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Part II. An Experimental Study of an Isothermal System

An experimental study was undertaken to verify the theoretical predictions that for a certain range of operating conditions an isothermal crystallizer would produce oscillating outputs even when the inputs were maintained constant. An interesting feature of the results is that even though a power-law model and Volmer's model for nucleation kinetics provided equivalent descriptions of the steady state data, predictions of transient responses based on Volmer's equation were much better than the power-law results, and the observed behavior of the oscillating system was described well with Volmer's expression, whereas the power-law equation predicted that the system would not oscillate.

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SCOPE

In recent years there have been significant advances in the theories used to predict the behavior of continuous crystallizers. Most of these studies have been concerned with steady state operation of the process or transient behavior between two steady states. In this study, a laboratory-scale crystallizer was designed to produce oscillatory outputs by use of the theory described in Part I of this paper. Only the simplest kind of continuous crystallizer was considered, that is, an isothermal, mixed-suspension, mixed-product removal (MSMPR) unit for a Class I system where high degrees of supersaturation are possible. Even for this simple process, the predictions of the existence of oscillatory operation are strongly dependent on the functional form chosen for the nucleation kinetics, that is, Volmer's model or a power-law model, and theoretical predictions indicate that oscillatory experiments are more sensitive to the magnitude of kinetic parameters than are steady state experiments.

CONCLUSIONS AND SIGNIFICANCE

Self-generated oscillations around the normal, steady state, exponential crystal size distribution were observed in a laboratory MSMPR crystallizer. The experimental values of the oscillatory output agreed very well with theoretical predictions based on steady state measurements of the growth rate and nucleation rate kinetic parameters, which is a very severe test of the elementary theory. For the very low range of suspension densities considered in the study, which does not correspond to normal industrial operation, Volmer's model provided an excellent description of the nucleation kinetics, whereas a power-law nucleation model failed to predict the existence of oscillations.

Even though self-generated oscillations have been observed for many years in industrial crystallizers (Miller and Saeman, 1947), they have seldom been encountered in laboratory studies (Nývlt and Mullin, 1970). Actually, there are two regions where oscillatory operation can occur (Randolph, et al., 1974). For high-order cycling, the instability occurs because the nucleation rate decreases much faster than the growth rate as the supersaturation driving force is lowered, and the system oscillates around the MSMPR exponential population distribution. For low-order cycling, the instabilities are caused by fines removal, product classification, and secondary nucleation effects. Low-order cycling is more representative of industrial operations, but high-order cycling should be easier to study in a laboratory. Moreover, an experimental demonstration of high-order cycling should provide additional verification of the simple theoretical models used to describe crystallizers, as well as providing some justification for using the theory of nonlinear oscillations to study the periodic operation of crystallizers as discussed in Part I.

In order to design a laboratory crystallizer that will oscillate even when the inputs are maintained constant, it is necessary to obtain values of the stability parameter b/g greater than about 12 for a Class I system (where high degrees of supersaturation can be obtained) or greater than 21 for a Class II system (where only extremely small degrees of supersaturation are possible). It is common practice to assume that a power-law model can be used to describe the nucleation kinetics, and with this assumption the value of $b/g = m$ is independent of the operating conditions. (See Appendix.) Then, since crystallization data taken in laboratory units designed to simulate industrial processes normally lead to a value of b/g of 3 or less, although one value as high as 9 has been reported, it is not surprising that oscillatory systems are rarely encountered in the laboratory. However, as is shown in Part I, if Volmer's model is used to describe the nucleation kinetics rather than the power-law model, then the value of b/g depends on the operating conditions; according to Equation (7) in Part I, it should be possible to obtain large values of b/g by designing the crystallizer so that the steady state solute concentration approaches the saturation value. In other words, an extrapolation of crystallizer behavior into new operating regions based on Volmer's model gives different results than does one based on the power law model, and for this reason we should be able to devise a critical experiment that can be used to distinguish between the two models, at least for certain kinds of systems.

Perhaps it should be mentioned that an analogous situation concerning the interpolative vs. extrapolative characteristics of rate equations is encountered in reaction kinetics. For example, Weller (1956) showed that power-law models fit isothermal rate data as well as do the more complex Langmuir-Hinshelwood (or Hougen and Watson) models, but the study of Lumpkin et al. (1969), demonstrated that nonisothermal reactor designs based on these models could be quite different. Thus, the fact that a power law model can be shown to be equivalent to Volmer's model over a limited range of operating data, both theoretically and experimentally, does not necessarily imply that extrapolations based on the two models will give the same results.

One other analogy that may be drawn from reaction kinetic studies is that a highly underdamped transient system or an oscillatory process is much more sensitive to small changes in the system parameters than is a steady state experiment (Baccaro, et al., 1970). Thus, a second purpose in attempting to design an oscillating crystallizer is to determine whether or not a simple change in operating conditions may be used to distinguish between the abilities of the power-law model and Volmer's model to predict new kinds of operating behavior.

EXPERIMENTAL SYSTEM

In order to study self-generated oscillations in a crystallizer, a laboratory experiment was designed with equipment similar to that described by Larson and co-workers (Murray and Larson, 1965; Larson, 1967; Randolph and Larson, 1971). Mixtures of sodium chloride, water, and ethanol were studied so that the measured crystallization kinetics might be compared with the results obtained by previous investigators (Timm and Larson, 1968; Koros, et al., 1972). Also, with this system the crystallizer operates isothermally, a fact which simplifies the analysis and satisfies the assumptions listed in Part I. It should be noted, however, that it is not difficult to modify the theory to account for nonisothermal operation.

A cylindrical Pyrex vessel, 6 in. diameter by 15 in. high, was used as a crystallizer. The tank contained three baffles and a concentric draft tube, 4 in. diameter by 6 in. high, placed 2 in. above the bottom of the vessel. Under all operating conditions the tank contained 4 liters of solution, and a propeller type of agitator was used to provide the mixing. Some preliminary dynamic experiments involving the mixing of hot and cold water demonstrate that close-to-perfect mixing could be obtained.

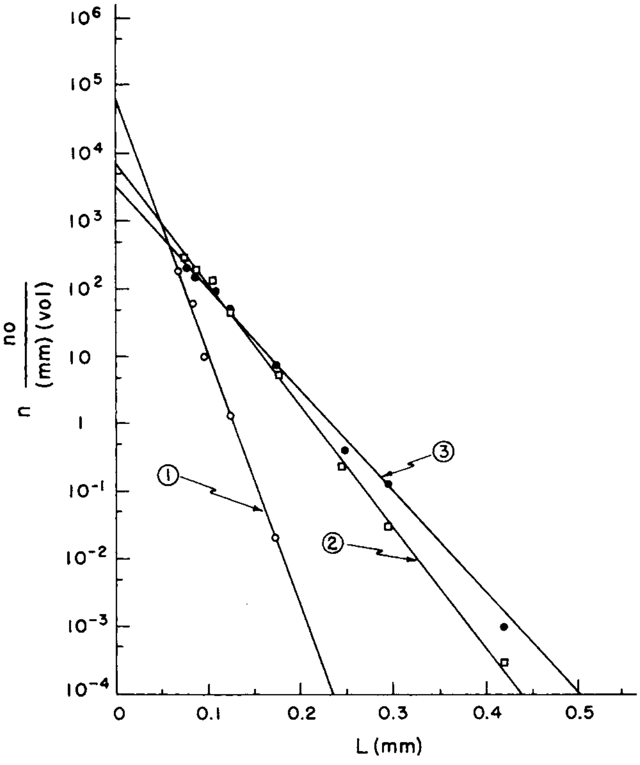

Fig. 1. Crystal size distribution

Denatured alcohol and a brine solution were metered and fed to the crystallizer from constant-head tanks, and the effluent flow rate was adjusted until the level in the tank remained constant. The product crystals were filtered from the effluent by use of a No. 1 filter paper; they were washed several times with acetone; and then they were allowed to dry before being placed in a set of Tyler standard 3-in. screens having the following mesh sizes: 20, 30, 40, 50, 60, 80, 100, 120, 140, 170, and 200. After shaking, each size fraction was weighed, and the resulting measurements were used to calculate the moments of the crystal size distribution function.

EXPERIMENTAL STUDIES AND RESULTS

The equilibrium solubilities of sodium chloride–water–ethanol mixtures were measured at various temperatures, and the results agreed almost exactly with the values reported in the International Critical Tables. Next, a set of steady state runs was carried out in order to check the validity of the model and to evaluate the kinetic constants in the nucleation-rate and growth-rate expressions. The brine concentration in these experiments was set at 0.304 g sodium chloride/ml; the brine to alcohol feed ratio was 5.0; the equilibrium solubility in the tank was 0.235 g sodium chloride/ml; and the feed rates were adjusted to correspond to retention times of 1/12, 1/4, and 1/3 hr. Data obtained from the screen measurements are plotted in Figure 1; losses in the screen analyses were about 1 or 2%. Table 1 contains a list of some of the process parameters for the steady state results, as well as the dynamic runs discussed later.

The data from the steady state measurements were used, along with Equations (9), (1), and (2) and the definition of ϵ given in Part I of the paper, to calculate

Table 1. System Parameters

Run	Type	θ (hr.)	$C_0 \frac{\text{g NaCl}}{\text{ml solu.}}$	$\frac{\text{Brine}}{\text{Alcohol}}$	$C_s \frac{\text{g NaCl}}{\text{ml solu.}}$	$n^0 \frac{\text{No.}}{\text{mm vol.}}$	$G \frac{\text{mm}}{\text{hr.}}$
1	Steady state	1/12	0.304	5	0.235	6.18×10^4	0.1385
2	Steady state	¼	0.304	5	0.235	7.36×10^3	0.0940
3	Steady state	1/3	0.304	5	0.235	3.04×10^3	0.0842
4	Transient	¼—1/12, FROM CONDITIONS AT RUN 2 TO CONDITIONS AT RUN 1					
5	Periodic	1	0.304	5	0.235		
6	Periodic	1	0.270	5	0.235		
7	Periodic	¾	0.304	6	0.265		

the kinetic constants appearing in Equations (1) and (2). The values obtained were

$$K_1 = 2.478 \left(\frac{\text{mm}}{\text{hr.}} \bigg/ \frac{\text{g NaCl}}{\text{ml}} \right)$$

$$K_2 = 7.029 \times 10^4 \frac{\text{crystals}}{\text{hr. mm}^3}$$

$$K_3 = 0.118$$

and a graph showing the fit of the data to Volmer's model, Equation (2), is presented in Figure 2. Also, the data were used with Equations (A2) and (A4) in the Appendix (Figure 3) to calculate the exponent in the simple power-law model of the nucleation kinetics. The exponent we calculated from the slope of Figure 3 was 7.9; whereas a value of 9 was reported by Timm and Larson (1968), and values in the range from 0.7 to 2.0 were published by Koros et al. (1972). However, as may be seen from Figure 4, the agreement between our data and Timm and Larson's is excellent. Thus, it seems as if a value of $m \approx 8$ corresponds to primary nucleation; whereas the lower value reported by Koros, et al., includes secondary nucleation and attrition effects. A comparison of Figures 2 and 3 shows that both types of nucleation models fit the data equally well.

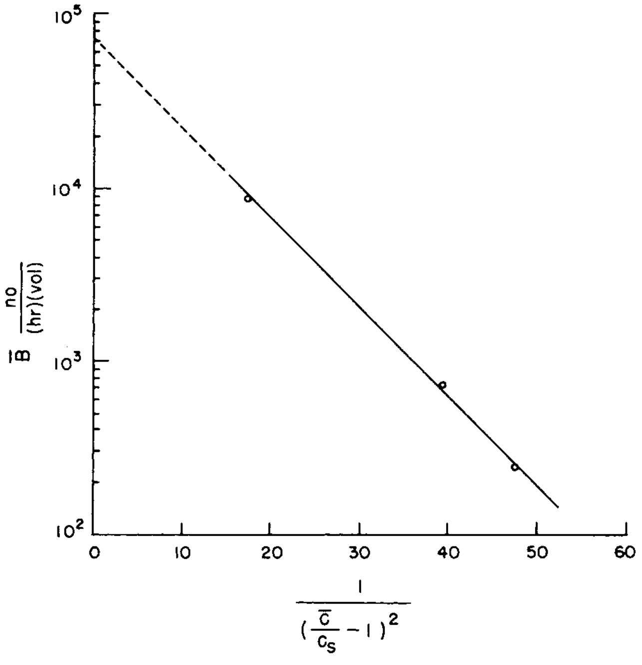

Fig. 2. Plot of Volmer's model.

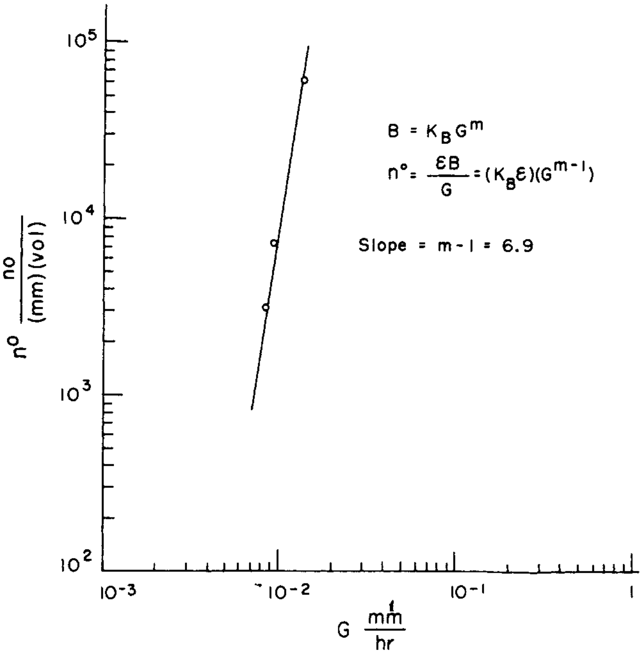

Fig. 3. Plot of power-law model.

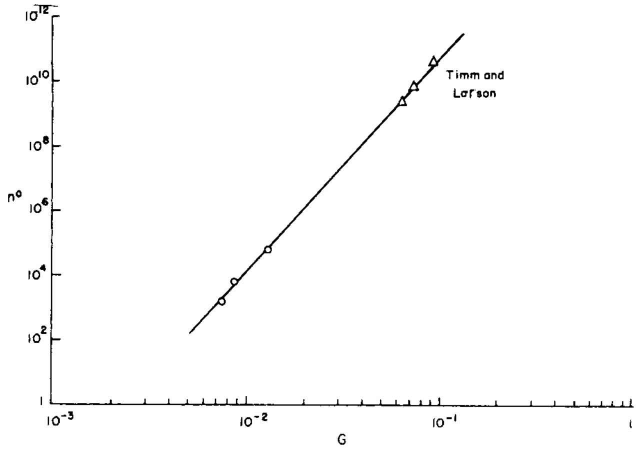

Fig. 4. Comparison with Larson's power-law model.

Using the estimates of the kinetic parameters in Volmer's model and the stability diagram given as Figure 5, we could verify that our steady state experiments corresponded to results from stable systems. The stability diagram based on a power-law nucleation model is identical to the previous result, except that the abscissa should be labeled as m rather than b/g. [See Equations (11) and (12) in Part I and Equation (A8) in the Appendix.] Since our measured value of m is unique, $m = 7.9$, we see that the power-law model predicts that the crystallizer

$B \frac{\text{No.}}{\text{hr. vol.}}$	ϵ	g	b/g	Period
8.62×10^3	0.994	0.234	4.2	
7.03×10^2	0.985	0.827	9.2	
2.6×10^2	0.983	1.045	11.2	
	0.980	1.620	19.50	4.5 θ
	0.994	0.462	23.58	5.4 θ
	0.996	0.322	21.40	5.5 θ

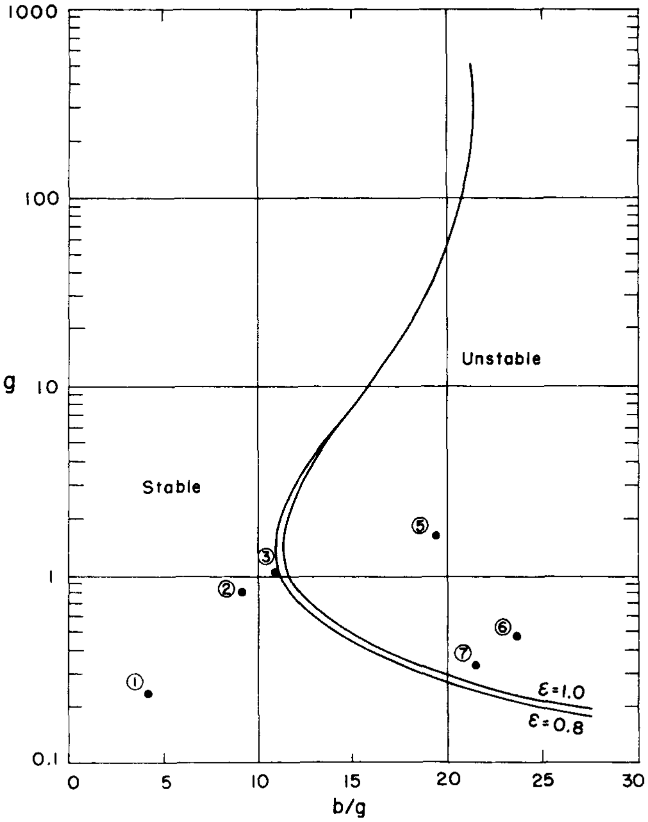

Fig. 5. Stability diagram.

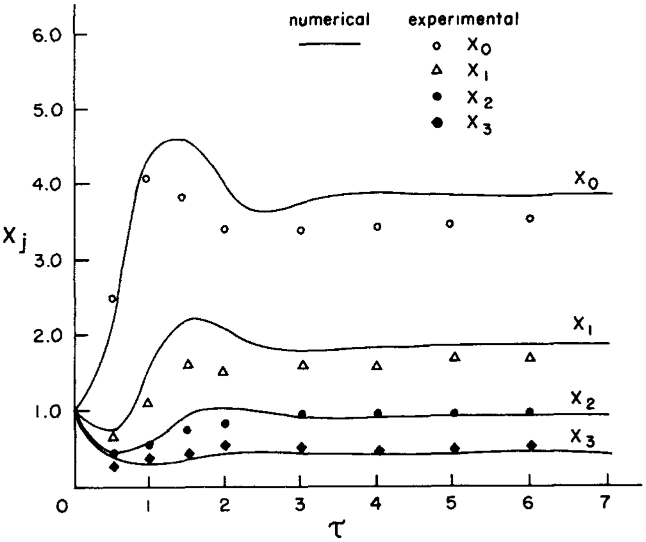

Fig. 6. Transient response with Volmer's model.

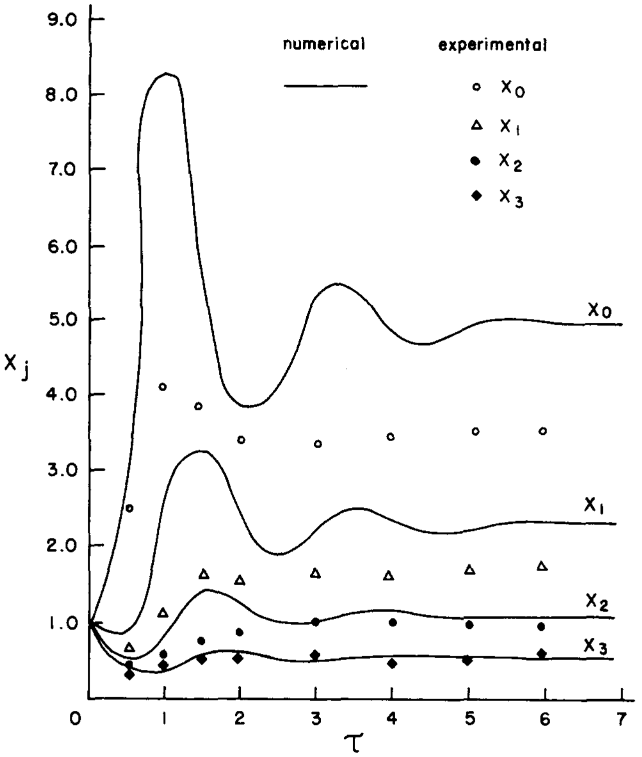

Fig. 7. Transient response with a power-law model.

will always be stable and that it will never be possible to observe self-generated oscillations. On the contrary, Volmer's model predicts that we can vary b/g by changing the feed rate to the crystallizer. Thus, we can use these conflicting predictions of stability characteristics to define a critical experiment that will distinguish between the ability of the two nucleation models to predict new types of behavior, at least for our system.

Before we attempted to achieve oscillatory operation in the crystallizer, however, we carried out a transient response experiment between two stable, steady state operating conditions by making a step change in the flow rate such that the retention time changed from 1/4 to 1/12 hr. The data and our numerical predictions based on the two nucleation models are presented in Figures 6 and 7. It is apparent that our ability to predict transient results with kinetic constants based on steady state measurements is better with Volmer's nucleation model, Figure 6, than with a power-law expression, Figure 7. Of course, we could use statistical techniques to detremine the kinetic constants that provide the best fit of each model to both the steady state and dynamic data. We did not follow this approach, however, because we have already been able to define a critical experiment that can be used to test the validity of the models. Instead, we showed that if the kinetic constants obtained from steady state measurements are changed ± 5%, the transient predictions bracket the experimental data. (See Figures 8 and 9.)

In the final set of experiments we changed the operating conditions so that our mathematical model with Volmer's nucleation expression predicted an unstable steady state. (See Figure 5.) After we had waited for any system transients to decay, data were taken at periodic time intervals. The results, as well as the predictions, are shown for a case where $c_0 = 0.304$, brine/alcohol = 5, and $\theta =$ 1 hr. in Figure 10; for a case where $c_0 = 0.27$, brine/alcohol = 5, and $\theta = 1$ hr. in Figure 11; and for a case where $c_0 = 0.304$, brine/alcohol = 6, and $\theta = 0.75$ hr. in

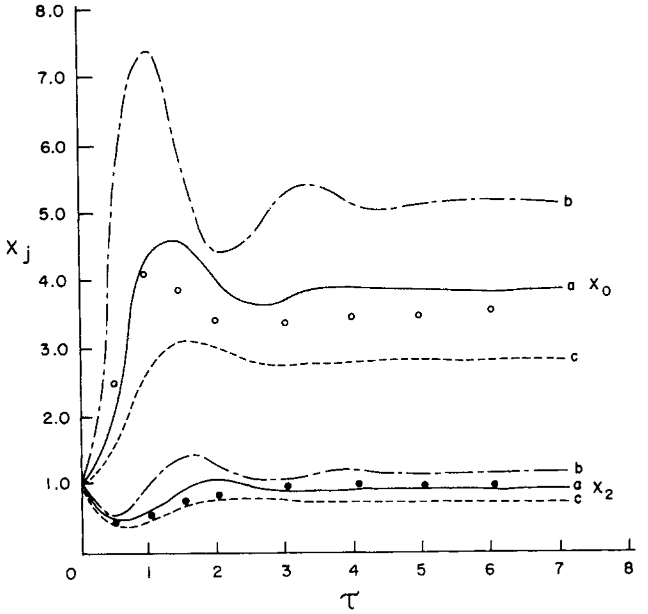

Fig. 8. Sensitivity of transient response;
a) $\bar{\epsilon} = 0.985$, $g = 0.827$, $b/g = 9.2$, θ from 1/4 to 1/12
b) $\bar{\epsilon} = 0.982$, $g = 0.945$, $b/g = 10.79$, θ from 1/4 to 1/12
c) $\bar{\epsilon} = 0.985$, $g = 0.739$, $b/g = 7.77$, θ from 1/4 to 1/12

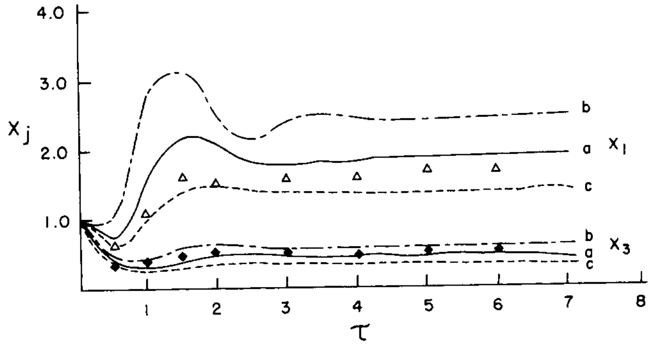

Fig. 9. Sensitivity of transient response;
a) $\bar{\epsilon} = 0.985$, $g = 0.827$, $b/g = 9.2$, θ from 1/4 to 1/12
b) $\bar{\epsilon} = 0.982$, $g = 0.945$, $b/g = 10.79$, θ from 1/4 to 1/12
c) $\bar{\epsilon} = 0.985$, $g = 0.739$, $b/g = 7.77$, θ from 1/4 to 1/12

Figure 12. These graphs indicate that the period of the oscillation is about five times greater than the retention time, which is a behavior similar to that observed by Miller and Saeman (1947) for industrial crystallizers.

Even though the process parameters do not correspond to typical industrial operating conditions (the value of g was less than 2 rather than greater than 10; see Sherwin, et al., 1967), it is interesting to note that the predicted and observed time-average weight of crystals (which is proportional to x_3) produced by the oscillating crystallizer is greater than the steady state value, $x_3 = 1$. Moreover, we see from Figures 5 and 10 through 12 that the further the design conditions are from the stability boundary, the greater will be the improvement in crystal yield. The magnitude of the observed improvement was in the range of 5 to 15%. No attempt was made to find the operating conditions that would maximize this shift in the time-average operation, or to see whether there may be any unexpected limitations to periodic operation as the parameters are changed to increase the amount of instability in the system.

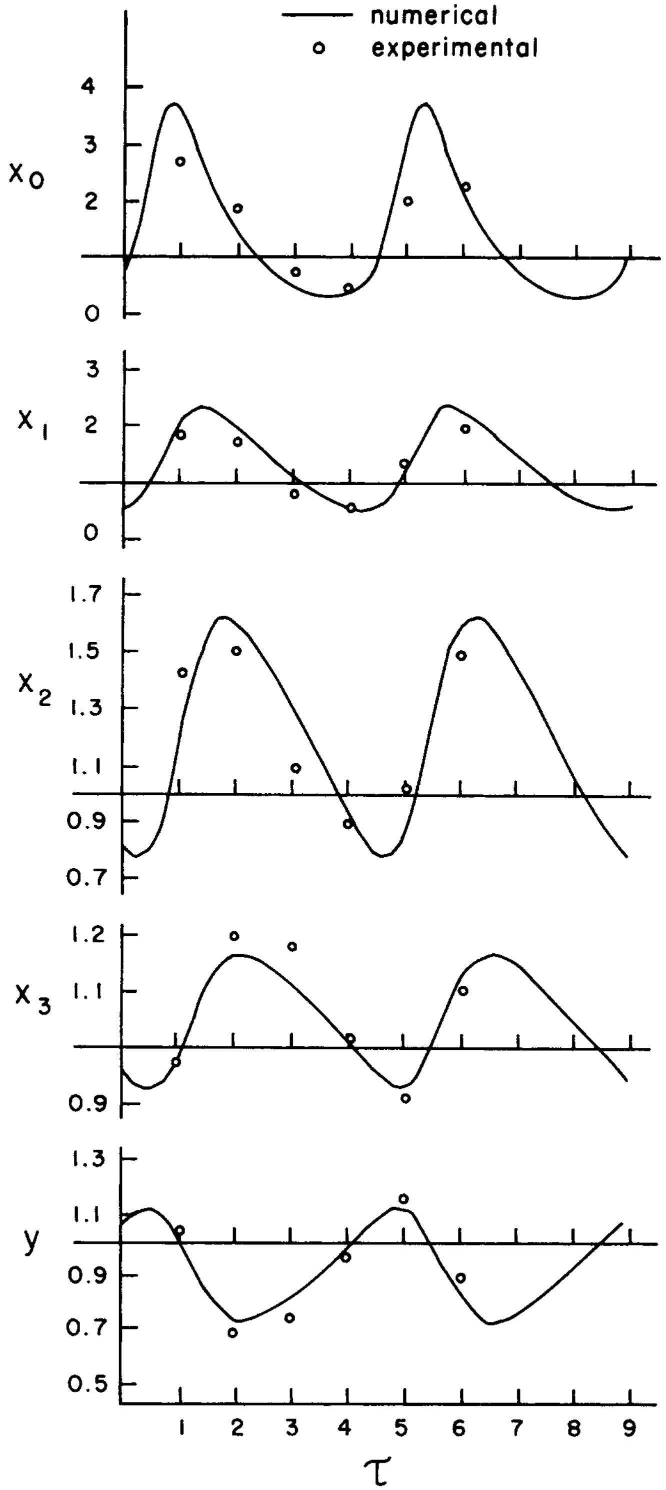

Fig. 10. Periodic operation, run 5.

Similarly, no attempt was made to determine the kinetic parameters that would provide the best fit for the three kinds of data, and the analytical solutions described in Part I were not used to estimate the crystallizer behavior. The best set of kinetic constants can be found in a straightforward fashion by use of conventional statistical techniques, but the additional effort did not seem to be warranted for the system under study. The analytical solutions are also straightforward, although tedious, and so few oscillatory runs were made that it was simpler to solve the nonlinear equations numerically.

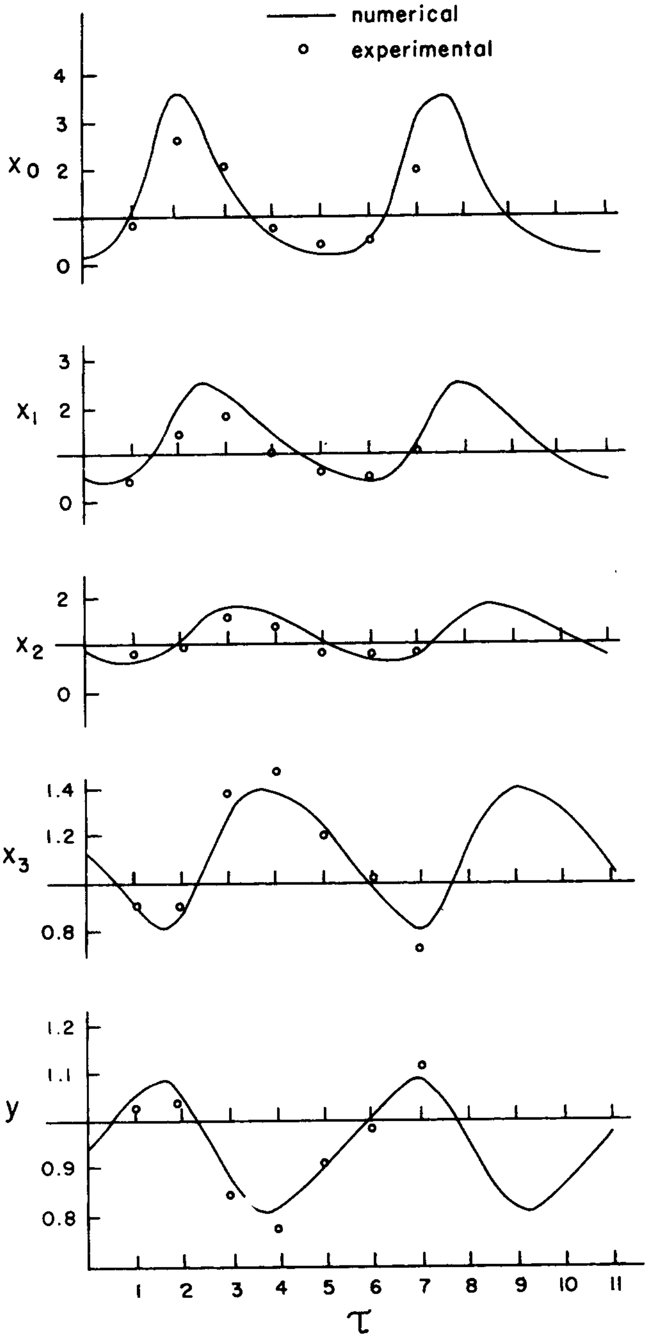

Fig. 11. Periodic operation, run 6.

DISCUSSION OF RESULTS

As the periodic operation described in this paper corresponds to the lower end of a high-order instability, in the terminology of Randolph and Larson (1971), the oscillations occur around the MSMPR exponential population distribution. Recently Randolph (1974) designed a crystallizer to oscillate at the high end of a low-order instability, which is a region of greater significance from a commercial viewpoint. It should be possible to use the analytical tools discussed in Part I to analyze Randolph's system, although no attempt has been made to do this as yet.

The experimental value of the exponent on the power-law model agrees very well with the results of Timm and Larson (1968) but is significantly different from the observation of Koros, et al. (1972). Very low suspension densities were maintained in the current study, $\epsilon > 0.98$,

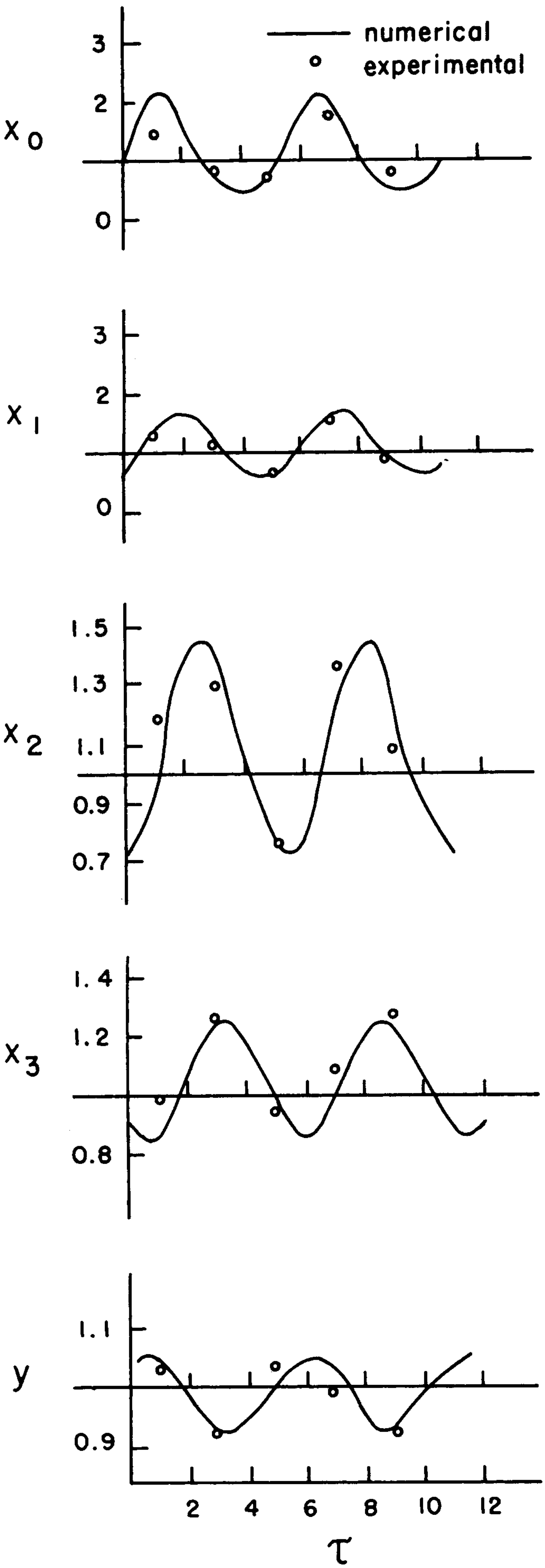

Fig. 12. Periodic operation, run 7.

and so it appears as if a value of $m \approx 8$ corresponds to primary nucleation, whereas the lower value obtained by Koros is influenced by secondary nucleation effects. (Also see Abegg, et al., 1968.) In this range of low suspension densities, we also found that Volmer's model for nucleation kinetics provided a better means of extrapolating the behavior of a crystallizer from one type of operating conditions to another, that is, from stable, steady state operation to transient conditions to oscillatory operation, than did the power law model.

ACKNOWLEDGMENT

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NOTATION

B = nucleation rate
b/g = $2K_3/[(\bar{c}/c_s) - 1]^2$
c = solute concentration
c_0 = feed concentration
c_m = metastable concentration
c_s = saturation concentration
G = growth rate
g = $(c_0 - \bar{c})/\bar{\epsilon}(\bar{c} - c_s)$
K_3, K_4, K_5, K_B = kinetic constants
L = crystal size
m = exponent in power law model
m_j = j^{th} moment
n = fraction of crystals having a size between L and $L + dL$ per unit volume
n^0 = number of crystals of zero size per unit volume
R_0 = $(1 - \bar{\epsilon})/\bar{\epsilon}$
t = time
V = crystallizer volume
W = feed rate
x_j = $m_j/\bar{m}_j$
y = $(c - c_s)/(\bar{c} - c_s)$
ϵ = fractional volume which is liquid phase
θ = V/W = drawdown time
τ = t/θ
overbar = steady state value
prime = deviation from steady state

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APPENDIX: USE OF A POWER-LAW, NUCLEATION MODEL

Larson has suggested replacing the metastable concentration c_m in Mier's model for nucleation kinetics

$$B = \begin{cases} K_4(c - c_m)^m & \text{if} \quad c > c_m \\ 0 & \text{if} \quad c \leq c_m \end{cases} \tag{A1}$$

by the saturation concentration c_s. Thus, he proposes the expression

$$B = K_5(c - c_s)^m \tag{A2}$$

This relationship can be combined with the growth rate equation, Equation (1) in Part I, to obtain

$$B = K_B G^m \tag{A3}$$

Moreover, from the steady state solution for the particle size distribution, the first expression in Equation (9) in Part I, we see that the number of nuclei, that is, the number of particles at zero size, is

$$n^0 = \frac{\bar{\epsilon}\bar{B}}{\bar{G}} = K_B\,\bar{\epsilon}\,\bar{G}^{\,m-1} \tag{A4}$$

Thus, from a log-log plot of n^0 vs. $\bar{G}$ based on steady state experiments, we can determine the kinetic parameters K_B and m. We expect that this approximation will be valid when $c_m - c_s$ is very small compared to $c - c_s$, which would correspond to the precipitation of highly insoluble compounds.

The moment equations, given by Equations (6) in Part I, are unchanged, except that we use Equation (A2) for B in the first expression, rather than Equation (2) in Part I. Similarly, only the first relationship in Equations (8) in Part I is changed, and this becomes

$$\frac{dx_o}{d\tau} = \left(\frac{1}{\epsilon} - R_o x_3\right) y^m - x_o \tag{A5}$$

With this modification, the first expression in Equation (10) in Part I becomes

$$\frac{dx_o'}{d\tau} = -x_o' - R_o x_3' - my' \tag{A6}$$

The characteristic equation given by Equation (11) in Part I is not affected, but the definition of a_4 in Equation (12) becomes

$$a_4 = 1 + 3g + gm + R_o \tag{A7}$$

Thus, the stability characteristics must be the same as we had before, except that we replace the parameter b by gm, or we let

$$m = b/g \tag{A8}$$

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