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PHYSICO-CHEMICAL BACKGROUND OF PHOSPHORIC ACID  
MANUFACTURE BY WET PROCESSES

(with special reference to the semihydrate method)

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SUMMARY

It is shown that nucleation occurs for supersaturated systems only above a threshold value and that the rate of crystal growth at technical state of things is proportional to the supersaturation. The theoretical background is outlined. At continuous crystallization there is a Poisson-distribution of the crystal size. Three modifications of calcium sulphate, namely dihydrate,  $\alpha$ -semihydrate, and anhydrite II are formed in phosphoric acid processes.

Equilibrium curves obtained in different ways are compared, and an equilibrium diagram for phosphoric acid - sulphuric acid mixtures is given.

The consequences of nucleation conditions applied to phosphoric acid processes are discussed. Sanfourche's curve and the blocking of the reactions are thereby explained. The non-workable zone between the dihydrate and the semihydrate processes depends on simultaneous formation of dihydrate nuclei and semihydrate nuclei.

Shape and size of calcium sulphate crystals depends to a large extent on specific impurities in the phosphate rocks.

The kinetics of nucleation and transformation of the different calcium sulphate modifications are discussed and the formation of dihydrate and semihydrate in the stability region of anhydrite II explained.

## INTRODUCTION

A variety of wet processes for the manufacture of phosphoric acid have been developed over a long period. From a chemical point of view they have a common feature. Phosphate rock or other suitable phosphate raw material is treated with sulphuric acid with liberation of phosphoric acid and formation of calcium sulphate in one or more of its crystal forms, followed by mechanical separation of the solids from the liquid. There are other common features. The laws of formation and growth of calcium sulphate crystals are the same irrespective of the crystal form. A knowledge of these laws is a necessity for a proper understanding of the processes. Other physico-chemical phenomena determine the conditions under which the different process types, i.e. dihydrate or gypsum, semihydrate and anhydrite processes, are possible.

It is the aim of this paper to link the process types together and provide a background for the whole complex problem with special reference to the semihydrate process.

## FORMATION OF CRYSTAL NUCLEI

It is possible to show that the laws for formation of nuclei at crystallization from solutions, at allotropic transformations, at solidification of melts, and so on can be strictly derived from the general kinetic theory without introducing any hypothetical assumptions /1/. In a solution there occur local, thermodynamically stipulated concentration variations, called fluctuations. The smaller the inter-connected entropy change, the greater is the probability for the occurrence of such a fluctuation. For this reason great specific changes are limited to small masses. The simplest fluctuation consists of complexes with two molecules. Some of these are split into their constituents, while others catch a third molecule. In this way the building up continues until small complexes are formed with a lattice of orientated molecules of the same crystalline nature as the dissolved material in solid form. Part of the fluctuations reach a size possessing the same thermodynamic potential as the surrounding solution. A nucleus is defined as a fluctuation fulfilling this condition. Fluctuations smaller than this critical size possess a predominant tendency to split, while those greater than this size possess a predominant tendency to grow. A second definition of a nucleus can be given. A nucleus is a crystal formation for which formation out of the old phase a maximum of formation work is necessary / Ref. 1 p.126/.

Turnbull and Fisher /2/ have studied the nucleation problem according to the theory of absolute reaction rates by Eyring and his school /3/. Using this work as a basis Hirano /4/ investigated the influence on nucleation by electric charges on nuclear surfaces in electrolyte solution and stated that these charges play an important rôle. The derived relations are particularly complicated and have not as yet been completely experimentally verified or rejected. A partial verification has been presented by Amstler /5/. Here we content ourselves with the following relation between nucleation frequency and supersaturation, keeping all other factors constant.

$$J = a \frac{10^{-b(\log s)^{-2}}}{\log s}$$

Eq.1.

where

$J$  = nucleation frequency

"a" and "b" are constants

$s = \frac{c}{c_0}$  = supersaturation quotient

$c$  = concentration in the solution

$c_0$  = concentration in saturated solution

In Fig.1 this relation is visualized for different values of the exponential factor "b". We observe that up to a certain critical supersaturation, nucleation is practically non-existent. After passing this critical point the rate of nucleation increases rapidly. The transition has almost the character of a knee on the curve. Thus we can state that the formation of a new phase is impossible along and immediately on the other side of the coexistence boundary (equilibrium curve and solubility curve). For this formation to take place the coexistence boundary must be exceeded to such an extent that a threshold value (the knee) is passed. This fact is of essential importance for wet phosphoric acid processes.

#### CRYSTAL GROWTH

We distinguish between two kinds of crystal surfaces - plane and step-formed. The step height of the step-formed surfaces is of molecular dimensions. An ideal crystal surface with a step in the surface grows owing to the presence of a great number of thermally stipulated unevennesses in the step front, i.e. Frenkel-kinks.

During growth the step front advances to the corner of the crystal leaving a complete crystal surface. When all steps are eliminated through formation of complete layers, further growth is only possible if new steps are formed. This may happen owing to the formation of two-dimensional nuclei or molecular islands on the crystal surface. This assumption, however, would lead to the non-appearance of growth at supersaturations lower than the threshold value for nucleation. As a matter of fact real crystals grow at an observable rate at supersaturations of 1% and lower, while the threshold value has an order of size of about 25-50%. The most regular and well built crystals are obtained at a low supersaturation.

This leads to the conclusion that crystal growth at low supersaturation can only be explained by the fact that real crystals are not perfect. This conception was introduced by Burton and Cabrera /6/ and Frank /7/ and gives us a mechanism according to which the crystal surface remains step-formed irrespective of how far the step front advances. Thus no obstacle to growth at low supersaturation is involved.

According to Frank /7/, all surfaces of a real crystal must contain a number of dislocations with a screw component, which results in the surface forming steps that do not disappear during growth. Extensive microscopic investigations by Verma /8/ agree with this theory.

The dislocation theory of crystal growth gives a relation between rate of growth and supersaturation which is demonstrated in Fig.2. Thus above a certain supersaturation, proportionality exists. In most technical connections the non-proportional part at low supersaturation need not be considered.

Likewise, according to the theory of two-dimensional nuclei, proportionality is obtained above a certain supersaturation, but the lower part of the curve is different. Generally, growing crystals have a rate of growth proportional to the supersaturation at supersaturations much lower than the threshold value according to the theory of two-dimensional nuclei. The proportionality has been experimentally verified e.g. by Chretien and Heubel /9/.

### CONTINUOUS CRYSTALLIZATION

Assume a reaction vessel with a certain volume of crystal suspension. To this reaction system we continuously add material for crystallization. At the same time we draw off an equivalent amount of crystal suspension. The system is well agitated and uniformity is achieved in the whole system. At the stationary state there is a constant rate of nucleation and a constant rate of growth, as the supersaturation is constant. Thus the size distribution of the crystal population becomes unchanged. The following expression of the size distribution is obtained:

$$n(r) = \frac{n_0}{f(\alpha)} \cdot e^{-\frac{v(r-r_k)}{f(\alpha)}} \quad \text{Eq.2.}$$

where  $n(r)$  = number of crystals per volume unit suspension with average dimension "r"

$n_0$  = number of nuclei formed per volume unit in unit time

$f(\alpha)$  = a function of supersaturation ( $\alpha = \frac{c}{c_0} - 1$ )

$v$  = volume suspension drawn off in unit time and volume unit of reaction volume

$r_k$  = average dimension of a nucleus.

On a graph with  $\log n(r)$  against  $r$  ( $r_k$  is neglected) a straight line is obtained from which  $f(\alpha)$  and  $n_0$  may be determined.

Besides the number distribution the weight distribution is of interest and we put

$$w(r) = \gamma \cdot n(r) \cdot r^3 \cdot \rho \quad \text{Eq.3.}$$

where  $w(r)$  = weight of crystals per volume unit suspension with average dimension "r"

$\gamma$  = shape factor (sphere  $4\pi/3$ )

$\rho$  = density of crystal

This function has a maximum for the particle size  $r_{\max}$ .

$$r_{\max} = \frac{3 f(\alpha)}{v} \quad \text{Eq. 4.}$$

The nucleation rate  $n_0$  may also be obtained from

$$n_0 = \frac{v}{6 \cdot \gamma \cdot S} \cdot \left( \frac{3}{r_{\max}} \right)^3 \quad \text{Eq. 5.}$$

where  $\gamma$  = weight of crystals drawn off per time unit and volume unit of reaction volume

$n(r)$  and  $W(r)$  may be determined by a photoelectric sedimentometer /11/.

Branson et al. /10/ have obtained very good experimental evidence of the equations 2 and 3. The experiments confirm that there is a Poisson-distribution of  $W(r)$  and that the linear rate of growth is independent of "r".

#### THE CRYSTAL FORMS OF CALCIUM SULPHATE

The old literature on calcium sulphate and its crystal forms is highly confused. To explain existing data, several varieties of dihydrate, semihydrate and anhydrite were postulated. The excellent work by Kelley et al. /12/ has, however, rendered all this intelligible. Often the nomenclature has not been clear. Here the nomenclature suggested by Kreis and Späth /13, 14/ will be used, as it excludes the mistakes.

From the crystallographic and thermodynamic point of view there exists only one form of dihydrate, even if the external geometric shape varies. The semihydrate exists in two forms. The  $\alpha$ -semihydrate is crystalline and is formed by crystallization from solution or by slow dehydration in a saturated water vapour atmosphere. Its lattice allows deviations from the semihydrate formula in both directions. The normal state is an overstoichiometric content of crystal water. That this is the case is indicated by an asterisk,  $\alpha$ -semihydrate\*. With phosphoric acid processes, the overstoichiometric  $\alpha$ -semihydrate is formed. The  $\beta$ -semihydrate is microcrystalline (crystal size  $< 10^{-4}$  cm), voluminous and flocky. It is formed by rapid dehydration in an unsaturated water vapour atmosphere. This crystal form is of no interest in so far as the present problem is concerned.

On atmospheric dehydration of  $\alpha$ -semihydrate and  $\beta$ -semihydrate at not too high a temperature  $\alpha$ -anhydrite III and  $\beta$ -anhydrite III (formerly called soluble anhydrite) are formed respectively. Their properties show many similarities to the corresponding semihydrates.

Under suitable conditions anhydrite II (formerly called insoluble anhydrite) is formed by dehydration of semihydrate or dihydrate or by crystallization from solution. This unreactive variety is formed in some phosphoric acid processes.

Anhydrite I is a high temperature modification, stable above 1195°C, and is of no practical interest.

Thus for phosphoric acid processes we have three modifications of calcium sulphate to consider: dihydrate,  $\alpha$ -semihydrate\* and anhydrite II.

EQUILIBRIA OF CALCIUM SULPHATE IN ACID SOLUTIONS

In their work Kelley et al. (12) have given equations for the temperature dependence of the free energy for all real and hypothetical reactions in the system  $\text{CaSO}_4 - \text{H}_2\text{O}$ . When the activity of water differs from unity, as in electrolyte solutions, an additional term must be put to the equations, which then have the general form:

$$\Delta F^\circ = A \cdot T + B \cdot T^2 + C \cdot T \cdot \ln T + D + nRT \cdot \ln \frac{p}{p_0} \quad \text{Eq. 6.}$$

where

- $\Delta F^\circ$  = the free energy of the reaction
- T = the temperature  $^\circ\text{K}$
- R = the general gas constant
- n = moles of water in the reaction formula
- p = the water vapor pressure of the electrolyte solution at temperature T $^\circ\text{K}$
- $p_0$  = the vapor pressure of pure water at temperature T $^\circ\text{K}$
- A, B, C, and D are constants

If we now put  $\Delta F^\circ = 0$ , we get the equilibrium conditions between the two modifications of calcium sulphate in the reaction formula - the transition temperature as a function of the relative water vapor pressure, that is the activity of water in the electrolyte solution.

From water vapor pressure data of electrolyte solutions we get the relation between water activity in the solution and the concentration at different temperatures. On combining the two relations, transition temperature as a function of concentration is obtained.

In this way the thermodynamic equilibrium curves for the transitions dihydrate - anhydrite II and dihydrate -  $\alpha$ -semihydrate\* in pure phosphoric acid solutions have been calculated. The curves are shown in Fig. 3. Vapor pressure data used are taken from Ref. 15.

From this figure it is clear that there exist only two stable modifications of calcium sulphate - dihydrate and anhydrite II, the former stable below the transition curve and the latter stable above the curve. Apart from this fact, the curve dihydrate - anhydrite II has no practical consequences in phosphoric acid manufacture.

$\alpha$ -semihydrate\* is the metastable form in the region above the thermodynamic dihydrate- $\alpha$ -semihydrate\* curve, whereas dihydrate is metastable in the region between the two thermodynamic curves.

The equilibrium curve obtained from solubility measurements by Taperova and Shul'gina (16) and Hultbom-Lehrecko's curve (17) from the reaction between sulphuric acid and phosphate rock agree very well with the thermodynamic curve between 30 and 40%  $P_2O_5$ . Sanfourche's curve (18) is not an equilibrium curve and will be discussed later.

In practice pure phosphoric acid solutions are seldom present, whereas mixtures of phosphoric acid and sulphuric acid are frequent. The equilibrium diagram for dihydrate -  $\alpha$  - semihydrate\* in such mixtures is given in Figure 4. The points for the system sulphuric acid-water are thermodynamically calculated using vapour pressure data from Ref. 19 after correlation. The curve for the system phosphoric acid-water is the same as in Figure 3. The other curves are prepared from data by Ikono et al. (20).

### CRYSTALLIZATION AND NUCLEATION IN PHOSPHORIC ACID PROCESSES

We have already stated that under technical state of things the rate of crystal growth of a single crystal is proportional to the supersaturation. Further, the solid deposited per unit of time is proportional to the available crystal surface area, thus for a given quantity of seed material growth is proportional to the specific surface of the crystal mass. In a reaction system the conditions deviate from the completely reacted state. There is a trend in the system to such a displacement of the reactions that a supersaturation arises, so that the combination of nucleation and crystal growth is just capable of removing an amount of crystal mass equivalent to the reactants added during the same time. This is easily seen by following the  $SO_4^{--}$ -ion concentration during the lapse from completely reacted state to dynamic equilibrium or stationary state.

The greater the deviation from the completely reacted state, the larger the production per unit of reaction volume is obtained in this part of the system. On the other hand the need for reaction volume for the after-reactions grows at the same time, since a fully reacted sludge is wanted as a final result. The possibilities of working with a high supersaturation are, however, limited, as blocking of the reactions may occur.

During the reaction between phosphate rock and acid a diffusion of  $Ca^{++}$ -ions takes place from the phosphate rock grains and at the same time a diffusion of  $SO_4^{--}$ -ions occurs towards the phosphate rock grains. At a certain distance from the grains, owing to mechanical agitation, we may assume a nearly unchanged composition of the liquid phase, which acts as a substrate for nucleation and growth of suspended crystals of calcium sulphate. Owing to the  $SO_4^{--}$ -ion concentration in the substrate some nucleation may take place within the diffusion zone around the grains. Should the supersaturation in the solution near to a grain pass the threshold value for nucleation, nucleation will occur on the surface of the grain itself. If a certain part of the grain surface is inactivated in this way by adherent crystals (partial encasing), the transport of material by diffusion from the remaining free surface cannot keep pace with the addition of reagents. We then get a blocking, and the amount of unreacted phosphate rock and sulphuric acid concentration will rise continuously. In view of the sharp threshold value for nucleation a rather sharp critical limit of supersaturation is to be expected and, for



simplification, this is represented by the  $\text{SO}_4^{--}$ -ion concentration in the mother liquor. The limiting value of the  $\text{SO}_4^{--}$ -ion concentration will depend on other process variables influencing on the  $\text{Ca}^{++}$ -ion concentration and the activation energy of nucleation. It is also affected by the  $\text{P}_2\text{O}_5$ -concentration and temperature influencing the viscosity of the mother liquor and thus the diffusion.

If blocking occurs and the supply of new reagents ceases, there is further attack on the remaining free grain surface and adherent crystals are liberated. Only in the case of complete encasing will there be a loss of phosphate rock.

In the development of the Saint-Gobain gypsum process (18) the same blocking of reaction was reported. This was also the case in the development of the continuous semihydrate process.

Taking an arbitrary phosphoric acid concentration we may examine the solubility curves of dihydrate and  $\alpha$ -semihydrate<sup>x</sup> as a function of temperature. The curves in Fig.5. are prepared from solubility data by Taperova and Shul'gina /16/. At increasing temperature the solubility curve of dihydrate approaches that of semihydrate until they cross each other at the point of equilibrium, and at a still higher temperature they leave each other. At temperatures lower than the equilibrium temperature dihydrate is more stable than semihydrate, but still metastable and at higher temperatures semihydrate is more stable than dihydrate, but still metastable. In a dihydrate process there is always a certain supersaturation and thus we cross the solubility curve of semihydrate at a lower temperature than the equilibrium temperature. However, any changes in the process do not occur until the semihydrate curve is surpassed to such an extent that the supersaturation relative to semihydrate has reached the threshold value for nucleation of semihydrate. The highest possible working temperature in a dihydrate process thus depends on the highest supersaturation in the reaction system. If all parts of the reaction system, as in the Saint-Gobain gypsum process in a single vessel (18) have a low supersaturation, it is possible to work at temperatures above the equilibrium temperature without any formation of semihydrate. Sanfourche's curve in Fig.3 shows how far the equilibrium curve may be surpassed under favourable conditions.

From Fig.3. we find that Sanfourche's curve lies about  $8^\circ\text{C}$  higher than the thermodynamic curve at 32%  $\text{P}_2\text{O}_5$ ,  $12^\circ$  at 38% and  $16^\circ$  at 43%  $\text{P}_2\text{O}_5$ . From Fig.5 we find that at temperatures higher than the equilibrium temperature the dihydrate and semi-hydrate curves diverge more sharply at 32%  $\text{P}_2\text{O}_5$  than at the two higher concentrations and that the least deviation is obtained at the highest concentration. This means that at a weaker phosphoric acid concentration the threshold value is reached at a lower excess temperature at higher concentrations. There is thus a qualitative agreement between information obtained from solubility data and Sanfourche's curve relative to the thermodynamic equilibrium curve.

## "STABLE" AND "UNSTABLE" SEMIHYDRATE

In their experiments Hultbom and Lehrecke (17) found that the washed out filter cake from sludge formed in a region above their equilibrium curve would harden within 24 hours and that the cake from sludge formed below the region was still soft after 24 hours. They introduced the notations stable and unstable semihydrate. From the crystallographic point of view, however, it is now quite clear that two such modifications of semihydrate do not exist.

Within a transition region formation of semihydrate nuclei as well as dihydrate nuclei will take place, with a trend towards semi-hydrate at the higher temperatures. At a certain temperature the supersaturation relative to dihydrate will not reach the threshold value for nucleation of dihydrate, and pure semihydrate will be formed. Analogously to the preceding paragraph it follows that the lowest possible working temperature for a semihydrate process depends on the highest supersaturation in the reaction system. When washing out the filter cake the environment and the equilibrium conditions will change. We will now look at what happens to pure semihydrate in water. By simple thermal measurements (heat of hydration) in a Dewar flask, Weiser and Moreland (21) have studied the seeding effect of finely ground dihydrate on hydration of semihydrate, Figs. 6 and 7. We see here that even very small additions of dihydrate considerably shorten the induction period. This shows that it is essential to run a semihydrate process so that no dihydrate is formed. With reference to the previous presentation it is clear that the better the processes are designed regarding crystallization, the narrower the "prohibited zone" will be. Other factors in the environment affect the relative stability of semihydrate. Residues of sulphuric and phosphoric acid and impurities in the washed filter cake influence the rate of dihydrate nucleation and the rate of growth of dihydrate as well as the rate of dissolution of semi-hydrate. So do inorganic surface films formed on the crystals.

## REGULATION OF CRYSTALLIZATION BY IMPURITIES AND ADDITIONS

In the gypsum industry different organic and inorganic compounds are to a large extent used to regulate the crystal formation in the manufacture of semihydrate by hydrothermal calcination (22) and by ordinary gypsum cooking, as well as in hydration of semihydrate and anhydrite to give dihydrate (13). Of interest here is the fact that certain organic compounds, especially high-molecular ones, act as nucleation poisons. By selective adsorption on certain crystal surfaces they may have a specific influence on their growth, thereby modifying the crystal habit. Even small amounts of such compounds may have a marked effect on the size and shape of the crystals formed.

It is a well known fact that in phosphoric acid manufacture different phosphate rocks may behave very differently. Some of them give good filterable crystals of calcium sulphate whereas others give very poor crystals. Experiments at Landskrona have shown that a poor phosphate rock together with a circulating acid containing amounts of a good phosphate rock gives fairly good crystals. A moderate admixture of a good phosphate rock to a poor one has the same result. This indicates that a good phosphate rock, like P bble, contains some favourable impurities, probably of organic origin, which are entirely absent, or present in too small amounts, in

poor phosphate rocks.

On the other hand the nuclei follows the laws of colloid chemistry. It may therefore happen that in the presence of sufficient amount of protective colloids only well shaped individual crystals will form, while in the absence or presence of insufficient amount of protective colloids nuclei tend to condensate, and the crystals formed get an irregular shape. In the anhydrite as well as the semihydrate process some phosphate rocks give individual very minute crystals while others give larger dense and irregular shaped aggregates or loosely jointed agglomerates.

The subject has not yet been investigated. However, it opens potential possibilities for using any phosphate rock independently of its origin for the manufacture of phosphoric acid by wet processes.

### REACTION KINETICS

It has already been shown that all phosphoric acid processes are carried out under conditions where anhydrite II is the stable modification of calcium sulphate. However, the metastable varieties dihydrate and semihydrate are formed and very slowly transformed into the stable anhydrite II under the conditions prevailing in the dihydrate and semihydrate processes. For formation of a nucleus the reacting ions and molecules must be brought to a certain activation energy, sufficient to force a potential barrier. The higher the barrier the smaller the number of ions and molecules that have the opportunity to attain it. There is a stream in both directions along the reaction coordinate. Which one will dominate depends on the conditions. If different reaction coordinates have potential barriers of different heights, the reactions predominantly run along the coordinate with the lowest barrier, even if a reaction product richer in energy is formed. In such a case the result is a temporary storage of metastable compounds.

A low activity of water (that is a high acid concentration), a high content of reacting ions (high sulphuric acid conc.) and a high temperature increase the opportunity to exceed the potential barrier for anhydrite nucleation. E.g. local excess concentrations of sulphuric acid in a mother liquor with 40-45%  $P_2O_5$  cause extensive anhydrite nucleation even at 90°C while in a homogenous system with the same composition even at a higher temperature only semihydrate nuclei are formed. At a  $P_2O_5$ -percentage above 50 and moderate sulphuric acid excess there is also extensive anhydrite nucleation.

In the Nordengren anhydrite process (23) with intermittent reactor charging there is, in addition to anhydrite nucleation, a considerable semihydrate nucleation. During the maturing period the semihydrate formed will partly or completely redissolve and precipitate on the anhydrite crystals already in the slurry.

The kinetics of transformations of calcium sulphate in phosphoric acid solutions at 40° to 90°C have been investigated by Taperova and Shul'gina (24). The precipitation was done by suddenly adding an equivalent amount of concentrated sulphuric acid to a pure phosphoric acid containing such an amount of CaO that calcium phosphate could not precipitate.

The experiments were done in an unseeded system. In all trials the primary precipitation was semihydrate independent of temperature and  $P_2O_5$ -concentration. Within the metastability region of dihydrate, a transformation into dihydrate then occurred. At higher temperatures within the region there occurs afterwards a very slow transformation into anhydrite. At lower temperatures the latter does not take place to an observable extent. Within the metastability region of semihydrate there is a direct transformation from primarily formed semihydrate into anhydrite. At the beginning there is no observable change in the crystal water content. During this period nuclei are formed and not until their number is sufficiently large can a change be observed, the start of the growth period. The duration of the induction period is approximately in inverse proportion to the rate of nucleation.

Taparova and Shul'gina stated the following relation between the duration of the induction period and the phosphoric acid concentration

$$\log t = a + b.P \quad \text{Eq. 7.}$$

where

t = duration of induction period

P = %  $P_2O_5$

"a" and "b" are constants depending on temperature and kind of transformation.

These investigations are very illustrative but not quantitatively applicable to practical problems, where an excess of sulphuric acid, other supersaturations, impurities and seeding exist.

## CONCLUSIONS

In this presentation of the physico-chemical background of wet phosphoric acid processes the author has endeavoured to collate, correlate and apply the knowledge of various branches of science to this specific problem, and where necessary to supplement the details with his own theoretical views.

Hitherto no interest has been taken in a pure semihydrate process. However, great possibilities are connected with it. It is evident that it is possible to work the semihydrate process if the following two main conditions are fulfilled:

sufficiently long induction period for anhydrite nucleation during the process,

sufficiently long induction period for dihydrate nucleation when washing out the filter cake.

These conditions can be fulfilled under technically acceptable conditions.

REFERENCES

1. Max Volmer; Kinetik der Phasenbildung.  
Verlag von Theodor Steinkopff, Dresden und Leipzig 1939.
2. D.Turnbull and J.C. Fisher: Rate of nucleation in  
condensed systems.  
J. Chem. Phys. 17 /1949/ 71-73.
3. S.Glasstone, K.J.Laidler and H.Eyring: The theory of rate  
processes. McGraw-Hill, New York 1941.
4. Koichi Hirano: On the rate of nucleation of supersaturated  
solution. I. Some trials of the theoretical estimation of  
the nucleation rate in the electrolyte solution.  
The Science Reports of the Tohoku University. Series I,  
Volume.38, No.2, 97-103 /1954/ /Japan/.
5. J.Amsler: Nucleus formation in supersaturated solutions  
Helv. Phys. Act. 15 /1942/ 699-732.
6. W.K. Burton and N. Cabrera: Crystal growth and surface  
structure pp. 33-48 in Crystal Growth. A general  
discussion of the Faraday Society No.5. Gurney and  
Jackson, London 1949.
7. F.C. Frank: The influence of dislocations on crystal  
growth. Ibid. pp. 48-54.
8. A.R. Verma: Crystal Growth and dislocations.  
Butterworths Sci. Publ., London 1953.
9. A Chretien et J. Neubel:  
Compt. rend. 242 /1956/ 2837.
10. S.H. Branson, W.J. Dunning and B. Millard: Kinetics of  
crystallization in solution.  
Crystal Growth. A general discussion of the Faraday  
Society No.5, pp. 83-95. Gurney and Jackson, London 1949.
11. H.S. Branson and W.J. Dunning: The determination of  
particle-size distribution by means of the photoelectric  
sedimentometer.  
J. Soc. Chem. Ind. /London/ 68 /1949/ 80-84.
12. K.K. Kelley, J.C. Southard, and C.T. Anderson:  
Thermodynamic properties of gypsum and its dehydration  
products. U.S. Bureau of Mines Techn. Paper 625. U.S.  
Government Printing Office, Washington D.C., 1941.

13. A.Kruis and H.Spáth: Forschungen und Fortschritte auf dem Gipsgebiet seit 1939.  
Tonindustrie-Zeitung und Keramische Rundschau 75 /1951/  
341-351, 395-399.
14. Ullmanns Encyklopädie der technischen Chemie. Band 8, p.97  
3rd Ed, Urban & Schwarzenberg, München-Berlin, 1957.
15. Phosphoric acid. Its physical and chemical properties.  
Monsanto Technical Bulletin No. P-26. November 1, 1946.  
Monsanto Chemical Company, Phosphate Division, St.Louis, Mo.
16. Physico-chemical analysis in the field of sulphuric acid  
treatment of phosphates.  
IV. A.A. Taperova: The system  $\text{CaSO}_4 - \text{H}_3\text{PO}_4 - \text{H}_2\text{O}$   
J.Appl. Chem. USSR 13 /1940/ 643-652.  
V. A.A. Taperova and M.N.Shul'gina: The solubility of  
calcium sulphate in aqueous solutions of phosphoric acid at  
 $40^\circ$ ,  $60^\circ$  and  $90^\circ$ .  
Ibid. 18 /1945/ 521-528.
17. H. Lebrocke: Die modernen Methoden der Phosphorsäureherstellung insbesondere auf nassem Wege.  
Die Chemische Fabrik 6 /1933/ 505-507.
18. Bigot: Manufacture of wet-process phosphoric acid. The possibility of making 45%  $\text{P}_2\text{O}_5$  phosphoric acid by the gypsum process.  
Paper presented at the Technical Meeting of the International Superphosphate Manufacturers' Association, Madrid 1957.
19. J.H. Perry: Chemical Engineers' handbook. 2nd Ed, pp.398-399  
McGraw-Hill, New York 1941.
20. Sukemasa Ikeno, Keiji Kaji, and Tamotsu Tsuda: Studies on the transition temperature of calcium sulphate in mixed acid  $/\text{H}_3\text{PO}_4, \text{H}_2\text{SO}_4/$ . I.  
Gypsum & Lime /Japan/ 1958, No.33, 1607-1611.
21. H.B. Weiser and F.V. Moreland: The setting of plaster of Paris  
J. Phys. Chem. 36:1 /1932/ 1 - 30.
22. J.J. Eberl and A.R. Ingram: Process for making high-strength plaster of Paris. Ind. & Eng. Chem. 41/1949/ 1061 - 1065
23. S. Nordengren, I.Francia and R. Nordengren: The first installation of a phosphoric acid plant according to the anhydrite method at Vercelli, Italy.  
The Fertiliser Society Proceedings No.33, 1955.
24. A.A. Taperova and M.N. Shul'gina: Kinetics of transformations of crystal hydrates of calcium sulphate in the presence of phosphoric acid. J.Appl. Chem. USSR 23 /1950/ 27 - 46

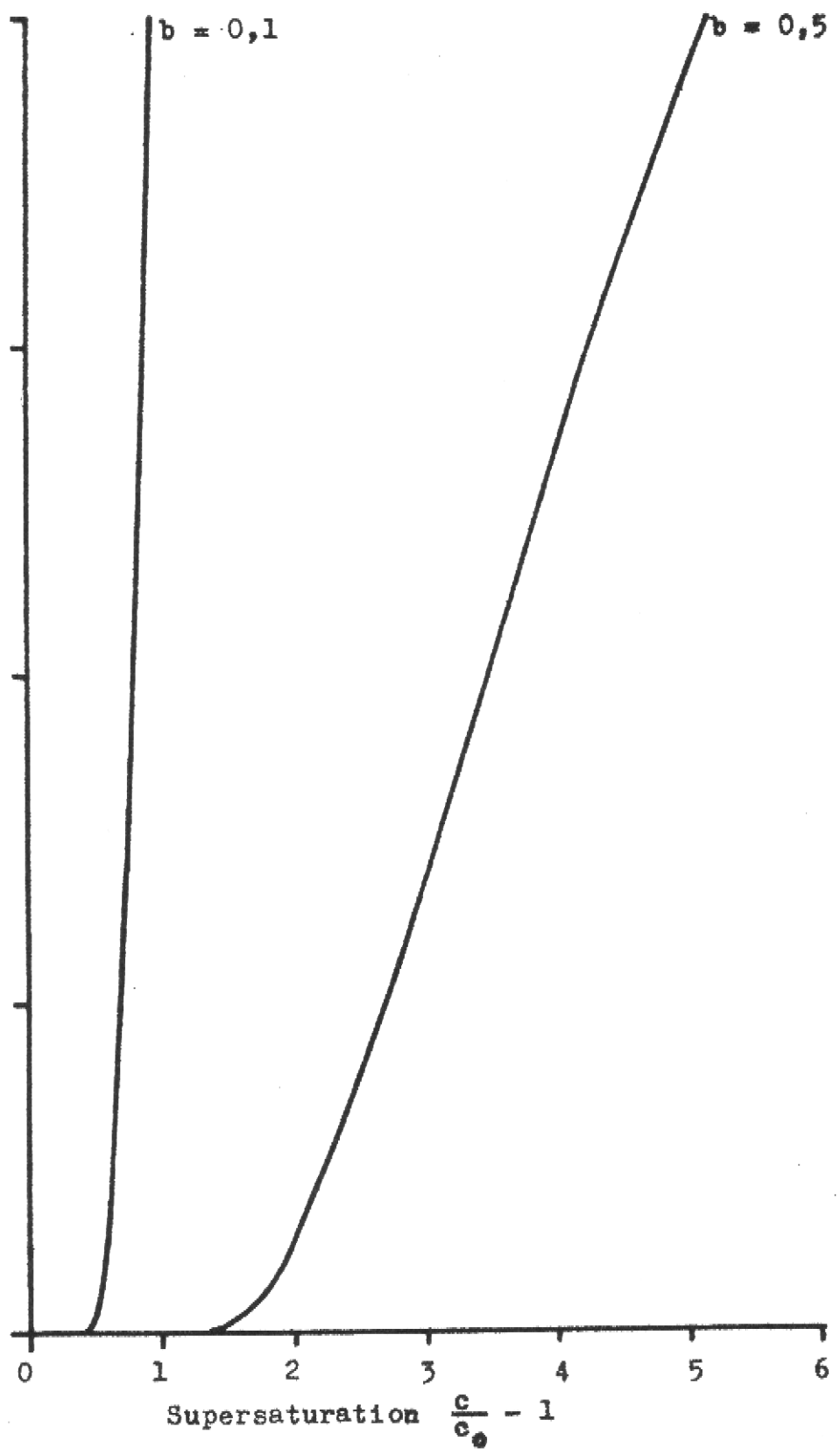
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fabriker  
Landskrona  
Sweden

Relation between nucleation frequency  
and supersaturation as to the Volmer-  
Weber theory

Figure 1  
Dahlgren

Nucleation  
frequency

Arbitrary linear scale

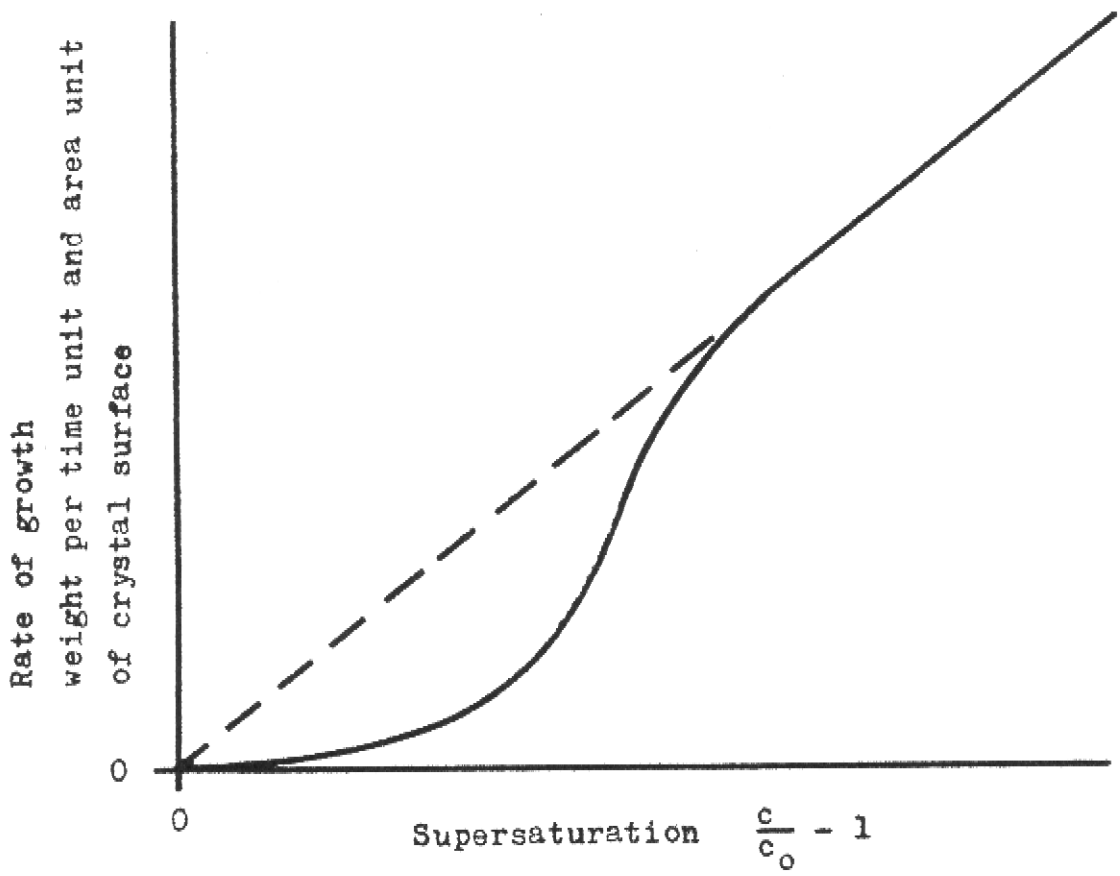


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Relation between supersaturation and  
rate of crystal growth as to the  
dislocation theory

Figure 2

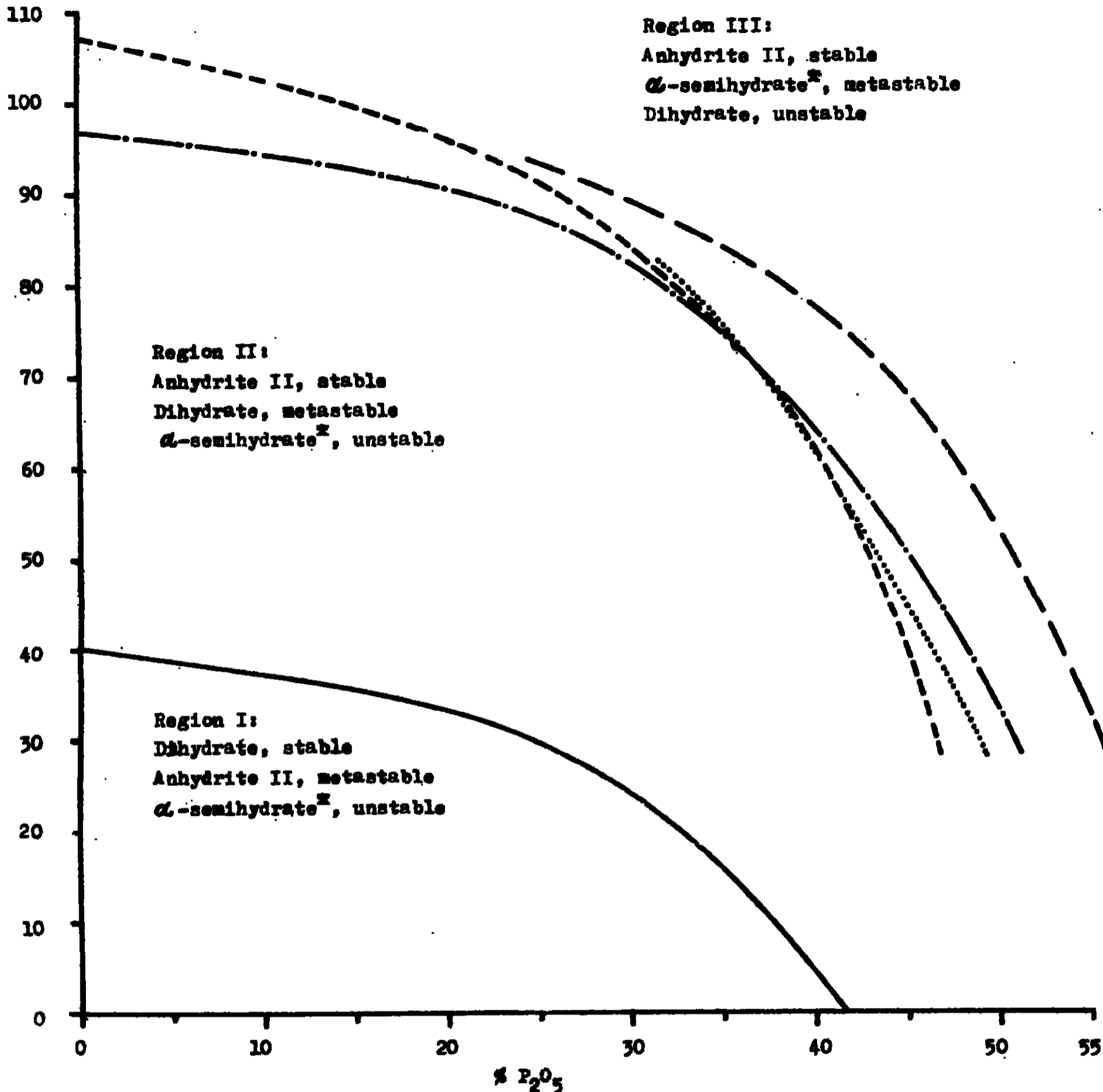
Dahlgren





Temperature

°C



Region II:  
Anhydrite II, stable  
Dihydrate, metastable  
 $\alpha$ -semihydrate\*, unstable

Region III:  
Anhydrite II, stable  
 $\alpha$ -semihydrate\*, metastable  
Dihydrate, unstable

Region I:  
Dihydrate, stable  
Anhydrite II, metastable  
 $\alpha$ -semihydrate\*, unstable

- Dihydrate - anhydrite II  
 ————— thermodynamic calculated equilibrium curve from vapor pressure of pure fosforic acid using the thermodynamic relations given by Kelley et al.
- Dihydrate -  $\alpha$ -semihydrate\*  
 -.-.-.- thermodynamic calculated equilibrium curve from vapor pressure of pure fosforic acid using the thermodynamic relations given by Kelley et al.
- Hultbon-Lehrecke's curve  
 ..... equilibrium curve from solubility measurements by Taperova and Shul'gina  
 - - - - Sanfourche's curve

The asterisk indicates an over-stoichiometric crystal water content

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The transitions  
dihydrate -  $\alpha$ -semihydrate\* and  
dihydrate - anhydrite II in  
fosforic acid solutions

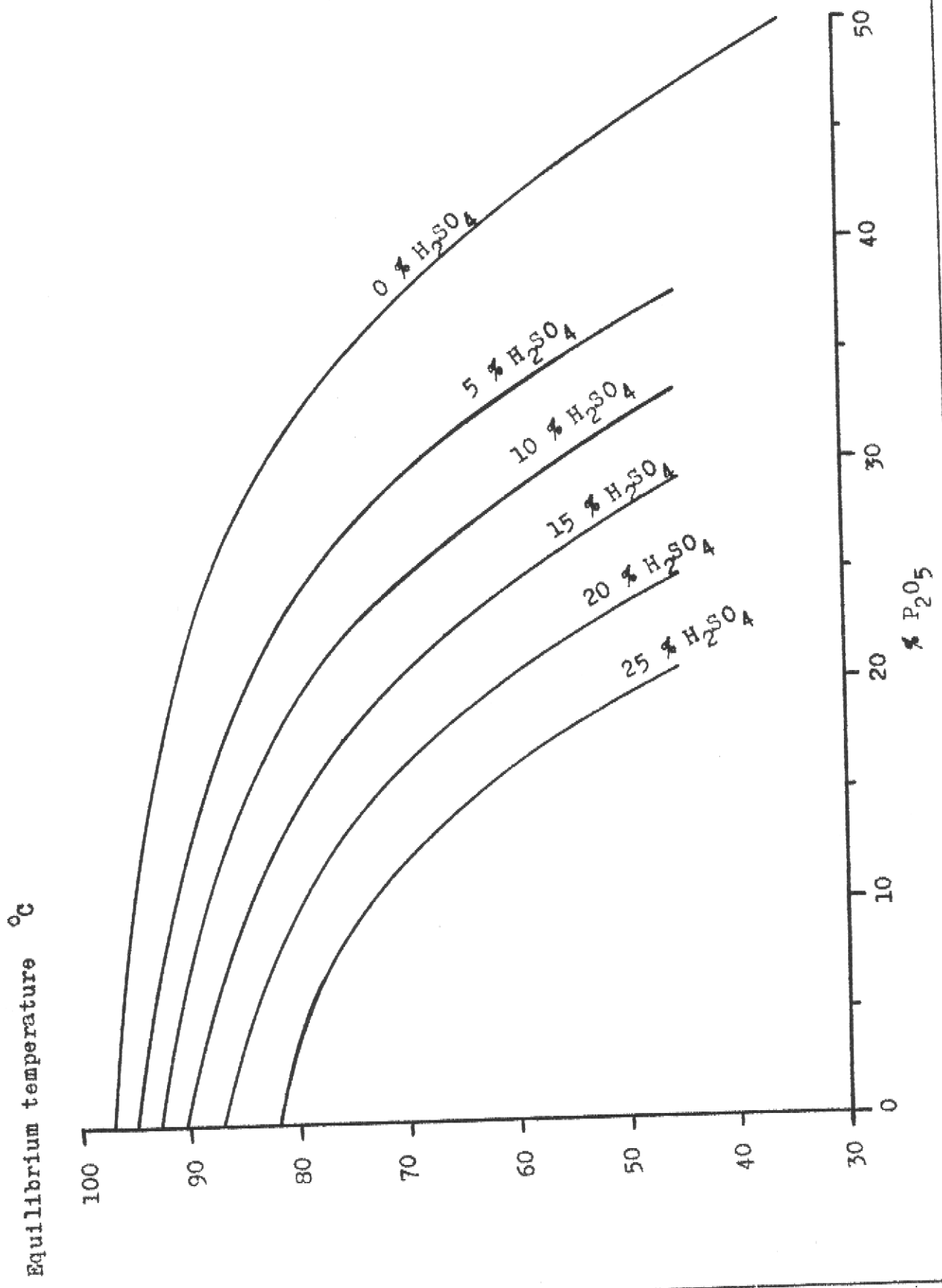
Figure 3  
Dahlgren

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Equilibrium diagram for  
dihydrate -  $\alpha$ -semihydrate<sup>Ⓢ</sup> in  
mixtures of  $H_3PO_4$  and  $H_2SO_4$

Figure 4

Dahlgren

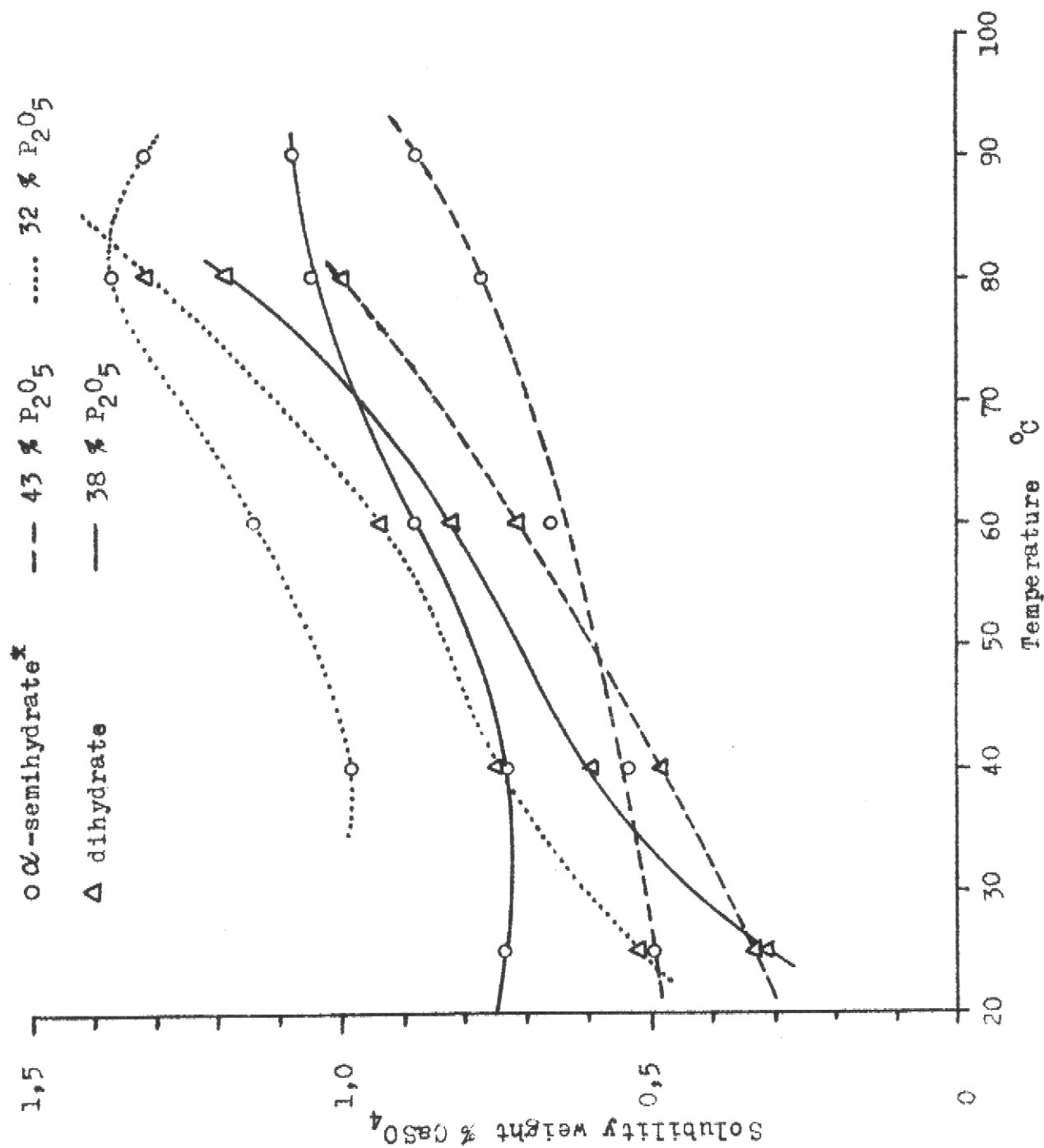


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Solubility of  $\alpha$ -semihydrate\* and  
dihydrate at different temperatures  
and  $P_2O_5$ -concentrations. Prepared  
from data by Taperova and Shul'gina

Figure 5

Dahlgren



Temperature rise

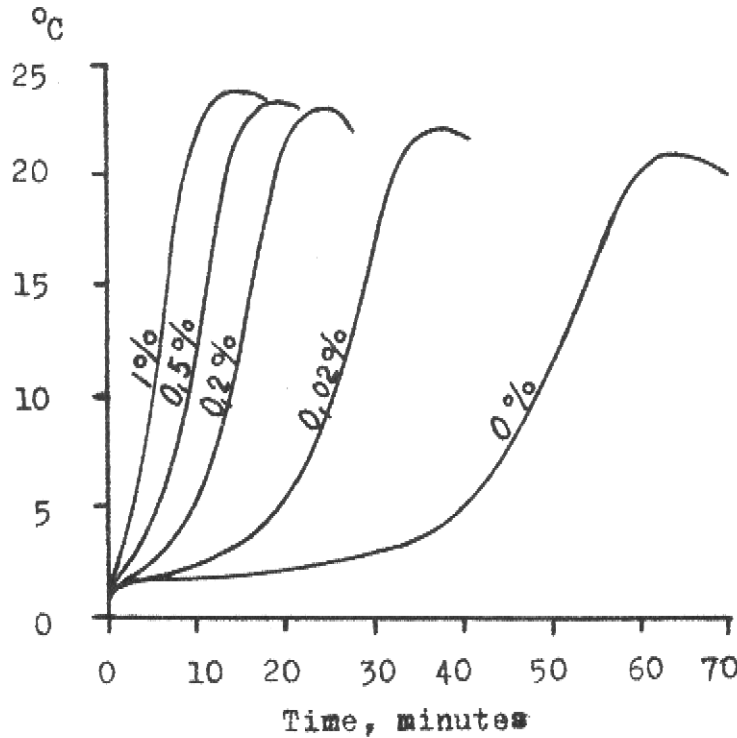


Figure 6. Heat development at hydratization of semi-hydrate with varying addition of finely milled dihydrate

Time to obtain maximum  
temperature, minutes

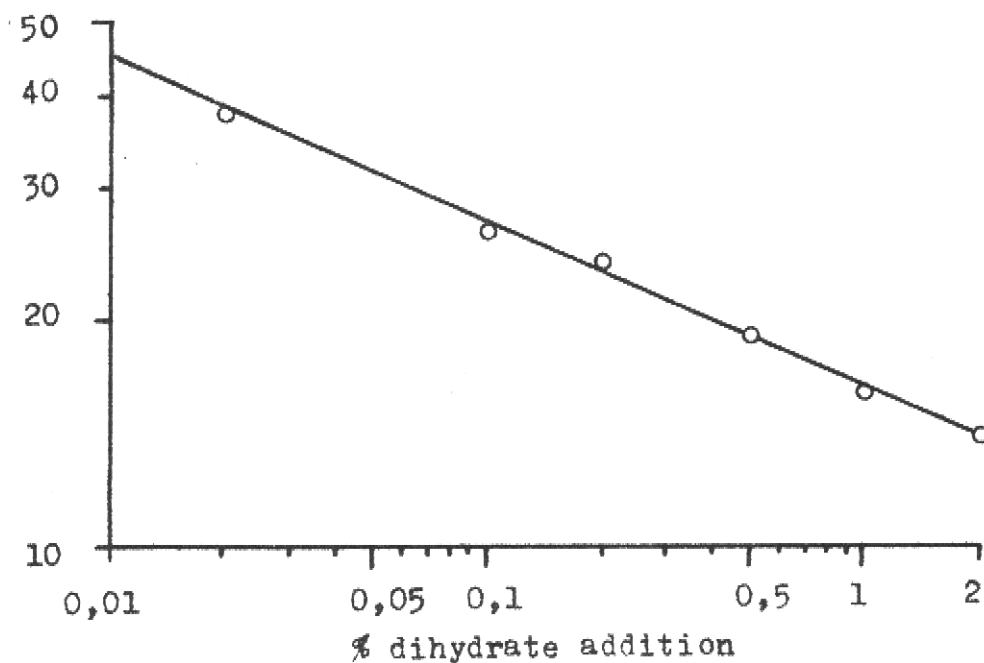


Figure 7. Relation between dihydrate addition and time to obtain maximum temperature