Determination of Solubility Curves by the Schlieren Method. Computer Control of Growth and Dissolution

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A system for computer control of growth and dissolution processes is described. The main components of the system are: An He–Ne laser as light source, a tv camera as monitor, a microprocessor as controller of temperature and concentration, and a medium size computer which controls the state of growth or dissolution on time sharing basis. By application of the schlieren technique the system has been used to determine solubility curves for K_2SO_4 , $KBrO_3$, and $KAl(SO_4)_2 \cdot 12H_2O$.

Application of a digital computer makes it possible to survey and to control growth and dissolution processes dynamically. The control signal can be produced by a TV camera if the solution is transparent. Quantitative measures can then be obtained for the size and for the convexity of the boundary of a crystal. Determination of solubility curves¹ using the schlieren technique can be made automatically and in a detailed way. This is illustrated by three examples in the present paper. Work on the experimental determination of the concentration variation near the surface of a growing crystal, using the schlieren technique, is in progress.

SCHLIEREN APPARATUS

The schlieren method² has been applied in studies of solid phase – solution processes.³ A general comparison of schlieren technique with interferometric techniques is given by Brown,⁴ and a review of the schlieren method by Shardin.⁵

The photo, Fig. 1, shows the construction used in the present work. All parts are mounted on an

optical bench of length 1.5 m. The arrangement is classical, however, the following two remarks may be worth mentioning. Two vertical knife edges, Fig. 1 F, are applied, one after the other, to generate in principle symmetrical schlieren effects. This allows elimination of a possible optical skewness by the later data treatment.

The sample container, Fig. 1 D, is made of stainless steel plate and is formed as a thermostated cylindrical mantle of volume 1400 cm.³ The sample is made of glass filter (mesh 10–20 μ m) cut as an orthogonal prism with dimensions $2 \times 4 \times 4$ mm³ and filled with the solid under investigation.

Fig. 1. Schlieren apparatus. A: He–Ne laser, output 0.5 mW, wavelength 632.8 nm (Spectra Physics, 155). B: Shutter, activated by a suction magnet. C: Beam expander (Melles Griot LBX 005). D: Sample container. E, G: Biconvex lenses, $f=250$ mm, diameter=75 mm (Melles Griot LDX 229). F: Knife edges, shifted vertically by a suction magnet. H: Screen of white, matt paper. I: TV camera (ITC IKEGA-MI, model CTC-4500 M).

TEMPERATURE CONTROL

A pump supplies the mantle of the sample container with water from a thermostat bath. The temperature of the bath is PID-controlled by a microprocessor, MC6800,⁶ coupled to a transducer (Analog Devices 590 series) and a modified commercial thermostat (Heto 02 T 923). The microprocessor also monitors the temperature in the container. Calibration of the measured temperature is performed in ice water/(0.000 °C) and in Na₂SO₄/Na₂SO₄·10H₂O (32.384 °C). The measured values are assumed to depend linearly on the temperature in the range 0–64 °C. 12 hours tests show that for constant setpoint the variance of the temperature measured in the container is less than 9×10^{-6} °C.²

PICTURE ANALYSIS

384 condensators (3×SAM 64) convert the video signal from the TV camera 1 line at a time. The grey tone of each point is digitized to values between 0 and 16. Each point represents an area of 0.003 mm² at the sample position. The picture is analyzed by a medium size computer, RC4000.⁷

Using the schlieren method, the maximum light intensity near the vertical sides of the picture of the sample is measured to decide

whether the sample is growing, dissolving or in equilibrium with the solution. As discriminator is chosen:

$$I_d = I_r^1 - I_l^1 - (I_r^2 - I_l^2) \quad (1)$$

where the superscripts refer to the intensities obtained with each of the two knife edges in position, and the subscripts refer to the intensities at the right and left boundary of the sample.

The sign of I_d indicates whether the sample is growing or dissolving. The magnitude of I_d measures approximately the deviation from equilibrium.

12 hours tests show that for a steel rod in air, the average value of I_d is 0.0 grey tone and the sample variance is 0.01 (grey tone).² A deviation of more than ± 0.2 grey tone is thus considered significant. For a solid sample of KBrO₃ in equilibrium with saturated solution either a temperature change of the solution of 0.01 °C or a relative change in concentration of the solution of 0.5 % is sufficient to produce a significant change in I_d .

DETERMINATION OF SOLUBILITY CURVES

The solid sample, and a solution saturated at the temperature in the range 25–50 °C where the solubility is highest, are placed in the sample container. The temperature is adjusted until I_d is 0. The MC6800 is instructed to keep a specified temperature gradient, and the RC4000 takes over the solubility determination. With specified time intervals a set of pictures is taken and analyzed, and I_d is calculated. If I_d indicates that the sample is growing, RC4000 instructs MC6800 to add a volume of solvent proportional to the magnitude of I_d . The values of the temperature, the volume of water added, and I_d are recorded by the computer. After the next time interval the procedure is repeated. In this way the actual concentration oscillates around the decreasing equilibrium concentration until the final wanted temperature is reached. A chemical analysis of the saturated solution at the beginning of the experiment combined with the results recorded by the computer makes it possible to calculate the equilibrium concentration as a function of temperature on an absolute scale.

Fig. 2. Vertical sections of the sample container parallel (1) and perpendicular (2) to the optic axis. A, inlet; B, outlet for thermostat water; C, optic glass windows, 3 mm thick; D, temperature probe; E, inlet for solvent; F, sample holder; G, sample; H, step motor.

Fig. 3. Experimental solubility curves for K_2SO_4 , $KBrO_3$ and $KAl(SO_4)_2 \cdot 12H_2O$. The mol percent in the solution is for water free salt. Values from the literature: $KAl(SO_4)_2 \cdot 12H_2O$: + x $\square$ $\triangle$.⁸ $KBrO_3$: $\blacktriangle$.⁹ K_2SO_4 : + x $\square$ $\blacktriangle$ $\triangle$ ∇ .¹⁰

The method was tested using three salts, K_2SO_4 , $KBrO_3$, and $KAl(SO_4)_2 \cdot 12H_2O$. Fig. 3 shows the experimental results. The ordinate is given in mol % (=mol fraction $\times$ 100) of water free salt. Each curve is composed of more than 1000 points and represents running times of approximately 48 h. In all cases, the temperature gradient was -0.01 $^{\circ}C/min$. Comparisons of the final concentration on each curve with the concentration obtained from a chemical analysis at the end of experiment show relative deviations between 0.2 and 1.3 %. These are probably due to an inherent weakness in the method: The many (up to 700) small additions of solvent with the risk of accumulating errors.

The curves were fitted by the eigenvalue method to functions of the type

$$x = A \exp [B/(RT)] \quad (2)$$

where T is the Kelvin temperature in the container and R is the gas constant. Table 1 gives the values of A and B together with root mean square deviations of T and x . All experimental points on the curves were used despite that they all must deviate a little from the equilibrium values because of the oscillatory character of the method.

A calculation where T was replaced by $T + k_d \times I_d$, and k_d varied between 0.0 and 0.2 did not change neither the A or the B values nor the root mean square deviations significantly.

A calculation where x was replaced by

$$x + (c_2 x^2 + c_1 x + c_0) \quad (3)$$

and c_i found by the least squares method did not change the A and B values but diminished the root mean square deviations significantly in

Table 1. Values of A and B with root mean square deviations for the expression $x = A \exp(B/(RT))$. T is the Kelvin temperature.

$$rms_T = \left(\sum_{i=1}^n (T_{\text{obs}} - T_{\text{calc}})^2 / n \right)^{1/2} \quad rms_x = \left(\sum_{i=1}^n (x_{\text{obs}} - x_{\text{calc}})^2 / n \right)^{1/2}$$

$$T_{\text{calc}} = B / \{ R / [\ln(x_{\text{obs}}) - \ln(A)] \} \quad x_{\text{calc}} = A \exp [B / (RT_{\text{obs}})]$$

Compound	Curve	A	B (kJ/mol)	rms_T (°C)	rms_x (x 10 ⁵)
KAl(SO ₄) ₂	1	444	-28.3	0.22	6.4
KAl(SO ₄) ₂	2	356	-27.8	0.27	7.9
KBrO ₃	3	102	-23.2	0.14	4.9
KBrO ₃	4	116	-23.5	0.17	7.1
K ₂ SO ₄	5	0.742	-10.1	0.12	2.2
K ₂ SO ₄	6	0.445	-8.8	0.19	3.2

Table 2. Values of c_2 , c_1 and c_0 with root mean square deviations corresponding to rms_T and rms_x of Table 1.

Compound	Curve	c_2	c_1 (x 10 ²)	c_0 (x 10 ³)	rms_T (°C)	rms_x (x 10 ⁵)
KAl(SO ₄) ₂	1	-18.84	30.08	-1.135	0.04	1.0
KAl(SO ₄) ₂	2	-19.24	29.08	-1.016	0.02	0.7
KBrO ₃	3	-2.52	6.279	-0.3697	0.14	4.6
KBrO ₃	4	8.789	-22.04	1.308	0.04	1.7
K ₂ SO ₄	5	11.91	-34.14	2.423	0.05	0.8
K ₂ SO ₄	6	-4.554	13.04	-0.9786	0.19	3.1

several cases. The results are given in Table 2. The use of a second degree polynomial is purely empirical. Its physical meaning is not obvious. It may be an expression for experimental error.

The B values are related to the heats of solution, but as the solutions are far from ideal, the exact relationship is difficult to evaluate. Values of x calculated from (2) and with A and B from Table 1 were compared with values of x calculated from the expression¹³

$$\log x = Q1 + Q2/T + Q3 \times \log T \quad (4)$$

with $Q1$, $Q2$, and $Q3$ as given in the reference. The relative deviations for a given T in the range 298 to 323 K were in all cases less than 4.5 % and in most cases less than 2 %.

In the experiments on KAl(SO₄)₂·12H₂O (curves 1 and 2), the chemical analysis was made

on sulfate.¹¹ Among the three salts the method worked best for KAl(SO₄)₂·12H₂O which is illustrated by the similarity of the two curves and of the corresponding c_1 values.

In the experiments on KBrO₃ (curves 3 and 4), the chemical analysis was made on bromate.¹² The two curves deviate significantly from each other. The reason may be that KBrO₃ has a very limited metastable region of supersaturation, so that during one of the experiments some KBrO₃ has precipitated in the container for a while. At the end of the experiment corresponding to curve 3 a small crystal was observed on the stirrer. The introduction of the second degree polynomial reduces the root mean square deviations very little for curve 3.

In the experiments on K₂SO₄ (curves 5 and 6), the chemical analysis was the same as used for KAl(SO₄)₂·12H₂O. K₂SO₄ represents the most

difficult of the three cases. Several experiments were done on that salt. The two curves show the two sets of results which deviated most from each other. As for curve 3, the root mean square deviations for curve 6 are not reduced significantly by introduction of a second degree polynomial.

A report with a more detailed description of the schlieren equipment and the control system can be obtained from the author on request.

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