

## PROBABLE MECHANISM OF THE EFFECT OF THERMAL HISTORY OF SOLUTION ON THE METASTABLE ZONE WIDTH

Jaroslav NÝVLT

*Institute of Inorganic Chemistry,  
Czechoslovak Academy of Sciences, 160 00 Prague 6*

Received July 12th, 1983

The metastable zone width of an aqueous solution of  $\text{FeSO}_4$  has been measured as a function of the temperature of solution overheating. For the solution overheated to a temperature lower than that of hydrate transformation, the data fit to a continuous, smooth curve, while points obtained in overheating the solution above the hydrate transformation temperature lie distinctly above the extension of the curve. Of hypotheses advanced in the literature to explain the thermal history of solution, only that based on redistribution of subcritical cluster sizes of crystallizing substance seems compatible with the observations.

A previous communication<sup>1</sup> gave a summary of hypotheses advanced in the literature to explain the effect of thermal history on the behaviour of solution. The hypotheses are based on the concepts of *a*) kinetics of redistribution of subcritical cluster sizes of crystallizing substance, *b*) kinetics of dissolution of microscopic and/or submicroscopic solid particles of crystallizing substance, *c*) permanent or temporary deactivation of foreign solid particles, and *d*) destruction of foreign heterogeneous particles. Results obtained for the effect of thermal history of KCl solutions on the metastable zone width eliminated hypotheses (*c*) and (*d*) from consideration, but did not permit decision to be made between the hypotheses of subcritical cluster size redistribution and dissolution of microcrystals in pores of heterogeneous impurities.

The aim of this work was to present experimental material which would give a basis for deciding on the validity of either of these hypotheses.

### THEORETICAL

All experimental data available for the effect of the temperature of solution overheating on the metastable zone width follow the same general pattern<sup>2</sup>: the attainable undercooling is smallest for solutions which have not been overheated, and the metastable zone width,  $\Delta T_{\text{max}}$ , increases as the solution overheating,  $\Delta T_{\text{H}}$ , is increased. A plot of  $\Delta T_{\text{max}}$  against  $\Delta T_{\text{H}}$  is initially a steeply rising curve whose slope gradually decreases until at great overheatings the undercooling approaches a limiting value characteristic of a particular system and experimental conditions employed. The

curve is continuous and smooth, and may formally be fitted with the empirical equation

$$\Delta T_{\max} = \Delta T_0 + a \Delta T_H^b \quad (1)$$

or

$$\ln(\Delta T_{\max} - \Delta T_0) = a + b \ln \Delta T_H. \quad (2)$$

For a system whose crystallizing component undergoes a hydrate transformation at a temperature above the saturation temperature, hypotheses (a) and (b) imply the following behaviour of the metastable zone width.

Hypothesis (a) (redistribution of subcritical cluster sizes of crystallizing substance): at the temperature of hydrate transformation there are also changes in temperature dependences of a number of physicochemical properties of solution and hence, a change in the structure, or arrangement of particles in solution, may be assumed to occur. At temperatures below the hydrate transformation temperature the corresponding hydrate will precipitate from supersaturated solution, and the effect of solution overheating will be described by Eq. (1). Overheating the solution above the hydrate transformation temperature will, however, induce the formation of subcritical clusters of anhydrous compound or a lower hydrate. After cooling the solution rapidly to the saturation temperature, the particle groupings will persist for a time, resulting in a widening of the metastable zone, *i.e.* a deviation from the dependence expressed by Eq. (1), on subsequent cooling. This is in line with Ostwald's law of transient stages,<sup>3</sup> according to which a metastable phase separates preferentially under certain conditions and only after a time does it transform into the equilibrium stable phase.

Hypothesis (b) (dissolution of microscopic and/or submicroscopic solid particles of crystallizing substance) assumes that microcrystals of the solid phase surviving in micropores of heterogeneous impurities and/or micropores of the vessel walls grow up in saturated solution to fill the capillary mouth, where they start functioning as nuclei<sup>4</sup>. If these microcrystals can survive even in overheated solution, they will be unaffected either by increasing the temperature beyond that of hydrate transformation (recrystallization usually occurs *via* solution), and a plot of  $\Delta T_{\max}$  against  $\Delta T_H$  will show no discontinuities. This effect should be even more reflected in the measured metastable zone width if a seed crystal of the hydrate is immersed in the solution on cooling to saturation temperature.

## EXPERIMENTAL

The measurements of the metastable zone width were made on the system  $\text{FeSO}_4\text{-H}_2\text{O}$ . This choice was not fortuitous. The requirements for the system were that it should undergo a change in the number of molecules of hydration water or a modification transformation in the experi-

mentally accessible temperature range, and also show suitable solubility. The transformation temperature had to be such as to allow reliable overheating of solution by at least 10 K below and above its value, as well as controlled cooling at a constant rate of 20K/h in the region below the saturation temperature, this being performed on the same apparatus as used in previous studies. In practical terms, the solution had to be saturated at about 40°C (an attainable temperature gradient with respect to the surrounding of at least 8°C), and the transformation temperature had to be below 60°C (owing to difficulties in overheating above 75°C). Of the broad range of systems<sup>5</sup>, NaBr-H<sub>2</sub>O, with a hydrate transformation temperature of 51°C, and FeSO<sub>4</sub>-H<sub>2</sub>O were singled out as the best candidates. With NaBr, seeding with a crystal kept above the solution during overheating proved unfeasible — the crystal dissolved. This left us with FeSO<sub>4</sub>-H<sub>2</sub>O as the only readily available system suited to our purpose. Ferrous sulphate crystallizes<sup>5</sup> as heptahydrate in the range 0 to 56.5°C, as tetrahydrate in the range 56.5 to 63.5°C, and as monohydrate above 63.5°C. A solution saturated at 40°C was prepared by mixing 111.27 g FeSO<sub>4</sub>·7 H<sub>2</sub>O (Lachema, analytical grade) in 100 g of distilled water. The solution was filtered, and a faint turbidity arising from the presence of Fe<sup>3+</sup> was removed by adding a small amount (0.025 mass %) of ascorbic acid (a test confirmed that this addition had no effect on the metastable zone width).

The study of the effect of thermal history of solution on the metastable zone width was carried out using the same apparatus as described earlier<sup>6</sup>. Magnetically stirred solution was overheated for 180 min by a temperature difference  $\Delta T_H$ , and then cooled down at a rate of approximately 100 K/h. On reaching the saturation temperature, the solution was seeded with a crystal of heptahydrate fixed on a holder, and cooled again at a rate of 20.0 K/h until visible crystals separated. The seed crystal was then removed, and the solution was heated slowly to check the saturation temperature  $T_{eq}$  by the last-crystal-dissolution method. Measurements were carried

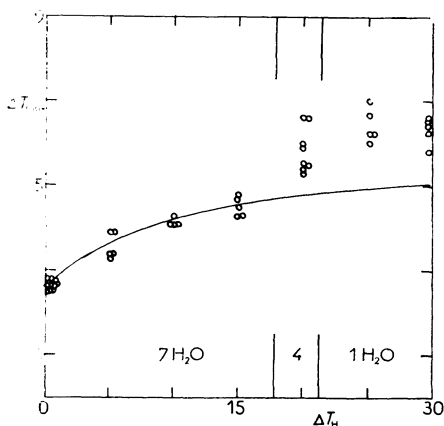


FIG. 1

Effect of thermal history of FeSO<sub>4</sub> solution on the metastable zone width (a solution saturated at 40°C, overheating  $\Delta T_H$  for 180 min)

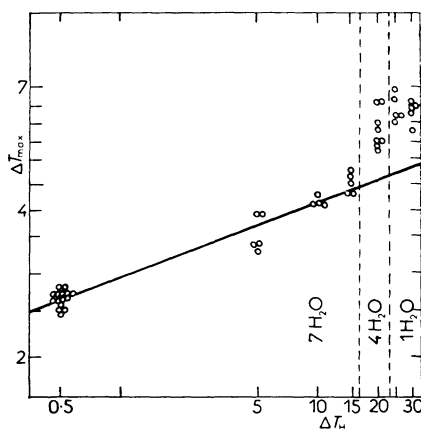


FIG. 2

Correlation of experimental results by Eq. (3)

out for  $\Delta T_H = 0.5$  K (a total of 15 runs, including check measurements in other series of experiments),  $\Delta T_H = 5, 10,$  and  $15$  K (5 to 8 runs at each temperature, with time lapses of at least 16 h between the successive experiments),  $\Delta T_H = 20$  K (the region of the equilibrium existence of tetrahydrate), and finally  $\Delta T_H = 25$  and  $30$  K (the monohydrate region). Results of the measurements are shown in Fig. 1.

#### DISCUSSION AND CONCLUSIONS

Results from the measurements of the metastable zone width of ferrous sulphate saturated at  $40^\circ\text{C}$  for  $\Delta T_H = 0.5, 5, 10,$  and  $15$  K were correlated by Eq. (2). The constants  $a$  and  $b$  were evaluated for chosen values of  $\Delta T_0$  by the method of least squares, and correlation coefficients,  $R$ , were calculated. The highest correlation coefficient,  $R = 0.976$ , was found for  $\Delta T_0 = 1.9$  K. The correlating equation

$$\ln(\Delta T_{\max} - 1.90) = -0.0426 + 0.364 \ln \Delta T_H \quad (3)$$

or

$$\Delta T_{\max} = 1.90 + 0.958 \Delta T_H^{0.364} \quad (4)$$

is represented by the straight line in Fig. 2, where experimental points are also shown for comparison. Calculated and average experimental values of  $\Delta T_{\max}$  and their deviation,  $\Delta$ , for various overheatings  $\Delta T_H$  are given in Table I.

From Fig. 2 and data of Table I the values of the metastable zone width for overheatings exceeding the hydrate transformation temperature are seen to lie distinctly above the extension of the line drawn through points obtained at lower tempera-

TABLE I

Effect of overheating,  $\Delta T_H$ , on the metastable zone width,  $\Delta T_{\max}$ , of  $\text{FeSO}_4$  in aqueous solution saturated at  $40^\circ\text{C}$

$\Delta T_H$	$\Delta T_{\max}$		$\Delta$
	experimental	calculated	
0.5	2.65	2.64	-0.01
5	3.58	3.62	+0.04
10	4.15	4.12	-0.03
15	4.52	4.47	-0.05
20	5.85	4.76	-1.09
25	6.42	5.00	-1.42
30	6.32	5.21	-1.11

tures. The difference is statistically significant: inclusion of all 47 measured values of  $\Delta T_{\max}$ , i.e. for  $\Delta T_H$  up to 30°C, yields a correlation coefficient of 0.856, which is too low compared with the above value  $R = 0.976$ . In view of the considerations presented in Theoretical, it may be concluded that the effect of thermal history of solution on the metastable zone width may, in the given case, be explained in terms of the hypothesis of subcritical cluster size redistribution.

#### REFERENCES

1. Nývlt J.: This Journal 49, 559 (1984).
2. Vacek V.: Chem. Listy, in press.
3. Ostwald W.: *Lehrbuch der Allgemeinen Chemie*, Vol. II, p. 444. Engelmann, Leipzig 1896 to 1902 (cited according to *Nucleation* (A. C. Zettlemoyer, Ed.), p. 62. (M. Dekker, New York 1969).
4. Turbull D.: J. Chem. Phys. 18 (2), 198 (1950).
5. Broul M., Nývlt J., Söhnel O.: *Solubility in Inorganic Two-Component Systems*. Academia, Prague-Elsevier, Amsterdam 1981.

Translated by M. Škubalová.