4. Magnesium sulfate

Magnesium sulfate forms various hydrates in aqueous solution. Experiments have been conducted with two phases, the heptahydrate, MgSO_4 \cdot 7\text{H}_2\text{O}, also referred to as epsomite, and the hexahydrate, MgSO_4 \cdot 6\text{H}_2\text{O}, known as hexahydrite. A comprehensive study of the influence of additives on thermodynamics and kinetics of crystallization of magnesium sulfate hydrates is presented. Furthermore, phase transformations in pure and impure solutions have been studied, particularly with regard to induction times in dependence on the purity of the system or temperature, respectively.

4.1 Influence of additives on thermodynamics and kinetics of crystallization

The effect of several additives on the solubility, metastable zone width, growth rate and on the crystal habit has been determined experimentally. For a better basis for discussion, certain additives have been chosen of which the influence on some features of the crystallization process had already been published (see e.g. /KARP84, NYV95/). Furthermore, all additives chosen may occur as solution by-products in actual industrial crystallization processes.

4.1.1 Solubility

Due to the addition of an impurity, the solubility of a given substance may increase, decrease or not change at all within detectable limits. With magnesium sulfate, all three effects mentioned can be observed. The influence of twelve different additives on the solubility is qualitatively illustrated in Figure 4.1-1.

![Figure 4.1-1](image)

**Fig. 4.1-1.** Influence of additives on the solubility of epsomite
As can be taken from Figure 4.1-1, KCl is the only impurity that does not noticeably influence the solubility of epsomite. Some additives increase the solubility:

KH₂PO₄, K₂SO₄, Na₂B₄O₇ · 10H₂O, NaOH

However, most additives lead to a decrease in solubility:

CaSO₄ · 2H₂O, FeSO₄ · H₂O, H₂SO₄, MgCl₂, NaCl, Na₂SO₄, NiSO₄ · 6H₂O

Quantitative solubility data can be found in the appendix / section 14.4 and 14.5.

4.1.2 Metastable zone width
Additives might also exert an influence on the width of the metastable zone. Many cases of additives widening the metastable zone can be found in literature and only few examples are known in which an impurity decreases the metastable zone width. In Figure 4.1-2, the influence of twelve additives on the metastable zone width of magnesium sulfate solutions is illustrated. Since different amounts of additives are used, the respective amount is indicated in each column. The additives are listed in alphabetical order.

![Fig. 4.1-2. Influence of additives on the metastable zone width](image-url)

The metastable zone width, or in other words the maximum possible supercooling, can be distinctly influenced by additives (see Figure 4.1-2). In Figure 4.1-2 mean values of five measurements are shown, all of which have been carried out with the ultrasonic measuring technique. Most additives exert only little influence on the metastable zone
width. However, two additives have a pronounced effect: borax (Na₂B₄O₇·10H₂O) and sodium hydroxide. The addition of borax causes a significant widening of the metastable region, whereas the addition of sodium hydroxide, i.e. the shift of pH into the alkaline region, reduces the maximum possible supercooling.

Comprehensive data on the influence of these additives on the metastable zone width of magnesium sulfate solutions is shown in the appendix, section 14.6. In this section, solely further information about the effect of potassium chloride (KCl) and di-sodium tetraborate decahydrate (borax) will be given.

![Diagram showing the influence of KCl on the maximum supercooling](image)

**Fig. 4.1-3.** Influence of KCl on the maximum supercooling

The influence of different amounts of KCl on the maximum supercooling is shown in Figure 4.1-3. In this diagram the cooling rate – which has been kept constant in all experiments – is depicted above the maximum possible supercooling. Although for all experiments thermostatic baths have been programmed with a cooling rate of 10 K/h, the actual cooling rate ranged from approximately 8 to 9 K/h. Nevertheless, the influence of variations in the cooling rate have been neglected.

For pure magnesium sulfate solutions the maximum possible supercooling varies between 3.3 and 4.0 K. By the addition of KCl no distinct changes in the supercooling-behavior can be observed. Even amounts as high as 2 wt% KCl only have a negligible effect on the temperature at which nucleation takes place. Since the addition of KCl does not change the solubility of epsomite in aqueous solution within detectable limits, no significant effect of this additive on the metastable zone width is detected (see Figure 4.1-3).

As already shown in Figure 4.1-2, borax distinctly influences the metastable zone width. In the following diagram, Figure 4.1-4, the maximum supercooling of aqueous magnesium
sulfate solutions in dependence of the impurity concentration is illustrated. Experiments have been carried out in the same manner as described for KCl and, again, an almost constant cooling rate is employed. The maximum supercooling increases significantly even with additive amounts as low as 0.1 wt%. Experiments have been conducted with additive-concentrations ranging from 0.1 to 5 wt% borax. Up to 5 wt% borax a continuous increase in the width of the metastable zone with increasing additive concentration can be observed.

![Graph showing the influence of borax on the maximum supercooling](image)

**Fig. 4.1-4.** Influence of borax on the maximum supercooling

The influence of borax on the metastable zone width is also illustrated in *Figure 4.1-5.*

![Graph showing the influence of borax on the metastable zone width](image)

**Fig. 4.1-5.** Influence of borax on the metastable zone width
The black line is the result obtained with the ultrasonic measuring technique for a pure magnesium sulfate solution. The medium gray and light gray lines represent results for solutions with 2 and 5 wt% borax, respectively. In each case, the ultrasonic velocity increases almost linearly with temperature. Only when nucleation starts, a sudden decrease of the ultrasonic velocity can be observed. Saturation and nucleation temperatures for each condition are marked with a black dot. The saturation temperature for pure solutions is 30.5°C. With increasing amount of borax, saturation as well nucleation temperatures are shifted towards lower temperatures. However, the influence of borax on the nucleation temperature is stronger than on the saturation temperature and therefore the metastable zone width broadens. The metastable zone width in dependence on the amount of borax is also emphasized by the striped field (see Figure 4.1-5).

In addition, also experiments with varying cooling rates have been carried out with the same additives, KCl and borax. All solutions are saturated at approximately 30.5°C. A comparison between the maximum supercooling in pure and impure solutions in dependence on the cooling rate is presented in Figure 4.1-6.

Both additives have been used in quantities of 0.5 wt% and mean values of five measurements are taken as basis for the diagram / Figure 4.1-6. On an average, solutions with KCl exhibit a slightly smaller metastable zone than pure solutions. In contrast to it, solutions with borax can be supercooled to a larger extent than pure solutions, independent of the cooling rate employed. It is also apparent from Figure 4.1-6, that the metastable zone is a function of the cooling rate. The metastable zone broadens with increasing cooling rate, for pure solutions as well as for solutions containing additives.
Magnesium sulfate

The metastable zone width for the heptahydrate and the hexahydrate is depicted in Figure 4.1-7. It can be seen in Figure 4.1-7 that the width of the metastable zone is not independent of temperature. The higher the temperature, the smaller the metastable zone width of both hydrates. According to literature /OTT02/, the transition temperature is approximately 48.1°C, indicated by the dotted line in Figure 4.1-7. Although the solubility curves are in good agreement with data published in literature /SEI65/ (see appendix, section 14.4), the experimentally obtained transition temperature is slightly higher, at ca. 50°C.

Fig. 4.1-7. Metastable zone width: epsomite and hexahydrite

The solubility as well as the supersolubility curves for each hydrate can be approximated by linear trendlines, listed in Table 4.1-1.

Table 4.1-1. Solubility and supersolubility of epsomite and hexahydrite

<table>
<thead>
<tr>
<th></th>
<th>solubility</th>
<th>supersolubility</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epsomite</td>
<td>c = 0.5471 ( T + 22.375 )</td>
<td>c = 0.4906 ( T + 26.179 )</td>
</tr>
<tr>
<td>Hexahydrite</td>
<td>c = 0.4274 ( T + 28.358 )</td>
<td>c = 0.4114 ( T + 30.356 )</td>
</tr>
</tbody>
</table>

Quantitative data of the solubility and supersolubility of magnesium sulfate hexahydrate and heptahydrate is listed in the appendix, section 14.4.
4.1.3 Growth rate
Experiments concerning the influence of additives on the growth rate have been carried out in two ways: measurements of single crystals in a microscopic cell, and measurements with populations of crystals in a fluidized bed. Two additives, KCl and borax, have been used. The results from measurements in a fluidized bed are illustrated as the overall growth rate versus the supersaturation ratio. The supersaturation ratio, a common expression of supersaturation /MUL00/, is defined by

\[ S = \frac{c}{c^*} \]  

(4.1-1)

In Figure 4.1-8, the growth and dissolution rate of magnesium sulfate heptahydrate crystals are shown. Experiments have been carried out in a fluidized bed, the solution having a saturation temperature of approximately 34°C.

![Growth rate of magnesium sulfate heptahydrate](image)

**Fig. 4.1-8.** Growth rate of magnesium sulfate heptahydrate

It can clearly be seen from Figure 4.1-8, that the growth rate is lower than the dissolution rate of the epsomite crystals. At a supersaturation ratio of 1.02 the growth rate is ca. \(2 \times 10^{-7}\) m/s\(^{-1}\), whereas the dissolution rate at a supersaturation ratio of 0.98 is approximately \(7 \times 10^{-7}\) m/s\(^{-1}\).

The influence of KCl on the growth and dissolution rate of epsomite crystals is illustrated in Figure 4.1-9. Measurements have been carried out with 1 and 5 wt% KCl, however, the results for the two different additive concentrations show no significant difference. It is obvious from Figure 4.1-9, that the dissolution rate of the epsomite crystals is reduced due to the addition of KCl. At a supersaturation ratio of 0.98, an overall dissolution rate of
Magnesium sulfate

$5 \times 10^{-7}$ ms$^{-1}$ has been measured, in contrast to $7 \times 10^{-7}$ ms$^{-1}$ for solutions containing no additive. Regarding the influence of KCl on the growth rate, no clear result is obtained. With both additive concentrations, the growth rate is not distinctly influenced, although the results give the impression that the growth rate slightly increases due to the addition of KCl. When 5 wt% KCl are added to the solution, the saturation temperature is slightly increased (about 0.2 K), i.e. the solubility is decreased. This effect has already been considered in Figure 4.1-9, the curve has been shifted to the zero point to show only the kinetic effect.

![Figure 4.1-9](image)

**Fig. 4.1-9.** Influence of KCl on the growth rate of magnesium sulfate heptahydrate

The influence of borax on the growth rate of epsomite crystals is already known /NYV95/. Therefore, no experiments with borax in the fluidized bed have been conducted. However, in order to find out about the influence of borax on single faces of a crystal, growth rate measurements have been carried out in a microscopic cell. For the same reason, also additional experiments with the additive KCl have been conducted in the microscopic cell.

In all experiments carried out in the microscopic cell, crystals have been measured according to the scheme shown in Figure 4.1-10.

![Figure 4.1-10](image)

**Fig. 4.1-10.** Magnesium sulfate hexahydrate (Mg6) and heptahydrate (Mg7) crystals as measured in the microscopic cell
Results of experiments having been conducted in the microscopic cell with both additives, KCl and borax, are shown in Figure 4.1-11. The additive concentration amounts to 5 wt% in all experiments, and mean values of crystal growth rates from seven measurements are taken.

Experiments from growth rate measurements of single crystals in a microscopic cell show that the linear change in size in both directions increases with KCl, whereas it decreases due to the addition of borax. When borax is added, the growth rate of the epsomite crystals is almost the same in x- and y-direction.

Growth rates for crystals grown in pure solutions and in solutions with the respective additive are depicted in Table 4.1-2.

<table>
<thead>
<tr>
<th></th>
<th>x-direction</th>
<th>y-direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epsomite</td>
<td>$1 \times 10^{-7}$ ms$^{-1}$</td>
<td>$5 \times 10^{-8}$ ms$^{-1}$</td>
</tr>
<tr>
<td>+ 5 wt% KCl</td>
<td>$2 \times 10^{-7}$ ms$^{-1}$</td>
<td>$6 \times 10^{-8}$ ms$^{-1}$</td>
</tr>
<tr>
<td>Epsomite</td>
<td>$4 \times 10^{-8}$ ms$^{-1}$</td>
<td>$5 \times 10^{-8}$ ms$^{-1}$</td>
</tr>
<tr>
<td>+ 5 wt% borax</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In the microscopic cell also the influence of KCl and borax and the growth rate of the hexahydrate has been measured. Results of these measurements are shown in Figure 4.1-12.
Magnesium sulfate

Fig. 4.1-12. Influence of additives on the growth rate of magnesium sulfate hexahydrate

In pure solutions, crystals of the hexahydrate grow in the same magnitude in both directions. When KCl is added to the solution, the crystals grow more slowly than in pure solutions. The linear change in size in the presence of KCl is influenced to the same extent in both, the x- and y-direction. Due to the addition of borax, the growth rate is decreased more distinctly. However with borax, the growth rate in the x-direction is reduced stronger than in the y-direction.

Growth rates of the hexahydrate with and without additives are comprised in Table 4.1-3.

Table 4.1-3. Growth rates of hexahydrate crystals in single crystal measurements

<table>
<thead>
<tr>
<th>Hexahydrate</th>
<th>x-direction</th>
<th>9 \cdot 10^{-8} \text{ ms}^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>y-direction</td>
<td>9 \cdot 10^{-8} \text{ ms}^{-1}</td>
</tr>
<tr>
<td>Hexahydrate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>+ 5 wt% KCl</td>
<td>x-direction</td>
<td>8 \cdot 10^{-8} \text{ ms}^{-1}</td>
</tr>
<tr>
<td></td>
<td>y-direction</td>
<td>8 \cdot 10^{-8} \text{ ms}^{-1}</td>
</tr>
<tr>
<td>Hexahydrite + 5 wt% borax</td>
<td>x-direction</td>
<td>3 \cdot 10^{-8} \text{ ms}^{-1}</td>
</tr>
<tr>
<td></td>
<td>y-direction</td>
<td>4 \cdot 10^{-9} \text{ ms}^{-1}</td>
</tr>
</tbody>
</table>

4.1.4 Crystal habit

The habit of magnesium sulfate heptahydrate, which belongs to the rhombic-disphenoidal class /GME53/, is illustrated in Figure 4.1-13. The crystal shown in Figure 4.1-13 b, has been grown in a microscopic cell at low supersaturation, and thus, with a relatively slow growth rate. It can be seen from Figure 4.1-13 b that the faces of the epsomite crystal are well-developed.
Magnesium sulfate

**Fig. 4.1-13.** Habit of epsomite crystals
a) theory /SGU87/, b) experiment

**Fig. 4.1-14.** Habit of magnesium sulfate heptahydrate crystals
a) without additive, b) with 5 wt% KCl, c) with 5 wt% borax

Comparing both crystals, the resemblance between the epsomite crystal obtained experimentally and the habit known from literature is emphasized (see *Figure 4.1-13*).
Epsomite crystals which are grown in a pure magnesium sulfate solution are shown in Figure 4.1-14 a. It is obvious that even crystals grown in pure solutions show differences in their habit. Among crystals having the typical orthorhombic form, also shortened crystals with a higher length to width ratio are grown. In Figure 4.1-14 b, the influence of KCl on the habit of epsomite crystals is shown. Due to the addition of KCl, all crystals exhibit a shortened habit compared to the crystals grown in a pure solution. By the addition of borax, this effect is even more pronounced (see Figure 4.1-14 c). The epsomite crystals grown in the presence of borax do not have the typical orthorhombic form anymore, but look rather wedge-shaped.

Fig. 4.1-15. Habit of magnesium sulfate hexahydrate crystals
   a) without additive, b) with 5 wt% KCl, c) with 5 wt% borax

Both additives influence the habit of the hexahydrite crystals to a similar degree as they influence the habit of the epsomite crystals. In Figure 4.1-15 a, crystals of the hexahydrite grown in a pure solution are shown. Compared to the crystals grown without additive, KCl exerts only little influence on the habit whereas borax changes the external form of the hexahydrite more distinctly (see Figures 4.1-15 b and 4.1-15 c). The generally hexagonal habit of the hexahydrite crystals is changed to an almost rhombic habit due to the addition of borax.
4.2 Phase transformation
The transition temperature between magnesium sulfate heptahydrate and hexahydrate is approximately 48.1°C /OTT02/. Above the transition point, the hexahydrate is the stable phase and the heptahydrate is metastable, below this point the opposite applies. Phase transformations of magnesium sulfate heptahydrate to the hexahydrate and in reverse order have been observed in a microscopic cell. For the transformation of the hexahydrate to the heptahydrate, solutions have been prepared being saturated at ca. 30.5°C. During the experiment, the solution is slightly supersaturated with regard to the heptahydrate. A seed crystal of the hexahydrate, without special prior treatment, is added to the solution. The course of the transformation is illustrated in Figure 4.2-1. It can be seen that the crystal of the metastable hexahydrate gradually dissolves while the stable heptahydrate nucleates and grows onto the dissolving crystal of the hexahydrate.

Fig. 4.2-1. Phase transformation of magnesium sulfate hexahydrate to the heptahydrate

A transformation in reverse order has been carried out in a solution saturated at 55°C. During the experiment, the solution is slightly supersaturated with respect to the hexahydrate. A seed crystal of the heptahydrate, without special prior treatment, is added to the solution. In Figure 4.2-2, the course of the phase transformation is shown. The crystal of the metastable heptahydrate gradually dissolves and simultaneously the hexahydrate nucleates and grows onto the dissolving crystal of the heptahydrate.
Fig. 4.2-2. Phase transformation of magnesium sulfate heptahydrate to the hexahydrate

Besides the phase transformation experiments in the microscopic cell, studies have also been carried out in a crystallizer. The transformation of the hexahydrate to the heptahydrate in these experiments has been monitored with the ultrasonic measuring technique. A schematic of how the phase transformation experiments are conducted is given in Figure 4.2-3.

Single steps of the phase transformation experiments carried out in the crystallizer are as follows:
(1) cooling, addition of seed crystal, nucleation hexahydrate
(2) constant temperature, depletion of supersaturation by crystal growth
(3) cooling, growth hexahydrate
(4) nucleation epsomite, dissolution hexahydrate and growth epsomite

In this context, the induction time for nucleation of the stable phase is defined as the period of time starting when the final transformation temperature is reached until nucleation of the stable phase starts.

The course of a phase transformation monitored by the ultrasonic measuring technique is depicted in Figure 4.2-4. Both, ultrasonic velocity and temperature, have been measured in-line with the ultrasonic sensor. All solution-mediated transformations of the metastable
hexahydrate to the stable heptahydrate have been carried out as schematically shown in Figure 4.2-3.

![Figure 4.2-3. Solution-mediated phase transformation: hexahydrate to heptahydrate](image)

In the phase transformation experiments, solutions with a saturation temperature of 56°C are cooled to 53°C. If nucleation of the hexahydrate does not start within 15 minutes, a seed crystal is added to induce nucleation. After depletion of supersaturation by nucleation and crystal growth, the suspension is cooled to the final transformation temperature below the transition point. In this series of experiments, the solution-mediated phase transformation has been carried out at a constant temperature of 45°C. After reaching the final temperature of 45°C, the ultrasonic velocity increases linearly with time until nucleation of the stable phase starts. The starting point of nucleation of the heptahydrate is indicated by a distinct increase in ultrasonic velocity and by a temperature peak. In the pure solution, nucleation of the stable phase starts after an induction period of approximately 19 hours, as can be read from Figure 4.2-4.

The two additives, KCl and borax, significantly influence the induction time for nucleation of the heptahydrate. The effect of KCl on the phase transformation can be seen in
Adding KCl obviously accelerates the transformation. In solutions with 0.5 wt% KCl, nucleation of the heptahydrate already starts after an induction time of 45 minutes. In contrast to it, transformation in the presence of 0.5 wt% borax is distinctly prolonged (see Fig. 4.2-6). Nucleation of the stable phase can only be observed after an induction time of approximately 70 hours. In both cases, nucleation of the heptahydrate is accompanied by a distinct increase of the ultrasonic velocity and an increase in temperature.

Fig. 4.2-4. Phase transformation of magnesium sulfate heptahydrate to hexahydrate

Fig. 4.2-5. Phase transformation of magnesium sulfate with 0.5 wt% KCl

However, the induction times reported for the above mentioned phase transformations cannot be taken as given. Even if repetitive experiments are carried out in analogous
manner, the induction times until nucleation of the heptahydrate starts may vary experiment-to-experiment. In the case of pure solutions, nucleation of the heptahydrate starts after 10 to 19 hours. With 0.5 wt% KCl the induction times vary between 30 and 45 minutes, whereas with 0.5 wt% borax induction times from 27 to 70 hours have been monitored with the ultrasonic measuring technique.

![Fig. 4.2-6. Phase transformation of magnesium sulfate with 0.5 wt% borax](image)

The phase transformation experiments have been monitored by means of the ultrasonic measuring technique. Furthermore, for optical evaluation of the progress of transformation, samples have been taken during a phase transformation experiment in pure solution. The crystals have been withdrawn from solution, filtered and dried at ambient conditions. After

![Fig. 4.2-7. Times of sampling in a phase transformation experiment](image)
drying, all samples have been evaluated by optical microscopy. Times of sampling are indicated in Figure 4.2-7. The first sample (1) is taken at the beginning of cooling still above the transition temperature and the last sample (6) at the end of the transformation, when only crystals of magnesium sulfate heptahydrate are present in the slurry. Photographs of these samples are shown in Figure 4.2-8. Since different modifications are used, a scalar is plotted in each photograph.

Fig. 4.2-8. Course of the phase transformation of magnesium sulfate hexahydrate to the heptahydrate

1 53°C, 45min
2 45°C, 2h 40min
3 45°C, 4h 45min
4 45°C, 19h 05min
5 45°C, 20h 25min
6 45°C, 22h 55min
In the first photograph, taken at the beginning of cooling, only crystals of the hexahydrate can be seen. The fifth photograph, which is taken when nucleation of the heptahydrate is detected by the ultrasonic measuring technique, shows crystals of both phases, the hexahydrate as well as the heptahydrate. However, already before noticeable nucleation of the heptahydrate starts, single crystals of the heptahydrate can be found in the suspension, shown in the photographs (2), (3) and (4). About two and half hours after noticeable nucleation of the heptahydrate has started, no crystals of the hexahydrate can be observed anymore (see sixth photograph).

4.2.1 Induction times
Magnesium sulfate solutions with a saturation temperature of 56°C have been prepared. In the course of the experiments, solutions are cooled to 53°C into the metastable zone of the hexahydrate. If nucleation of the hexahydrate does not start within 15 minutes, a seed crystal is added to induce nucleation. After nucleation of the hexahydrate, the suspensions have been kept at a constant temperature of 53°C for at least 30 minutes to assure depletion of supersaturation by nucleation and growth of the crystals. Subsequently, the suspensions have been cooled to varying temperatures below the transition temperature, which is reported to be 48.1°C /OTT02/.

All experiments have been monitored by means of the ultrasonic measuring technique. The induction time is defined as the period of time between reaching the final transformation temperature and the start of nucleation of the stable heptahydrate. Thus, an induction time of zero means that nucleation of the heptahydrate starts instantaneously when the transformation temperature is reached. An example for instantaneous nucleation in a phase transformation experiment is shown in Figure 4.2-9.

![Figure 4.2-9. Instantaneous nucleation at 30°C](image-url)
Nucleation of the heptahydrate starts directly when the final transition temperature of 30°C is reached (see Figure 4.2-9). An arrow marks the onset of nucleation, which is accompanied by an increase in ultrasonic velocity and a temperature peak.

An example for varying induction times at one constant temperature can be seen in Figure 4.2-10. Both transformation experiments have been carried out at 45.5°C. At this temperature, the induction times do not differ distinctly. In one experiment, nucleation of the heptahydrate starts after almost 4 hours, in the other experiment an induction time of 5 hours has been monitored.

![Graph](image1.png)

**Fig. 4.2-10.** Different induction times at 45.5°C in phase transformation experiments

![Graph](image2.png)

**Fig. 4.2-11.** Induction times for magnesium sulfate solutions as a function of temperature
Induction times as a function of temperature are depicted in Figure 4.2-11. Experiments have been carried out in the temperature range between 30 and 46°C. Temperatures below 30°C could not be reached, because in the respective experiments nucleation already started during cooling, i.e. before the final transition temperature has been reached. All experiments between 30 and 43°C have been repeated three times with very reproducible results. In this temperature range, nucleation always starts within one hour. Experiments at temperatures higher 46°C have been interrupted, because the induction times exceed 200 hours.

5. Discussion of the results for magnesium sulfate

The study of the influence of KCl and Borax has shown that the influence of KCl is often neglectable whereas borax has a strong inhibiting effect in every respect. Concerning the influence of additives on phase transformations it could be demonstrated that both is possible, a reduction as well as a prolongation of induction times attained with KCl and borax, respectively. However, it is also shown that a reliable prediction of induction times is not possible, neither in pure systems nor in systems with additives.

5.1 Influence of additives on thermodynamics and kinetics of crystallization

5.1.1 Solubility and metastable zone width

Even small traces of additives can influence the solubility and metastable zone width (see Figures 4.1-1 and 4.1-2). It is known that a pH more alkaline or acidic can influence the solubility as well as the amount of supersaturation tolerated by a system /EGL63/. Since all of the additives used in the experiments have changed the pH of the solution to some extent, this can be taken as a possible explanation for the influence of these additives on the solubility. The pH of a pure magnesium sulfate solution is approximately 6.4, a pH distinctly more acidic being obtained by adding e.g. 1 wt% FeSO₄ • H₂O (pH: 4.6) or 1 wt% KH₂PO₄ (pH: 3.2). It is possible that the additive either only increases the ionic strength I of the solution without forming complexes with the solute or the additive increases the ionic strength and simultaneously forms soluble complexes with the solutes /EGL63/. However, a possible formation of complexes has not been further prosecuted.

Concerning the influence of additives on the metastable zone width, two contrary effects have been observed: On the one hand, a slight decrease of the width of the metastable zone with 0.5 wt% KCl (see Figures 4.1-3 and 4.1-6), and on the other hand, an increase of the metastable zone width with 0.5 wt% borax (see Figures 4.1-4 to 4.1-6). From the state of the art it is known that the solution-composition influences the interfacial free energy γ between the solvent and the solute. Since any adsorption onto the surface of a nucleus decreases the interfacial free energy, an increase of the nucleation rate should be observed when impurities are present in the solution. However, this would be the sole result of the thermodynamic effect and does not take into account the kinetic effect. Since the growth of a nucleus proceeds only via a few growth sites, merely a few adsorbed impurity molecules are necessary for inhibiting the growth of a nucleus /EGL63/. In this