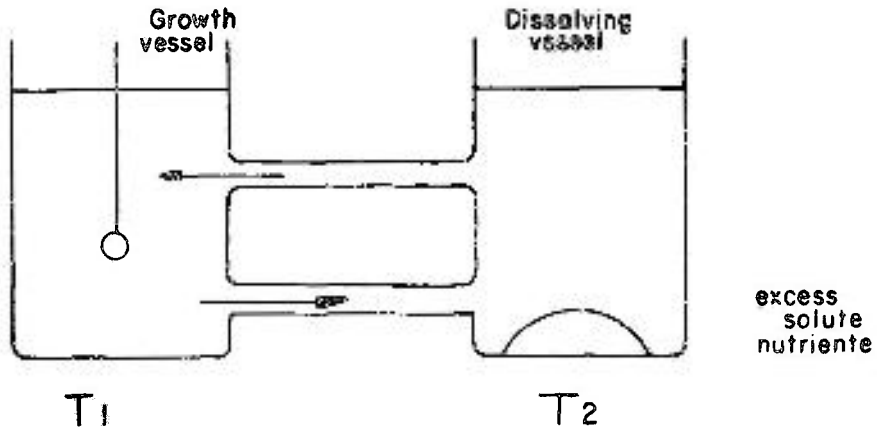


Fig. 4 - System for differential method to grow single crystals.

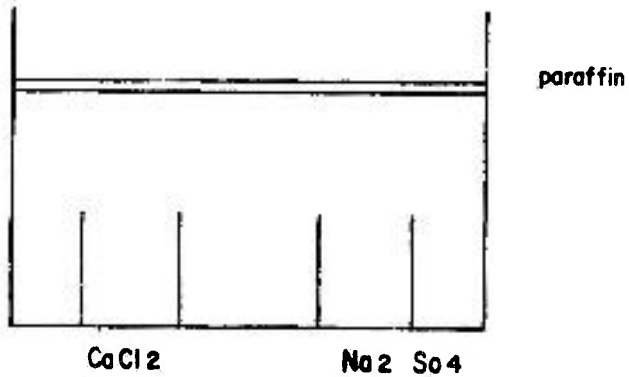


Fig. 5 - Growth of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ crystals using diffusion of reagents through water.

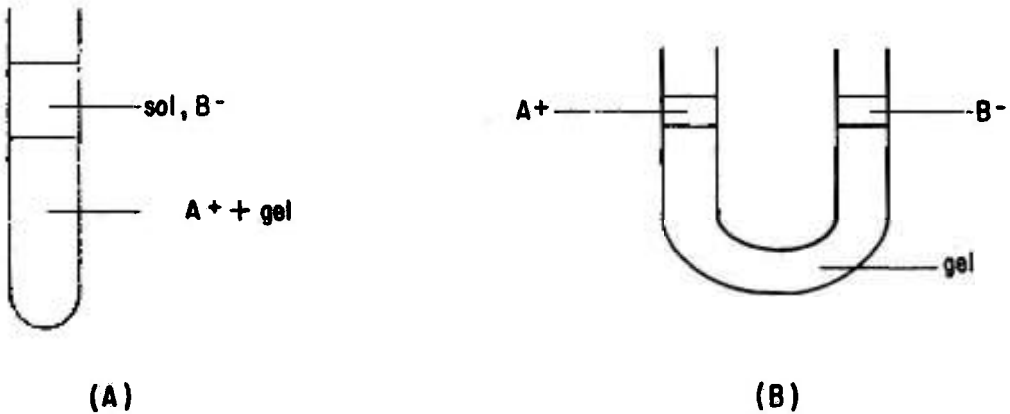


Fig. 6 - (A) - Gel containing A^+ (or B^-) ion is placed in a test tube and then on top of it a solution containing B^- (or A^+).

(B) - The gel is formed in a U tube, in one branch is deposited a solution of A^+ , in the other one a solution containing B^- .

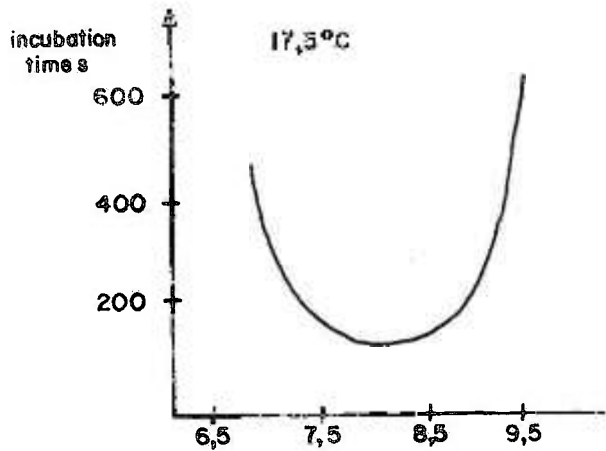


Fig. 7 - Curve of incubation time vs. pH.

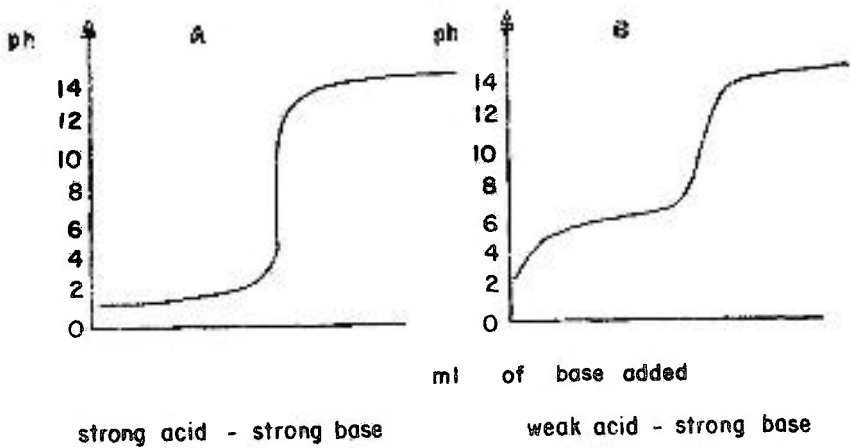


Fig. 8 - (A) - Curve of neutralization of a strong acid by a strong base.
 (B) - Neutralization of strong base with a weak acid solution.

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RESUMO

Algumas das propriedades químicas, bem como os métodos isotérmicos e não-isotérmicos de crescimento de microcristais de CaSO_4 são apresentados. Consideração especial é dada ao método de gelatina.

RÉSUMÉ

Qualques propriétés de CaSO_4 , aussi bien les méthodes isothermiques et non-isothermiques pour la croissance des leurs microcristaux sont présentés. Une consideration especial est faite sur la methode de gelatine.

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