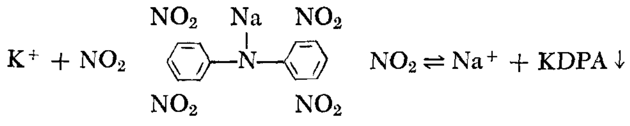
# Kinetics of Reaction and Crystallization in Condensed Phases: The Aqueous Potassium Dipicrylamine System

**H. R. SAVAGE, JOHN B. BUTT, and JOHN A. TALLMADGE**
**Yale University, New Haven, Connecticut**

**An apparatus and experimental technique were developed for the study of the kinetics of relatively rapid reaction and subsequent crystallization in condensed phases. The method employs *batch experiments to establish the integral of crystallization rate over ranges of pertinent external variables.***

**The crystallization of potassium dipicrylamine from aqueous solution, a system of potential interest in application to potassium recovery from brines, was studied experimentally. It is shown that both reaction and crystallization rate parameters may be determined from the data on the basis of the *consecutive rate model developed; application of the Burton-Cabrera-Frank theory of crystal growth to this system is demonstrated.***

Potassium reacts chemically with hexanitrodiphenylamine (dipicrylamine or DPA) and with some soluble metal salts of dipicrylamine such as sodium, calcium, and magnesium dipicrylame in aqueous solution to form potassium dipicrylamine, which is only slightly soluble in the solution. The reaction is apparently a simple exchange and may be written as



$$K^+ + \begin{array}{c} NO_2 \quad\; Na \quad\; NO_2 \\ NO_2 \; \bigcirc\!-\!N\!-\!\bigcirc \; NO_2 \\ NO_2 \qquad\quad NO_2 \end{array} \rightleftharpoons Na^+ + KDPA\downarrow$$

Particular interest in this system stems from the fact that it is apparently a good subject for the study of consecutive reaction and crystallization kinetics in condensed phases, and it has potential practical applications to recovery of potassium from saline sources. The latter has been dealt with in prior reports (*1*, *2*); our concern here is with the former area, and with particular regard to interpretation of crystallization kinetics in terms of modern crystal growth theory.

Previous work related to the chemical reaction has been predominately in the development of analytical techniques for the quantitative determination of potassium (*3*, *4*) and in extensions to development of processes for potassium recovery from brine sources (*1*, *2*, *5* to *7*). No prior studies of the kinetics of this reaction crystallization have been reported, and in this investigation a novel experimental technique and apparatus were developed for studying such rapid crystallizations resulting from reaction when two liquid solutions (reactants) are mixed.

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H. R. Savage is with Esso Research Laboratories, Baton Rouge, Louisiana.

John A. Tallmadge is at the Drexel Institute of Technology, Philadelphia, Pennsylvania.

## EXPERIMENTAL

The experimental approach to the study of crystallization kinetics involved measurement of the mass of KDPA crystals formed as a function of time under controlled conditions of temperature, initial reactants concentration, agitation level, and seed concentration. Each experiment involved a batch crystallization which gave one point on the curve relating mass of crystals formed to time of crystallization. Repeated experiments with different reaction times established the integral of the rate function for a given set of conditions over the time period studied. The reaction was initiated by rapidly mixing a solution of potassium chloride with a solution of sodium dipicrylamine in a stirred batch reactor and, after the desired time had elapsed, rapidly separating the crystals from the environmental solution.

This method gave integral curves which reflected both the rate of chemical reaction and the rate of crystal growth. These rates could not be measured individually, since it was not possible to analyze the solution for concentrations of the various substances present at any time when nondestructive analytical procedures are used. The rate of KDPA crystal growth is a function of the potassium dipicrylamine concentration in solution, and the rate of KDPA formation in solution is in general a function of $Na^+$, NaDPA, $DPA^-$, $K^+$, and KDPA concentrations. A detailed scheme may be written as

$$\begin{gathered} \mathrm{Na\,DPA} \rightleftharpoons \mathrm{Na}^+ + \mathrm{DPA}^- \\ \mathrm{K}^+ + \mathrm{DPA}^- \rightleftharpoons \mathrm{KDPA}\ (\mathrm{sol'n}) \\ \mathrm{K}^+ + \mathrm{Na\,DPA} \rightleftharpoons \mathrm{KDPA}\ (\mathrm{sol'n}) + \mathrm{Na}^+ \\ \mathrm{KDPA}\ (\mathrm{sol'n}) \rightleftharpoons \mathrm{KDPA}\ (\mathrm{solid}) \end{gathered}$$

Some distinctions among these steps are possible on the basis of experimental observation, as described subsequently, but suitable quantitative analytical procedures for this do not exist.

The apparatus and technique developed for this study permitted variation of the important independent variables one at a time. The crystallization experiments were carried out under isothermal and essentially constant volume conditions. Initial concentrations of sodium dipicrylamine and potassium could be varied independently, and the level of agitation within the reaction vessel was externally controlled and measured. It is important to note that relatively few data on crystallization kinetics in condensed phases have been reported in which experimental conditions have been well defined or which exist in a form which may be interpreted in terms of the fundamental rate processes occurring; hence experimental considerations are relatively important in this research.

### Apparatus

The apparatus employed was designed to accomplish the rapid mixing of measured amounts of two liqud phase reactants and the rapid separation of the resulting crystalline precipitate from the reaction solution. Provision was made for setting and maintaining a constant temperature, for agitation of the reaction volume, and for measuring the time of reaction. A schematic diagram of the reactor system is given in Figure 1. The reactor proper was a jacketed, brass, pressure vessel with internal baffles, a sloping bottom, and a center outlet tube in the bottom. Internal agitation of the reactor and agitator geometry was determined on the basis of experimentation to minimize mixng dead spaces (*8*). The top of the reactor was a separate brass plate bolted in place; all inlet lines, the stirrer, and the thermocouple passed through the top. The reactor could be pressurized to 600 lb./sq. in gauge for rapid filtration of its contents at the desired moment. The injection section was a jacketed pressure vessel with a ball valve at each end for charging sodium dipicrylamine solutions rapidly into the reactor. A coating of tygon was placed on the interior walls of the injector to retard wetting and retention of droplets during injection, so that reproducible amounts of liquid could be discharged to the reactor. Injector volumes of 50 and 100 ml. were used in experimentation, requiring 0.5 and 1.0 sec., respectively, for discharge. The filters used to separate crystals from the reaction mixture were made of porous, sintered, stainless steel in the shape of a cylindrical cup. The filter was positioned in the reactor outlet line so that the closed end was downstream; the material to be filtered then entered the tip, and crystals were retained in the cup as the liquid passed through. The filter elements employed were machined to uniform size; they weighed approximately 9 g. and contained a volume of approximately 3 ml. Temperature control was accomplished by pumping fluid from a constant temperature bath through the reactor and injector jackets. Connecting lines and the reactor and injector were insulated with fiber glass; temperature in the bath was maintained either by a base plus swing load immersion heater or by an external refrigerator. Temperature in the reactor was measured by a chromel-alumel thermocouple to within ± 0.05°C.; bath temperature was controlled in all cases to less than ± 0.05°C. Reaction times were measured with an electronic timer switched on and off automatically as the injector outlet valve and reactor outlet valve were actuated. All reagents employed in the experimentation were reagent grade or analytical reagent grade.

### Procedure

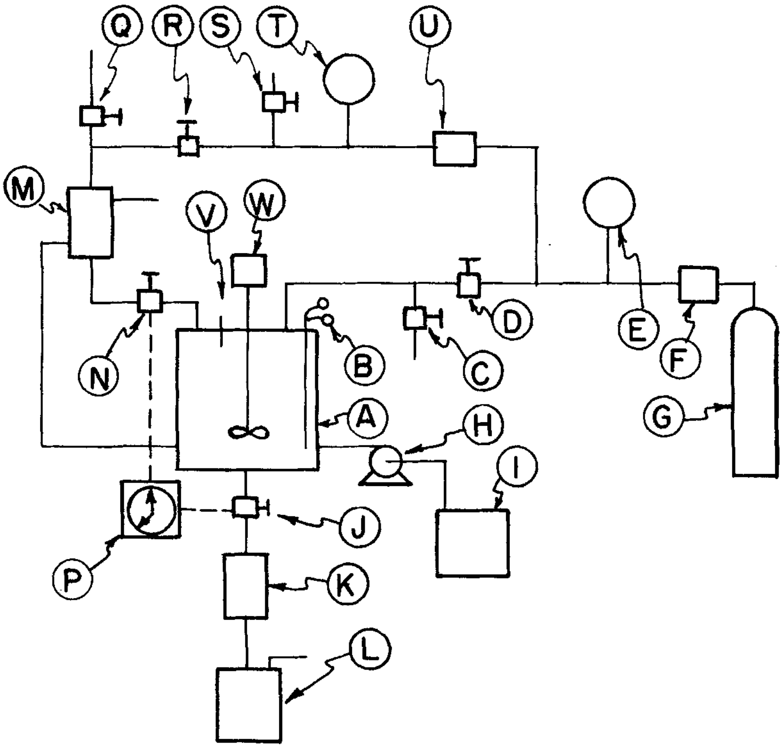
The experimental procedure can be divided conveniently into three major areas; synthesis of sodium dipicrylamine, procedure for making a run, and calculation of desired quantities from the raw data. Each of these is discussed below.

*Synthesis of Sodium Dipicrylamine.* This material is not available commercially, so the reagent employed in the crystallization experiments was prepared in the laboratory. Dipicrylamine and sodium carbonate decahydrate in 100% excess were placed in distilled water at room temperature and stirred until all solids dissolved, giving a dark red solution of sodium depicrylamine. The solution was evaporated to dryness leaving red crystalline sodium dipicrylamine mixed with sodium carbonate. This residue was then treated with acetone to separate the desired product, soluble in acetone, from the insoluble carbonate. This extraction was repeated twice by evaporating the acetone solution and redissolving the solids. Purity of the product was verified by microscopic examination, since the presence of carbonate crystals in the solid is easily detected by this method.

*Operating Procedure.* Initially all valves were closed except the reactor vent valve C (see Figure 1). The stirrer control was off, the air cylinder main valve was opened, and the constant temperature bath thermostat was set to approximately the desired point. A clean, tared filter element was placed in filter K, and filtrate receiver L was put in place. The unit was then ready to be charged.

Potassium chloride solution was charged to the reactor through charge port V by a pipette. Seed crystals from a previous crystallization were weighed and charged to the reactor through a dry funnel. Seeds from a single batch were used in all experiments. The charge port cap was replaced and the reactor stirrer started and set to the desired speed by means of a variac and a volt meter. Sodium dipicrylamine was charged to the injector by a pipette, and the injector inlet valve Q was closed. A final adjustment of the constant temperature bath thermostat was made to bring thermocouple B reading to the desired value, and a minimum of 30 min. was allowed for the thermal equilibrium to be established as indicated by temperature measurement. Pressure regulators F and U were adjusted to pressurize the injector. The timer control switches were set in the proper position and the timer set to zero. At this point the unit was completely charged and equilibrated.

The reaction was started by opening the injector outlet valve N for 3 or 4 sec., allowing the sodium dipicrylamine to mix in the reactor with the potassium chloride solution and the seed crystals. The timer was actuated automatically as valve N was opened. The injector outlet valve N and the reactor vent valve C were then closed. A few seconds before the reactor contents were to be discharged, the reactor pressurization valve D was opened, and 1 to 2 sec. prior to discharge the reactor stirrer motor control was set to motor stop



LEGEND

A - REACTOR
B - THERMOCOUPLE
C - VENT VALVE
D - REACTOR PRESSURIZATION VALVE
E - PRESSURE GAGE
F - PRESSURE REGULATOR
G - GAS BOTTLE
H - PUMP
I - CONSTANT TEMP. BATH
J - REACTOR OUTLET VALVE
K - FILTER
L - FILTRATE RECEIVER
M - INJECTOR
N - INJECTOR OUTLET VALVE
P - TIMER
Q - INJECTOR INLET VALVE
R - INJECTOR PRESS. VALVE
S - VENT VALVE
T - PRESSURE GAGE
U - PRESSURE REGULATOR
V - CHARGE PORT
W - STIRRER MOTOR

**Fig. 1. Schematic diagram of reactor system.**

in order to prevent crystals from being thrown against the reactor walls and top as the liquid surface reached the stirrer level during discharge. At the desired instant reactor outlet valve J was opened and the reactor contents discharged through filter K which retained the crystals. Air was blown through the crystals for a few seconds to remove any adhering solute. Direct measurements showed this to be effective for removing solute except for negligible amounts. The reactor pressurization valve D was closed, reactor vent C opened, and the filter element and crystals removed from the unit and placed in the oven for final drying. The mass of crystals was determined by direct weighing.

Crystals remaining in the reactor and outlet line after filtration were recovered by dissolution in acetone. The concentration of KDPA in the acetone solution was measured spectrophotometrically, and the mass of crystals recovered in the acetone was calculated and added to the crystals weighed. Blank runs were made to determine what portion of the seed crystals charged to the reactor dissolved in the potassium chloride solution prior to injection of the sodium dipicrylamine solution. The unit was set up and charged as described above, except that no NaDPA was charged to the injector and the run operating procedure was carried out.

*Treatment of Raw Data.* The treatment of raw data was straightforward, consisting mainly of applying corrections to obtain the true mass of crystals grown in a given experiment. Reaction time was measured directly. Initial reactants concentrations were calculated based on the total volume of potassium chloride and sodium dipicrylamine solutions which was taken to be the pipette volume of each less the amount retained by the injector (1.2 ml. by calibration). The mass of crystals formed in each experiment was calculated as follows: mass of crystals formed = (mass of filter plus crystals therein) — (tare weight of filter) + (mass of crystals washed out in acetone) — (mass of seed crystals present at beginning of the reaction).

## KINETIC DATA

Rates were measured in a total of ninety-six runs, made in eight sets, in which the effects of temperature, initial reactants concentrations, seed crystal concentration, and stirrer speed were determined. The range of experimental

TABLE 1. SUMMARY OF EXPERIMENTAL CONDITIONS

| Run set | | Temp., °C. | Initial concs. K, mg./liter | Initial concs. NaDPA, g./liter | Agitator speed, rev./min. | Mass of seeds, g. |
|---|---|---|---|---|---|---|
| RC | a | 5.0 | 200 | 3.6295 | 900 | 0.0500 |
| | b | 5.0 | 200 | 3.6295 | 1,364 | 0.0500 |
| | c | 5.0 | 200 | 3.6295 | 2,060 | 0.0500 |
| RD | a | 5.0 | 100 | 1.8148 | 900 | 0.0500 |
| | b | 5.0 | 100 | 1.8148 | 1,364 | 0.0500 |
| | c | 5.0 | 100 | 1.8148 | 2,060 | 0.0500 |
| RE | a | 29.7 | 100 | 1.8148 | 900 | 0.2000 |
| | b | 29.7 | 100 | 1.8148 | 1,364 | 0.2000 |
| | c | 29.7 | 100 | 1.8148 | 2,060 | 0.2000 |
| RF | a | 16.8 | 100 | 1.8148 | 900 | 0.0700 |
| | b | 16.8 | 100 | 1.8148 | 1,364 | 0.0700 |
| | c | 16.8 | 100 | 1.8148 | 2,060 | 0.0700 |
| RG | | 29.7 | 100 | 1.8148 | 1.364 | 0.1200 |
| RH | | 5.0 | 100 | 3.6295 | 1,364 | 0.0500 |
| RJ | | 5.0 | 300 | 5.3420 | 1,364 | 0.0500 |
| RK* | | 5.0 | 100 | 1.8148 | 1,364 | 0.0500 |

* Synthetic sea water, recipe of Lyman and Fleming (9), employed in place of potassium chloride solution.

conditions investigated is summarized in Table 1. A number of runs were duplicated to determine reproducibility of the data in terms of crystals formed after set reaction time under varying conditions. The average deviation (defined as run value minus average for duplicate run divided by average for the duplicate runs) for twenty-four of these replicate runs was 0.5% with the maximum observed deviation being 3.8% . Further details of this are given elsewhere (*8*).

### Experimental Observations

Observations on the gross effects of major experimental variables on the kinetics are discussed below. The experimental data presented have been corrected for the mass of seeds present at time zero and are normalized with respect to the equilibrium yield of crystals determined from the reaction stoichiometry and KDPA solubility (*1*) under the conditions of the experiment. The ordinate of the plots, therefore, represents the fractional approach to equilibrium yield of crystals.

*Effects of Temperature* The effect of temperature on the kinetics of KDPA crystallization was determined experimentally at 5.0°, 16.8°, and 29.7°C. Typical results, as summarized in Figure 2, indicate that the rate of crystallization increases with temperature, suggesting that the rate of chemical reaction which produces KDPA might be sufficiently slow to have an effect on the overall crystallization rate.

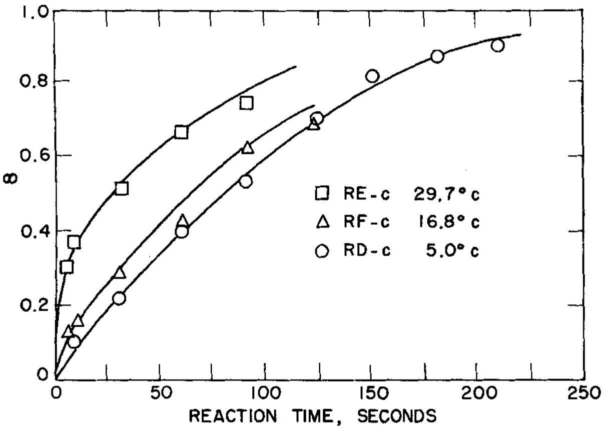


Fig. 2. Effect of temperature, experimental.

Consider the case of extremely rapid chemical reaction. The concentration of KDPA in solution at any time would then be determined by the crystal growth rate only. Also, suppose that the rate of growth depends on two things: a rate constant related to diffusion rates, and the supersaturation. While the rate constant for crystal growth certainly increases with temperature, the supersaturation decreases with temperature owing to increased solubility, since the solubility of KDPA in water increases with temperature (*1*). At 0.7°C. the solubility is 259 mg./liter, and at 30°C. the solubility is 1,098 mg./liter. If the latter effect dominates, which is likely in many systems because of the relatively weak dependence of diffusion rate on temperature, the result will be a net decrease in the rate of crystal growth with temperature.

Consider now a slower chemical reaction. The supersaturation at any time in this case depends on the difference in the rates of chemical reaction and crystal growth. One would expect the chemical rate to be more strongly temperature dependent than the crystal growth rate, resulting in an increase in supersaturation with temperature. In this case, then, both the supersaturation and the rate constant for crystal growth increase with temperature, and an overall increase in growth rate must be expected.

*Effect of Initial Concentrations.* The effect of initial potassium concentration on the crystallization kinetics was determined at three levels; 0.1, 0.2, and 0.3 grams potassium/liter, in runs at 5.0°C. (see Figure 3). For initial NaDPA concentration effects, two levels, 1.8148 and 3.6295 g./liter, were employed in runs at 5.0°C. with 0.1 grams potassium/liter. These figures represent NaDPA in excess of the stoichiometric amount by 50 and 200%, respectively. Results are also given in Figure 3.

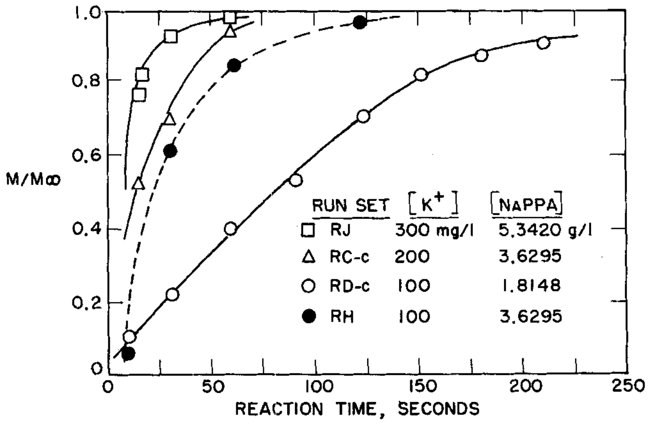


Fig. 3. Effect of initial potassium and NaDPA concentration.

*Effect of Seed Crystal Concentration.* Two run sets were made at 29.7°C., involving 0.2000- and 0.1200-g. seeds initially added to the reactor. It is assumed that the number of seeds is directly proportional to the mass; the effect shown in Figure 4 also includes the effect of seed size due to the fact that a portion of each seed crystal dissolved and that portion differed with the number of seeds.

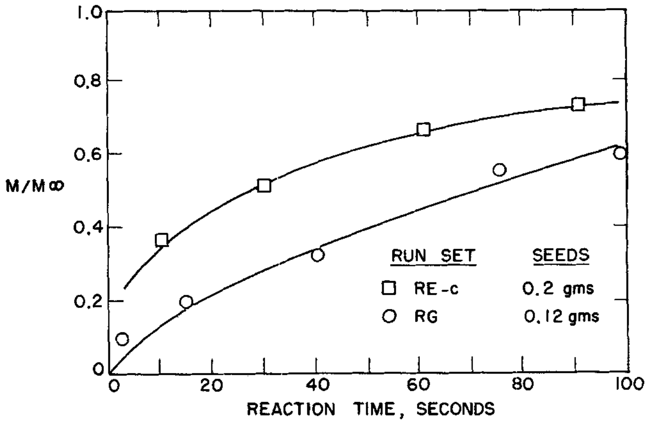


Fig. 4. Effect of seed crystal concentration.

*Effect of Agitation.* The effect of stirrer speed on the observed kinetics was determined at the three temperatures and two initial potassium concentration levels. Three stirrer speeds were employed, and an example of the results is given in Figure 5. In all cases, the rate of crystallization was found to increase with increasing agitation. The highest Reynolds number attained was the maximum possible with the experimental apparatus.

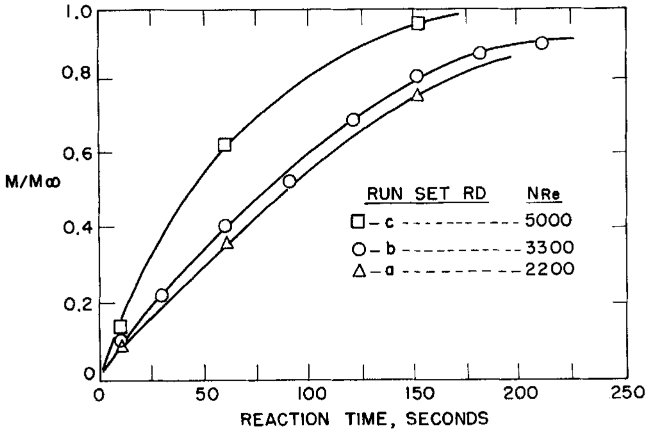


Fig. 5. Effect of agitation level.

## THEORY

It is apparent from the experimental observations noted above that the reaction-crystallization process involved in KDPA formation is a complex one. The development of a detailed approach to the kinetics of the system requires determination of the relative importance of reaction and crystallization rates and a knowledge of the chemical reactions involved. The importance of the chemical rate is suggested by the variations in overall crystallization rate with initial reactants concentrations and temperature, and by the absence of spontaneous nucleation effects in the experimentation (arising from large supersaturations if there is fast reaction). The absence of spontaneous nucleation is indicated by the reproducibility of the data. More than one hundred unseeded experiments were run in which spontaneous nucleation occurred, and the entire set of these experiments was characterized by the nonreproducibility of the results (*8*).

### Chemical Reactions Involved

The three following reactions, written in simplified form, are possible in the experimental system:

$$\mathrm{NaDPA} \rightleftharpoons \mathrm{Na}^+ + \mathrm{DPA}^- \qquad (1)$$

$$\mathrm{K}^+ + \mathrm{DPA}^- \rightleftharpoons \mathrm{KDPA} \qquad (2)$$

$$\mathrm{K}^+ + \mathrm{NaDPA} \rightleftharpoons \mathrm{KDPA} + \mathrm{Na}^+ \qquad (3)$$

Reactions (1) and (2) are known to be reversible, but reaction (3) may not be. The effects of initial potassium and sodium dipicrylamine concentrations can be explained on the basis of (1) and (2), or (3), or all three reactions; however, the kinetics observed in runs RK at very high sodium concentrations were identical to those of similar runs (RD-b) in potassium chloride solution. Clearly, (1) and (2) cannot be selected as the model reactions because the rate of KDPA formation in solution would decrease with increasing $\mathrm{Na}^+$ concentration. In the subsequent analysis, reaction (3) governs the chemical rate; it is likely, of course, that all three reactions take place, but the effective equilibrium in (1) is far to the left, thus diminishing the importance of (2).

### Formulation of the Overall Kinetic Expressions

The most widely accepted modern theory of crystal growth is that of Burton, Cabrera, and Frank (*10*) postulating growth from screw dislocations as a favored alternative to two-dimensional nucleation in the building up of a crystal face. Considerable evidence has been accumulated (*11*) in support of this theory, and we shall subsequently demonstrate its application in the present experiment.

The growth rate equation is derived on the basis of considering both the rate of diffusion of molecules to the surface of the crystal and the rate of surface migration of adsorbed molecules. Details of the development are given in reference *10*; the result is

$$R_i = \left[ \frac{a_1 RT \ln S}{2\ \sigma_{cs} V_c} \cdot \frac{D N_o \Omega (S-1)}{X_o} \right] \cdot \left[ 1 + \frac{2\pi a_1 (\delta - Y_o)}{X_o Y_o} + \frac{2a_1}{X_o} \ln \frac{Y_o}{X_o} \right]^{-1} \qquad (4)$$

where $Y_o = (4\pi\ \sigma_{cs}\ V_c)/(RT \ln S)$ and $R$ is the rate of crystal growth in a direction perpendicular to the plane of the surface $i$ in units of distance per time. It may be shown that at low supersaturations the third term in the denominator of Equation (4) predominates, and the rate becomes approximately proportional to $(S-1)^2$. At high supersaturations the second term in the denominator becomes important, and the rate of crystal growth approaches proportionally to $(S-1)^1$. Burton et al. (*10*) estimate that the linear dependence is correct when $(S-1) > 0.01$. This linear dependence is assumed in the following development, since rather large supersaturations are to be expected unless the chemical rate is very slow. The rate expression for crystal growth then simplifies to

$$R_i = k_i (S-1) \qquad (5)$$

The rate at which an entire crystal grows is dependent on the growth rates of each of its sides, which are in general not the same; hence, to describe the rate of accumulation of mass on a crystal, one must account for its macroscopic geometry.

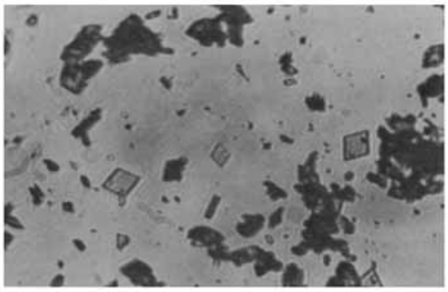


Fig. 6*a*. Photomicrograph of KDPA crystals.

Potassium dipicrylamine crystals grow as rhombohedra, depicted in the photomicrograph of Figure 6*a*. The mass of such a crystal is given by the equation

$$M = \rho abc \sin\alpha \qquad (6)$$

Differentiating with respect to time, one gets

$$\frac{dM}{dt} = \rho \sin\alpha \left[ bc\frac{da}{dt} + ac\frac{db}{dt} + ab\frac{dc}{dt} \right] \qquad (7)$$

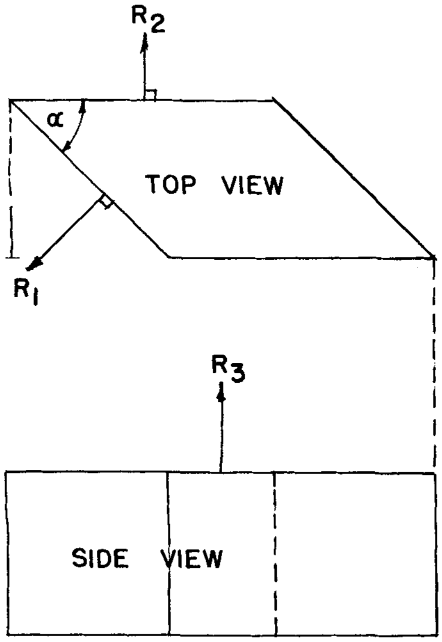


Fig. 6b. Schematic of rhombic geometry.

Growth rates of parallel sides can be summed to give three values which uniquely describe the overall rate. These are shown in Figure 6b as $R_1$, $R_2$, and $R_3$ and are given by Equation (5). Taking the component of the rate vector in the direction of the crystal side most nearly parallel to the vector, one can write:

$$\frac{da}{dt} = R_1 \sin\alpha = k_1 \sin\alpha (S - 1) \tag{8}$$

$$\frac{db}{dt} = R_3 = k_3 (S - 1) \tag{9}$$

$$\frac{dc}{dt} = R_2 \sin\alpha = k_2 \sin\alpha (S - 1) \tag{10}$$

In the case, such as the subject experiment, where growth is from initial dimensions, $a_o$, $b_o$, $c_o$, then crystal size is given by

$$\begin{aligned} a &= a_o + \int_o^t k_1 \sin\alpha (S - 1) dt \\ b &= b_o + \int_o^t k_3 (S - 1) dt \\ c &= c_o + \int_o^t k_2 \sin\alpha (S - 1) dt \end{aligned} \tag{11}$$

Substituting Equations (8) to (11) into the general expression, Equation (7), one obtains

$$\frac{dM}{dt} = (S - 1) \left[ K_1 + K_2 \int_o^t (S - 1)\, dt + K_3 \left\{ \int_o^t (S - 1)\, dt \right\}^2 \right] \tag{12}$$

and

$$K_1 = \rho[a_o c_o k_3 \sin\alpha + (b_o c_o k_1 + a_o b_o k_2) \sin^2\alpha]$$
$$K_2 = 2\rho[(c_o k_1 k_3 + a_o k_2 k_3) \sin^2\alpha + b_o k_1 k_2 \sin^3\alpha]$$
$$K_3 = 3\rho\, k_1 k_2 k_3 \sin^3\alpha$$

Equation (12) refers to an individual crystal; for the approximation in which all crystals are the same size, the total rate of mass accumulation is given by Equation (12) multiplied by the total number of crystals $N$.

The growth rate expression must be combined with the chemical reaction rate expression to formulate the overall kinetic equations. It is assumed that order corresponds to stoichiometry, so the rate of production of KDPA in solution is equal to

$$r_c = k_R [K^+] [\text{NaDPA}] \tag{13}$$

The rate of change of [KDPA] in solution is equal to its rate of production by chemical reaction minus its rate of removal by crystallization, or from Equations (12) and (13)

$$\frac{d[\text{KDPA}]}{dt} = k_R [K^+] [\text{NaDPA}] - \frac{N}{V} \frac{dM}{dt} \tag{14}$$

For the ionic concentration of potassium

$$\frac{d[K^+]}{dt} = -k_R [K^+] [\text{NaDPA}] \tag{15}$$

Thus, overall material balances for $[K^+]$ and [NaDPA] are

$$[K^+] = [K^+]_o - \{[\text{KDPA}] - [\text{KDPA}]_o\} - (M/V) \tag{16}$$

$$[\text{NaDPA}] = [\text{NaDPA}]_o - \{[\text{KDPA}] - [\text{KDPA}]_o\} - (M/V) \tag{17}$$

From (16) and (17)

$$[\text{NaDPA}] = [K^+] + (RR - 1) [K^+]_o \tag{18}$$

where:

$$RR = \frac{[\text{NaDPA}]_o}{[K^+]_o}$$

Substitution of Equation (18) into (14) and (15) gives the two final equations which describe the system:

$$\frac{d[K^+]}{dt} = -k_R \{[K^+]^2 + (RR - 1) [K^+]_o [K^+]\} \tag{19}$$

$$\frac{d(S - 1)}{dt} = \frac{k_R}{[\text{KDPA}]_s} \{[K^+]^2 + (RR - 1) [K^+]_o [K^+]\} - \frac{N(S - 1)}{[\text{KDPA}]_s V} \left[ K_1 + K_2 \int_o^t (S - 1)\, dt + K_3 \left\{ \int_o^t (S - 1)\, dt \right\}^2 \right] \tag{20}$$

The *simultaneous* solution of this pair with appropriate initial conditions gives $S = S(t)$; from this, Equation (12) is directly integrated to find $M$ as a function of time. The fit of the data to this kinetic model is discussed in the next section.

### Interpretation of Data

Equations (19) and (20) are highly nonlinear; removal of the integral terms from (20) as an approximation allows analytical solution, but even in this case the solution is not in closed form. The set is easily solved by analogue computer; this was the method employed in the present research, and details are discussed elsewhere (8). The curves computed for all experimental runs, sets RC — RJ, are shown with the experimental data in Figures 7 to 11. The kinetics observed at 5.0°C. were fitted with a reaction rate constant ($k_R$) of 21 liter/mole-sec. It was also determined for this case, as for all temperature levels investigated, that best fit was obtained with $K_2$ and $K_3$ of Equation (12) equal to zero. The implications of zero values for these two constants are discussed subsequently.

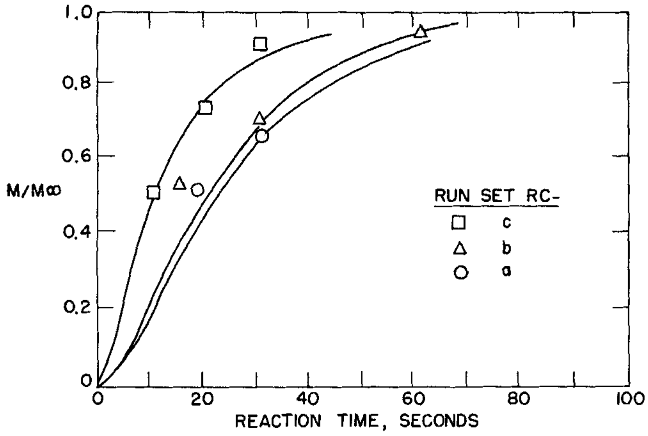


Fig. 7. Data of run set RC with calculated curves.

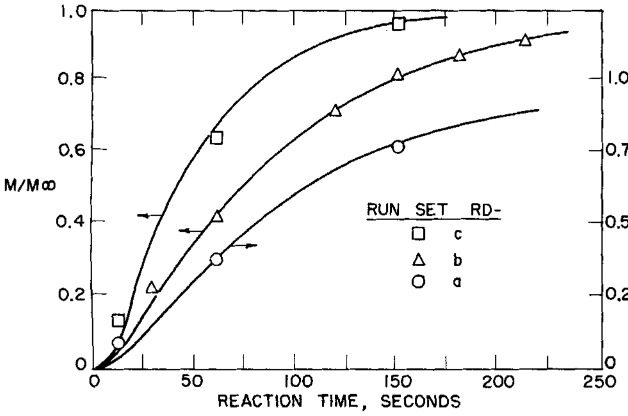


Fig. 8. Data of run set RD with calculated curves.

Values of $(S - 1)$ generated by the best fit solution were found to be above 0.01, as assumed in the development of the model, except for a very short time at the start of the reaction period. Indeed, rather large supersaturations ($\sim$ 2) are observed in some cases, indicating relatively rapid initial production of KDPA in solution with subsequent depletion by crystallization.

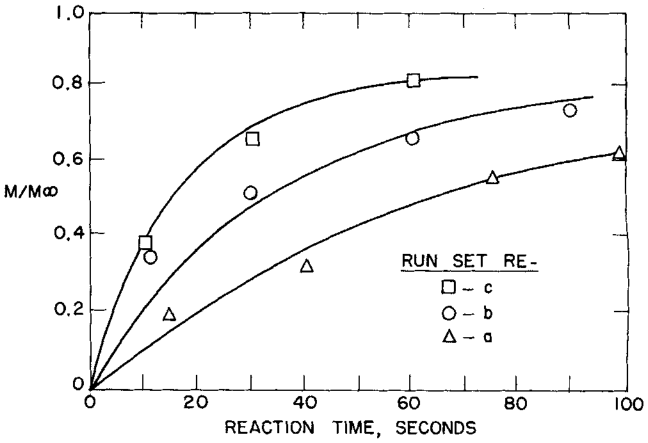


Fig. 9. Data of run set RE with calculated curves.

In fitting the data for the runs at 16.8 and 27.9°C. it was found that values of $k_R > 100$ liter/mole-sec. were required; these values indicate very rapid reaction rates, so data for these conditions were fit by assuming $k_R >> K_1$, and $K_2 = K_3 = 0$. A simple calculation, based on the results finally obtained, shows that little error is introduced by assuming infinite reaction rate for these runs. Equation (19) can be integrated directly, and the time necessary for 90 per cent conversion of the $[K^+]$ can be calculated. For example, if the reaction has an activation energy of 25 kcal/mol the times required for 90 per cent conversion are 13 and 2 sec. respectively, by extrapolation of the rate constant determined for 5.0°C. This is compared to approximately 86 sec. for 90 per cent conversion at 5.0°C. Values of the constants, $NK_1$, of the crystal growth rate expression are summarized in Table 2.

Table 2. Summary of Crystal Growth Rate Constants

| Run set | | $NK_1 \times 10^{16}$ | $N \times 10^{-6}$ | $a_0$, $\mu$ | $K_1 \times 10^{12}$ moles/sec. | $k_1 \times 10^5$ cm./sec. | $\left(\frac{K_2}{K_1}\right) \times 10^3$ | $\left(\frac{K_3}{K_1}\right) \times 10^6$ |
|---|---|---|---|---|---|---|---|---|
| RC | a | 3.94 | 2.14 | 25 | 1.84 | 3.13 | 25.0 | 125 |
| | b | 4.38 | 2.14 | 25 | 2.05 | 3.49 | 27.9 | 140 |
| | c | 17.5 | 2.14 | 25 | 8.18 | 13.9 | 111 | 555 |
| RD | a | 0.768 | 2.14 | 25 | 0.356 | 0.604 | 4.83 | 2.42 |
| | b | 0.874 | 2.14 | 25 | 0.408 | 0.695 | 5.56 | 2.78 |
| | c | 1.86 | 2.14 | 25 | 0.869 | 1.48 | 11.8 | 5.90 |
| RE | a | — | 8.54 | 22 | — | — | — | — |
| | b | 10.6 | 8.54 | 22 | 1.24 | 2.72 | 24.7 | 124 |
| | c | 33.2 | 8.54 | 22 | 3.89 | 3.14 | 28.5 | 143 |
| RF | a | 1.55 | 2.99 | 22 | 0.518 | 1.14 | 10.4 | 52 |
| | b | 1.61 | 2.99 | 22 | 0.538 | 1.18 | 10.7 | 54 |
| | c | 2.67 | 2.99 | 22 | 0.893 | 1.96 | 17.8 | 89 |
| RG | | 5.43 | 5.12 | 18.5 | 1.06 | 3.29 | 35.6 | 178 |
| RH | | 1.89 | 2.14 | 25 | 0.883 | 1.50 | 12.0 | 60 |
| RJ | | 15.8 | 2.14 | 25 | 7.38 | 12.6 | 101 | 505 |
| RK | | 0.874 | 2.14 | 25 | 0.408 | 0.695 | 55.6 | 278 |

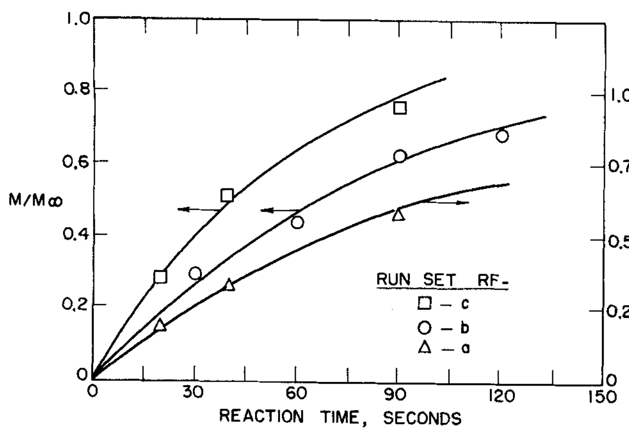


Fig. 10. Data of run set RF with calculated curves.

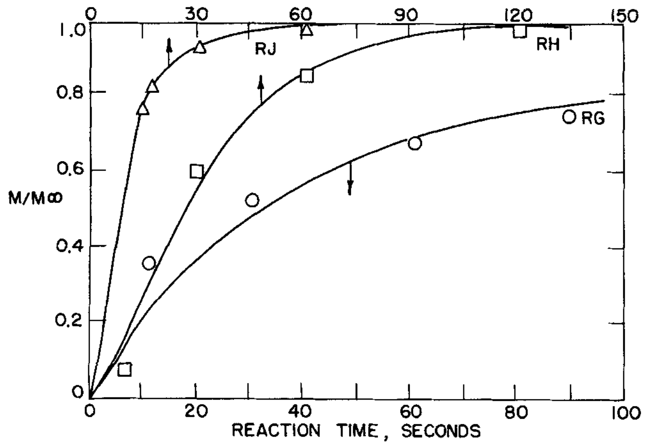


Fig. 11. Data of run sets RG, RH, RJ with calculated curves.

### Discussion of the Model

The form of the crystal growth expression, Equation (12), applies uniformly to any crystal which has three sets of parallel sides and two or three 90° angles between the sides—such as cubic, tetragonal, orthorhombic or monoclinic. The value of $\alpha$, of course, is specific to a given crystalline material, as well as the three constants of Equation (12), which must be determined experimentally for a given material.

It is important to note especially how the constants of Equation (12) relate to the more basic parameters of the system. If the crystal grows much more slowly in any one direction than in the other two, then $K_3$, say, approaches zero; if this is the case in two directions then both $K_3$ and $K_2$ approach zero. Note also that $K_1$ is more strongly dependent on seed crystal size than $K_2$, and that $K_3$ is independent of seed crystal size. The relative dependency of these constants on $k_1$, $k_2$ and $k_3$ is reversed; $K_3$ is most dependent and $K_1$ least dependent.

The kinetic data reported in the present study were best fit with $K_2 = K_3 = 0$. This result is best understood by calculating approximate values of $k_1$, $k_2$, and $k_3$ from the measured values of $K_1$, then comparing $K_1$, $K_2$, and $K_3$. In order to do this it is necessary to characterize more completely the seed crystals. These crystals were measured with a calibrated microscope and found to be uniform in size, 25 $\mu$ long on each side. With an estimated apparent density of 1.5 g./cc. used, the number of crystals added in each run could be computed. Since a portion of each crystal dissolved in the potassium chloride solution, the size of the seed crystals was adjusted by the one-third power of the ratio of masses before and after dissolution. The results of these calculations are given in Table 2.

In order to determine estimates for $k_1$, $k_2$, and $k_3$, the following approximations are made:

$$\begin{aligned} \alpha &= \pi/2 \\ k_1 &= k_2 = k_3 \\ a_o &= b_o = c_o \end{aligned} \tag{21}$$

It is known that $k_1$ and $k_2$ are equal from the photomicrograph, Figure 6a, which shows that the lengths of two sides of the crystals are always equal. Hence their growth rates must be equal. Whether $k_3$ equals $k_1$ and $k_2$ or is much smaller has little effect on the present development, since order-of-magnitude values suffice. With the above assumptions, then, we have that

$$K_1 = 3\,\rho(a_o)^2 k_1 \tag{22}$$

$$K_2 = 6\,\rho a_o(k_1)^2 \tag{23}$$

and

$$K_3 = 3\,\rho(k_1)^3 \tag{24}$$

Table 2 contains the values of $K_1$, $k_1$, $(K_2/K_1)$, and $(K_3/K_1)$ computed in accordance with the above. The value of $K_2$ is as much as 200 times smaller than $K_1$, and $K_3$ is as much as $10^5$ times smaller than $K_1$. The integral terms of Equations (12) and (20), thus, are relatively smaller than the linear term, and there is an a posteriori justification for the neglect of $K_2$ and $K_3$.

It is interesting to compare the magnitude of $k_1$ for potassium dipicrylamine crystal growth with values of the same constant for growth of crystals of other large molecules. Booth and Buckley (*12, 13*) have reported direct measurements of the growth rate of single crystals of ethylene diamine tartrate and ammonium dihydrogen phosphate from which values of the rate constant have been determined. These constants are of the same magnitude as those determined in the present research. Table 3 presents a comparison of the three systems.

TABLE 3. RELATIVE VALUES OF CRYSTAL GROWTH RATE CONSTANT

| | | Temp. range, °C. | $k_1$ range, cm./sec. |
|---|---|---|---|
| Potassium dipicrylamine | | 5.0-29.7 | $6.04 \times 10^{-6}$-$1.39 \times 10^{-4}$ |
| Ethylene diamine tartate | (100) | 27.5-42 | $7.29 \times 10^{-6}$-$5.55 \times 10^{-5}$ |
| | (110) | 27.5-42 | $7.07 \times 10^{-5}$-$3.0 \times 10^{-4}$ |
| Ammonium Dihydrogen Phosphate | (Pyramidal) | 31-38.5 | $1.03 \times 10^{-4}$-$3.83 \times 10^{-4}$ |
| | (Prismatic) | 31-42.5 | $3.40 \times 10^{-5}$-$1.72 \times 10^{-4}$ |

### Correlation of Growth Rate with Operating Conditions

The range of crystallization rate constant $k_1$ given in Table 3 represents variation with the operating variables of temperature, agitation level, and initial reactants concentration. Inspection of Equations (4) and (5) shows that the constant $k_1$ is a function of temperature, the diffusion coefficient, the crystal-solution interfacial free energy, and some constant parameters. The effect of liquid boundary-layer thickness is also lumped into $k_1$. The diffusion coefficient is a function of temperature and of concentration level, and the interfacial free energy is certainly a function of temperature and chemical composition to some extent. It is thus obvious that the observed variation of $k_1$ with temperature is consistent with the model. The boundary-layer thickness is a function of agitation level; hence the dependence of $k_1$ on this variable is reasonable. Variation of $k_1$ with reactants concentration is not obvious from the model equations but is most probably related to variation of diffusivity and interfacial free energy with composition. Some quantitative aspects of the variations of $k_1$ with operating conditions are discussed in the following paragraphs.

Temperature dependence can be correlated by means of an Arrhenius expression with an apparent activation energy of 9,000 cal./g.-mole and a frequency factor slightly dependent on agitation level. The experimental data have an average deviation of ± 10.4% from calculated values with this correlation (*8*). The magnitude of the activation energy is also an indication of the influence of boundary-layer effects on $k_1$, since typical values for diffusion in liquids are in the range of 3,000 cal./g.-mole and apparent activation energies for growth rates when $\delta$ in Equation (4) is small range up to approximately 20,000 cal./g.-mole (*14*). Observed variation of the overall constant $k_1$ is proportional to Reynolds number ($2{,}200 \leq N_{Re} \leq 5{,}000$) to the 1.2 power, within the range predicted by the correlations of Middleman (*15*) for mass transfer in agitated vessels.

The number and size of seeds affect the magnitude of constants in Equation (12) for the overall system but should have no effect on the value of the specific growth rate constant. Thus, $k_1$ values for runs RE-c and RG should agree; values computed for these runs are $2.72 \times 10^{-5}$ and $3.29 \times 10^{-5}$ cm./sec., respectively, which deviate ± 10% from their mean value.

Concentration variation of growth rate constants in the range of 20% with initial potassium ion and sodium dipicrylamine concentration was observed, the constant decreasing with increasing concentration. The reasons for this variation are not as clearly defined as they are for changes with temperature and agitation level; however, diffusivities and interfacial energies are concentration dependent, and it is not unreasonable to attribute $k_1$ variation with concentration level to the variation of these quantities.

## SUMMARY

An interpretation of the crystallization kinetics of KDPA in aqueous solution has been derived through application of the theory of crystal growth from screw dislocations. The overall system is considered to be one of sequential rates: chemical reaction and crystallization. The interpretation indicates that the chemical reaction of major importance is the irreversible combination of potassium ions and molecular sodium dipicrylamine, and that the rate of this reaction measurably retards the overall rate of crystallization at the lowest temperature studied, 5°C. The growth rate equation based on the dislocation theory is shown to reduce to a linear rate law under certain conditions and for certain values of the basic parameters of the model. Crystal growth rate constants for potassium dipicrylamine, calculated from the model, have reasonable values and are shown to agree in order of magnitude with those determined by direct means for other large molecules in the corresponding temperature range.

## NOTATION

$a_1$ = step height in dislocation model, cm.
$a, b, c$, = length of a side of a crystal, cm. (Figure 6*b*)
$d$ = stirrer blade diameter, cm.
$D$ = diffusion coefficient, sq.cm./sec.
$i$ = direction perpendicular to plane of crystal surface
$k_i$ = growth rate for surface $i$, cm./sec.
$k_R$ = reaction rate constant, [(g. moles NaDPA/cc.) — sec.]$^{-1}$
$k_1, k_2, k_3$ = growth rate constants for three directions, cm./sec. (Figure 6*b*)
$K_1, K_2, K_3$ = combined constants in growth rate equation, Equation (12)
$M$ = mass of crystals present at time $t$, g.
$M_\infty$ = mass of crystals present at equilibrium, g.
$N$ = number of crystals in the reactor
$N_o$ = saturation concentration, g. moles/cc.
$N_{Re}$ = Reynolds number; $N_{Re}$ = (RPM) $d^2/\nu$
$r_c$ = rate of production of KDPA by reaction, g./cc. — sec.
$R$ = gas constant
$R_1, R_2, R_3$ = rate of crystal growth for three directions, cm./sec. (Figure 6*b*)
$R_i$ = rate of crystal growth in direction $i$, cm./sec.
$RR$ = reactants ratio
$S$ = supersaturation, actual concentration divided by the saturation value
$t$ = time, sec.
$T$ = temperature, °K.
$V$ = reactor volume, cc.
$V_c$ = molal volume of crystal, cc./g. mole
$X_o$ = distance between kinks in a step (*10*)
$Y_o$ = distance between steps (*10*)

### Greek Letters

$\alpha$ = crystallographic angle (Figure 6*b*).
$\delta$ = liquid film thickness at crystal surface, cm.
$\rho$ = crystal density, g./cc.
$\sigma_{cs}$ = crystal solution interfacial free energy
$\nu$ = kinematic viscosity, sq.cm./sec.
$\Omega$ = molecular volume, cc.

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