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THE EFFECT OF VARIOUS FACTORS UPON THE VELOCITY OF CRYSTALLIZATION OF SUBSTANCES FROM SOLUTION[1,2]

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This investigation is an attempt to determine the effect of a number of factors upon the velocity of crystallization (V. C.) of substances from supersaturated solutions in the hope that the results will throw some light upon the mechanism of this very important phenomenon.

The question of the order of reaction of the crystallization process has provoked considerable discussion. The equation of Noyes and Whitney[3,4] for the velocity of solution of crystals in a solvent of the first order is

$$\frac{dC}{dt} = KS(C_s - C) \tag{1}$$

where K is the so-called velocity constant, S is the surface area of the crystal or crystals, C_s is the concentration of the saturated solution, and C is the concentration of the solution at any time t. If the processes of solution

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[1] The work included in this paper is from the thesis presented by John D. Jenkins in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin. This investigation was conducted under the supervision of Professor J. H. Walton.

[2] This investigation was made possible by a grant from the Research Committee of the University of Wisconsin, Dean C. S. Slichter, Chairman.

[3] Noyes and Whitney, *Z. physik. Chem.*, **23**, 689 (1897).

[4] (a) Nernst and Brunner, *ibid.*, **23**, 196 (1897). (b) LeBlanc and Schmandt, *Z. Elektrochem.*, **16**, 114 (1910); (c) *Z. physik. Chem.*, **77**, 614 (1911). (d) Nernst, "Theoretical Chemistry," MacMillan Co., **1923**, 5th ed., p. 670; (e) *Z. physik. Chem.*, **47**, 52 (1904). (f) Brunner, *ibid.*, **47**, 56 (1904).

For an excellent general discussion of crystallization and solution, see Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans and Co., **1922**, Vol. 1, 627.

and crystallization are exactly reciprocal, then this equation must also be valid for the latter process.

Many recent investigations, particularly those by Marc,[5] who has made a rather thorough study of the crystallization of some inorganic salts from water, and also by Fischer,[6] indicate that this may not always be the case. Marc reports that most of his crystallizations were "second order" reactions. He used small crystals in a vigorously stirred, supersaturated solution. By controlling conditions, Fischer claims to have altered the reaction from first order to second order at will in the same type of system. Unfortunately, details of Fischer's work were not available to the author. In the present work it was found that in all but a few cases, which have been noted, the process was very closely first order throughout; consequently, the rate has been calculated from the above equation in its integrated form

$$0.4343\ KS = \frac{1}{t}\log\frac{C_0 - C_s}{C - C_s} \qquad (2)$$

where C_0 is the initial concentration of the supersaturated solution. Whatever the significance of the first-order reaction rate may be, it serves its purpose in providing a means of expressing the relative velocities of the processes under consideration and this is considered as justification for its use.

Experimental Part

Materials.—The methyl and ethyl alcohols were refluxed for several hours over lime and fractionated, the middle fraction being used. Amyl alcohol was fractionated from the purest obtainable material. Ethyl ether was dried by refluxing over sodium for several hours and then fractionated. Benzene, ethyl acetate, and in the experiments with ammonium nitrate, the glycerol, were redistilled, the latter under reduced pressure, from the purest materials obtainable. The lactic acid was a good quality of C. P. material and was not further purified.

Naphthalene was purified by twice recrystallizing, and urea and ammonium nitrate by once recrystallizing, from pure dry methyl alcohol, and all were dried for two days at room temperature. Lactose and acetanilide were twice recrystallized from distilled water.

Seed crystals were made for each of the above solutes by saturating the respective solvents, as indicated above, at about 50°, then cooling the saturated solution, in a 500cc. Florence flask, under the tap, during vigorous shaking.

Apparatus.—The apparatus used in the first part of this work is illustrated in Fig. 1. It consists of a cell A so made that the prism of a Zeiss dipping refractometer R may be placed directly in the solution. A stirrer S was attached to the stirring motor by means of a flexible coupling. Seed crystals were dropped into the solution through the tube F. Due to the great rapidity of the crystallization of these compounds under the conditions employed, it was found necessary to use a chronograph to follow the process with

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[5] Marc, *Z. physik. Chem.*, **61**, 385 (1908); **67**, 470 (1909); **73**, 685 (1910); **75**, 710 (1911); **79**, 71 (1912); *Z. Elektrochem.*, **15**, 679 (1909); **16**, 201 (1910); **17**, 134 (1911); **18**, 161 (1912).

[6] Fischer, *C. A.*, **7**, 1883 (1914).

sufficient accuracy. This consisted of a clockwork arrangement for marking second intervals upon a smoked drum rotated at constant speed. Another stylus actuated by a small electromagnet and controlled by a key, made a simultaneous record of the readings of the refractometer on the same drum.

Method.—The procedure in making a run was as follows. A known volume, usually 25 cc., of the solution was pipetted into the cell A. The stopper carrying stirrer and seeding tube was fitted into the mouth of the cell and the cell placed in the thermostat and allowed to stand for several minutes, while the liquid was rapidly stirred, until it had come to the temperature of the bath. A known weight of standard seed crystals was then quickly dropped in, and at the same time the key was pressed to mark the beginning of the run on the chronograph drum. As the crystallization proceeded, the refractive index of the solution decreased, so that the dark field in the refractometer moved down the scale. Each time the border crossed an even division the key was pressed to mark the time on the drum; from these readings the V. C. constant was calculated.

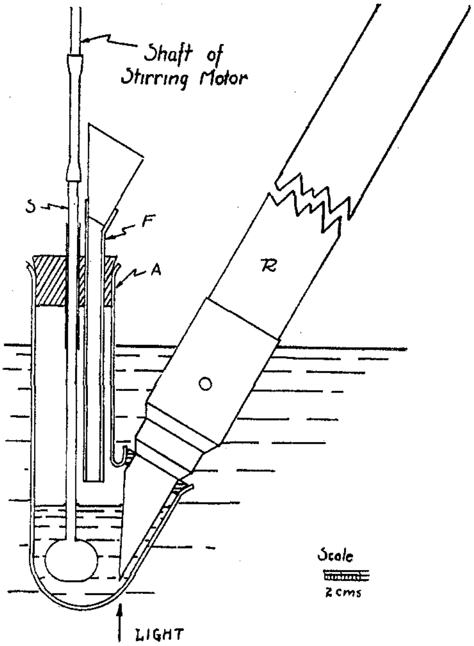


Fig. 1.—Refractometer cell.

This method has distinct advantages over some others used in this field. It is quite rapid. By stirring at 1000 r.p.m. it is possible to follow a reaction which is half completed in ten seconds, with an average deviation from the mean of from 3 to 5%. When the lighting is proper the field is clearly discernible even in the presence of 8 to 10 g. of crystals per 100 cc. of solution. It is applicable to any solution whose refractive index does not exceed 1.36. When the type of refractometer with interchangeable prisms is available, the value of the refractive index may be as high as 1.45. This method is accurate to about 0.01 g. per 100 cc. of solution, so that small supersaturations may be used and still show reasonable exactness.

Results.—Since most of the previous work on crystallization has been done in aqueous solutions it was thought desirable to extend these observations to non-aqueous solvents. For this purpose a solution of naphthalene in methyl alcohol was chosen. Naphthalene has the advantage that it is easily purified, stable, and readily forms supersaturated solutions from which it crystallizes well and at the same time slowly enough for accurate measurements. These and all subsequent runs were made at 0°, largely because of the slower rate of crystallization at that temperature. A number of determinations were made in which various foreign substances were added to the solution to determine the effect of these compounds upon the V. C. of the naphthalene. The solution used contained 4.15 g. of naphthalene in 100 cc. of solution, measured at room temperature, about 24°. This gave a supersaturation of from 0.30 to 0.40 g. per 100 cc. at 0°.

Since it is nearly impossible to make two preparations of seed crystals of exactly the same surface per gram, each preparation was standardized by several runs in the pure supersaturated solution. From the data obtained relative surfaces can be calculated. The constants are expressed as K and K_1, K being the calculated constant on the basis of 1 g. of the particular seed crystals used in 100 cc. of solution, as the unit of surface. K_1 for the same run is obtained by dividing K by the constant for the same seed crystals in pure alcoholic solution. This gives a relative figure which makes values comparable for all runs in the series.

A typical run to indicate the "constancy" of the "constants" is given in Table I.

TABLE I

VELOCITY OF CRYSTALLIZATION OF NAPHTHALENE FROM METHYL ALCOHOL AT 0°

Stirring rate, 1000 r.p.m.

t Seconds	$C-C_s$	W_0S/S_0	$K \times 10^3$
0.0	0.594	0.500	
		.71	(75)
5.1	.452		
		.79	90
8.8	.347		
		.85	101
13.0	.242		
		.91	106
18.9	.137		
		.96	93
24.4	.084		
		.99	91
35.4	.031		
		Av.	96
∞	.000		

The third column gives the surface correction factor. This correction is made necessary by the fact that in the determination of K by (2) the surface area is continuously increasing due to the growth of the crystals. It is easily shown mathematically that as a crystal of any form increases in weight without an alteration in form, the ratio at any time of the surface S to the initial surface, S_0 is

$$\frac{S}{S_0} = \left(\frac{W_0 + W}{W_0}\right)^{2/3} \qquad (3)$$

where W_0 is the initial weight and W is the increase in weight. W is calculated from the decrease in refractive index of the solution. To reduce this to the basis of 1 g. of seed crystals as the unit of surface it is necessary to multiply by the weight of seed crystals used.

$$W_0S/S_0 = (W_0 + W)^{2/3}\, W_0^{1/3} \tag{4}$$

To permit computation from reading to reading the constants for Table I and all subsequent runs have been calculated from a modification of the rate formula. The formula used is the following.

$$0.4343\ K = \frac{S_0}{W_0S(t_2 - t_1)} \log \frac{C_1 - C_s}{C_2 - C_s} \tag{5}$$

where C_1 and C_2 are concentrations at time t_1 and t_2, respectively, and S is the average surface between the two times.

This method of computation allows a greater fluctuation in the individual values of the constants since it does not have the averaging effect of computing each one from the initial point; however, it gives a much truer picture of the course of the crystallization and is much more sensitive to changes in the order of the reaction. It also permits the surface correction to be easily applied, for by simply dividing each constant by its surface factor the corrected constant is obtained.

The first constant is always low, as it takes a second or so for the crystals to become properly distributed in the solution. There is no question about the equation for the first order being the only applicable one. The constants show a tendency to go through a maximum value and then decrease slightly. This is explained by the fact that the process liberates heat, slightly increasing the temperature of the solution as shown by thermometric measurements. This has two effects, (1) the slowing down of the crystallization by reducing the supersaturation, and (2) decreasing the refractive index of the solution, thus *apparently* increasing the rate of the process. These effects partially neutralize each other but the second is the greater, so the rate is apparently increased in the earlier, and retarded in the later part of the run. To get an accurate determination in very rapid runs corrections must be made for this effect, but in most cases the error is not great enough to warrant the tedious process necessary for this correction.

The results of the runs with naphthalene are listed in Table II.

It is rather surprising that in this whole list there is only one substance, collodion, which has any great inhibiting effect, such as Marc found for the influence of dyes on the rate of crystallization of metallic salts from water solution. Picric acid, methylene blue, Pontammine Green Gx(direct), iodine and colloidal calcium carbonate have some action. The Pontammine Green Gx was picked from among a number of dyes as the one most strongly adsorbed by the naphthalene, as determined by making colorimetric measurements on the decolorizing action of naphthalene crystals on the dyes dissolved in a saturated solution of naphthalene. Even in the extreme dilution used (greater concentration was impossible due to

TABLE II

INFLUENCE OF VARIOUS SUBSTANCES UPON THE VELOCITY OF CRYSTALLIZATION OF NAPHTHALENE FROM METHYL ALCOHOL

Temp. 0°

The stirring rate for Nos. 1–10 was 1000 r.p.m.; for Nos. 11–23, 1200 r.p.m.

No.	Added substance	G./100 cc. of soln.	Seed	$K \times 10^3$	K_1
1	Control (4 runs)	...	A	93	1.00
2	Shellac	0.07	A	93	1.00
3	Sodium oleate	.40	A	87	0.94
4	Picric acid	.06	A	67	0.72
5	Control (3 runs)	...	B	163	1.00
6	Methylene blue (2 runs)	.015	B	144	0.88
7	Methylene blue	.031	B	132	.81
8	Methylene blue	.046	B	121	.75
9	Methylene blue	.062	B	143	.88
10	Methylene blue	.093	B	129	.79
11	Control (2 runs)	...	C	128	1.00
12	Pontammine Green Gx	.0056	C	91	0.71
13	Quinine	.125	C	145	1.13
14	Stearic acid	.400	C	136	1.06
15	Potassium hydroxide	.350	C	132	1.03
16	Urea	1.250	C	136	1.06
17	Iodine	0.146	C	97	0.76
18	Mercuric chloride	1.00	C	136	1.06
19	Colloidal calcium carbonate	0.010	C	99	0.77
20	Radium tube inserted	...	C	132	1.03
				Second order $K \times 10^3$	
21	Collodion	0.042	C	12.6	
22	Collodion	.047	C	12.7	
23	Collodion	.0188	C	16.6	

the strong color of the dye) it is as effective as methylene blue in sixteen times the concentration. This is in agreement with Marc's findings, that those dyes which stained or were adsorbed by the crystals were most effective in impeding crystallization. Methylene blue is only very slightly adsorbed, and its inhibiting effect is in consequence slight. It is difficult to determine how much collodion is adsorbed in such dilutions, but it is probable that the adsorption is quite marked.

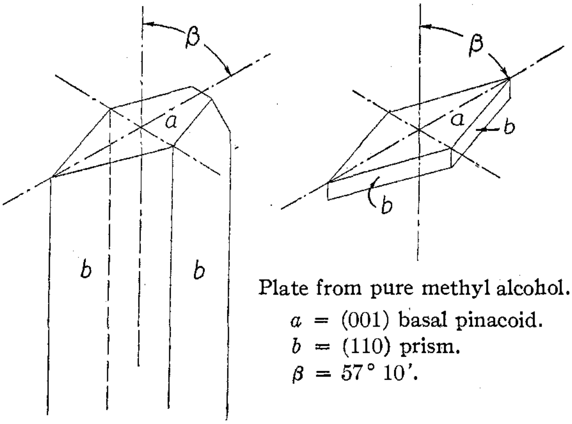
The action of collodion is very interesting. It inhibits the crystallization very strongly, and at the same time changes the process from first to second order. The form of the crystals is also greatly altered. Crystals of naphthalene grown in a solution containing 0.050 g. of collodion in 100 cc. of solution were needle shaped instead of having the form of thin plates. The collodion appears to suppress the deposition upon the lateral edges of the plate or prism (110) faces so that the growth can take place only upon the flat or basal pinacoid (001) face, thus elongating the crystal into a needle. Comparative sketches of the crystals grown in collodion solution and in pure methyl alcohol are shown in Fig. 2. The complete change in the order of the process is illustrated in Table III.

TABLE III

VELOCITY OF CRYSTALLIZATION OF NAPHTHALENE FROM METHYL ALCOHOL SOLUTION CONTAINING 0.042 GRAMS OF COLLODION PER 100 CC.

t Seconds	$C-C_s$ G./100 cc.	W_0S/S_0	$K \times 10^3$ monomol.	$K \times 10^3$ bimol.
0.0	0.500	0.500		
6.0	.394			
		.600	39.7	11.8
19.0	.289			
		.646	30.2	11.5
29.2	.237			
		.678	25.2	12.1
44.0	.184			
		.707	18.9	12.2
63.4	.131			
		.736	12.6	12.4
118.2	.079			
				Av. 12.0
∞	.000			

The strongest evidence that this is an actual change in order of the process, and not simply a distortion of the first-order curve due to inhibition by the collodion is the fact that the second-order "constants" are so "constant" for different concentrations of collodion.



Needle from collodion solution.

Plate from pure methyl alcohol.

a = (001) basal pinacoid.
b = (110) prism.
β = 57° 10'.

Fig. 2.—Naphthalene crystals from pure methyl alcohol and from methyl alcohol containing collodion.

The collodion solution was prepared by dissolving a weighed amount of "Parlodion" in methyl alcohol free from ether.

The effect of adding various amounts of water and benzene to the alcohol is shown in Table IV, which is self-explanatory. Decreasing the solubility of the naphthalene from 3.72 to 1.16 g. per 100 cc. by adding water had practically no effect on the V. C. The low value of Expt. 3 and probably also of Expt. 8, is doubtless partially due to the low initial supersaturation, as this was later shown to have considerable effect. Increasing the solubility by adding 7% of benzene was also without much effect, although some decrease in rate apparently took place.

TABLE IV

VELOCITY OF CRYSTALLIZATION OF NAPHTHALENE FROM MIXED SOLVENTS

Stirring rate, 1200 r.p.m,

No.	% by volume CH_3OH	H_2O	C_6H_6	Initial supersatn.	$K \times 10^3$
1	100	..	..	0.67	128
2	94	6	..	.54	128
3	87	13	..	.21	88
4	87	13	..	.37	125
5	93	..	7	.66	103
6	100	(new soln.)		.52	123
7	93	..	7	.51	95
8	93	..	7	.31	82

Velocity of Crystallization of Urea from Methyl Alcohol

Using the same procedure with urea as with naphthalene, the effect of four different substances upon both the V. C. and the velocity of solution (V. S.) was determined. The V. C. was measured upon the same solution as that in which the V. C. was determined, by pipetting in at the end of the crystallization just enough pure solvent, previously cooled, to redissolve the amount of urea which had crystallized. The constants were corrected for surface change by just reversing the procedure for similar corrections of the V. C. In Table V, which gives the results of these observations, it will be seen that in the concentrations used none of the substances added had any appreciable effect upon either the V. C. or V. S., the deviations all being within the limit of experimental error.

TABLE V

EFFECT OF FOREIGN SUBSTANCES UPON THE VELOCITY OF CRYSTALLIZATION AND OF SOLUTION OF UREA IN METHYL ALCOHOL

Stirring rate, 1200 r.p.m.

Added substance	G./100 cc. Solution	V. C. $K \times 10^3$	V. S. $K \times 10^3$
Control, av. 4 runs		53	..
Control, 1 run		..	86
Methylene blue	0.0125	56	..
Methylene blue	.025	50	78
Picric acid	.020	55	87
Picric acid	.029	51	82
Collodion	.0076	55	..
Collodion	.038	51	83
Sodium oleate	.0284	56	78

The great specificity of inhibiting agents is illustrated by the inertness of collodion toward urea, though it so strongly affected the naphthalene.

Solvate of Urea

In one of the solutions of urea made up for the experiments described above it was noticed that while being rapidly stirred, the solution suddenly became filled with minute white crystals different in form and much less soluble than those of the ordinary urea. Upon examination they appeared to be a solvate of urea, probably of the formula, $(NH_2)_2CO.CH_3OH$. The crystals were unstable above about 10°, giving off alcohol and changing to the ordinary needle-like form. The solvate crystallized in the form of rhomb-shaped tablets. In the air, even at 0° the solvate gave off alcohol rapidly and changed to the unsolvated form. Further work has been done on this compound by Dr. J. H. Walton and Mr. R. V. Wilson of this Laboratory.[7]

Effect of Initial Supersaturation upon the Velocity of Crystallization

The effect of varying the initial supersaturation was noticed in the runs with naphthalene, but appeared to be more important in the case of urea. It was therefore decided to investigate the influence of this factor, and for this purpose a number of runs were made in which the initial supersaturation was varied. The results are shown in Table VI.

TABLE VI

EFFECT OF INITIAL SUPERSATURATION ON THE VELOCITY OF CRYSTALLIZATION OF UREA FROM METHYL ALCOHOL

Stirring rate, 1500 r.p.m.

Initial supersatn.	0.49	0.51	0.76	0.97	1.19	1.33	1.36	2.07
$K \times 10^3$	51	49	46	60	56	110	67	142

Below a supersaturation of about 1.0 g./100 cc. of solution the results are quite constant, but above this value they increase and at the same time become erratic. It was first supposed that this was due to the presence of very fine crystal dust in the seed crystals which was capable of seeding the more concentrated solutions but was too fine to grow in the less concentrated ones. Agitating the crystals with a saturated solution for several minutes, however, failed to modify the action; consequently, it was concluded that the explanation was the spontaneous formation of fine crystals at the time of seeding. This effect of the appearance of a large number of small crystals upon seeding a supersaturated solution is a matter of common experience for high supersaturations[8] and may be the correct explanation of the above effect. However, no method of experimentally proving this assumption was devised and it is offered only as a suggestion.

[7] Walton and Wilson, THIS JOURNAL, **47**, 320 (1925).

[8] Miers, *J. Oxford U. Jr. Sci. Clubs,* **1911.**

Velocity of Crystallization of Urea from Mixed Solvents

In this series of experiments a number of common solvents were added to the methyl alcoholic solution to alter the solubility of the urea, and change the chemical and physical properties of the medium. Table VII gives the results of these experiments. A new preparation of seed crystals was used in these tests, and consequently the values are not comparable with those in Table VI.

TABLE VII

VELOCITY OF CRYSTALLIZATION OF UREA FROM MIXED SOLVENTS

Stirring rate, 1200 r.p.m.

No.	Solvent: % by vol. in CH_3OH		Supersatn. G./100 cc.	Spec. viscosity of satd. soln.	$K \times 10^3$
1	Water	10	0.65	1.16	24.3
2	Glycerol	4	.45	0.96	24.3
3	Amyl alcohol	23	.73	.80	30.0
4	Amyl alcohol	23	.55	.80	34.2
5	Methyl alcohol	..	.51	.76	33.8
6	Ethyl acetate	33	.25	.57	48.4
7	Ethyl acetate	33	.31	.57	41.8
8	Ethyl ether	15	.45	.51	(23.0)
9	Ethyl ether	15	.56	.51	(19.2)
10	Ethyl ether	50	.42	.41	74.0

From these experiments there appears to be a close connection between the V. C. and the viscosity. Expts. 8 and 9 gave abnormal results for which no explanation is offered. The specific viscosity of the saturated solution as given in the table is referred to water at 0°, as 1.000.

Thermometric Measurements of Velocity of Crystallization

At this point it seemed desirable to extend measurements of V. C. of urea to other pure organic solvents. Since the interchangeable prisms for the refractometer were not at the time available, some other method of measurement became necessary. The method adopted was a thermometric one, the apparatus for which is shown in Fig. 3.

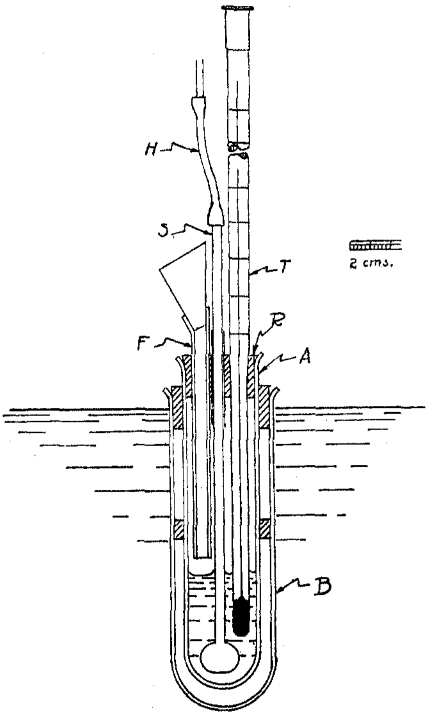


Fig. 3.—Cell for thermometric determination of rate of crystallization.

Apparatus.—A large test-tube A which served as the crystallizing cell was fitted with a stirrer S, Beckmann thermometer T and seeding tube F. In order to cut down conduction as much as possible the cell was placed in a larger test-tube B and the whole apparatus immersed in the thermostat.

Method.—A definite volume (20 cc. in all cases) of the solution to be investigated was pipetted into the cell, care being taken not to splash it on the sides of the tube where it might evaporate and inoculate the rest of the solution. The cell was then stoppered and placed directly in the ice-bath. In cooling, considerable distillation took place from the solution to the cell wall, washing down and dissolving any crystal dust. When the cell with solution had reached the temperature of the bath it was quickly removed and placed in the larger tube. It was necessary to cool the thermometer and stirrer separately in an air-bath; otherwise distillation took place from drops inadvertently splashed on them causing crystallization which seeded the whole solution. By cooling the thermometer and stirrer separately it was possible to stir the supersaturated liquid vigorously for some time without spontaneous crystallization taking place.

Calculation of Corrections.—There are four disturbing factors in these measurements: (1) the lag of the thermometer, (2) heating due to stirring, (3) cooling by conduction and convection, and (4) decrease of supersaturation due to the rise in temperature of the solution. Let T' be the thermometer reading, and T the true temperature of the solution at time t. Then

$$T = T' + \frac{1}{K_L}\left(\frac{dT'}{dt}\right) \tag{6}$$

where K_L is the "lag constant" of the thermometer, determined by standard calorimetric methods. The temperature-time curve may then be constructed graphically from Equation 6.

The problem is, of course, to find the form which the T, —t curve would have had, had it not been distorted by cooling and heat from stirring. We may call this the ideal curve. The ideal temperature, Θ at time t is given by the expression

$$\Theta = T + K_c\int_0^t (T - T_\infty)dt \tag{7}$$

where T_∞ is the temperature of the cell when $t = \infty$, and K_c is the cooling constant. This may be determined by warming the cell to a temperature, T_0, slightly above the bath temperature, then allowing it to cool, and measuring the T, —t curve. Then

$$K_c = \frac{1}{t}\, ln\, \frac{T_0 - T_\infty}{T - T_\infty} \tag{8}$$

The construction of the Θ, —t curve may be greatly simplified without material loss in accuracy by applying the corrections given in Equation 7 directly to the T', —t curve, eliminating the construction of the T, —t curve, since after the first few seconds the two curves are practically parallel as is shown in Fig. 4. Thus

$$\Theta' = T' + K_c\int_0^t (T' - T_\infty)dt \text{ (approx.)} \tag{9}$$

This may be demonstrated mathematically for strictly first-order reactions, but is not quite true for these curves as they are not exact first-order equations, due to the change in surface of the seed crystals, and loss of heat by conduction. However, these factors may be neglected, being in the nature of corrections on a correction. This ideal temperature curve is constructed graphically from the measured T' curve, and values interpolated from it are used to calculate the V. C. constant, K.

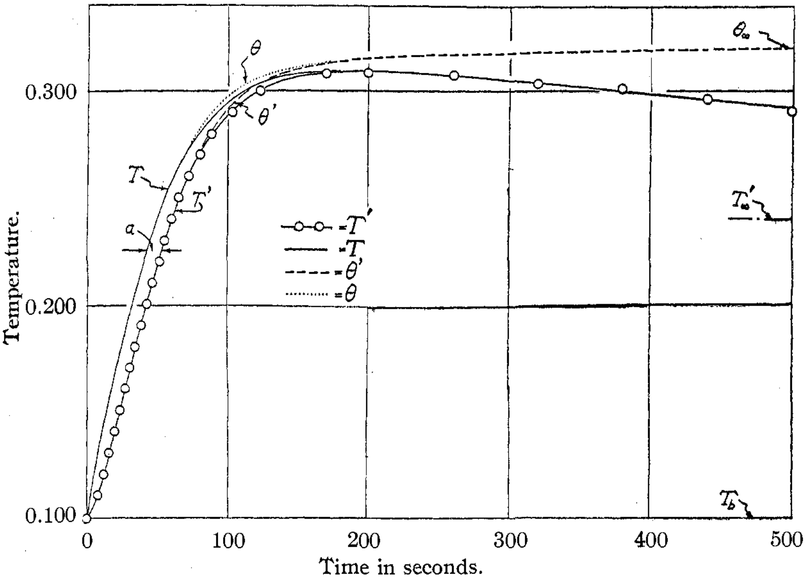


Fig. 4.—Temperature-time curves for Table VII.

T' = thermometer reading; T = true temperature; θ' = T', corrected by Equation 7; θ = T, corrected by Equation 9; θ_∞ = final ideal temperature; T_∞' = final thermometer reading; T_b = bath temperature.

The other factor mentioned above is the lowering of the supersaturation due to increased solubility at the higher temperature. Let a small amount, W, of solute crystallize from solution. The temperature rise, T, is given by the expression

$$W = aT \qquad (10)$$

where a is a constant. For a small range of temperature the solubility may be assumed to be a linear function of the temperature; therefore the reduction in supersaturation, W', due to temperature rise is

$$W' = bT \qquad (11)$$

where b is a constant. The total decrease in supersaturation then is

$$W + W' = (a + b)T \qquad (12)$$

It follows from Equations 10 and 12 that

$$W = \frac{a}{a + b}(W + W') \qquad (13)$$

or the total reduction in supersaturation is directly proportional to the amount crystallized. This allows us to calculate the V. C. from the temperature rise without regard to the change in solubility, since K is simply an expression of the *fractional* reduction in supersaturation in unit time. The heat of stirring and loss of heat by conduction will again tend to make this inexact, but these effects may be neglected.

The Θ, —t curves constructed from Equations 7 and 9 are shown in Fig.

TABLE VIII

VELOCITY OF CRYSTALLIZATION OF AMMONIUM NITRATE FROM WATER

Initial supersatn. = 1.00 g./100 cc. Stirring rate, 1000 r.p.m.
Bath temperature, 0.100° = T_b W_0 = 1.0 g./100 cc.

Data on run	
(sec.)	T'
0.0	0.100
7.5	.110
11.5	.120
15.1	.130
18.8	.140
22.4	.150
26.3	.160
29.9	.170
33.5	.180
38.0	.190
41.9	.200
46.2	.210
51.0	.220
54.4	.230
59.4	.240
65.0	.250
72.0	.260
79.8	.270
89.2	.280
103	.290
123	.300
170	.308
200	.308
260	.307
320	.303
380	.301
440	.296
500	.290
∞	.240

Calculation of K

(a) From Θ, $-t$ curve calcd. from Eq. 7

t(sec.)	$(\Theta_\infty - \Theta)$	$(T - T_\infty)$ intermediate	W_0S/S_0	$K \times 10^4$
10	0.179			
20	0.148	−0.093	1.18	162
30	.121	− .054	1.25	161
40	.097	− .030	1.31	168
50	.076	− .007	1.38	176
60	.060	.012	1.43	166
70	.047	.027	1.46	167
80	.037	.038	1.48	163
90	.029	.047	1.51	162
100	.023	.054	1.53	152
110	.018	.060	1.54	160
			Av.	164

(b) From the Θ,$'-t$ curve calcd. from Eq. 9

t(sec.)	$(\Theta_\infty - \Theta')$	$(T' - T_\infty)$ intermediate	W_0S/S_0	$K \times 10^4$
20	0.178			
30	.150	−0.094	1.18	(145)
40	.123	− .057	1.24	161
50	.099	− .032	1.31	166
60	.078	− .010	1.37	174
70	.061	.010	1.42	173
80	.048	.026	1.46	164
90	.038	.037	1.48	158
100	.030	.046	1.51	157
110	.023	.054	1.53	173
120	.018	.060	1.54	160
			Av.	165

Total ideal change in temperature = 0.220° corresponding to crystallization of 1.000 g. of NH_4NO_3, therefore

$$1^\circ \Leftrightarrow 4.55 \text{ g. } NH_4NO_2$$

$$W_0S/S_0 = (1.000 + 4.55\Theta)^{2/3}$$

4, and values of K calculated therefrom, in Table VIII. K is calculated from the following equation similar in form to (5),

$$0.4343\ K = \frac{S_0}{W_0 S(t_2 - t_1)} \cdot \log \frac{\Theta_\infty - \Theta_1}{\Theta_\infty - \Theta_2} \tag{14}$$

where Θ_1, Θ_2 and Θ_∞ are the ideal temperatures at the times t_1, t_2 and $t = \infty$, respectively. There is no essential difference in the values of K as calculated from the two curves, nor is there any noticeable trend of the values of K, indicating that the method of calculation is sufficiently exact for all practical purposes.

In this manner the V. C. of urea, acetanilide and ammonium nitrate from various solvents was investigated. The results are given in Table IX. All measurements are at 0°.

TABLE IX

VELOCITIES OF CRYSTALLIZATION

UREA FROM VARIOUS SOLVENTS

No.	Solvents % by volume	%	Stirring rate R.p.m.	$K \times 10^4$	Specific viscosity
1	Methyl alcohol Ethyl ether	50	1000	392	0.41
2			1000	388	.41
3	Methyl alcohol		925	272	.76
4			925	256	.76
5	Ethyl alcohol		800	158	1.47
6			1200	183	1.47
7	Ethyl alcohol Glycerol	76 24	1300	55	9.90
8	Methyl alcohol Glycerol	50 50	1500	35.6	37.3
9			1650	32.2	37.3

ACETANILIDE FROM VARIOUS SOLVENTS

No.	Solvents % by volume	%	Stirring rate R.p.m.	$K \times 10^4$	Specific viscosity
1	Ethyl acetate		1000	460	0.390
2			1000	450	.390
3	Methyl alcohol		1000	273	.701
4			1000	212	.701
5	Amyl alcohol		1500	85	5.9
6			1500	75	5.9
7	Glycerol Methyl alcohol	50%	1000	16.4	56.0

AMMONIUM NITRATE FROM VARIOUS SOLVENTS

No.	Solvents % by volume	%	Stirring rate R.p.m.	$K \times 10^4$	Specific viscosity
1	Methyl alcohol		1000	166	0.682
2			1000	158	.682
3	Water		1000	165	1.195
4			1000	129	1.195
5	Glycerol Methyl alcohol	50 50	1000	25.1	19.39
6	Lactic acid Methyl alcohol	77 23	1000	9.4	77.2

The last column gives in each case the specific viscosity of the saturated solution at 0° (as referred to water at the same temperature).

These results are shown in the graph, Fig. 5, in which the logarithm of the constant K is plotted against the logarithm of the specific viscosity of the saturated solution. A very close relation between the V. C. and the viscosity is at once apparent, and there appears to be *no appreciable effect due to any other factors such as changes in solubility or the chemical nature of the solvent.* This is somewhat unexpected in the light of the specificity of the effect of certain impurities upon crystal growth. It would seem that there are two independent effects which a foreign substance may have upon the V. C.: (1) a highly specific inhibitive action, such as the action of collodion on naphthalene, and (2) a general effect, due to the alteration of the viscosity of the medium.

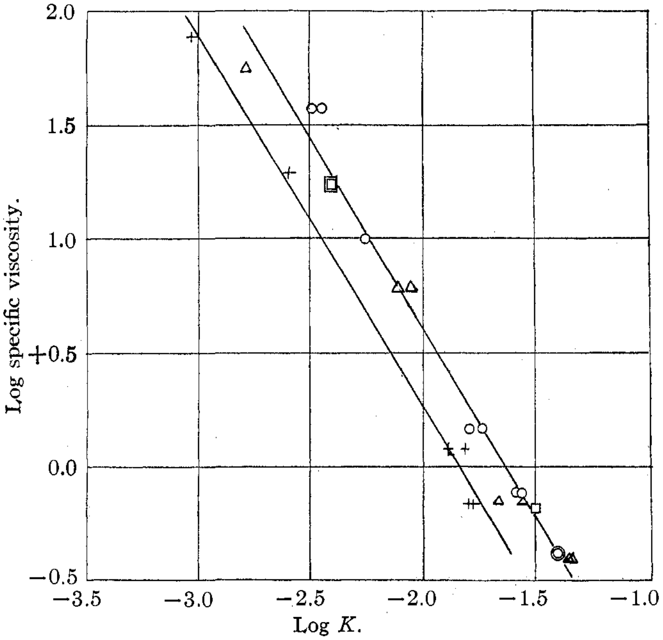


Fig. 5.—The plus signs indicate NH_4NO_3 at 0°; the triangles, urea at 0°; the circles, acetanilide at 0°; the squares, acetanilide at 20°.

It is interesting to note that in all three of the curves the slope is practically the same, —1.70. Expressing this relation mathematically we get

$$-1.70 \log K = \log \eta - \log \text{Const.}$$

or

$$K = \frac{\text{Const.}}{\eta^{0.59}} \qquad (15)$$

where η is the viscosity.

This equation would seem to show that diffusion processes are of relatively much less importance in the process of crystallization than in solution. Nernst[4e] replaced the constant K in the solution formula (1) by the expression D/δ, giving

$$K = D/\delta \tag{16}$$

and

$$\frac{dC}{dt} = \frac{DS}{\delta}(C_s - C) \tag{17}$$

where D is the diffusion constant, and δ is the thickness of the layer of solution in contact with the crystal through which diffusion must take place. It has been shown,[9] however, that

$$D = \frac{\text{Const.}}{\eta} \tag{18}$$

where η is again the viscosity. Substituting this in (16) we have

$$K = \text{Const.}/\eta\delta \tag{19}$$

If we dip a glass plate in a liquid, then withdraw it and allow it to drain a definite time, we find that for two liquids of the same density but with different viscosities the relative volumes retained on the plate will be approximately $V_1/V_2 = \sqrt{\eta_1/\eta_2}$. It is reasonable to conclude that δ will increase with η at least in proportion to the square root, or

$$K = \text{Const.}/\eta\sqrt{\eta} = \text{Const.}/\eta^{1.5} \text{ (approx.)} \tag{20}$$

instead of the experimental value of $K = \text{Const.}/\eta^{0.59}$. In other words the viscosity does not exert nearly as great an influence upon the rate of crystallization as is called for by the diffusion theory, and this would seem to be a serious objection to extending this theory to the velocity of crystallization.

Berthoud[10] has proposed a formula for the V. C. based upon the hypothesis that there are two independent effects operative in modifying the V. C., (1) the diffusion process, as outlined by Noyes and Whitney, and (2) a slow process of some sort on the surface of the crystal, the true V. C. He replaces K in Equation 1 by

$$K = D/(\delta + D/k) \tag{21}$$

Equating (15) and (21) and solving for k, where k is the true V. C. on the surface

$$k = 1/(\eta^{0.59}/\text{Const.} - \delta/D) \tag{22}$$

When δ/D becomes small compared to $\eta^{0.59}/\text{Const.}$, the expression reduces to

$$k = \text{Const.}/\eta^{0.59}$$

which is the same form as Equation 15 and suggests that what we are actually measuring is the true V. C. or slow process on the crystal surface, rather than the diffusion process, and that we have reduced the thickness of the stationary diffusion layer to such an extent that its effect is negligible. This same conclusion was reached by Marc from his experiments on the effect of changes in the rate of stirring on V. C.

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[9] Walden, *Z. physik. Chem.*, **55**, 426 (1906).

[10] Berthoud, *Jour. chim. phys.*, **10**, 624 (1912).

The results of this investigation seem to indicate that the inhibiting action of dyes and such materials is not due to their ability to alter the "capillary constant"[11] of the crystal face, since if this were the case certainly changing the solvent entirely would greatly alter this value. However, there appears to be no effect on changing the solvent which is not explained entirely by change in viscosity. Marc's explanation of the action of inhibiting agents, as due to the formation of rather stable adsorption complexes which slow down the orientation of the dissolved molecules to the crystal surface, seems the most satisfactory one from the standpoint of the above results.

The Temperature Coefficient of the Velocity of Crystallization

For the purpose of determining the temperature coefficient, some measurements were made upon the V. C. of acetanilide at 20°. The results are tabulated in Table X, and have been plotted in Fig. 5. Apparently the only effect of temperature change in this system is due to the effect of diminution of the viscosity of the solvents; when this effect is considered the temperature coefficient is nearly equal to one.

Table X

Velocity of Crystallization of Acetanilide at 20°

Stirring rate, 1000 r.p.m.

Solvent, % by vol.	Methyl alcohol	Methyl alc. 50% Glycerol 50%	
$K \times 10^4$	311	100	100
Sp. visc.	0.636	17.0	17.0

Velocity of Crystallization of Lactose from Water

Some interesting observations have been made upon the V. C. of lactose from water. This substance crystallizes so slowly that a method of sampling through a filter paper and analyzing by means of an Abbé refractometer was used. The crystallization was carried out in a cell very similar to that shown in Fig. 3, but without the outer jacketing tube B. A solution having an initial supersaturation of 35 g. of lactose in 110 g. of solution was seeded with 5 g. of fine seed crystals. The results of four runs are shown in Table XI.

Table XI

Velocity of Crystallization of Lactose from Water

Temperature 30° Stirring rate, 900 r.p.m.

$K \times 10^6$	33	39	121	112
Remarks	Pure lactose	Pure lactose	In 0.0166 *N* NH_4OH	In 0.067 *N* NH_4OH

It is interesting to note that a small amount of ammonia more than

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[11] Curie, *Bull. soc. min.*, 7, 89, 414 (1884).

triples the V. C. This is probably because it catalyzes the reaction:[12] Lactose anhydride + $H_2O \rightleftharpoons$ lactose hydrate. This system is in equilibrium in the solution, initially, but as soon as crystallization starts it is disturbed, and since only the hydrate can crystallize the slow hydration reaction effectively slows up the process. This hypothesis is strengthened by the fact that the constants started high and fell off in the first and second experiments, but in the presence of ammonia, in the third and fourth, no such rapid fall in the constants was noticed.

Rates of Solution in Various Solvents

For the case of a crystal dissolving in a volume of solution so large that the concentration is not appreciably altered we get

$$-\mathrm{d}x/\mathrm{d}t = KS(C_s - C) \qquad (23)$$

where x is the mass of the crystal at time t, $(C_s - C)$ is the unsaturation of the solution in grams per unit volume, this remaining constant as the surface S varies. Expressing S as a function of the mass of the crystal assuming its form does not vary,

$$S = Mx^{2/3} \qquad (24)$$

M being a proportionality constant. Substituting (24) in (23), and integrating, letting x_0 be the initial weight of the crystal, and putting $K_1 = KM$

$$K_1 = \frac{3}{t(C_s - C)}(x_0^{1/3} - x^{1/3}) \qquad (25)$$

It will be noticed that when $x = 0$, that is, when the crystal is completely dissolved, the time t_0 is still finite and equal to

$$t_0 = 3\,x_0^{1/3}/K_1(C_s - C) \qquad (26)$$

This equation may be used for a rough determination of K_1, by observing the time required for complete solution of the crystals. Obviously, the crystals must be of very nearly uniform size. This method is particularly applicable in cases where the rate of solution is too great to be measured in the usual manner. The rates of solution of ammonium nitrate in pure water and solutions of various concentrations have been measured in this manner and are given in Table XII.

TABLE XII

VELOCITY OF SOLUTION OF AMMONIUM NITRATE IN WATER AND SOLUTIONS OF DIFFERENT CONCENTRATIONS

Temperature 0° Stirring-rate, 1000 r.p.m.

$C_s - C$	65.0	52.0	39.0	26.0	13.0	6.5
t_0, sec.	4.5	5.4	6.7	11.1	16.2	30.2
$K_1 \times 10^4$	102	107	111	104	143	153

Each value of t_0 is the average of four or more determinations. There is a tendency for K_1 to decrease as the unsaturation increases. This may

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[12] Hudson, THIS JOURNAL, **30**, 1767 (1908).

be due to the fact that at these rapid rates of solution the local cooling due to the solution of the crystal is great enough to increase the viscosity materially and decrease the effective unsaturation. Due to the difficulty of determining the point of total solution with accuracy, the method must be considered as an approximation only.

A number of determinations of the velocity of solution of ammonium nitrate crystals in various solvents were made by means of the refractometer cell described in the first part of the paper. This was done to find whether the same generalizations held true for V. S. as for V. C. in various solvents. The results seemed to show that the V. S. was much more affected by the viscosity of the medium than the V. C., but the results were not concordant, and appeared to indicate the influence of other factors than viscosity. As yet, no relation between the results has been found.

Individual runs in most cases gave fairly good constants, thus indicating the accuracy of the equation. A typical run is shown in Table XIII where Equation 25 was used to calculate K_1.

Table XIII

Velocity of Solution of Ammonium Nitrate in a Mixture of 75% of Ethyl Alcohol and 25% of Glycerol

Temperature, 0° Stirring rate, 1000 r.p.m.
Specific viscosity, 5.56 $x_0 = 1.0$ g./100 cc.
Initial $C_s - C = 7.7$ g./100 cc.

t, sec.	0.0	30	60	90	120	150	180	210	
x	1.000	0.716	0.486	0.296	0.175	0.092	0.041	0.015	
$K_1 \times 10^{5a}$		140	145	170	150	156	153	146	Av. 151

[a] K_1 is corrected for change in $C_s - C$ during the process by point-to-point computation.

As is apparent, the equation applies with fair exactness throughout the whole process.

The author is greatly indebted to Professor J. H. Walton, under whose direction this work was carried out, for his kind advice and assistance, and to the Research Committee of the University of Wisconsin for the grant which made the investigation possible.

Summary

1. A rapid refractometric method for the determination of velocity of crystallization (V. C.) is described and used to find the effect of the following factors upon the V. C. of urea and naphthalene from methyl alcohol solutions; (a) various foreign substances; (b) initial supersaturation (urea only); (c) added solvents. In the case of the last it appeared that the viscosity of the solution was an important factor in the V. C. from mixed solvents.

2. A new solvate of urea has been prepared and briefly described.

3. A thermometric method for the determination of the V. C. has been devised and the apparatus and calculations are described.

4. Measurements of the V. C. of three solutes, urea, acetanilide and ammonium nitrate made in various solvents and mixtures by the thermometric method, indicate that the important factor in altering the V. C. of a given solute in such solvents and mixtures is the viscosity of the solution. The relation between the viscosity of the solution, η, and the velocity constant, K, is given by the expression: $K = \text{Const.}/\eta^{0.59}$.

5. The results of these experiments have been discussed in relation to some of the present theories of crystallization.

6. The temperature coefficient of the V. C. of acetanilide in two solvents was found to be due only to the decrease in viscosity of the solution at the higher temperature.

7. Measurements of the V. C. of lactose from water indicate that the process is retarded by the slow formation of the hydrate in solution by the reaction: lactose anhydride + $H_2O \rightleftharpoons$ lactose hydrate. Ammonia in very dilute solution greatly increases the V. C.

8. Some determinations of the rate of solution have been made and a formula has been suggested and tested for the rate of solution of small crystals in a medium whose volume is so great that its concentration is not appreciably altered during the process.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF NEVADA]

CRITICAL STUDIES ON THE FUSION OF RARE-METAL ORES
I. THE PYROSULFATE FUSION OF TITANIUM ORES[1]

BY GEORGE W. SEARS AND LAURENCE QUILL

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Although fusion methods have long been in use for the decomposition of ores, apparently no very careful study of the reactions taking place or of the conditions affecting these reactions has been made. When the analyst is forced to use fusion for the decomposition of his sample, he receives little help from the literature as to the method of procedure, the proportion of flux necessary, the time of fusion or the temperature most desirable. Furthermore, he is not always sure of obtaining a complete decomposition in one fusion but often finds a second and sometimes a third fusion necessary. Because of this lack of definiteness in the treatment of ores and a desire to clarify if possible the reactions concerned, a series of investigations is being carried on in this Laboratory in a critical study

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[1] Presented at the Joint Session of the several California sections of the American Chemical Society, held in conjunction with the Pacific Division of the American Association for the Advancement of Science at Stanford University, June 25–28, 1924.