STUDIES ON NUCLEATION FROM AQUEOUS SOLUTION

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By

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SCOPE AND CONTENTS:

The major part of the present work dealt with adapting the droplet technique to the study of nucleation from solution of some analytically important metal chelates. Precipitation from homogeneous solution was introduced as the means of gradually increasing the supersaturation in the droplets. This new method of producing supersaturation enabled the extention of the droplet technique to nucleation studies of sparingly soluble substances.

In addition, a second novel way of achieving supersaturation in the droplets was devised. In contrast to the first method, which increased the amount of solute at constant droplet volume, the second method maintained the amount of solute constant, while gradually reducing the volume of the droplet. This permitted studies on nucleation from solution of soluble substances to be carried out isothermally.

The two techniques mentioned above were applied successfully to the study of nucleation from solution of four analytically important metal chelates and to several inorganic salts, respectively.

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I. INTRODUCTION

I.A. Statement of the Problem

The purpose of this investigation was to study the nucleation from solution of various compounds of widely different compositions, structures and properties. It was desired to search for correlations between the properties of the compounds studied and the experimental data obtained with them. Further, it was proposed to assess the validity of the classical nucleation theory as applied to nucleation from solution. This required the development of new techniques for studying nucleation from solution.

I.B. Historical Background

Crystallization is undoubtedly among the oldest techniques employed in the chemical laboratory. It has been used for the purification of substances for over one thousand years. A vast amount of effort has been devoted to its study, but much remains unknown about the process. Knowledge gained in this area is of considerable interest to workers in a wide variety of fields.

Metallurgists are interested in the problem because many of the properties of metals and alloys are to a large extent determined by the conditions employed in their solidification. Much of the theoretical and experimental work on crystallization has been carried out by workers in this field.

Crystallographers are also actively engaged in the study of the crystallization process. It is known, for example, that many semiconducting substances would be very useful as radiation detectors if they could be prepared as large single crystals. Also, single crystals would find important applications in other branches of industry and in research.

Meteorologists have much to gain from any advancements in the understanding of phase transformations. Many successful experiments in rain-making have been performed, but, in general, the techniques available are far from satisfactory. Improvements in these techniques and in the general area of weather control would certainly have important world-wide economic consequences.

Analytical chemists are interested in the problem because it is recognized that many of the difficulties which are encountered in their work frequently arise from lack of sufficient fundamental knowledge of the crystallization process. Examples of these difficulties are the coprecipitation of impurities in gravimetric analyses, the unfilterability of certain types of precipitates, the poor quality of some electrolytic deposits in electrogravimetric determinations, and the problems associated with the purification of primary standards by recrystallization.

The first significant observation related to the crystallization process was made by Ostwald[1] near the end of the 19th century. He found that many substances could be maintained in solution in concentration exceeding their normal solubility, provided that the excess of solute, or supersaturation, was kept within certain limits. Also, he found that, if this limit were exceeded, crystallization would take place spontaneously. More than twenty-five years later Tamman[2] and von Weimarn[3] observed that crystallization could occur in the metastable region described by Ostwald if the solution were kept in that state for a sufficiently long period of time.

From the observations reported by Ostwald, Tamman and von Weimarn it was deduced that the crystallization process probably consisted of two separate steps. The first step was called nucleation and was presumed to be the formation of very small aggregates which acted as sites upon which the second phase continued to develop. The second step was called growth and involved the development of nuclei into macroscopic particles. Of these two steps, nucleation has proved by far the least susceptible to independent experimental study. This is partly due to the fact that nuclei are of the order of 30 Å or less in diameter and therefore are not subject to direct physical examination or measurement.

Historically, the theories describing nucleation of a liquid from a supersaturated vapor were developed before those for nucleation in condensed systems. The generally accepted theory for homogenous nucleation of liquids in vapors is due largely to Volmer and Weber[4] and Becker and Döring[5]. The theory was later extended by Turnbull and Fisher[6] to account for the nucleation of crystals in condensed systems. Because it is supported by much of the experimental evidence that has been gathered during the last twenty years, the theory has been accorded a wide measure of acceptance. In 1962, however, the theory was challenged on theoretical grounds by Lothe and Pound[7], who, employing statistical mechanical methods, obtained values for the nucleation rate which were many orders of magnitude higher than those predicted by the classical theory. Recently, Abraham[11] reached the conclusion that "the apparent success of the Becker-Döring theory to predict the nucleation rate of polar liquids is fortuitous". The situation at the present time can be described by saying that, in spite of recent advances, much more theoretical and experimental work is needed before the theory can be fully assessed.

I.C. Classical Nucleation Theory

I.C.1. Qualitative Considerations

It was recognized long ago that the phenomenon of supersaturation implied the existence of an energy barrier which opposed nucleation. The objective of any nucleation theory is to account for this barrier and, further, to derive an expression for the nucleation rate.

Qualitatively, the condensation of a vapor can be described in the following way. Within any vapor there exists clusters of molecules of various sizes. If such clusters are smaller than a certain critical size, their vapor pressures will be higher than the pressure of the surrounding supersaturated vapor[12]. Normally these clusters tend to evaporate and disappear. As the supersaturation is increased, however, the frequency of cluster-molecular collisions increases so rapidly that an appreciable number of clusters attain the critical size and are in metastable equilibrium with the supersaturated vapor. Continued addition of molecules to these critical clusters results in a decrease in the Gibbs free energy; consequently, they grow to macroscopic size.

I.C.2. Quantitative Theory

I.C.2.a. Nucleation of liquid droplets from the vapor

Several workers[4-10], employing a wide variety of mathematical techniques, have developed the qualitative ideas outlined above (I.C.1) into a quantitative theory. The details of these derivations can be found in the literature cited. Recently, an excellent review of the main points of the theory has been published[13].

The main ideas involved in the quantitative development can be described as follows. A saturated vapor contains single molecules in equilibrium with clusters whose concentrations decrease with increasing cluster size. The clusters are built up by the incorporation of single molecules at a time; thus,

$$\begin{array}{rcll} A + A & \rightleftarrows & A_2, & (1) \\ A_2 + A & \rightleftarrows & A_3, & (2) \\ \vdots \quad \vdots & & & \\ A_{i-1} + A & \rightleftarrows & A_i, & (3) \end{array}$$

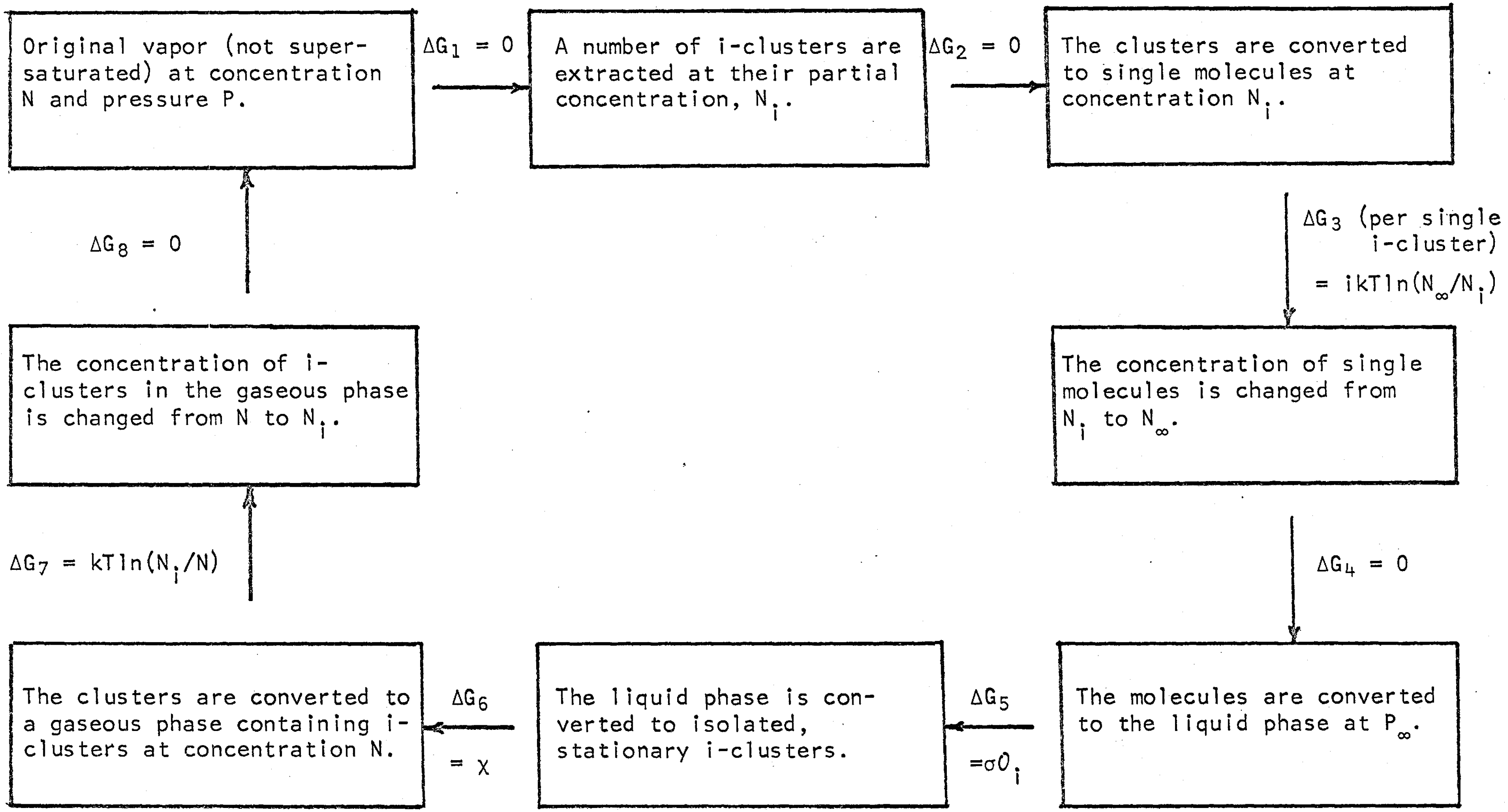
where A_i represents a cluster containing i molecules. By performing the cycle of reversible isothermal operations shown in Figure 1 on a vapor that is in complete thermal and mechanical equilibrium it is possible to derive a distribution function giving the concentrations, N_i, of the clusters as a function of i, the number of molecules in each cluster. (The total pressure on the vapor phase is kept constant throughout the entire cycle.)

The quantities ΔG_1, ΔG_2, ΔG_4 and ΔG_8 are equal to zero. Since the overall change in free energy must be zero, it follows that:

$$\Delta G_{Total} = \Delta G_3 + \Delta G_5 + \Delta G_6 + \Delta G_7 = 0, \tag{4}$$

$$ikT\ln\frac{N_\infty}{N} + \sigma O_i + \chi + kT\ln\frac{N_i}{N} = 0 \tag{5}$$

FIGURE 1. Cycle of Reversible Isothermal Operations on a Vapor



and $$N_i = N\exp[-\frac{1}{kT}(\sigma O_i - ikT\ln\frac{N_i}{N_\infty} + \chi)] \qquad (6)$$

or $$N_i = N\exp(\frac{-\Delta G_i}{kT}). \qquad (7)$$

In these and the following equations:

k is the Boltzmann constant;

T is the absolute temperature in degrees Kelvin;

N is the total number of molecules (including clusters) per unit volume;

N_1 is the total number of single molecules per unit volume;

N_i is the total number of i-clusters per unit volume;

N_∞ is the total number of molecules per unit volume in equilibrium with bulk liquid;

P is the total pressure on the vapor phase;

P_∞ is the saturation vapor pressure of liquid with plane surface;

σ is the surface free energy per unit area of the liquid;

O_i is the surface area of an i-cluster;

ΔG_i is the difference in free energy between the concentration levels N_i and N; and

χ is the difference in free energy between a stationary cluster and a cluster dissolved in a vapor phase at concentration N.

Most investigators have assumed that χ (equations 5 and 6) is equal to zero. Recent statistical mechanical calculations, however, have produced rather large values of χ. Until this controversy is settled, the assumption that χ equals zero will remain one of the weak points in the theory.

In order to derive a mathematical expression for the nucleation rate it must be realized that a cluster may gain molecules by condensation and lose them by evaporation. Therefore, the net stream of condensation, J_i, must be the difference between these two processes. Thus,

$$J_i = j_c f_{i-1} O_i - j_e f_i O_i, \tag{8}$$

where j_c and j_e are the gross molecular condensation and evaporation fluxes, respectively, and the f_i's are the concentrations of i-clusters in the non-equilibrium distribution associated with the condensation process. Some investigators have used O_{i-1} instead of O_i in the first term of equation (8). However, as Strickland[13] points out, it is probably more correct to accept Volmer's[14] contention that "there is a surface close to, and outside of, the actual surface of a spherical drop, which represents the boundary of the field of force. The condensing molecule is inside the drop when its center of gravity has passed inside the boundary, and the reverse is true for evaporation, O_i being the boundary common to both processes."

The equation for J_i can be converted into the following differential equation:

$$\frac{df_i}{di} + \left(\frac{j_e}{j_c} - 1\right) f_i = \frac{-J_i}{O_i j_c} \tag{9}$$

This equation is very difficult to solve because both J_i and f_i are functions of i and time. The solution can be simplified by mentally supplying to the system a stream of single molecules and removing from the system all clusters which have grown larger than the critical size. In the resulting steady-state process the f_i's are independent of time and J_i is independent of both time and i and can be represented simply by J. The equation then becomes a first order linear differential equation with coefficients that are functions of i only. Thus it can be integrated with the aid of the integrating factor $\frac{1}{N_i}$.

The final equation describing the stream of clusters in the steady-state system is

$$J = 2Nvj_c \quad (\frac{\sigma}{kT})^{\frac{1}{2}} \exp(\frac{-\Delta G_n^*}{kT}), \tag{10}$$

where v is the molecular volume of the liquid, n is the number of molecules in the critical cluster and ΔG_n^* is the free energy barrier to nucleation.

I.C.2.b. Nucleation of crystals from the melt

Equation (10), which was developed for the rate of condensation of liquid droplets from the vapor, was modified by Turnbull and Fisher[6] in order to apply it to the nucleation of crystals from the liquid phase. These investigators assumed that a molecule which is located at the interface between the liquid and a crystal nucleus is analogous to the activated complex of transition state theory. According to their theory the rate of transfer of molecules from the liquid phase to the nucleus is then given by

$$\text{rate} = \frac{kT}{h} \exp(\frac{-G_D}{kT}), \tag{11}$$

where h is Planck's constant and G_D is the free energy of activation for diffusion. The term $\frac{kT}{h}$ represents the frequency with which a molecule acquires the energy necessary to enable it to move into the crystal face from the liquid. Since the number of molecules per square centimeter at the solid-liquid interface is of the order of $v^{-2/3}$, where v is now the molecular volume of the solid phase, the rate of transition per square centimeter is given by

$$j_c = v^{-2/3} \frac{kT}{h}[\exp(\frac{-G_D}{kT})]. \tag{12}$$

The modified equation developed by Turnbull and Fisher is obtained by substituting the expression for j_c (equation 12) into the steady-state equation for the nucleation rate of liquid drops from the vapor (equation 10). The result is usually expressed as

$$J = 2v^{1/3}(\frac{\gamma}{kT})^{\frac{1}{2}}\frac{NkT}{h}\exp[\frac{-\Delta G_n^* - G_D}{kT}], \tag{13}$$

where the surface tension, σ, has been replaced by γ, an average surface free energy of the crystal in contact with its melt.

Turnbull and Fisher noted that the value of $2v^{1/3}(\frac{\gamma}{kT})^{\frac{1}{2}}$ is in many cases approximately equal to unity. This simplifies equation (13) to

$$J = \frac{NkT}{h}\exp[\frac{-\Delta G_n^* - G_D}{kT}]. \tag{14}$$

In addition they derived an expression for ΔG_n^* on the basis of a spherical nucleus, with an average value of γ in place of the true surface free energy per unit area of each face, γ_j. The resulting expression is

$$\Delta G_n^* = \frac{16\pi}{3}\frac{\gamma^3 v^2 T_M^{\ 2}}{\lambda_F^{\ 2}(\Delta T)^2}, \tag{15}$$

where T_M is the melting temperature, λ_F is the enthalpy of fusion per molecule and ΔT is the supercooling (the difference between the melting point and the experimental crystallization temperature). Equation (14) is often expressed as

$$J = A \exp\left(\frac{-\Delta G_n^*}{kT}\right), \tag{16}$$

where

$$A = \frac{NkT}{h} \exp\left(\frac{-G_D}{kT}\right). \tag{17}$$

I.C.2.c. Nucleation of crystals from solution

Nucleation from solution is usually treated similarly to nucleation from the melt. ΔG_n^* is usually expressed as

$$\Delta G_n^* = \frac{16\pi}{3} \frac{\gamma^3 v^2}{(kT\ln S)^2}, \tag{18}$$

where S is the supersaturation ratio, formally defined as the ratio of the actual activity to the saturation activity ($S = a/a_o$), but usually taken in practice as $S = N/N_o$, with concentrations replacing activities.

There are two other parameters which are of considerable interest in nucleation theory. One of these is n*, the number of molecules in the nucleus, the expression for which is[15]

$$n^* = \frac{32\pi\gamma^3 v^2}{3(kT\ln S)^3}. \tag{19}$$

The second is r*, the radius of the critical cluster. Its value can be calculated from equation (20)[15].

$$r^* = \frac{2\gamma v}{kT\ln S} \tag{20}$$

Equation (20) implies that the solubility of small crystals is greater than that of large crystals, a fact which has been known for a long time.

I.C.3. Agreement with Experiment

I.C.3.a. Nucleation from the vapor phase

Studies on the rate of nucleation from the vapor have been reported by many investigators. Those reported by Volmer and Flood[16] will be used here to illustrate the agreement between experimentally determined and theoretically calculated nucleation rates. In their experiments a saturated vapor was expanded suddenly and adiabatically. From this, Volmer and Flood determined the supersaturation ratio, P/P_∞, which just produced visible condensation. These data and the value of the surface free energy per unit area, σ, for the bulk liquid were used to calculate A, ΔG_n^* and the nucleation rate. For the nucleation of droplets of water from the vapor at 261°K they found a value of P/P_∞ of 5.0 and a value of $J \simeq 1\ \text{cm}^{-3}\text{sec}^{-1}$. Consequently they adopted $J = 1\ \text{cm}^{-3}\text{sec}^{-1}$ as the criterion for critical condensation and used it to calculate the values of P/P_∞ for other substances. The agreement between theory and experiment is shown in Table 1.

I.C.3.b. Nucleation from condensed phases

In general, good agreement between theory and experiment has been obtained in studies on nucleation from the melt. In a report by Hollomon and Turnbull[17] a dilatometric method was used to measure the nucleation rate of mercury drops emulsified in oil. They plotted the values of log J, obtained at different temperatures, versus $1/T(\Delta T)^2$ and obtained a straight line with an intercept value of 42.1. This differs considerably from the calculated value of log A = 35 for mercury but, considering the many approximations involved in the theory, this

TABLE 1

OBSERVED AND CALCULATED VALUES OF P/P_∞ (CRITICAL)[14]

Substance	Temperature (°K)	P/P_∞ (Critical) Calculated	P/P_∞ (Critical) Observed
Water	261	5.0	5.0
Water	275	4.2	4.2
Methanol	270	1.8	3.2
Ethanol	273	2.3	2.3
n-Propanol	270	3.2	3.0
Isopropanol	265	2.9	2.8
n-Butanol	270	4.5	4.6
Nitromethane	252	6.2	6.1

agreement has been considered satisfactory. Similar results have been reported by other investigators[18-20].

Compared with the results of experiments on nucleation from the melt, those on nucleation from solution do not agree so well with those theoretically calculated. The value of $A = 10^{30}\mathrm{cm}^{-3}\mathrm{sec}^{-1}$, which was computed by Turnbull and Vonnegut[21] for the homogeneous nucleation of most crystals from their supercooled melts, has usually been assumed[22] to apply to the nucleation of ionic salts from aqueous solution. Melia and Moffitt[23], however, have found experimental values of A lying in the range $10\text{-}10^{4}\mathrm{cm}^{-3}\mathrm{sec}^{-1}$ for the nucleation of various soluble ionic salts from their supersaturated aqueous solutions. A similar discrepancy between the theoretical and experimental values of A has been found by Dunning et al for the nucleation of cyclonite from aqueous nitric acid[24] and aqueous acetone solutions[24] and for the nucleation of sucrose from aqueous solution[25]. These findings point out the seriousness of the discrepancies which are so abundant in the literature on nucleation from solution.

There are various reasons which may be offered to explain why the theory of nucleation in condensed systems is more difficult to assess than the corresponding theory for the condensation of vapors. Firstly, the surface free energies of solids are usually unknown. Although the surface free energies of many ionic crystals in vacuum can be calculated, the crystal-solution interfacial energy, the parameter of interest, cannot be calculated. Secondly, the theory neglects the contributions of corners and edges to the interfacial energy and for very small crystals the value of these contributions may be large.

Thirdly, the nucleus is assumed spherical and an average interfacial energy is used instead of a separate value for each face of the crystal. Finally, and probably the most important, is the experimental difficulty of preparing a liquid system which is free of solid impurities. These foreign particles usually act as nucleating agents during the phase transformation and, if present, affect the results obtained in any given experiment.

When crystallization occurs on the surface of foreign particles present in the sample the process is termed heterogeneous nucleation. In the absence of foreign particles the nucleation process is said to be homogeneous and is governed only by the properties of the system under study. The theories referred to in the present study have been devised on the assumption that homogeneous nucleation is taking place in the system.

I.D. The Droplet Technique

I.D.1. Introductory Discussion

At the beginning of this century Ingersoll and Mendenhall[26] found that droplets of gold, platinum and rhodium, 50-100 μ in diameter, often could be supercooled over 100°C before freezing. At that time it was well known that bulk melts of these substances could not be supercooled more than a few degrees. The explanation for this phenomenon was given in 1948 by Vonnegut[27] and can be described as follows. Nucleation of substances in liquid systems normally takes place on foreign particles that are adventitiously present. This heterogeneously catalyzed nucleation occurs at relatively low supercoolings. When a melt is subdivided into sufficiently small drops, only a small fraction of them will contain foreign particles. Thus, the majority of the drops will solidify by homogeneous nucleation. This will take place only at much larger supercoolings.

This "droplet technique" has been employed by Vonnegut[27], Pound and La Mer[28], and Turnbull[29] in studying the solidification of metals. Also, it has been used by Bigg[30] for studying the freezing of water and by Melia and Moffitt[31], Newkirk and Turnbull[22] and White and Frost[32] in studies on the nucleation of inorganic salts from aqueous solutions. In addition to the sequestering of motes, the droplet technique enables the investigator to study several hundred samples in a single experiment.

In order to employ the droplet technique successfully in nucleation experiments, a method must be found which develops sufficient supersaturation in the droplets to overcome the barrier to nucleation. As already mentioned, the supersaturation ratio, S, is usually defined as the ratio of the concentration of solute in the supersaturated solution to the concentration of solute in the saturated solution (equilibrium solubility); that is,

$$S = \frac{\text{concentration of solute in supersaturated solution}}{\text{equilibrium solubility}}. \qquad (21)$$

It can be seen from equation (21) that supersaturation can be achieved either by increasing the numerator or by decreasing the denominator. The denominator can be decreased by changing the solvent or by lowering the temperature of the system. No means have yet been found of changing the medium, such as altering the solvent composition or the pH, of a solution which is contained in a microscopic droplet.

In fact, until recently the only method which had been used to produce supersaturation in droplets involved the reduction of the solubility by gradually cooling the droplets. In practice, this method of building up supersaturation limits the usefulness of the droplet technique to the study of highly soluble substances and to a temperature range from 100°C to 0°C. This situation led Melia[33], in his review on nucleation from aqueous solution, to state that "the development of a new method of producing supersaturation in droplets would represent a major technical advance".

I.D.2. Interpretation of Experimental Data from Droplet Experiments

In his studies on the supercooling of water, Bigg[30] discovered that the median freezing temperature of a droplet was directly proportional to the logarithm of its volume. This relationship enabled him to reduce the freezing temperature of a droplet of any size to that of a droplet of standard size. Also he found that, for a large population of droplets of any given size, the relative frequency of freezing was normally distributed with respect to the measured freezing temperature. Bigg recognized that, because of this statistical character of nucleation events, it was necessary to study a large number of samples in order to obtain characteristic and significant relationships.

To interpret his experimental data Bigg derived, from simple probability considerations, a relationship between freezing temperature, droplet volume and the duration of supercooling. Later the same equation was derived by Carte[34] in a more straightforward manner. The main ideas involved in the derivation can be described as follows. The probability of crystallization taking place in volume V within the time interval t to t + dt may be written as Vf(S)dt, where f(S) is a function of the supersaturation ratio. If the supersaturation in a large number, N, of non-communicating droplets of volume V is gradually increased at a constant rate and N_t droplets crystallize during the time interval 0 to t, then the probability of crystallization occurring during that interval is

$$P(V,t) = N_t/N. \tag{22}$$

The number of crystallized droplets during the interval 0 to t + dt will be

$$N_{t+dt} = N_t + (N-N_t)Vf(S)dt. \tag{23}$$

Division of both sides by N yields

$$P(V,t+dt) = P(V,t) + [1 - P(V,t)]Vf(S)dt \tag{24}$$

But
$$P(V,t+dt) = P(V,t) + \frac{\partial}{\partial t} P(V,t)dt. \tag{25}$$

Therefore,
$$\frac{\partial}{\partial t} P(V,t) = [1 - P(V,t)]Vf(S) \tag{26}$$

and
$$\frac{\frac{\partial}{\partial t} P(V,t)}{[1 - P(V,t)]} = \frac{-\frac{\partial}{\partial t}[1 - P(V,t)]}{[1 - P(V,t)]} \tag{27}$$

$$= -\frac{\partial}{\partial t} \ln[1 - P(V,t)] \tag{28}$$

$$= Vf(S). \tag{29}$$

Integration of equation (29) gives

$$\ln[1 - P(V,t)] = -\int_0^t Vf(S)dt. \tag{30}$$

If the droplets vary in volume, but a linear relationship exists between the median crystallization time and the logarithm of the droplet volume, then

$$\ln V = a\bar{t} + b, \qquad (31)$$

and

$$V = \exp(a\bar{t} + b). \qquad (32)$$

Equation (32) implies that, at any given time, t, there will be a certain drop of volume, $V = \exp(at + b)$, for which $P = 0.5$. The value of $\int_0^t f(S)dt$ can then be calculated from equation (30), thus

$$\int_0^t f(S)dt = \frac{-\ln 0.5}{\exp(at + b)}\Big|_0^t \qquad (33)$$

$$= 0.693 \exp(-b)[\exp(-at) - 1]. \qquad (34)$$

At any given time, the value of $\int_0^t f(S)dt$ is the same for all droplets. Therefore, it can be used to calculate the value of P for droplets of any standard size, V_s, thus

$$\int_0^t f(S)dt = \frac{-\ln[1 - P(V,t)]}{V_s}, \qquad (35)$$

and

$$\ln[1 - P(V,t)] = -0.693\, V_s \exp(-b)[\exp(-at) - 1]. \qquad (36)$$

Using the experimental values of a and b and suitable values of t, the probability of crystallization as a function of time can be calculated.

The derivative of equation (36) with respect to t, with V constant is

$$\left(\frac{\partial \ln[1 - P(V,t)]}{\partial t}\right)_V = -0.693\, V_s \exp(-b)[-a \exp(-at)]. \qquad (37)$$

But,
$$\left(\frac{\partial \ln[1 - P(V,t)]}{\partial t}\right)_V = \frac{\left(\frac{\partial}{\partial t}[1 - P(V,t)]\right)_V}{[1 - P(V,t)]} . \tag{38}$$

Therefore,
$$\left(\frac{\partial}{\partial t}[1 - P(V,t)]\right)_V = [1 - P(V,t)][0.693 \exp(-b)][a \exp(-at)]V_s \tag{39}$$

and
$$-\left(\frac{\partial P(V,t)}{\partial t}\right)_V = [1 - P(V,t)][0.693 \exp(-b)][a \exp(-at)]V_s \tag{40}$$

Since values of $\left(\frac{\partial P(V,t)}{\partial t}\right)_V$ are proportional to the crystallization frequencies, equation (40) can be used to calculate the relative frequency of crystallization as a function of time.

The number of droplets N_t crystallized at time t can be calculated by means of equation (41).

$$N_t = V_s \int_o^t J(t)dt \tag{41}$$

If total crystallization is represented by unity, then N_t becomes equal to the probability of crystallization and

$$P = V_s \int_o^t J(t)dt. \tag{42}$$

Differentiation with respect to t gives

$$J(t) = \frac{1}{V_s}\frac{dP}{dt} . \tag{43}$$

Equation (43) can be used to calculate the nucleation rate at any given time by dividing the corresponding slope of the probability curve by the standard droplet volume.

II. STUDIES ON FUNCTIONAL RELATIONSHIPS

II.A. Purpose of Studies

As mentioned in the Introduction (Section I.C.2.), the classical nucleation theory for condensed systems is embodied in equations (16), (17) and (18).

$$J = A \exp\left(\frac{-\Delta G_n^*}{kT}\right), \tag{16}$$

where

$$A = \frac{NkT}{h} \exp\left(\frac{-G_D}{kT}\right), \tag{17}$$

and

$$\Delta G_n^* = \frac{16\pi \gamma^3 v^2}{3(kT\ln S)^2}. \tag{18}$$

Because of the complexity of the expressions it is not easy to see how the variation of any one of the parameters J, γ, v, or S will affect the others. In order to facilitate a study of these variations a series of nomograms showing the relationship between the various parameters involved in the theoretical expression was prepared.

These diagrams must be used with reservations for the following reasons: 1) as already mentioned, most of the studies on nucleation from solution have yielded values of A which differ by many orders of magnitude from the theoretical value; 2) the correct theoretical value of ΔG_n^* is uncertain; 3) the factor $16\pi/3$ implies that the nucleus is spherical, an assumption which is justified only by the lack of experimental evidence concerning the actual shape of the nucleus; 4) the validity of applying macroscopic parameters such as the crystal-solution interfacial energy to the relatively small number of molecules or ions which compose the nucleus is questionable; and 5) equations (16), (17) and (18) are merely extensions of those derived for nucleation of liquid drops from the vapor. Consequently, they fail to take into consideration the ionic nature of the species present in electrolytic solutions and the significant solvation effects which are known to be present in such systems.

In spite of the above reservations the expressions are useful because 1) they embody the only accepted theory of nucleation at the present time, and 2) there is considerable evidence which supports the functional relationships found in them. For these reasons it was felt that generalized diagrams would facilitate the interpretation and correlation of experimental data. Also, they would aid in the selection of suitable compounds for study.

II.B. Variation of Interfacial Energy with Supersaturation, with Nucleation Rate and Volume Constant

In order to find the variation of γ with S at constant J and v, the equation for the nucleation rate was written in logarithmic form and solved for γ^3 to give

$$\gamma^3 = \frac{(30 - \log J)(2.3kT)^3(\log S)^2}{(16\pi/3)v^2}. \tag{44}$$

J was then set equal to 1 $cm^{-3}sec^{-1}$, which is generally considered to be its lowest measurable value. Similarly, the value of v was set equal to $10^{-23}cm^3$, since this value is close to the lowest obtainable value of v as computed from the expression

$$v = \frac{A_mB_n}{(m+n) \times d \times N}, \tag{45}$$

where A_mB_n represents the gram-formula weight of the solute, (m+n) is the number of ions contained in one formula unit of the solute, d is the density of the solute in g cm^{-3} and N is Avogadro's number. After substituting the lower limits of J and v given above, the simplified expression

$$\gamma^3 = 1.49 \times 10^7 (\log S)^2 \tag{46}$$

was obtained. Values of S from 2 to 9000 were then substituted into the equation and the corresponding values of γ computed. The procedure was then repeated, but using $J = 10^{10} cm^{-3} sec^{-1}$, which is close to the upper measurable limit for this parameter. The results of these calculations are shown in graphical form by the two upper curves in Figure 2. Similarly, the variation of γ with S for $v = 10^{-21} cm^3$, which is the order of magnitude of a large metal chelate molecule, and the same two values of J, was determined. The result appears as a single line in Figure 2.

II.C. Variation of Nucleation Rate with Supersaturation, with Interfacial Energy and Volume Constant

Following procedures similar to those described above, the variations of J with S for different fixed values of γ and v were obtained. The results are shown in Figure 3. It can be seen that, in an experiment with a substance of low v value ($\sim 10^{-23} cm^3$), homogeneous nucleation is expected to occur at very low values of S, unless the value of γ for the substance is extremely high. Similarly, if the substance involved in the experiment has a very large value of v ($\sim 10^{-21} cm^3$), homogeneous nucleation should occur at high values of S, unless the value of γ for the substance is very low.

II.D. Variation of the Radius of the Nucleus with Supersaturation, with

FIGURE 2. Interfacial Energy Versus Supersaturation Ratio, Nucleation Rate and Volume Constant

Curve	Volume (cm^3)	Nucleation Rate ($cm^{-3}sec^{-1}$)
1	10^{-23}	1
2	10^{-23}	10^{10}
3	10^{-21}	$1 - 10^{10}$

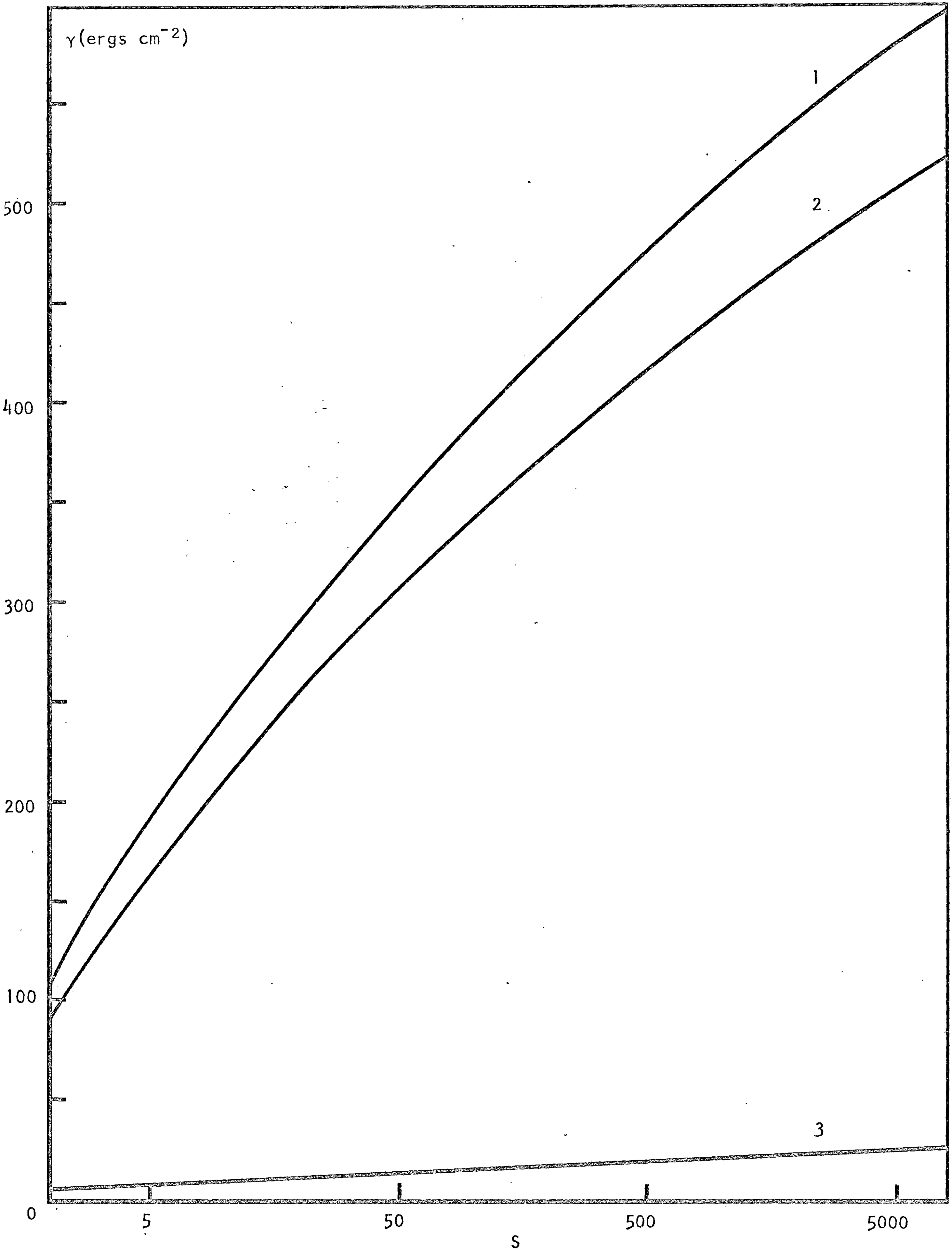
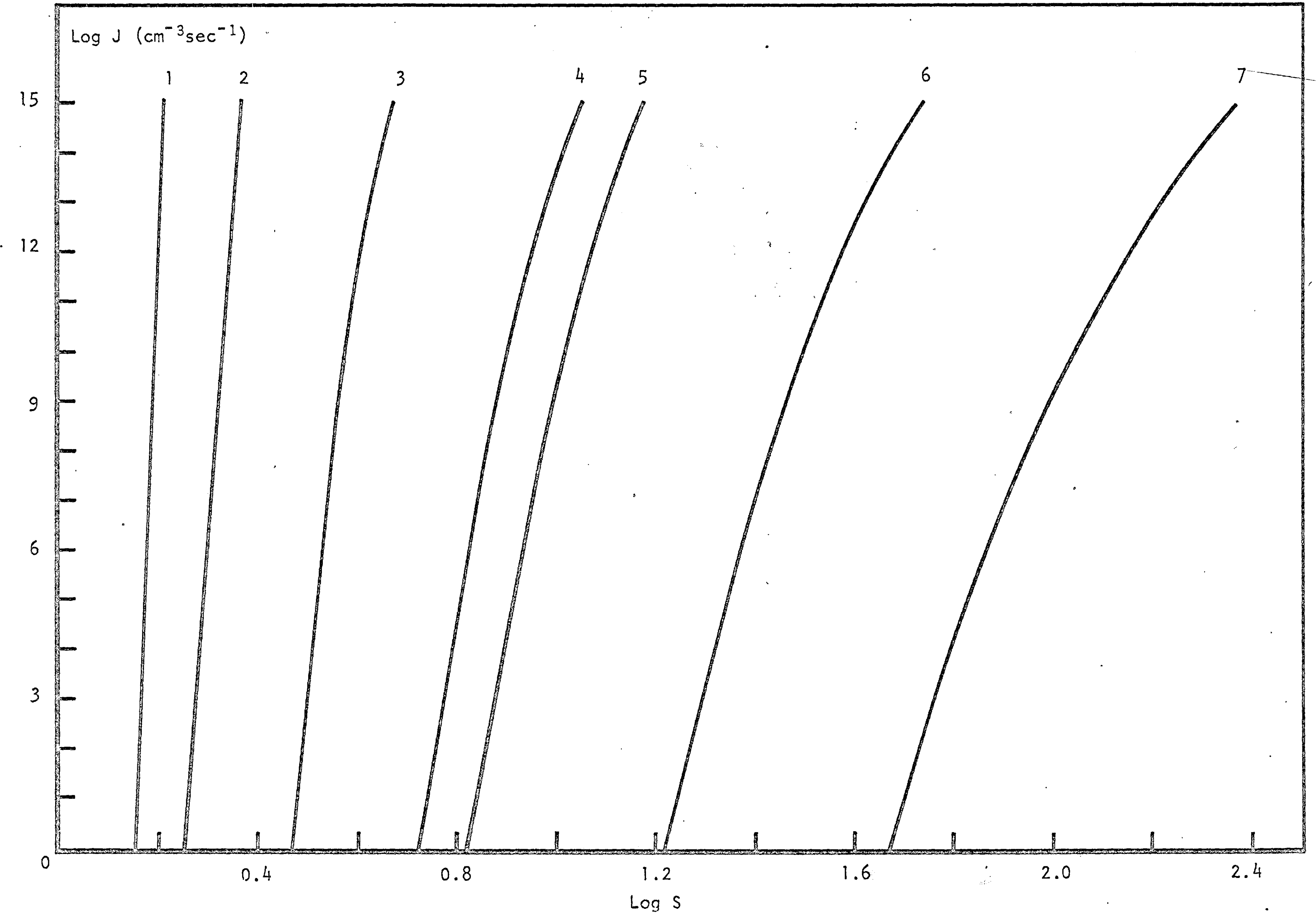

γ(ergs cm^{-2})
500
400
300
200
100
0
5
50
500
5000
S
1
2
3

FIGURE 3. Log Nucleation Rate Versus Log Supersaturation Ratio, Interfacial Energy and Volume Constant

Curve	Volume (cm^3)	Interfacial Energy (ergs cm^{-2})
1	10^{-23}	70
2	10^{-23}	100
3	10^{-23}	150
4	10^{-23}	200
5	10^{-21}	10
6	10^{-21}	13
7	10^{-21}	16



Log J (cm^{-3}sec^{-1})
15
12
9
6
3
0
1
2
3
4
5
6
7
0.4
0.8
1.2
1.6
2.0
2.4
Log S

Interfacial Energy and Volume Constant

The relationship between the size of the critical radius r^* and the supersaturation ratio S for several fixed values of γ and v was found by making the appropriate substitutions in the equation $r^* = \frac{2\gamma v}{kT\ln S}$. The results are shown in Figure 4. Like Figures 2 and 3, this Figure also emphasizes the important role played by the value of v, for any fixed value of γ, in determining the degree of supersaturation at which homogeneous nucleation occurs. Also it can be seen that the variation of r^* with S is much more pronounced for substances which nucleate at low values of S. However, it is not possible to estimate from Figure 4 the relative values of r^* for substances which nucleate at widely different values of S.

II.E. Variation of the Number of Molecules in the Nucleus with Supersaturation, with Interfacial Energy and Volume Constant

The variation of the number of molecules in the nucleus, n^*, as a function of S, for constant values of γ and v was found from the equation: $n^* = \frac{32\pi\gamma^3 v^2}{3(kT\ln S)^3}$. The results are shown in Figure 5.

The usefulness of these diagrams is enhanced by a correlation, found during the present studies, between the median supersaturation ratio and the solubility of the compound studied. This correlation and its limitations will be discussed in more detail later. It is useful because it enables one to estimate, from the solubility of a compound, the approximate value of S at which homogeneous nucleation will occur. This value of S can then be used in conjunction with Figure 2 to estimate the value of γ for the compound. The approximate values of the other parameters can be estimated with the aid of Figures 3, 4 and 5.

FIGURE 4. Radius of the Nucleus Versus Log Supersaturation Ratio, Interfacial Energy and Volume Constant

Curve	Volume (cm^3)	Interfacial Energy (ergs cm^{-2})
1	10^{-23}	70
2	10^{-23}	150
3	10^{-23}	200
4	10^{-21}	10
5	10^{-21}	13
6	10^{-21}	16

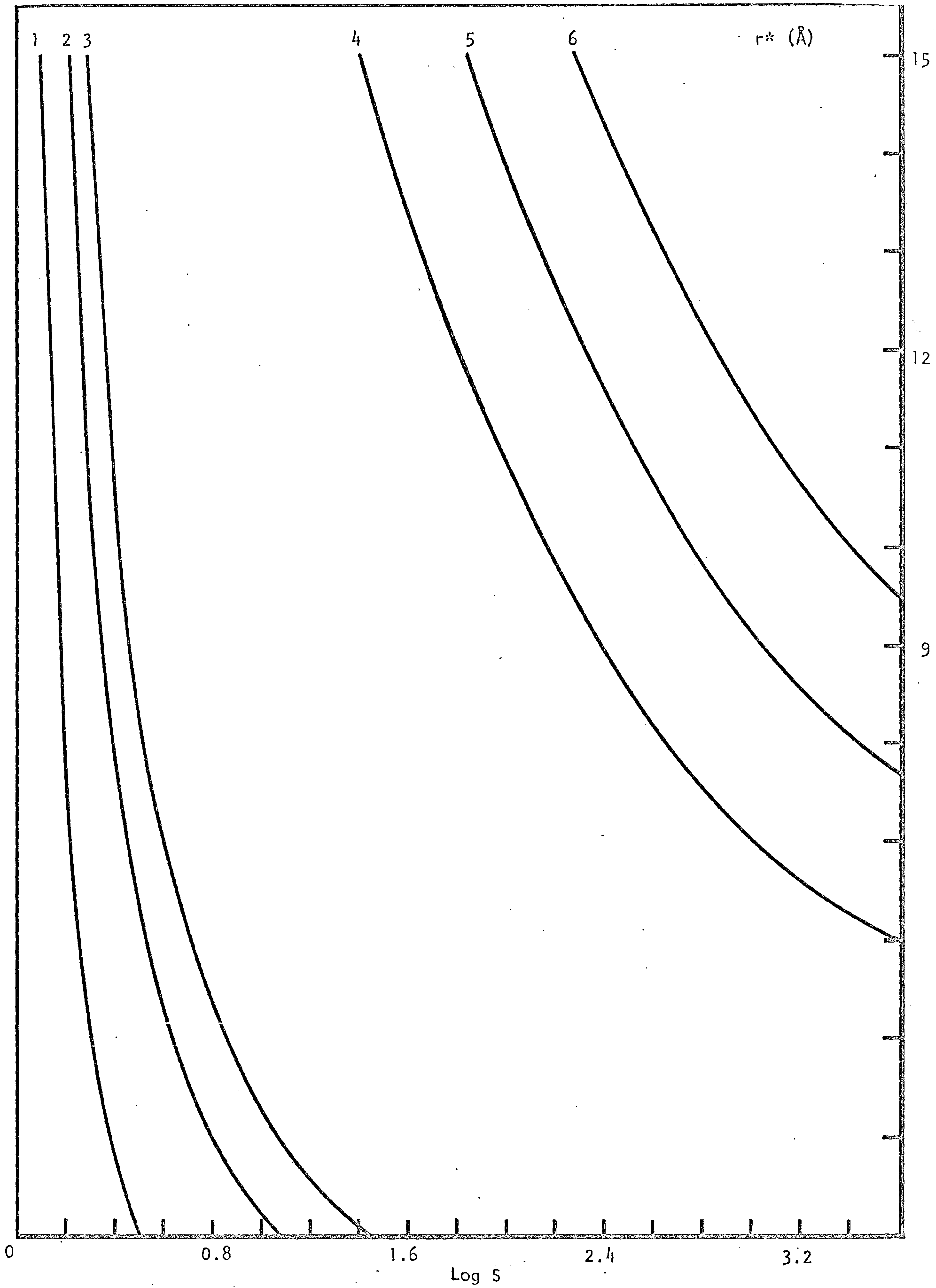
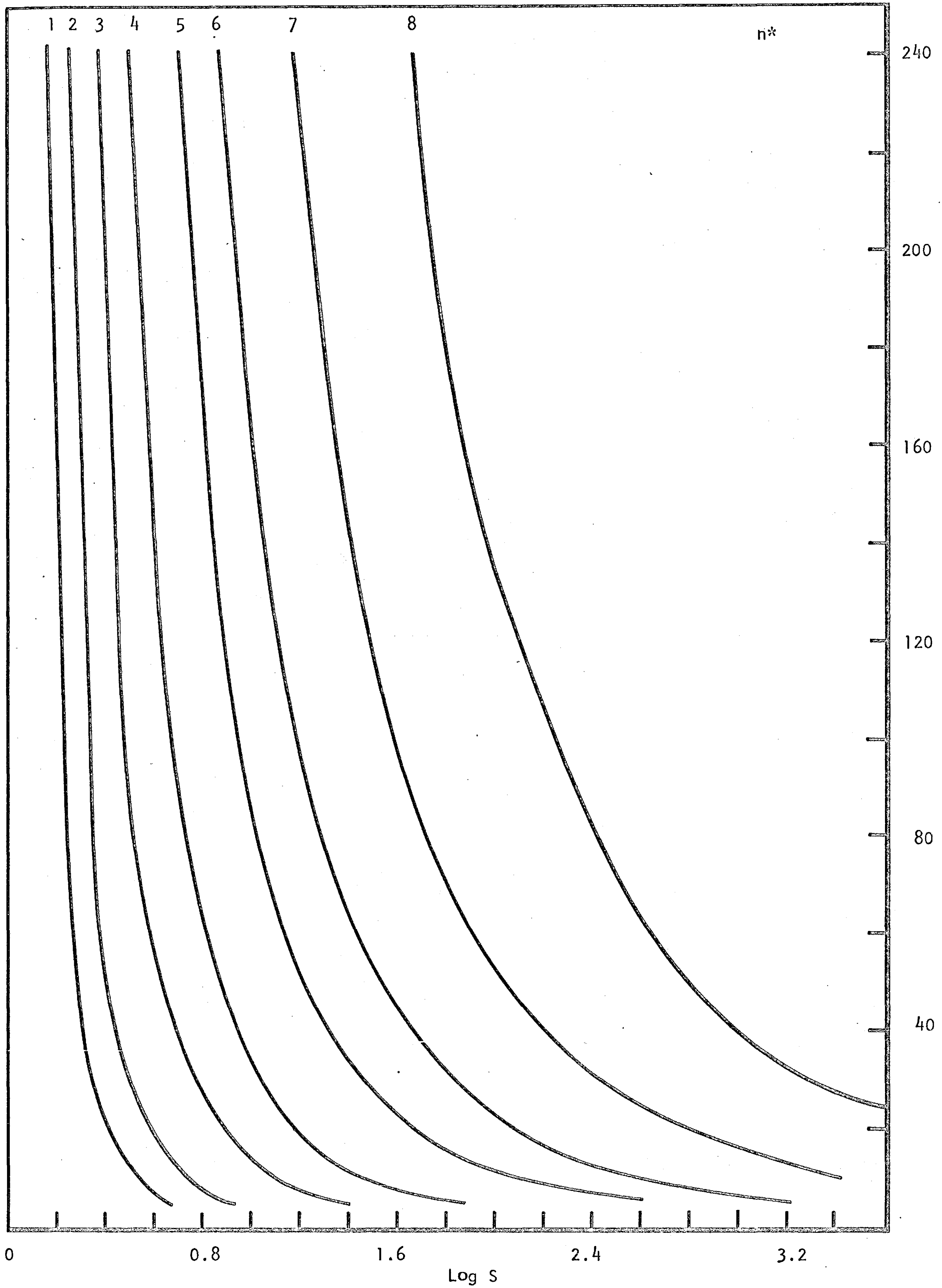

1
2
3
4
5
6
r* (Å)
15
12
9
0
0.8
1.6
2.4
3.2
Log S

FIGURE 5. Number of Molecules in the Nucleus Versus Log Supersaturation Ratio, Interfacial Energy and Volume Constant

Curve	Volume (cm^3)	Interfacial Energy (ergs cm^{-2})
1	10^{-23}	70
2	10^{-23}	100
3	10^{-23}	150
4	10^{23}	200
5	10^{-21}	13
6	10^{-21}	16
7	10^{-21}	20
8	10^{-21}	30


1
2
3
4
5
6
7
8
n*
240
200
160
120
80
40
0
0.8
1.6
2.4
3.2
Log S

III. EXPERIMENTAL

III.A. Preliminary Investigation

As mentioned in Section I.D.1. the droplet technique has several distinct advantages over all other methods which have been employed for studying nucleation in condensed systems. For this reason it was decided to adapt this technique for studies on the nucleation from solution of some analytically important metal chelates. Those selected for study were two dioximates of nickel and palladium. Because these compounds are sparingly soluble in water, a method other than supercooling a saturated solution was required to generate the supersaturation necessary to initiate nucleation. Thus, it was decided to explore the feasibility of employing precipitation from homogeneous solution to build up the necessary supersaturation to overcome the barrier to nucleation. A droplet experiment was planned which consisted of a) the preparation of a reaction mixture in which the precipitating agent was generated in the presence of a metal ion; b) the dispersion of the reaction mixture in some suitable oil; and c) the photographic recording of the crystallization occurring in the drops. As a necessary first step in the experimental work, a preliminary investigation of the methods of generating mono-sized water droplets dispersed in mineral oil was initiated. Later, optimum reaction conditions for generating the chelate in solution were determined.

III.A.1. Apparatus and Reagents

The dispersions were prepared with the aid of a Virtis microhomogenizer (Fisher Scientific Company) and a 7-ml flask which was obtained as an accessory.

The selection of a suitable number of drops within the desired size range was accomplished by means of an International clinical centrifuge (Central Scientific Company, Chicago, Illinois), which was adapted to enable the centrifuging of Nessler cups.

The Nessler cups (diameter 1.25 inch, height 1 inch) were made from Nessler tubes (Fisher Scientific Company).

The dispersions were examined with an MPS Lumex polarizing microscope (Fisher Scientific Company).

High intensity illumination for the microscope was provided by adapting an A O Spencer ortho-illuminator (Fisher Scientific Company) with a 3M-600 watt projector lamp.

Photographs of the dispersions were taken with an Olympus PM-6 microscope camera (Fisher Scientific Company).

The photographs were studied with the aid of a Leitz slide projector.

The slides were projected on a screen which was made by mounting graph paper on a cork board. This allowed accurate measurement of the drop diameters.

The solutions used in this preliminary investigation were prepared as follows.

A solution containing 32 mg of Pd(II) per ml was prepared by dissolving 5.34 g of $PdC\ell_2$ (Fisher Scientific Company, Fair Lawn, New Jersey) in 25 ml of 12 M hydrochloric acid and diluting to 100 ml with distilled water.

A 4 M solution of $NiC\ell_2 \cdot H_2O$ was prepared from the reagent grade chemical.

A solution of hydroxylamine hydrochloride in distilled water was prepared by dissolving 30 g of reagent grade $NH_2OH\cdot HC\ell$ in 100 ml of solution.

The 1,2-cyclohexanedione was purified as follows.

Approximately 3g of the commercial product (Aldrich Chemical Company, Inc., Milwaukee, Wisconsin) were placed in a 3-necked one liter round-bottom flask. A ground-glass stopper was placed in one of the side necks. The other side neck was connected to a vacuum line. A cold finger, reaching to within 1 cm of the bottom of the flask, was placed in the center neck. Water at 5°C was circulated through the cold finger. The pressure in the vacuum line was about 1-2 mm Hg.

Two grams of the sublimed dione were dissolved in 90 ml of distilled water and then diluted to 100 ml. The solution was stored at 5°C.

The 1,2-cycloheptanedione was prepared as follows.

A solution of 10.08 g of cycloheptanone in 21 ml of absolute ethyl alcohol was placed in a 150 ml flask fitted with a Glascol mantle, reflux condenser and a dropping funnel. A solution of 9.99 g of sublimed SeO_2 in a mixture of 15 ml of absolute ethyl alcohol and 48 ml of 95% ethyl alcohol was placed in a dropping funnel.

The cycloheptanone-alcohol solution was heated to refluxing; then the SeO_2 solution was added over a period of 1¼ hours. The resultant mixture was refluxed for an additional 6 hours and allowed to stand at room temperature for about 18 hours and then filtered. About 30 ml of alcohol were distilled from the filtrate at atmospheric pressure. The residue was then filtered again and the distillation continued under reduced pressure. The diketone came over as a deep yellow liquid. It was stored at 5°C.

III.A.2. Procedures

III.A.2.a. Initially it was intended to use reaction mixtures of compositions similar to those commonly used in analytical procedures. Under these conditions precipitation usually occurs in about 3-4 minutes and this limits the time available for the preparation of the dispersion to about 2-3 minutes.

The aim was to prepare a transparent dispersion which, upon microscopic examination with a magnification of 100 x, would enable the study of several hundred droplets with diameters in the size range 10 μ to 50 μ. It was important that the drops be on the same plane, stationary, and stable to coalescence. To study the conditions required for the preparation of a dispersion with the above characteristics, the following procedure was initially employed:

> Approximately 0.01 ml of distilled water was added, with the aid of a micropipet, to 6 ml of light mineral oil contained in a microhomogenizer flask and stirred for 5 seconds with the microhomogenizer operating at its lowest speed. A few drops of the dispersion were then transferred to the well of a hanging drop microscope slide. The dispersion was examined microscopically and the approximate number of drops and their size distribution in the field of view (magnification 100 x) was estimated.

This procedure was repeated many times, each time varying one of the following factors while keeping the others constant. The amount of distilled water was varied from 0.01 ml to 0.1 ml. The time of stirring was varied from 5 seconds to 20 seconds. The speed of the microhomogenizer from about 4000 rpm to about 35000 rpm. The oils used were mainly light and heavy mineral oils (viscosities 20 cts and 200 cts respectively), and silicone fluids (Dow Corning Fluids of 100 cts and 200 cts viscosity).

III.A.2.b. Varying the factors mentioned in the procedure above affected the number and size distribution of the drops in the dispersion. However, the results obtained were unsatisfactory because the dispersions were too turbid and the drops exhibited considerable movement and coalescence. In order to eliminate these objectionable features, the following procedure was devised: (Details concerning the criteria involved in the selection of this procedure will be discussed later).

> A counting cell was prepared by placing about 0.5 g of clear silicone fluid (viscosity 100,000 cts) in a Nessler cup and centrifuging it for about 30 seconds. The cup was then heated over a low flame for 1-2 minutes, centrifuged again to remove air bubbles which were trapped in the fluid. Then 1 ml of heavy mineral oil was added to it. The dispersion (6 ml) was prepared according to the procedure described previously, added to the cup, and centrifuged for about 15 seconds. The main part of the dispersion was then decanted and the cup centrifuged again for about 30 seconds. Using magnifications of 40 x and 100 x, the

dispersions were studied microscopically, as described in the previous section.

III.A.2.c. To find the optimum reaction conditions for studying the nucleation of the four metal chelate systems already mentioned, the following procedure was devised.

For studying bis(1,2-cyclohexanedione-dioximato)palladium(II) a reaction mixture was prepared by mixing stock solutions containing Pd(II), hydrochloric acid, hydroxylamine hydrochloride and 1,2-cyclohexanedione. The Pd(II) ion concentration in the mixture was varied from 10^{-4} M, which is the order of magnitude commonly found in analytical procedures, to about 0.3 M. The concentration of hydrochloric acid was varied from 0.1 M to 1.0 M. The concentrations of hydroxylamine hydrochloride and 1,2-cyclohexanedione were varied so that they were present in approximately stoichiometric amounts, relative to the metal ion. Immediately after the last reagent was added, the solutions were dispersed in light mineral oil. The dispersions were then examined with a polarizing microscope and 20 colored photographs taken at 30 second intervals. The film used was ANSCO 500 and the exposure time was 0.5 seconds. The photographs were developed, the slides projected on the calibrated screen and the number and size distribution of the crystallized droplets determined as a function of time. The optimum reaction conditions were considered those which produced few or no crystallized droplets in the first slide and a large number of crystallized droplets in the last slide.

Procedures similar to the one described above were used for determining the optimum reaction conditions for studying the nucleation of the other three metal chelates. With bis(1,2-cyclohexanedionedioximato)nickel(II), however, satisfactory conditions were found only after urea was added to the system. With bis(1,2-cycloheptanedionedioximato)nickel(II), phosphoric acid and ammonium acetate were found to improve the reaction conditions. The conditions employed for each system will be given later.

III.B. Studies on the Nucleation from Solution of Some Analytically Important Metal Chelates

III.B.1. Apparatus and Reagents

The same apparatus employed during the preliminary investigation were used for this study.

Having determined the optimum reaction conditions for a given system, and shortly before performing the droplet experiment, two stock solutions were prepared for that system. These solutions were prepared so that mixing them in a predetermined proportion would produce the desired reaction conditions in the final solution. The solutions were prepared as follows.

III.B.1.a. Bis(1,2-cyclohexanedionedioximato)nickel(II) system

Stock solution #1: Fourteen volumes of saturated urea solution, previously adjusted to pH 2.7 with 12 M hydrochloric acid were mixed with six volumes of 8 M hydroxylamine hydrochloride solution which had been previously adjusted to pH 0.3 with 12 M hydrochloric acid.

Stock solution #2: 1,2-cyclohexanedione was purified as described in Section III.A.1., a 0.9 M solution prepared and adjusted to pH 1.5 with 12 M hydrochloric acid. Twelve volumes of this solution were then mixed with one volume of a 4 M solution of reagent grade $NiC\ell_2\cdot 6H_2O$.

III.B.1.b. Bis(1,2-cycloheptanedionedioximato)nickel(II) system

Stock solution #1: One volume of 2 M $NiC\ell_2\cdot 6H_2O$ in 6 M phosphoric acid was mixed with four volumes of 1 M hydroxylamine hydrochloride in 2 M ammonium acetate solution.

Stock solution #2: 2.52 g of 1,2-cycloheptanedione were added to 80 ml of water containing 30 drops of concentrated hydrochloric acid. The mixture was stirred until all the dione dissolved. The solution was completed to 90 ml with distilled water and stored at 5°C.

III.B.1.c. Bis(1,2-cyclohexanedionedioximato)palladium(II)

Stock solution #1: Two volumes of 0.3 M $PdC\ell_2$ in 3M hydrochloric acid were mixed with one volume of 4.2 M hydroxylamine hydrochloride solution.

Stock solution #2 was a 0.4 M solution of 1,2-cyclohexanedione (purified as described in Section III.A.1.).

III.B.1.d. Bis(1,2-cycloheptanedionedioximato)palladium(II)

Stock solution #1: Equal volumes of 0.6 M $PdC\ell_2$ in 12 M hydrochloric acid and 3 M hydroxylamine hydrochloride were mixed.

Stock solution #2: Equal volumes of 0.5 M 1,2-cycloheptanedione and 12 M hydrochloric acid were mixed.

III.B.2. Procedures

A typical nucleation study involved three separate experiments; namely, a droplet experiment, a kinetic study and a solubility determination.

III.B.2.a. The following procedure was used for the droplet experiments:

A reaction mixture was prepared by mixing the appropriate stock solutions in such proportions as to produce the optimun reaction conditions previously determined. The relative amounts of the stock solutions used for the different compounds studied are shown in Table 2.

Immediately after mixing, a small drop (0.01-0.02 ml) of the reaction mixture was dispersed in 6 ml of light mineral oil and the dispersion photographed at regular intervals according to the procedure described in Section III.A.2. As described in the same section, the number and size of the crystallized drops was determined as a function of time.

III.B.2.b. The following procedure was used for the kinetic studies:

About 1 ml of light silicone oil (viscosity 1.0 cts) was added to each of 6 medium porosity sintered glass crucibles and allowed to stand for 5 minutes. The crucibles were then decanted and a suitable amount of the appropriate stock solution #1 was immediately added to each crucible. The corresponding amount of solution #2 was then added, the mixture stirred with a small glass rod and the time of addition recorded. Exactly 5 minutes after adding stock solution #2 to the last crucible, the vacuum was applied and the precipitate was filtered off, washed once with

TABLE 2

RELATIVE AMOUNTS OF STOCK SOLUTIONS EMPLOYED IN NUCLEATION STUDIES

Compound	Volume of stock solution #1	Volume of stock solution #2
$Ni(C_6H_9N_2O_2)_2$	1	1
$Ni(C_7H_{11}N_2O_2)_2$	1	3
$Pd(C_6H_9N_2O_2)_2$	1	1
$Pd(C_7H_{11}N_2O_2)_2$	1	10

hydrochloric acid solution of the same pH as the reaction mixture and then with water. The filtering operation was repeated with the other crucibles, always recording the time at which the vacuum was applied. The precipitates were then dried for one hour at 110°C and weighed.

III.B.2.c. The following procedure was used for the solubility determinations:

For each compound studied, a medium containing all components of the reaction mixture, except the metal ion and the α-diketone, was prepared as follows:

i) For the determination of the solubility of $Ni(C_6H_9N_2O_2)_2$, one liter of the medium contained 120 g of $CO(NH_2)_2$, 69 g of $NH_2OH{\cdot}HC\ell$, and enough $HC\ell$ to bring the pH to 1.5.

ii) For $Ni(C_7H_{11}N_2O_2)_2$, the medium contained 20 ml of 15 M H_3PO_4, 30 g of $NH_4C_2H_3O_2$, and 14 g of $NH_2OH{\cdot}HC\ell$ per liter.

iii) For $Pd(C_6H_9N_2O_2)_2$, the medium contained 83 ml of 12 M $HC\ell$ and 48 g of $NH_2OH{\cdot}HC\ell$ per liter.

iv) For $Pd(C_7H_{11}N_2O_2)_2$, the medium contained 500 ml of 12 M $HC\ell$ and 10 g of $NH_2OH{\cdot}HC\ell$ per liter.

The solid metal chelates were then added to the corresponding media and allowed to stand for one week with occasional shaking. The mixtures were then filtered and the filtrates evaporated slowly to a few milliliters in the presence of nitric acid. White solid residues which separated in some cases were filtered off. The evaporation process was repeated several times. Finally, 2 ml of 70% perchloric acid were added and the solution evaporated to the white fumes of the acid. The solutions were then diluted to 100 ml and the metal ion concentrations determined by EDTA titrations. Pd(II) was determined by a procedure given by Beamish[35] and Ni(II) was determined by a procedure described by Flaschka[36].

III.B.3. Numerical Analysis of the Experimental Data

One of the main purposes of the nucleation experiments which have been carried out with condensed systems has been to calculate the solid-liquid interfacial energy per unit area. This can be done if a single point in the J vs S curve is known. In these experiments the values of J and S at which 50% of the droplets had crystallized were chosen for the calculation of γ.

The value of S was determined as follows. From the photographs taken while performing the droplet experiment, the number of drops which crystallized within a given size range was determined as a function of time. As will be explained in more detail later, all drops were converted to standard size. The value of S corresponding to the median crystallization time for this standard size was used in the calculations.

From the kinetic study the weight of precipitate per unit volume was obtained as a function of time. This was assumed to be equal to the weight of monomers per unit volume per unit time in the supersaturated droplets.

The last quantity needed for the calculation of S was obtained from the solubility determination. The value of S was found by dividing the concentration of monomers in the supersaturated droplets at the median crystallization time by the solubility.

The manner in which J was calculated will be explained later. The values of J and S thus found were substituted in the theoretical equation for the nucleation rate and the value of γ calculated.

II.C. Studies on the Nucleation from Solution of Some Soluble Inorganic Salts

III.C.1. Apparatus and Reagents

The apparatus described previously were used in this study.

All solutions were prepared with reagent grade chemicals. The experiments were carried out with saturated solutions of NH_4NO_3, $NH_4C\ell$, NH_4SCN, $(NH_4)_2C_2O_4 \cdot H_2O$, $(NH_4)_2Cr_2O_7$ and $K_2Cr_2O_7$.

III.C.2. Procedure

The following procedure was used to study the nucleation of soluble inorganic salts.

> A counting cell was prepared as described previously and two ml of silicone oil (200 cts viscosity) added. The dispersion was then prepared by adding approximately 0.02 ml of a freshly filtered saturated salt solution to about 6 ml of light mineral oil contained in a microhomogenizer flask and stirring at about 10,000 rpm for 15 seconds. The dispersion was transferred to the counting cell and centrifuged for about 15 seconds. Nearly all the dispersion was decanted, 1 ml of silicone oil added, and the counting cell centrifuged again for 30 seconds. The dispersion was then examined with a microscope and a suitable set of droplets selected and photographed. The position of the

counting cell was noted and the readings of the microscope stage recorded to enable the same set of droplets to be located quickly. The counting cell was then removed to a desiccator containing phosphorus pentoxide. Subsequent photographs of the dispersion were taken at suitable intervals until all the droplets had crystallized.

III.C.3. Numerical Analysis of the Experimental Data

In these studies the diameter of each droplet was measured at the beginning of the experiment and after crystallization of the droplet. Since the amount of solute in the droplet was kept constant and the experiment was carried out at constant temperature, the supersaturation was produced as a result of the loss of water by the drop. An expression that enabled the calculation of the supersaturation ratio from the initial and final diameters of the drops, the density of the saturated solution, and the solubility of the salt was derived as follows.

If the saturated solution in the droplet contains x moles of solute and y moles of water, the mole fraction of a solute will be

$$N_s(\text{saturated}) = \frac{x}{x+y} . \qquad (47)$$

If the droplet loses z moles of water, the mole fraction of solute in the supersaturated droplet will be

$$N_s(\text{supersaturated}) = \frac{x}{x+y-z} . \qquad (48)$$

The value of the supersaturation ratio for the droplet will be

$$S = \frac{x+y}{x+y-z} \qquad (49)$$

Let d_1 and d_2 be the initial and final diameters of the droplet. Also, let V_1 and V_2 be the initial and final volumes (in ml) of the droplets. Therefore,

$$V_2 = V_1\left(\frac{d_2}{d_1}\right)^3. \tag{50}$$

The volume of water lost by the droplet can be expressed as

$$V_1 - V_2 = V_1\left[1 - \left(\frac{d_2}{d_1}\right)^3\right]. \tag{51}$$

The number of moles of water, z, lost by the droplet is

$$z = \frac{V_1\left[1 - \left(\frac{d_2}{d_1}\right)^3\right]d_w}{M_w}, \tag{52}$$

where d_w and M_w are the density and molecular weight of water, respectively.

Let d_s be the density of the saturated solution, W_s be the weight of solute per gram of solution, W_w be the weight of water per gram of solution and M_s be the molecular weight of the solute. It follows then that

$$x = \frac{V_1 d_s W_s}{M_s}. \tag{53}$$

and

$$y = \frac{V_1 d_s W_w}{M_w}. \tag{54}$$

Therefore,

$$S = \frac{\dfrac{V_1 d_s W_s}{M_s} + \dfrac{V_1 d_s W_w}{M_w}}{\dfrac{V_1 d_s W_s}{M_s} + \dfrac{V_1 d_s W_w}{M_w} - V_1\left[1 - \left(\dfrac{d_2}{d_1}\right)^3\right]\dfrac{d_w}{M_w}} \tag{55}$$

or

$$S = \frac{d_s\left(\dfrac{W_s}{M_s} + \dfrac{W_w}{M_w}\right)}{d_s\left(\dfrac{W_s}{M_s} + \dfrac{W_w}{M_w}\right) - \left[1 - \left(\dfrac{d_2}{d_1}\right)^3\right]\dfrac{d_w}{M_w}} \tag{56}$$

The manner in which the nucleation rate was calculated from the experimental data will be discussed later.

IV. RESULTS AND DISCUSSION

IV.A. Preliminary Investigation

As mentioned in Section III.A., one purpose of the preliminary investigation was to study methods of generating mono-sized water droplets dispersed in oil. To be useful for nucleation studies the following requirements had to be fulfilled.

1. The dispersion had to be available for microscopic examination in about 3 minutes. This was necessary because the aqueous solutions consisted of reaction mixtures in which precipitation occurred in about 3-4 minutes.

2. The dispersion had to be suitable for photographic study. This implied that the droplets be on the same plane, stationary, and stable to coalescence.

3. The dispersion had to provide several hundred drops with diameters preferably in the size range 10-50 μ. This number of drops was necessary in order to obtain statistically significant results. The desired size range was selected on the basis of preliminary tests which showed that crystallization was difficult to detect in droplets with diameters smaller than 10 μ. Droplets with diameters larger than 50 μ usually exhibited more than one crystal.

4. The dispersion had to be very transparent. Even though the microscopic study was to be carried out with crossed polarizers, the droplets had to be distinctly visible for accurate size measurements.

In order to establish a procedure which yielded droplets of the above characteristics some experiments were carried out to study the number, size distribution and stability of the droplets in a dispersion as conditions used in its preparation were varied. Because of the many variables involved in these experiments, the reproducibility of the results was not very good. Consequently, they will be discussed qualitatively.

As the proportion of aqueous phase in the dispersion was increased from 0.2% to 2%, the number and size of the droplets increased. Because of increased turbidity, coalescence and wider size distributions obtained with the larger amounts, a volume of 0.01-0.02 ml of aqueous phase in 6 ml of oil was selected for the nucleation experiments.

The time of stirring, measured from the time the microhomogenizer was turned on to the time it was turned off, was varied from 5 to 30 sec. As the time of stirring was increased, the number of droplets increased, their average size decreased and the turbidity of the dispersion increased. The time of stirring adopted for the final experiments was 15 seconds.

The speed of the microhomogenizer was varied from an estimated value of 4000 rpm to about 35000 rpm. The results were similar to those described above for the variation of the time of stirring. The best results were obtained at about 15000 rpm. If the time of stirring was limited to 5 seconds, however, satisfactory results could be obtained at 35000 rpm.

Mineral and silicone oils of various viscosities were used in the preliminary investigation. With light mineral oil (viscosity ~20 cts), the number and size of the droplets were found to be closer to the desired values and the dispersions obtained were more transparent than those prepared with heavy mineral oil (viscosity ~200 cts). With silicone oils of various viscosities (1.0-500 cts) and specific gravities (~0.8-1.1) the dispersions were considerably less stable than with mineral oils as the parent medium. Dispersions prepared with oils heavier than water were the least stable. Another objectionable feature observed with silicone oils was that the droplets of water gradually decreased in size and finally disappeared. After this observation was made the experiments with silicone oils were discontinued.

By varying the factors described above it was not possible to prepare a dispersion which could be considered satisfactory for a photographic study. The reasons for this were that many of the droplets were constantly moving across the field of view, considerable coalescence always occurred, and the presence of a large number of droplets with diameters from 1-5 μ produced undesirable cloudiness.

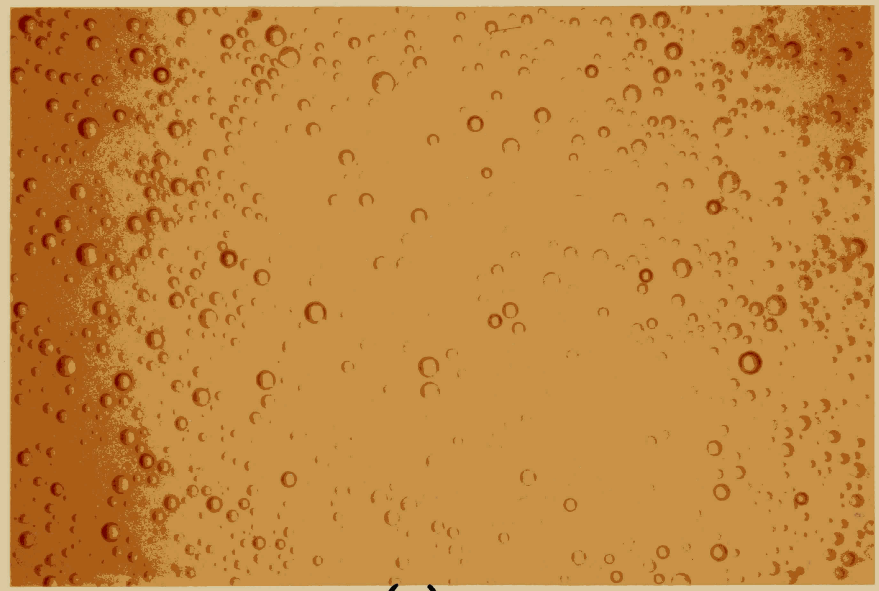
These undesirable characteristics were eliminated by placing the dispersion in a Nessler cup and centrifuging for about 15 seconds. During this time the larger droplets settled to the bottom of the cup and were embedded in a thin film of clear silicone grease. This enabled the very small droplets to be removed by decantation.

By following the procedure which finally emerged it was possible to obtain a single layer of several hundred stationary, non-communicating droplets, with diameters in the range 10-50 μ, and free of contact with any wettable surface. This can be seen in Figure 6, which shows photographs taken during the studies on bis(1,2-cycloheptanedionedioximato)-palladium(II). The largest droplets in these photographs are about 70 μ in diameter. Although a magnification of 70 x was used in some nucleation studies, these photographs were taken with a magnification of 40 x. In

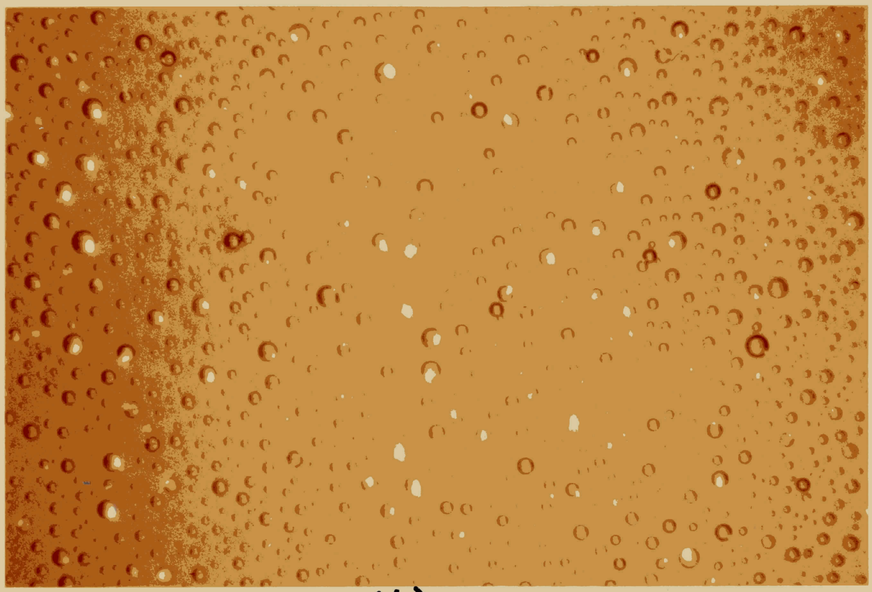
FIGURE 6. Photographs Taken During Studies on Nucleation of $Pd(C_7H_{11}N_2O_2)_2$:

(a) few droplets have crystallized;

(b) many droplets have crystallized.



(a)



(b)

general, because of the increased depth of field, this magnification resulted in photographs of better quality. In addition, it provided a larger number of droplets for study.

A second purpose of the preliminary investigation was to find a set of reaction conditions within the droplets which was suitable for the nucleation study. As mentioned in Section III.A., the first reaction conditions studied were similar to those commonly used in analytical procedures. Thus in the study of the nucleation of bis(1,2-cyclohexanedionedioximato)palladium(II), the following reaction conditions were initially employed:

Pd(II)	$[\mathrm{HC}\ell]$	$[\mathrm{NH_2OH \cdot HC}\ell]$	$[\mathrm{C_6H_8O_2}]$
2×10^{-4} M	0.1 M	10^{-3} M	4×10^{-4} M

Although a considerable amount of precipitate was formed in the beaker, no crystallization was observed in the droplets.

The reasons for this were recognized when the maximum amount of chelate monomers that could be produced in a 20 μ droplet was calculated. Assuming that the reaction goes to completion, the amount of precipitate formed corresponds to a monomer concentration of 2×10^{-4} M, or approximately 5×10^{8} molecules in a 20 μ droplet. If one single crystal is formed in the droplet, its mass will be approximately 3×10^{-13} g, which corresponds to a cube about 0.5 μ in an edge. A crystal of this size is probably very difficult to detect.

A second set of experiments was tried using higher reagent concentrations. At pH 1 the results were not satisfactory because the reaction proceeded so fast that crystallization occurred before the dispersion was ready for observation.

To reduce the reaction rate it was necessary to acidify the reaction mixture. As the pH was decreased, however, the extent of precipitation also decreased. The optimum reaction conditions were found to be critically dependent on the concentrations of reactants, pH, and the addition of secondary reagents.

The final reaction conditions used in the studies of the four metal chelate systems are summarized in Table 3.

It must be mentioned that, under the conditions described above, there were always droplets which, apparently, did not crystallize. This observation can be explained as follows.

1. Most of the droplets that failed to crystallize were very small and it is reasonable to assume that the total mass of monomers available in these droplets was insufficient to produce crystals of detectable size.

2. Since a polarizing microscope was being used to observe nucleation, it is possible that in some droplets the orientations of the crystals were such that they could not be detected.

IV.B. Studies on the Nucleation from Solution of Some Analytically Important Metal Chelates

After a set of suitable reaction conditions was found for a given system, a typical nucleation experiment was carried out on that system. The experiments consisted of the determination of the nucleation rate, J, and the median supersaturation ratio, $\bar{S}$, at which the drops of any given size crystallized. Then the values of other parameters of interest were calculated from the values of J and $\bar{S}$.

TABLE 3

REACTION CONDITIONS USED IN STUDIES ON THE NUCLEATION OF METAL CHELATE SYSTEMS

Compound Studied	Reaction Mixture Components and Molar Concentrations						
	Metal Ion	$NH_2OH \cdot HCl$	α-Diketone	Other Components			
				HCl	$CO(NH_2)_2$	H_3PO_4	NH_4Ac
$Ni(C_6H_9N_2O_2)_2$	0.2	1.0	0.4	pH1.5	2.0		
$Ni(C_7H_{11}N_2O_2)_2$	0.1	0.2	0.2			0.3	0.4
$Pd(C_6H_9N_2O_2)_2$	0.1	0.7	0.2	1.0			
$Pd(C_7H_{11}N_2O_2)_2$	0.03	0.2	0.3	6.0			

In order to determine the values of the nucleation rate and the median supersaturation ratio it was necessary to perform three separate experiments. The first was a droplet experiment, in which the values of J and the median crystallization time were measured. The second was a kinetic study, which yielded the concentration of monomers in the droplets as a function of time. The third was carried out to determine the solubility of the metal chelate at the conditions used in the nucleation study.

The droplet experiment was carried out by mixing the appropriate amounts of the stock solutions, dispersing the reaction mixture in mineral oil, and recording photographically the crystallization events with the aid of a polarizing microscope. Figure 6 shows photographs taken during the studies on bis(1,2-cycloheptanedionedioximato)palladium(II). The data were collected by projecting the 35 mm slides on a calibrated screen and recording the numbers of crystals and the diameters of the crystallized drops. Data obtained from more than one experiment were usually combined for analysis purposes. The results of droplet experiments on the nucleation of bis(1,2-cycloheptanedionedioximato)palladium(II) are shown in Table 4.

Examination of these results indicated that there was a linear relationship between the median crystallization time and the logarithm of the droplet volume. This empirical correlation is illustrated in Figure 7. These results are similar to those found by Bigg[30] in his experiments on the supercooling of water and by Melia and Moffitt[31] in their studies on the nucleation of inorganic salts from aqueous solution.

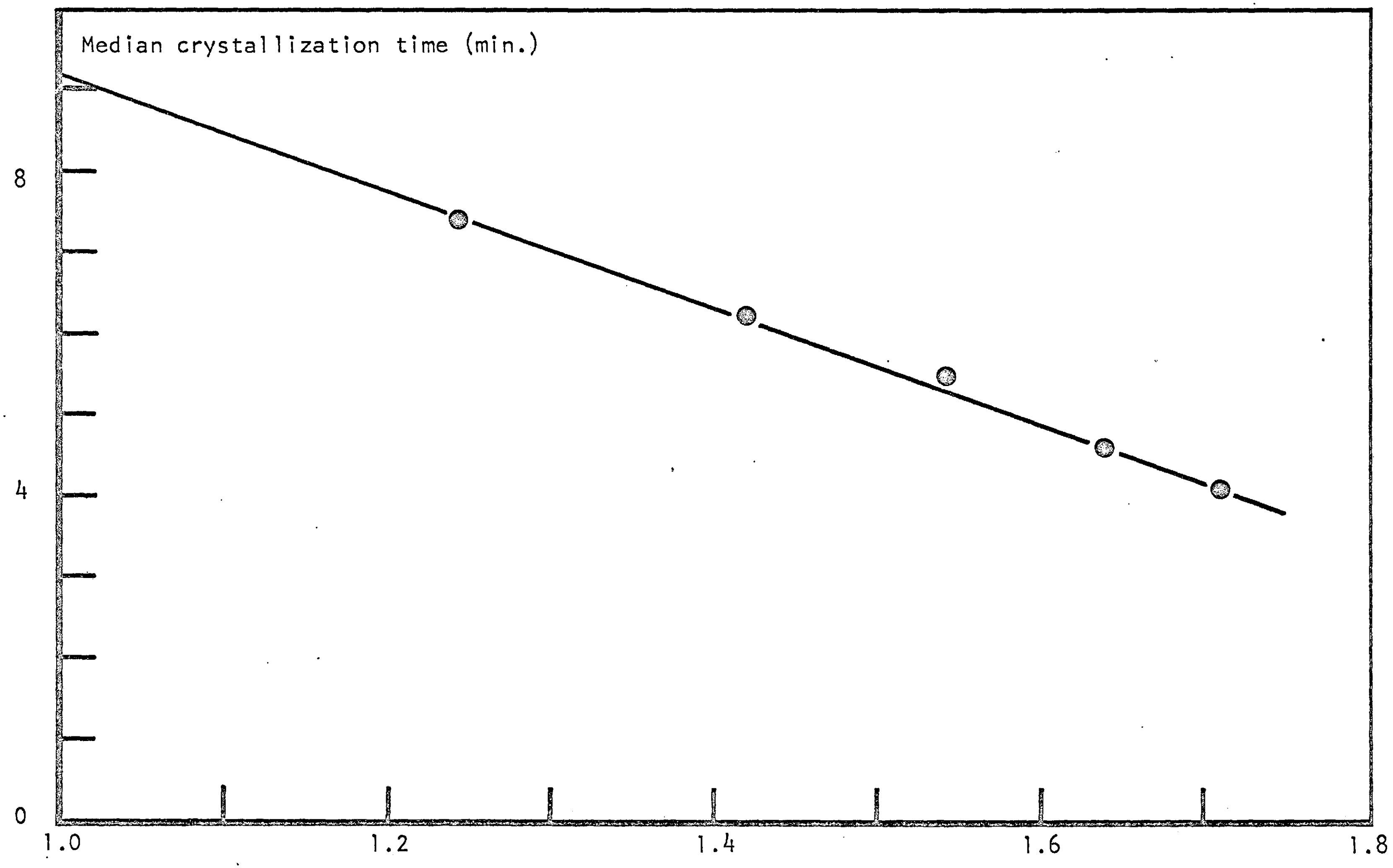
This linear relationship made it possible to reduce the crystallization time of any drop to that of a drop of standard size. Thus, the

TABLE 4

RESULTS OF DROPLET EXPERIMENTS ON THE NUCLEATION OF BIS(1,2-CYCLOHEPTANEDIONEDIOXIMATO)PALLADIUM(II)

Reaction time	Average drop diameters and numbers of new crystals				
(minutes)	17.5 μ	26.2 μ	35.0 μ	43.7 μ	52.5 μ
4.0		2	8	17	14
4.5		7	28	23	7
5.0	1	19	32	29	7
5.5	5	18	24	17	2
6.0	6	19	26	2	1
6.5	9	20	29	1	
7.0	12	23	23		
7.5	14	27	6		
8.0	9	12	5		
8.5	7	3	3		
9.0	9	3			
9.5	5				
10.0	7				
10.5	5				
Totals	89	153	185	89	31
M.C.t. (min.)	7.4	6.3	5.5	4.6	4.1

FIGURE 7. Median Crystallization Time Versus Log Drop Diameter for $Pd(C_7H_{11}N_2O_2)_2$



Median crystallization time (min.)
8
4
0
1.0
1.2
1.4
1.6
1.8
Log drop diameter (μ)

analytical expression for the line of Figure 7 was found to be $\overline{t} = -7.12 \log d + 16.3$. This equation was used to calculate the times at which droplets of any given size would crystallize if they were of average size (35 μ). Because the distributions of crystallization frequency versus time were approximately normal for any given droplet size, the results obtained were equivalent, within experimental error, to those obtained by shifting the various distributions as shown in Table 5.

As expected, the largest number of crystallized droplets occurred at the median crystallization time for the droplets of standard size. This number can be used to calculate the relative frequency of crystallization as a function of time. This is done by dividing the number of crystallized droplets at any given time by the number above. The results appear in Table 5 and are illustrated in Figure 8.

From Figure 8, the probability of crystallization as a function of time was calculated by dividing the area under the curve up to a given time by the total area. The results of these calculations are shown in Figure 9.

In order to check the consistency of the results obtained above, and thus the validity of the approximations used in the calculations, the probability of crystallization versus time and the relative frequency of crystallization versus time were calculated theoretically for 35 μ droplets. The basis for these calculations is described in Section I.D.2. There, the linear relationship between the median crystallization time and the logarithm of the droplet volume is expressed as

$$\ln V = a\overline{t} + b. \qquad (57)$$

TABLE 5

RESULTS OF THE CALCULATIONS TO REDUCE EXPERIMENTAL DATA ON $Pd(C_7H_{11}N_2O_2)_2$ TO STANDARD DROPLET SIZE OF 35 μ IN DIAMETER

Reaction time	Adjusted distributions					Totals	Relative frequency of
(minutes)	17.5 μ	26.2 μ	35.0 μ	43.7 μ	52.5 μ		crystallization
3.0	1	2				3	3.2
3.5	5	7				12	12.6
4.0	6	19	8			33	34.8
4.5	9	18	28			55	57.8
5.0	12	19	32	17		80	84.0
5.5	14	20	24	23	14	95	100.0
6.0	9	23	26	29	7	94	98.5
6.5	7	27	29	17	7	87	91.3
7.0	9	12	23	2	2	48	50.4
7.5	5	3	6	1	1	16	16.8
8.0	7	3	5			15	15.7
8.5	5		3			8	8.4

FIGURE 8. Relative Frequency of Crystallization Versus Reaction Time for Pd$(C_7H_{11}N_2O_2)_2$

Standard droplet diameter = 35 µ

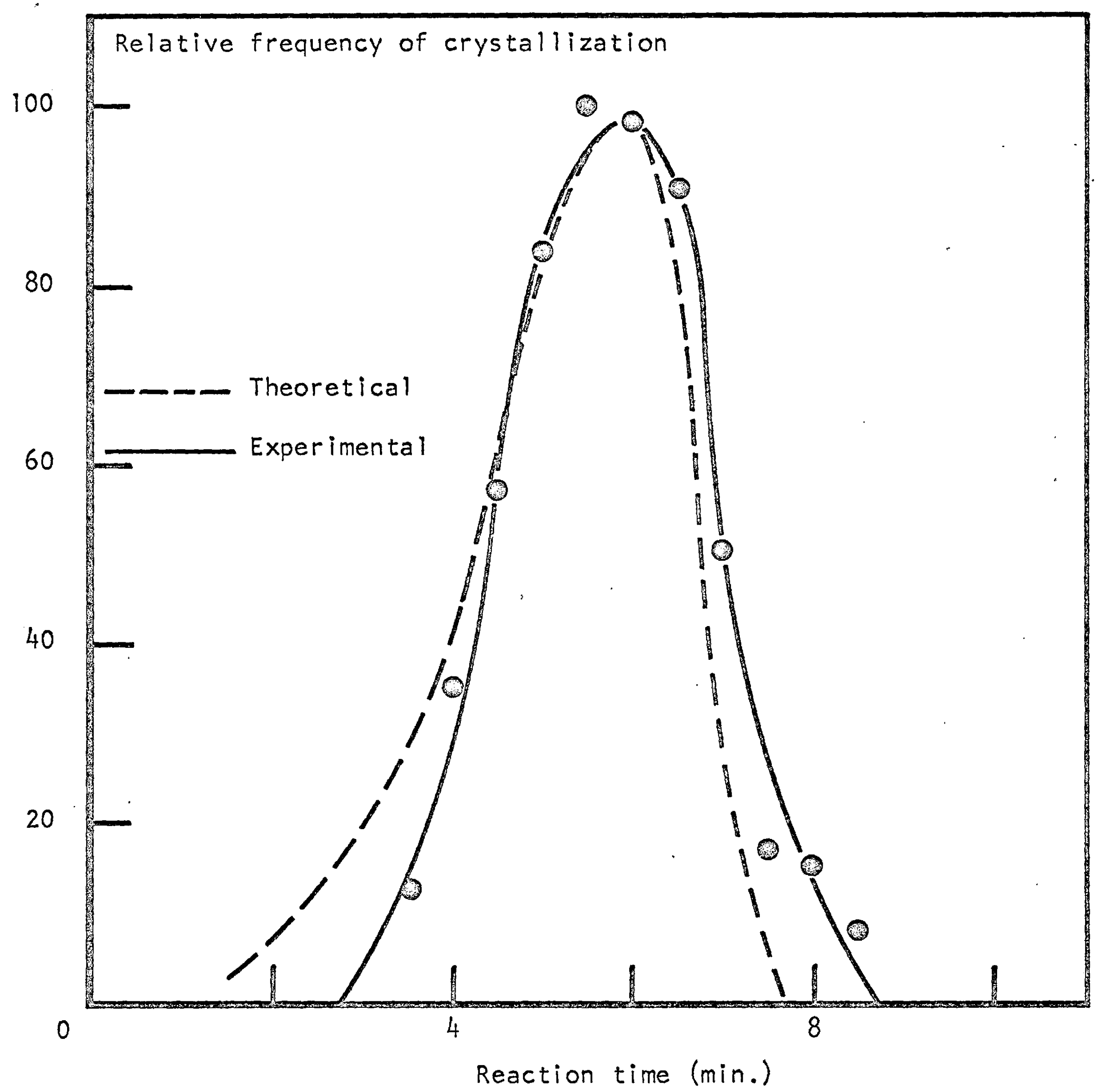
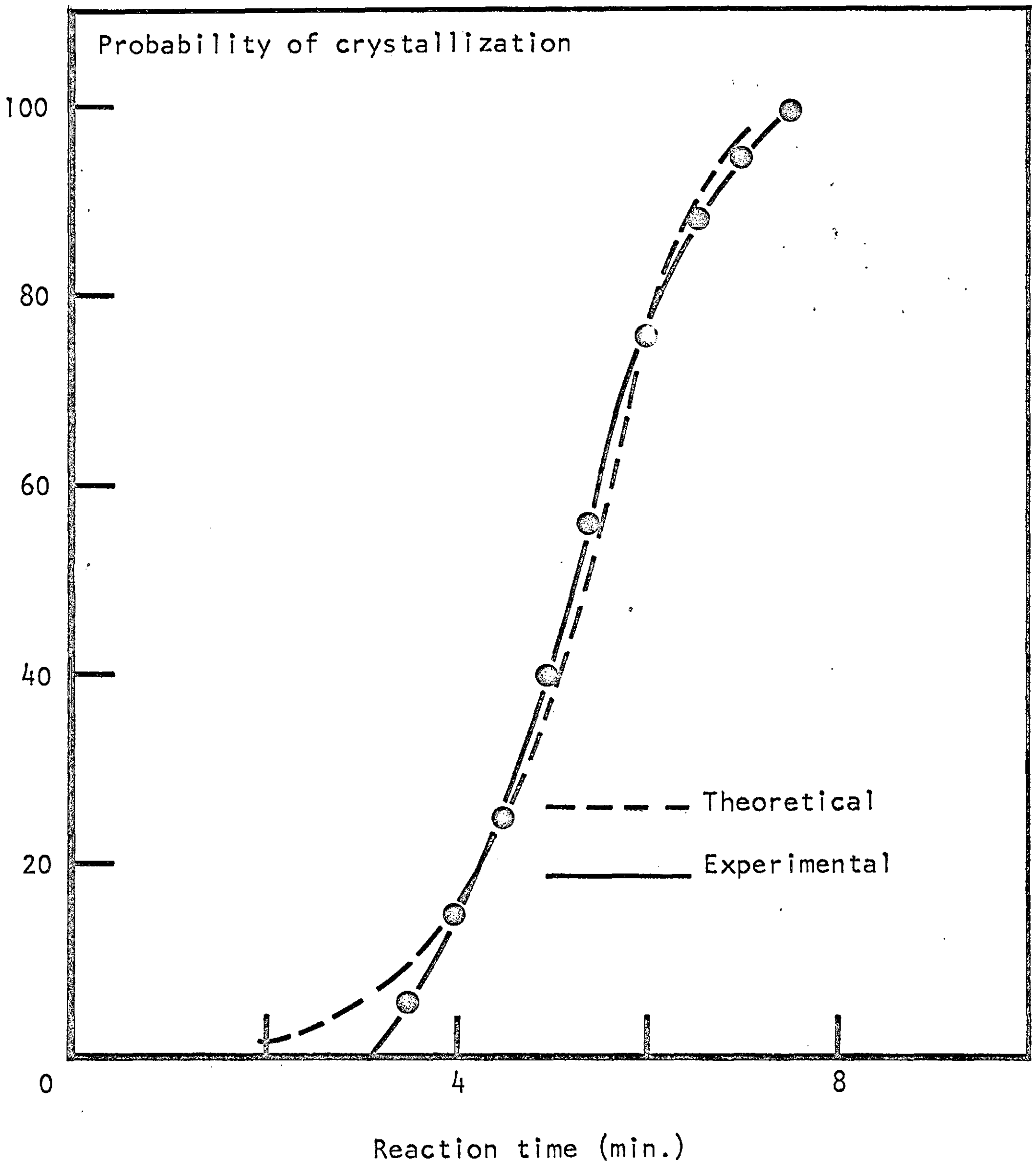

Relative frequency of crystallization
100
80
60
40
20
0
4
8
Reaction time (min.)
Theoretical
Experimental

FIGURE 9. Probability of Crystallization Versus Reaction Time for $Pd(C_7H_{11}N_2O_2)_2$

Standard droplet diameter = 35 μ


Probability of crystallization
100
80
60
40
20
0
4
8
Reaction time (min.)
Theoretical
Experimental

Experimentally, however, the diameters of the droplets were measured and for this reason it was more convenient to plot the relationship in the form

$$\bar{t} = m \log d + c. \tag{58}$$

To find the values of a and b in terms of m and c, equation (58) is written as follows.

$$\log d = \frac{1}{m}\bar{t} - \frac{c}{m} \tag{59}$$

The volume of a droplet of diameter d is

$$V = \frac{\pi}{6} d^3. \tag{60}$$

Therefore,

$$\log V = \log \frac{\pi}{6} + 3 \log d \tag{61}$$

and

$$\ln V = 2.3 \log \frac{\pi}{6} + 6.9 \log d. \tag{62}$$

By substitution,

$$\ln V = \frac{6.9}{m}\bar{t} + 2.3 \log \frac{\pi}{6} - \frac{6.9}{m} c. \tag{63}$$

From equation (63) it follows that

$$a = \frac{6.9}{m} \quad \text{and} \quad b = -(\frac{6.9}{m} c + 0.65).$$

At $\bar{t} = 0$, $b = \ln V$. Therefore, b can be calculated from the intercept of the plot shown in Figure 7. The following values of a and b were obtained.

$$a = -0.98, \ b = +15.3$$

Using these values and equation (36)

$$\ln[1 - P(V,t)] = -0.693\, V_s \exp(-b)[\exp(-at) - 1], \tag{36}$$

which was derived in Section I.D.2., the probability of crystallization as a function of time was calculated. Substituting the experimental values of a and b and $V = 2.4 \times 10^4 \mu^3$ reduced equation (36) to

$$\log\ (1 - P) = -1.58 \times 10^{-3}[\exp(-at) - 1] \tag{64}$$

The results of these calculations are shown in Table 6. The results shown in Table 6 are illustrated in Figure 9 (broken curve). The agreement between the two curves in Figure 9 justifies the approximations involved in reducing the experimental data to standard droplet size.

The relative frequency of crystallization as a function of time was calculated with the aid of equation (40), derived in Section I.D.2.

$$\begin{aligned} -\left(\frac{\partial \rho(V,t)}{\partial t}\right)_V &= [1 - P(V,t)][0.693\ \exp(-b)][a\ \exp(-at)]V_s \\ &= k[\exp(-at)](1 - P) \end{aligned} \tag{40}$$

The results of these calculations are shown in Table 7 and plotted as the broken curve of Figure 8.

Values of the nucleation rate of $Pd(C_7H_{11}N_2O_2)_2$ as a function of time were calculated with the aid of equation (43).

$$J = \frac{1}{V_s}\frac{dP}{dt} \tag{43}$$

The slopes of various tangents to the curve of Figure 8 were measured and divided by the standard droplet volume. The results of these calculations are shown in Table 8.

The experimental data and calculations involved in the nucleation studies on the three other chelates were similar to those described above for $Pd(C_7H_{11}N_2O_2)_2$. The results of the data analysis on these compounds

TABLE 6

RESULTS OF THE CALCULATION OF THE PROBABILITY OF CRYSTALLIZATION OF Pd$(C_7H_{11}N_2O_2)_2$ VERSUS TIME

Time (min.)	exp(-at) - 1	log (1 - P)	P
2.0	6.1	-0.0096	0.02
3.0	17.9	-0.0283	0.06
3.5	29.9	-0.0472	0.10
4.0	49.4	-0.0781	0.16
4.5	82.1	-0.130	0.27
5.0	133	-0.211	0.38
5.5	218	-0.345	0.55
6.0	359	-0.567	0.73
6.5	579	-0.915	0.88
7.0	954	-1.5	0.97
7.5	1570	-2.48	0.997

TABLE 7

RESULTS OF THE CALCULATION OF THE RELATIVE FREQUENCY OF CRYSTALLIZATION OF $Pd(C_7H_{11}N_2O_2)_2$ VERSUS TIME

Time (min.)	exp(-at)	1 - P	Relative frequency of crystallization
2.0	7.1	0.98	7.0
3.0	18.9	0.94	17.9
3.5	30.9	0.90	28.1
4.0	50.4	0.835	42.5
4.5	83.1	0.725	60.8
5.0	134	0.615	83.5
5.5	219	0.452	100.0
6.0	360	0.271	98.5
6.5	580	0.122	71.4
7.0	955	0.031	29.9
7.5	1570	0.003	4.8

TABLE 8

RESULTS OF THE CALCULATION OF THE NUCLEATION RATE OF $Pd(C_7H_{11}N_2O_2)_2$ VERSUS TIME

Reaction time (minutes)	Nucleation Rate ($cm^{-3}sec^{-1}$)
3.5	1.07×10^5
4.0	1.49×10^5
5.0	2.48×10^5
5.5	2.98×10^5

are shown in Tables 9 through 13 and Figures 10 through 12 for $Pd(C_6H_9N_2O_2)_2$, in Tables 14 through 18 and Figures 13 through 15 for $Ni(C_6H_9N_2O_2)_2$ and in Tables 19 through 23 and Figures 16 through 18 for $Ni(C_7H_{11}N_2O_2)_2$. Any slight modifications in the methods of calculations are indicated in the tables or in the figures. A summary of the values of m, c, a and b obtained for the four compounds studied is shown in Table 24.

The second experiment required in the nucleation study concerned the determination of the concentration of monomers in the droplets as a function of time. This was carried out by mixing the stock solutions in exactly the same proportions used for the droplet experiment and determining the weight of precipitate formed per unit volume as a function of time. The weight of the precipitate at any given time was assumed to be equal to the weight of monomers produced up to that time. Figures 19 through 22 show the results obtained in the kinetic studies of the four systems investigated.

The last experiment required for the calculation of S was the determination of the solubility of the metal chelate in the experimental medium employed. The results are shown in Table 25. Also, Table 25 shows the values of S, γ, r^* and n^*, calculated from equations (21), (16), (20) and (19) respectively.

The data obtained in nucleation experiments can be used to assess the validity of the classical nucleation theory. Usually, this is done by determining the experimental value of the pre-exponential term in equation (16) and comparing it with the theoretical value.

It can be seen from equation (16)

TABLE 9

RESULTS OF DROPLET EXPERIMENTS ON THE NUCLEATION OF $Pd(C_6H_9N_2O_2)_2$

Reaction time (minutes)	Average drop diameters and numbers of new crystals			
	10 μ	15 μ	20 μ	25 μ
8.5	1	3	7	11
9.0	6	20	14	13
9.5	11	28	15	6
10.0	10	25	9	7
10.5	20	18	5	2
11.0	25	13	1	
11.5	21	15		
12.0	25	9		
12.5	19	6		
13.0	18	1		
13.5	8			
14.0	2			
Totals:	166	138	51	39
M.C.T.: (min.)	11.2	9.9	9.1	8.8

FIGURE 10. Median Crystallization Time Versus Log Drop Diameter for $Pd(C_6H_9N_2O_2)_2$

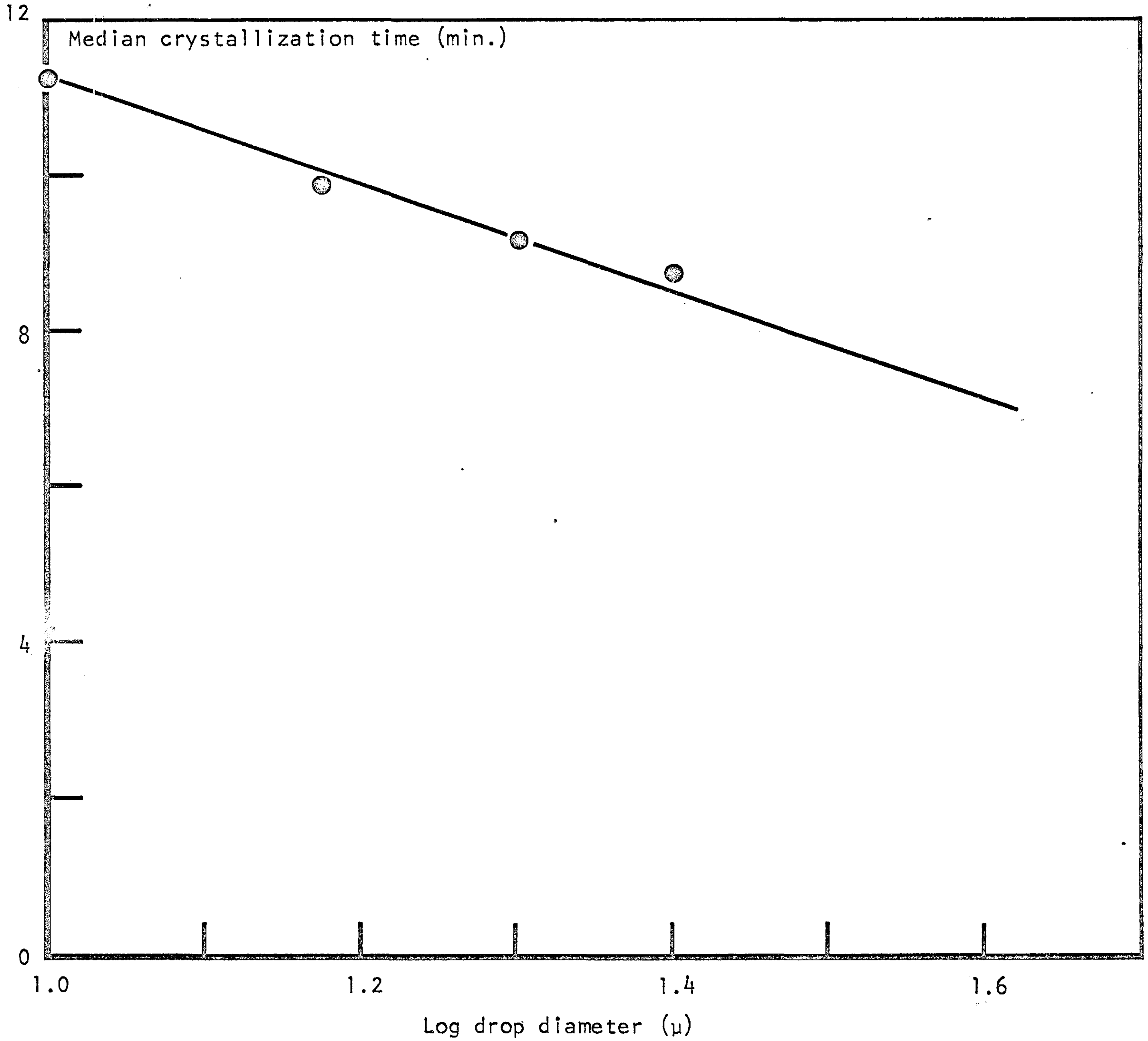

Median crystallization time (min.)
12
8
4
0
1.0
1.2
1.4
1.6
Log drop diameter (μ)

TABLE 10

RESULTS OF THE CALCULATIONS TO REDUCE EXPERIMENTAL DATA ON Pd$(C_6H_9N_2O_2)_2$ TO STANDARD DROPLET SIZE OF 15 μ IN DIAMETER

Reaction time (minutes)	Adjusted distributions 10 μ	15 μ	20 μ	25 μ	Totals	Relative frequency of crystallization
7.0	1				1	1.4
7.5	6				6	8.2
8.0	11				11	15.1
8.5	10	3			13	17.8
9.0	20	20			40	54.8
9.5	25	28	7	11	71	97.2
10.0	21	25	14	13	73	100.0
10.5	25	18	15	6	64	87.6
11.0	19	13	9	7	48	65.8
11.5	18	15	5	2	40	54.8
12.0	8	9	1		18	24.7
12.5	2	6			8	11.0
13.0		1			1	1.4

FIGURE 11. <u>Relative Frequency of Crystallization</u> Versus <u>Reaction Time</u> for $Pd(C_6H_9N_2O_2)_2$

Standard droplet diameter = 15 μ

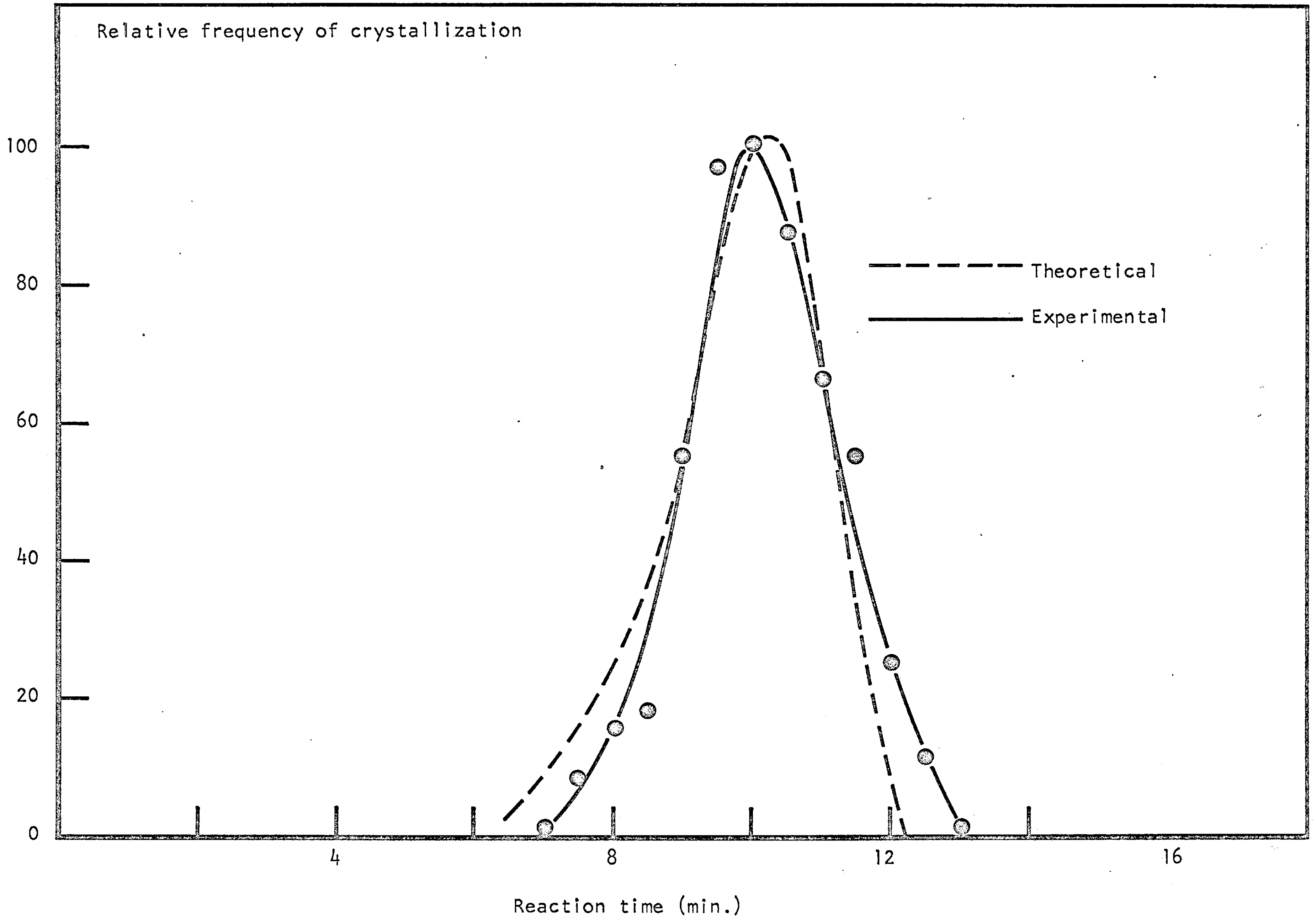

Relative frequency of crystallization
100
80
60
40
20
0
Theoretical
Experimental
4
8
12
16
Reaction time (min.)

FIGURE 12. Probability of Crystallization Versus Reaction Time for $Pd(C_6H_9N_2O_2)_2$

Standard droplet diameter = 15 μ

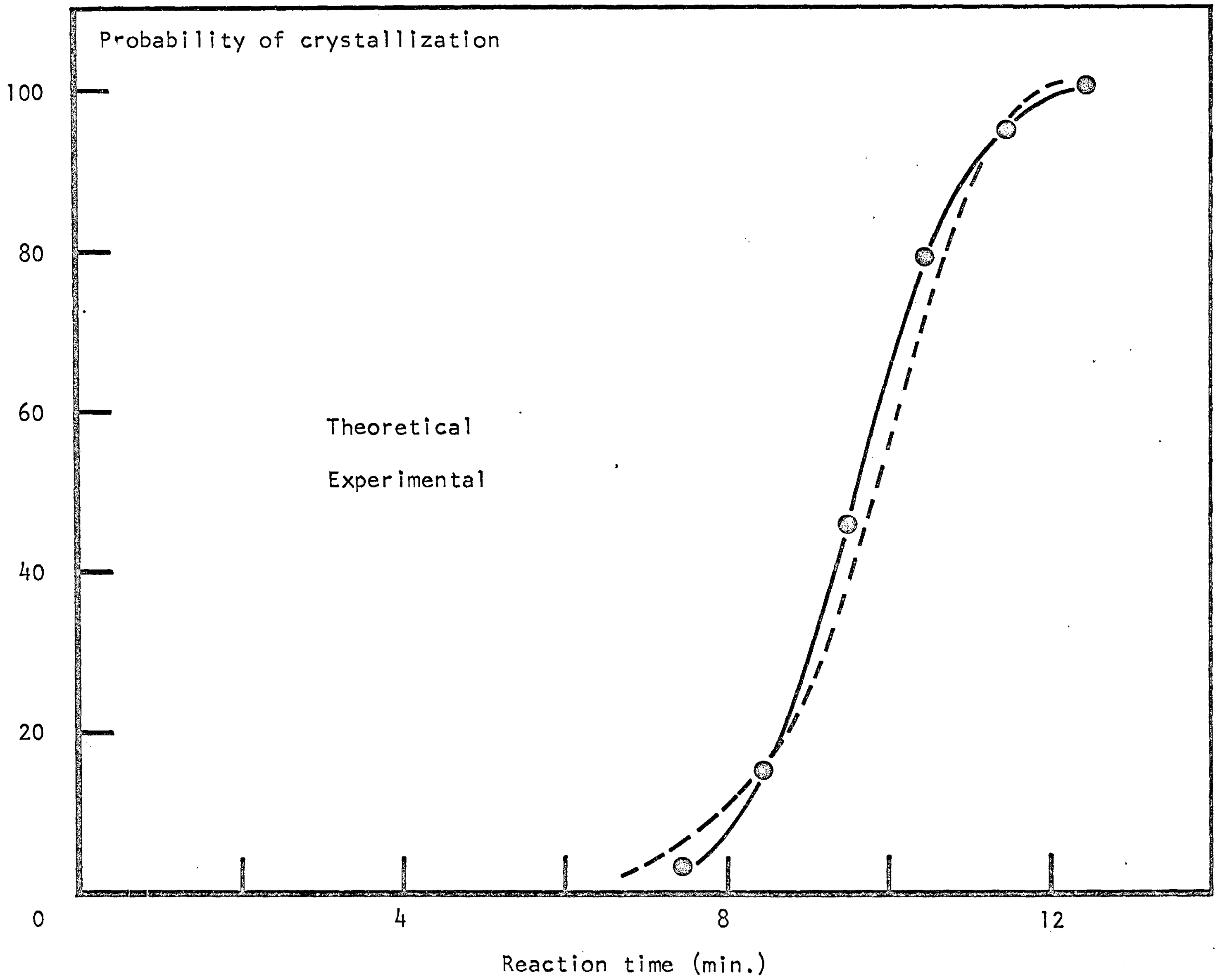

Probability of crystallization
100
80
60
40
20
0
4
8
12
Reaction time (min.)
Theoretical
Experimental

TABLE 11

RESULTS OF THE CALCULATION OF THE PROBABILITY OF CRYSTALLIZATION OF $Pd(C_6H_9N_2O_2)_2$ VERSUS TIME

Time (min.)	exp(-at) - 1	log(1 - P)	P
7.0	1177	-0.0157	0.04
7.5	1940	-0.0258	0.06
8.0	3200	-0.0426	0.10
8.5	5430	-0.0724	0.15
9.0	8950	-0.119	0.24
9.5	14770	-0.197	0.37
10.0	24000	-0.319	0.52
10.5	39800	-0.530	0.70
11.0	64600	-0.860	0.86
11.5	110,000	-1.46	0.96
12.0	178,000	-2.37	1.00

TABLE 12

RESULTS OF THE CALCULATION OF THE RELATIVE FREQUENCY OF CRYSTALLIZATION OF $Pd(C_6H_9N_2O_2)_2$ VERSUS TIME

Time (min.)	exp(-at)	1 - P	Relative frequency of crystallization
7.0	1177	0.96	9.5
7.5	1940	0.94	15.3
8.0	3200	0.90	24.1
8.5	5430	0.85	38.7
9.0	8950	0.76	57.1
9.5	14770	0.63	78.0
10.0	24000	0.48	96.8
10.5	39800	0.30	100.0
11.0	64600	0.14	76.0
11.5	110,000	0.04	37.0
12.0	178,000	0.004	6.0

TABLE 13

RESULTS OF THE CALCULATION OF THE NUCLEATION RATE OF $Pd(C_6H_9N_2O_2)_2$ VERSUS TIME

Reaction time (minutes)	Nucleation Rate (cm^{-3} sec^{-1})
7.5	6.7×10^5
8.5	18.8×10^5
9.0	25.6×10^5
9.5	39.2×10^5

TABLE 14

RESULTS OF DROPLET EXPERIMENTS ON THE NUCLEATION OF $Ni(C_6H_9N_2O_2)_2$

Reaction time (minutes)	Average drop diameters and numbers of new crystals			
	10 μ	20 μ	30 μ	40 μ
3.5		3	10	7
4.0		11	18	10
4.5		11	21	14
5.0		13	20	18
5.5		14	21	9
6.0	4	12	19	5
6.5	5	21	17	3
7.0	4	19	15	
7.5	7	22	19	
8.0	6	23	14	
8.5	15	20	13	
9.0	20	17	5	
9.5	15	14		
10.0	17	10		
10.5	21			
11.0	12			
11.5	9			
Totals:	135	210	192	66
M.C.T.: (min.)	9.2	7.0	5.7	4.6

FIGURE 13. Median Crystallization Time Versus Log Drop Diameter for $Ni(C_6H_9N_2O_2)_2$

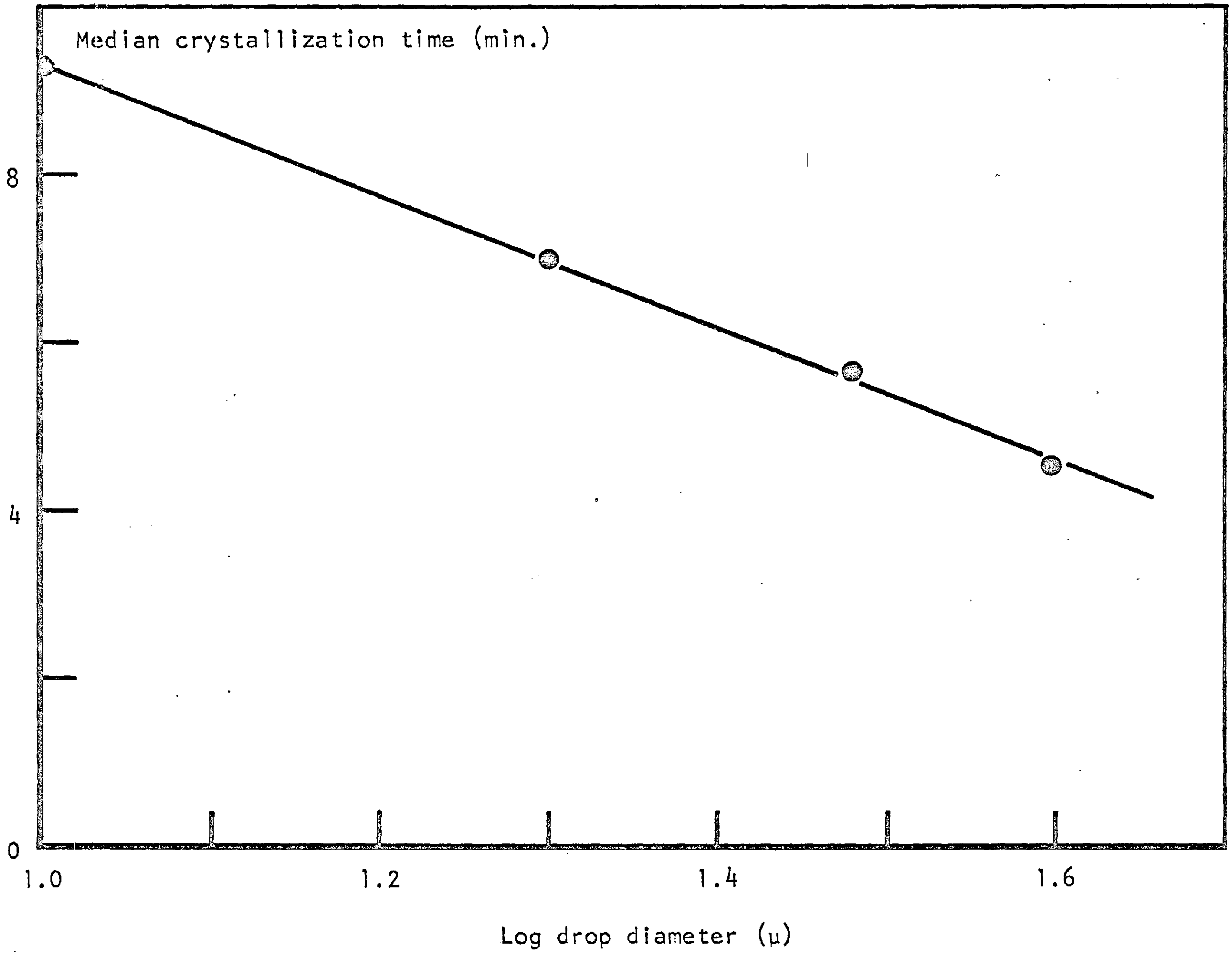

Median crystallization time (min.)
8
4
0
1.0
1.2
1.4
1.6
Log drop diameter (μ)

TABLE 15

RESULTS OF THE CALCULATIONS TO REDUCE EXPERIMENTAL DATA ON $Ni(C_6H_9N_2O_2)_2$ TO STANDARD DROPLET SIZE OF 20 μ IN DIAMETER

Reaction time (minutes)	Adjusted distributions 10 μ	20 μ	30 μ	40 μ	Totals	Relative frequency of crystallization
3.5		3			3	4.0
4.0	4	11			15	20.2
4.5	5	11			16	21.6
5.0	4	13	10		27	36.4
5.5	7	14	18		39	52.6
6.0	6	12	21	7	46	62.0
6.5	15	21	20	10	66	89.0
7.0	20	19	21	14	74	100.0
7.5	15	22	19	18	74	100.0
8.0	17	23	17	9	66	89.0
8.5	21	20	15	5	61	82.4
9.0	12	17	19	3	51	68.9
9.5	9	14	14		37	50.0
10.0		10	13		23	31.1
10.5			5		5	6.7

FIGURE 14. <u>Relative Frequency of Crystallization</u> Versus <u>Reaction Time</u> for Ni$(C_6H_9N_2O_2)_2$

Standard droplet diameter = 20 μ

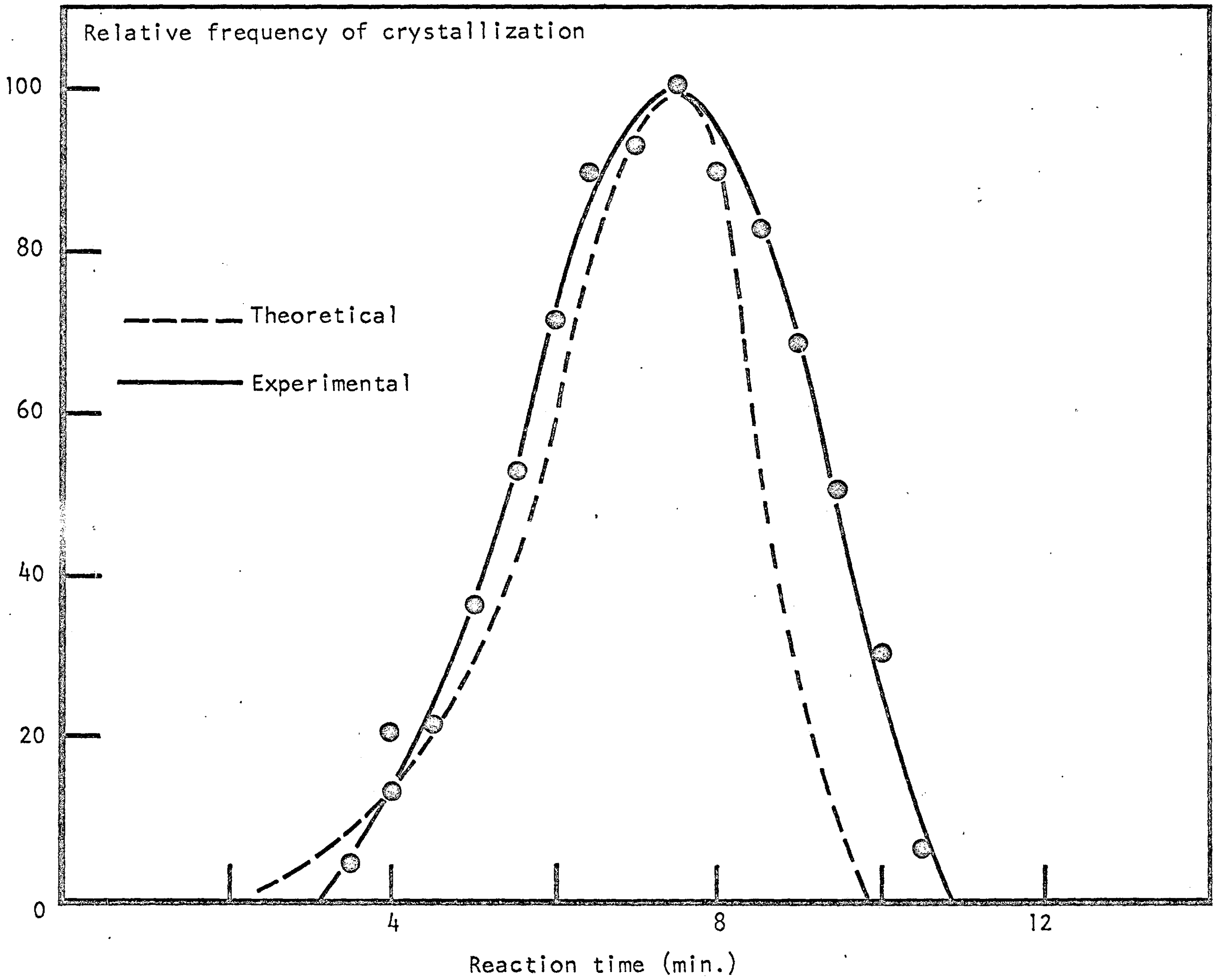

Relative frequency of crystallization
100
80
60
40
20
0
Theoretical
Experimental
4
8
12
Reaction time (min.)

FIGURE 15. <u>Probability of Crystallization</u> Versus <u>Reaction Time</u> for Ni$(C_6H_9N_2O_2)_2$

Standard droplet diameter = 20 μ

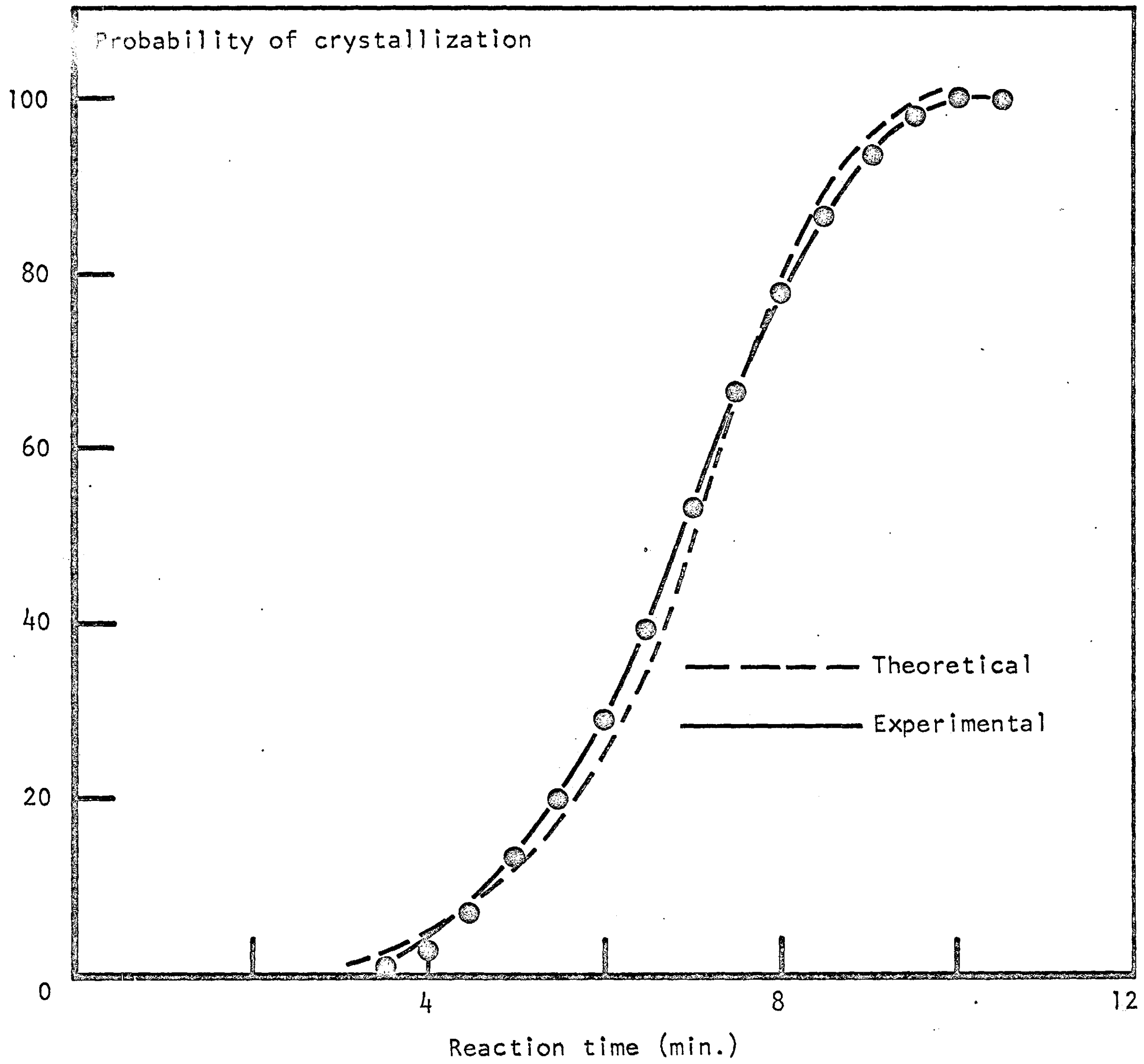

Probability of crystallization
100
80
60
40
20
0
4
8
12
Reaction time (min.)
Theoretical
Experimental

TABLE 16

RESULTS OF THE CALCULATION OF THE PROBABILITY OF CRYSTALLIZATION OF $Ni(C_6H_9N_2O_2)_2$ VERSUS TIME

Time (min.)	exp(-at) - 1	log (1 - P)	P
3.0	12.7	-0.0084	0.02
3.5	20.1	-0.0133	0.03
4.0	31.7	-0.0209	0.05
4.5	49.1	-0.0325	0.07
5.0	76.6	-0.0506	0.11
5.5	119	-0.0787	0.17
6.0	185	-0.122	0.25
6.5	287	-0.190	0.36
7.0	445	-0.294	0.49
7.5	690	-0.456	0.65
8.0	1070	-0.707	0.80
8.5	1660	-1.10	0.92
9.0	2570	-1.70	0.98
9.5	3890	-2.57	0.997

TABLE 17

RESULTS OF THE CALCULATION OF THE RELATIVE FREQUENCY OF CRYSTALLIZATION OF $Ni(C_6H_9N_2O_2)_2$ VERSUS TIME

Time (min.)	exp(-at)	1 - P	Relative frequency of crystallization
3.0	13.7	0.980	5.6
3.5	21.1	0.970	8.5
4.0	32.7	0.953	12.9
4.5	50.1	0.926	19.2
5.0	77.6	0.890	28.5
5.5	120	0.833	41.3
6.0	186	0.755	58.0
6.5	288	0.645	76.8
7.0	446	0.508	93.7
7.5	691	0.350	100.0
8.0	1070	0.196	86.8
8.5	1660	0.079	54.1
9.0	2570	0.020	21.2
9.5	3890	0.003	4.3

TABLE 18

RESULTS OF THE CALCULATION OF THE NUCLEATION RATE OF $Ni(C_6H_9N_2O_2)_2$ VERSUS TIME

Reaction time (minutes)	Nucleation Rate (cm^{-3} sec^{-1})
4	2.74×10^5
5	4.96×10^5
6	7.93×10^5
7	10.3×10^5
8	7.82×10^5

TABLE 19

RESULTS OF DROPLET EXPERIMENTS ON THE NUCLEATION OF $Ni(C_7H_{11}N_2O_2)_2$

Reaction time (minutes)	Average drop diameters and numbers of new crystals				
	17.5 μ	26.2 μ	35.0 μ	43.7 μ	52.5 μ
3.0					
4			2	1	4
5		1	2	4	5
6	1	1	13	14	4
7	1	4	14	12	6
8	3	7	12	13	3
9	2	6	14	2	
10	5	7	10	1	
11	8	4	6		
12	7	3			
13	2				
Totals:	29	33	73	47	22
M.C.T.: (min.)	10.3	8.6	7.5	6.4	5.5

FIGURE 16. Median Crystallization Time Versus Log Drop Diameter for $Ni(C_7H_{11}N_2O_2)_2$

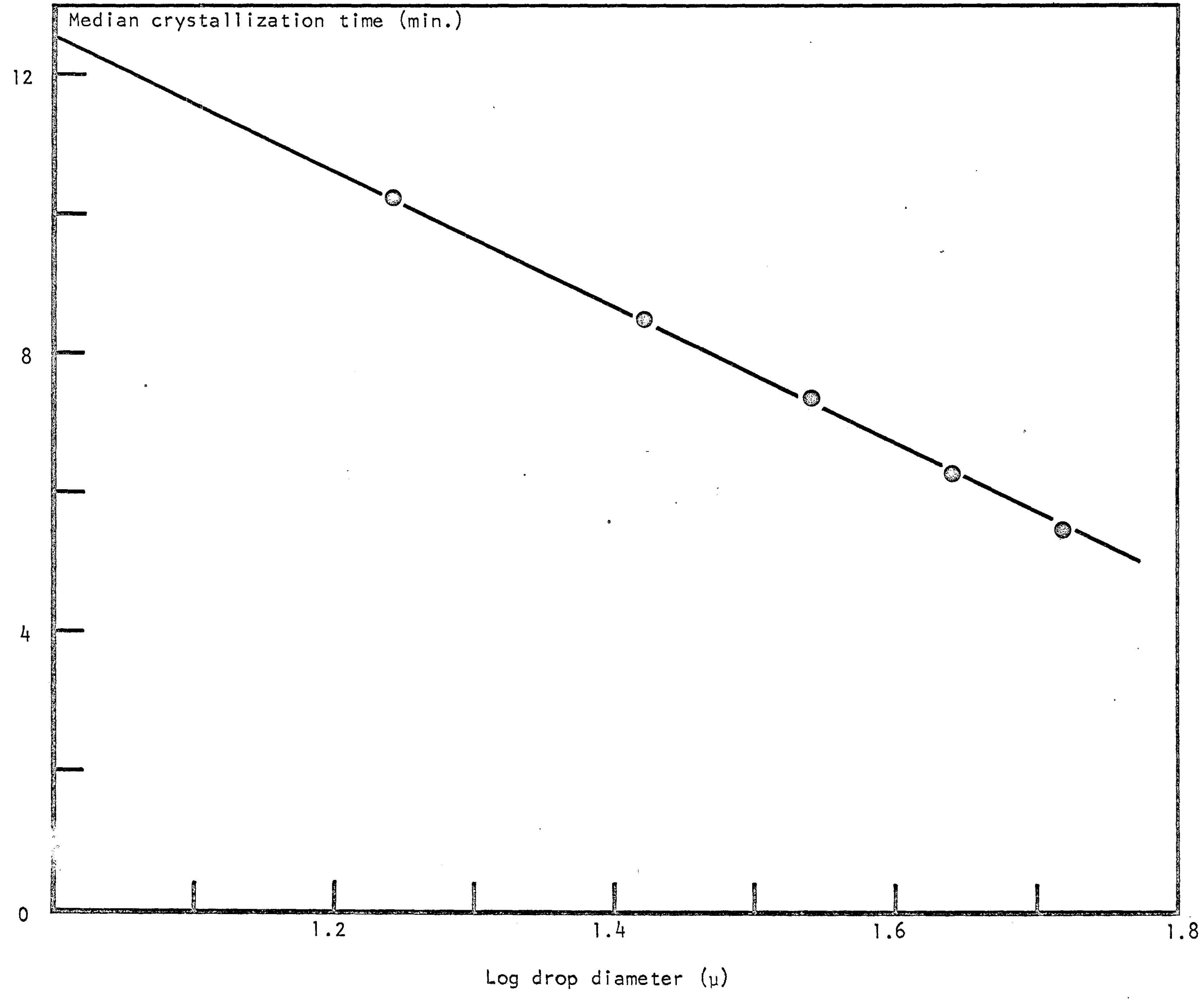

Median crystallization time (min.)
12
8
4
0
1.2
1.4
1.6
1.8
Log drop diameter (μ)

TABLE 20

RESULTS OF THE CALCULATIONS TO REDUCE EXPERIMENTAL DATA ON $Ni(C_7H_{11}N_2O_2)_2$ TO STANDARD DROPLET SIZE OF 35 μ IN DIAMETER

Reaction time (minutes)	Adjusted distributions					Totals	Relative frequency of crystallization
	17.5 μ	26.2 μ	35.0 μ	43.7 μ	52.5 μ		
3	1					1	2.1
4	1	1	2			4	8.5
5	3	1	2	1		7	14.9
6	2	4	13	4	4	27	57.4
7	5	7	14	14	5	45	95.7
8	8	6	12	12	4	42	89.3
9	7	7	14	13	6	47	100.0
10	2	4	10	2	3	21	44.6
11		3	6	1		10	21.2

FIGURE 17. <u>Relative Frequency of Crystallization</u> Versus <u>Reaction Time</u> for Ni$(C_7H_{11}N_2O_2)_2$

Standard droplet diameter = 35 μ

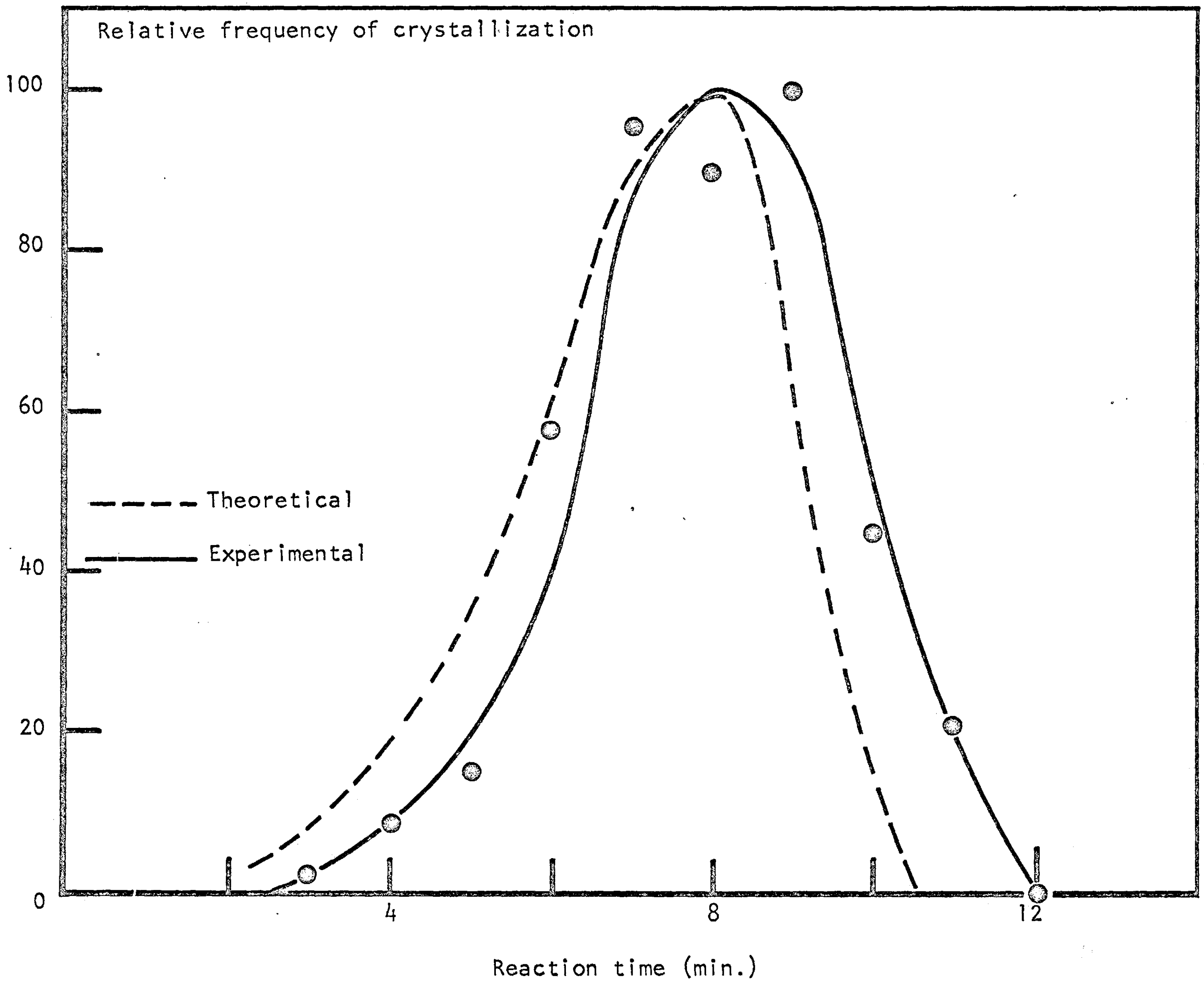

Relative frequency of crystallization
100
80
60
40
20
0
Theoretical
Experimental
4
8
12
Reaction time (min.)

FIGURE 18. <u>Probability of Crystallization</u> Versus <u>Reaction Time</u> for $Ni(C_7H_{11}N_2O_2)_2$

Standard droplet diameter = 35 μ

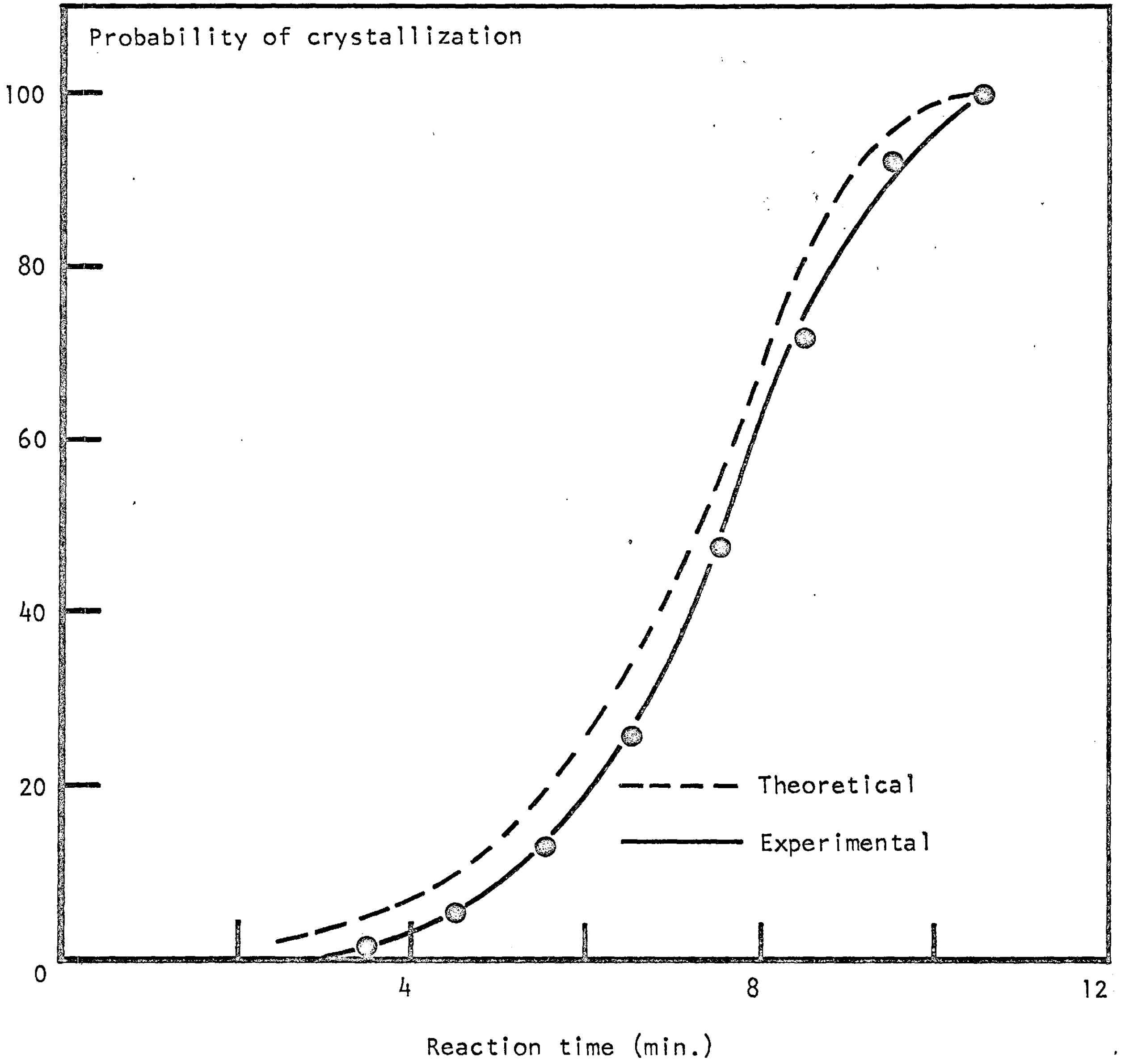

Probability of crystallization
100
80
60
40
20
0
4
8
12
Reaction time (min.)
Theoretical
Experimental

TABLE 21

RESULTS OF THE CALCULATION OF THE PROBABILITY OF CRYSTALLIZATION OF $Ni(C_7H_{11}N_2O_2)_2$ VERSUS TIME

Time (min.)	exp(-at) - 1	log (1 - P)	P
3	7.13	-0.014	.03
4	15.2	-0.029	.07
5	31.7	-0.062	.13
6	65	-0.126	.25
7	131	-0.255	.44
8	262	-0.510	.69
9	536	-1.04	.91
10	1070	-2.08	.99

TABLE 22

RESULTS OF THE CALCULATION OF THE RELATIVE FREQUENCY OF CRYSTALLIZATION OF $Ni(C_7H_{11}N_2O_2)_2$ VERSUS TIME

Time (min.)	exp(-at)	1 - P	Relative frequency of crystallization
3	8.1	0.97	9.8
4	16.2	0.93	18.5
5	32.7	0.87	35.0
6	66.0	0.75	60.8
7	132	0.56	91.0
8	263	0.31	100.0
9	537	0.09	59.3
10	1070	0.01	13.2

TABLE 23

RESULTS OF THE CALCULATION OF THE NUCLEATION RATE OF $Ni(C_7H_{11}N_2O_2)_2$ VERSUS TIME

Reaction time (minutes)	Nucleation rate ($cm^{-3}sec^{-1}$)
4	2.92×10^4
5	5.91×10^4
6	9.10×10^4
7	14.1×10^4
8	18.5×10^4

TABLE 24

VALUES OF m, c, a AND b FOR THE Ni(II) AND Pd(II) CHELATES

Compound	m	c	a	b
$Pd(C_7H_{11}N_2O_2)_2$	-7.1	16.3	-0.98	15.3
$Pd(C_6H_9N_2O_2)_2$	-6.8	18.0	-1.01	17.5
$Ni(C_6H_9N_2O_2)_2$	-7.9	17.3	-0.87	14.5
$Ni(C_7H_{11}N_2O_2)_2$	-9.8	22.4	-0.70	15.1

FIGURE 19. <u>Monomer Concentration</u> Versus <u>Reaction Time</u> for $Pd(C_7H_{11}N_2O_2)_2$

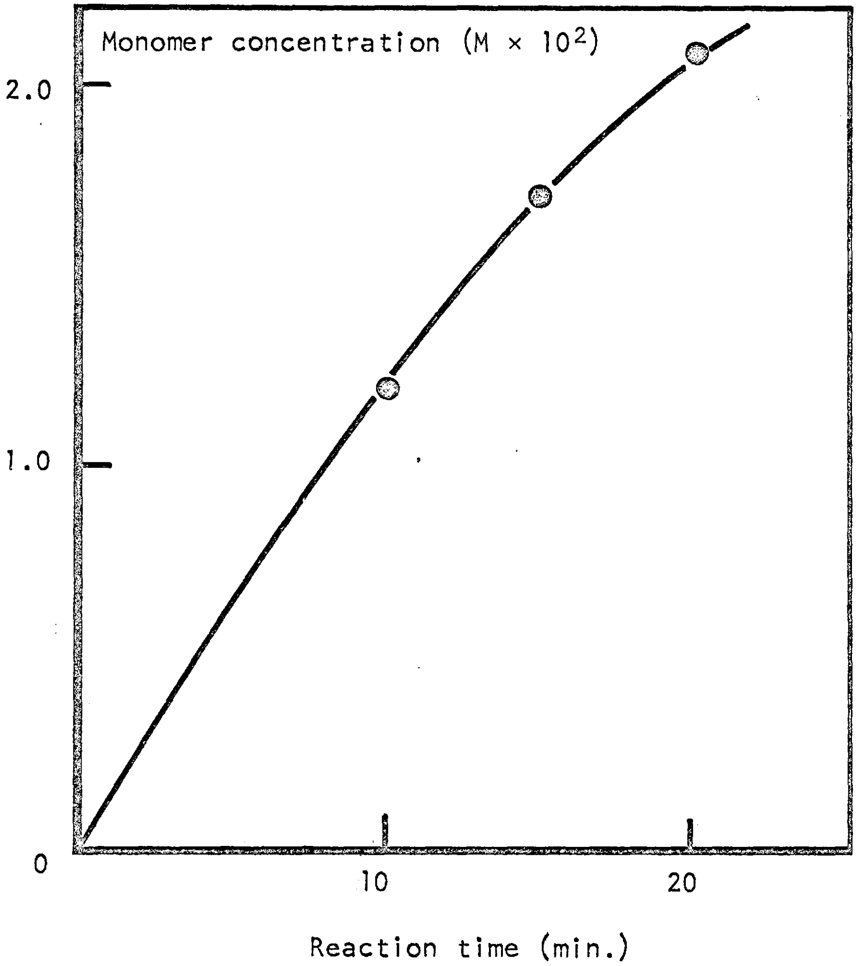

Monomer concentration (M × 10²)
2.0
1.0
0
10
20
Reaction time (min.)

FIGURE 20. Monomer Concentration Versus Reaction Time for $Pd(C_6H_9N_2O_2)_2$

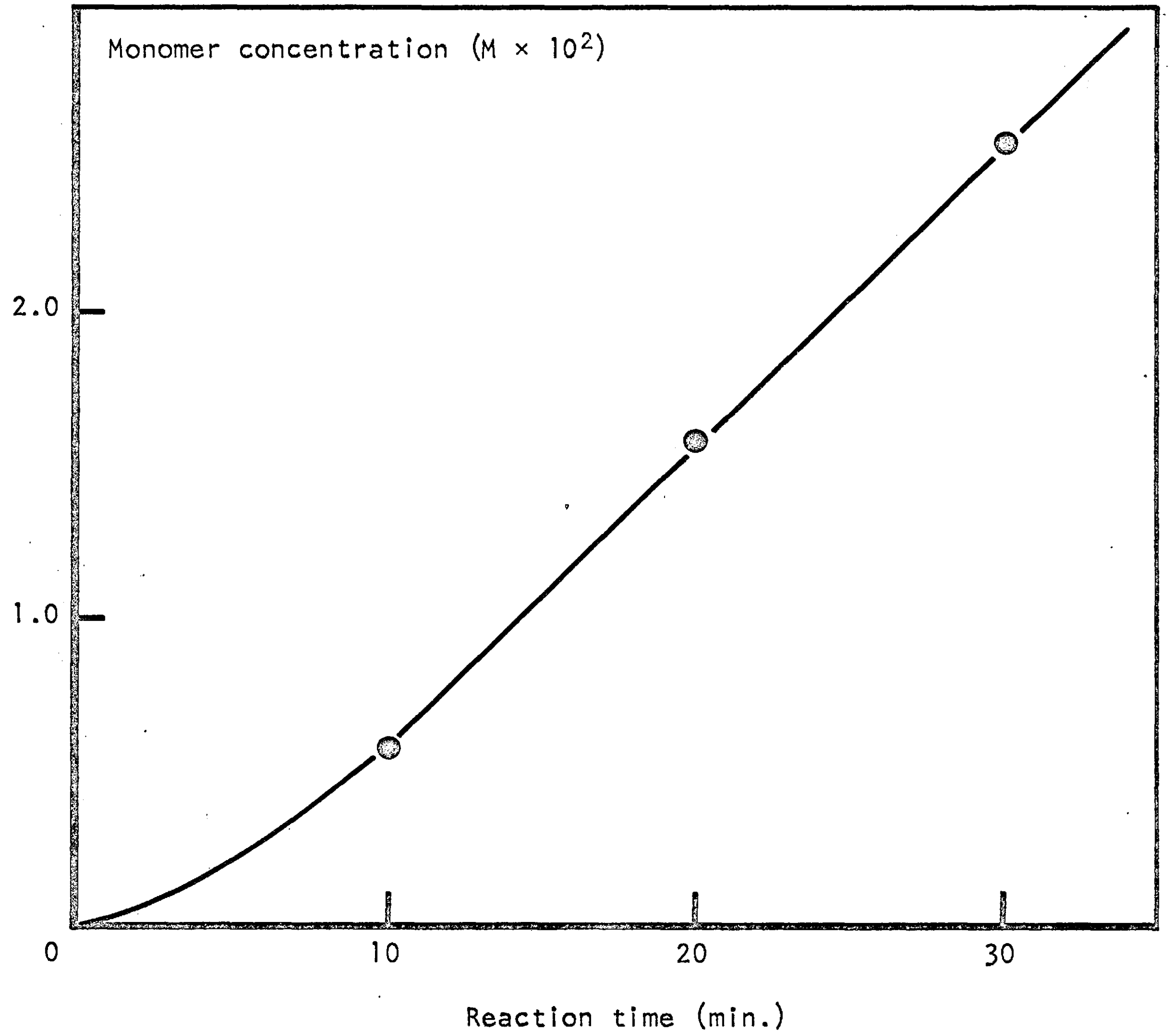
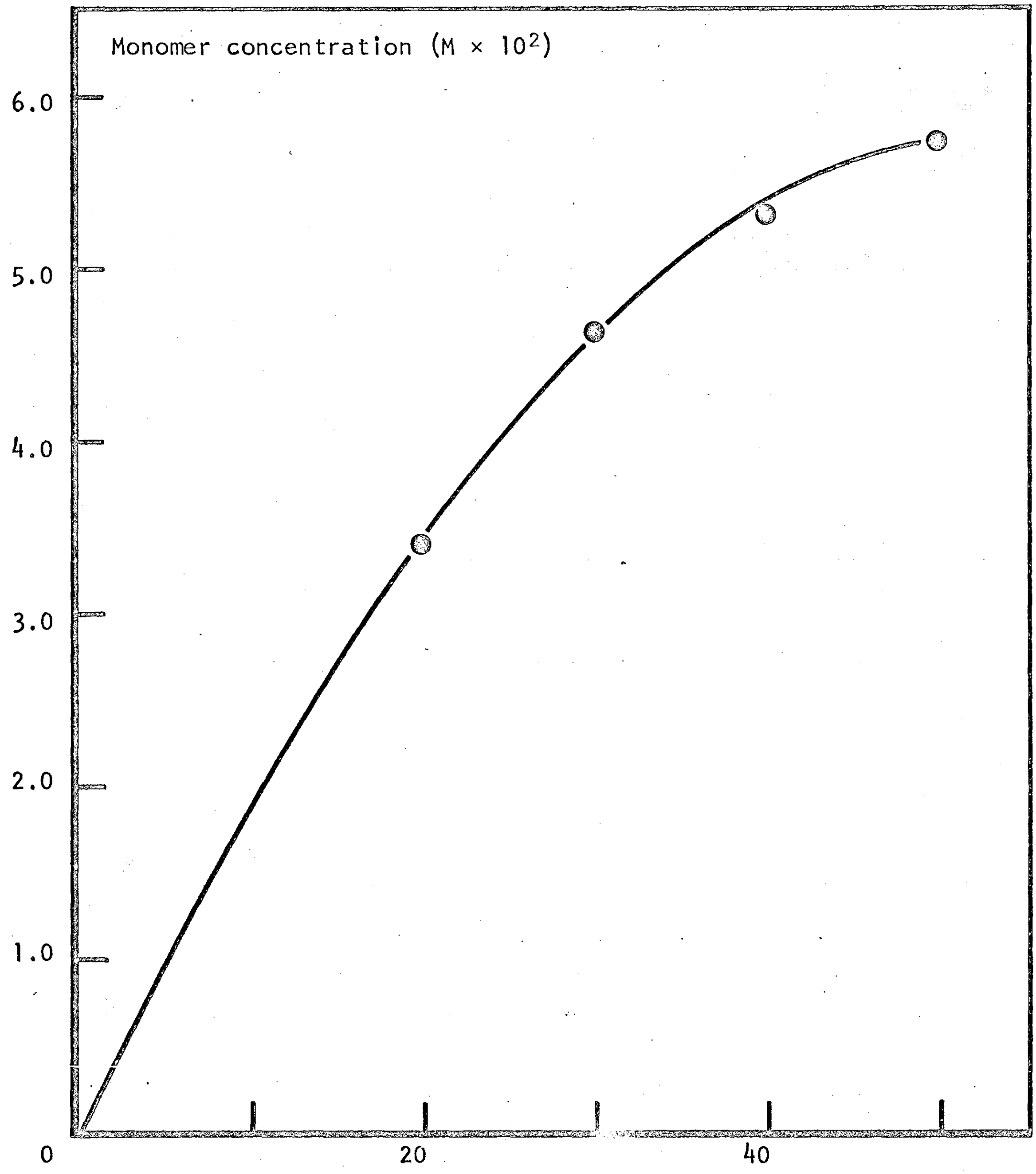

Monomer concentration (M × 10²)
2.0
1.0
0
10
20
30
Reaction time (min.)

FIGURE 21. Monomer Concentration Versus Reaction Time for $Ni(C_6H_9N_2O_2)_2$



Reaction time (min.)

FIGURE 22. Monomer Concentration Versus Reaction Time for $Ni(C_7H_{11}N_2O_2)_2$

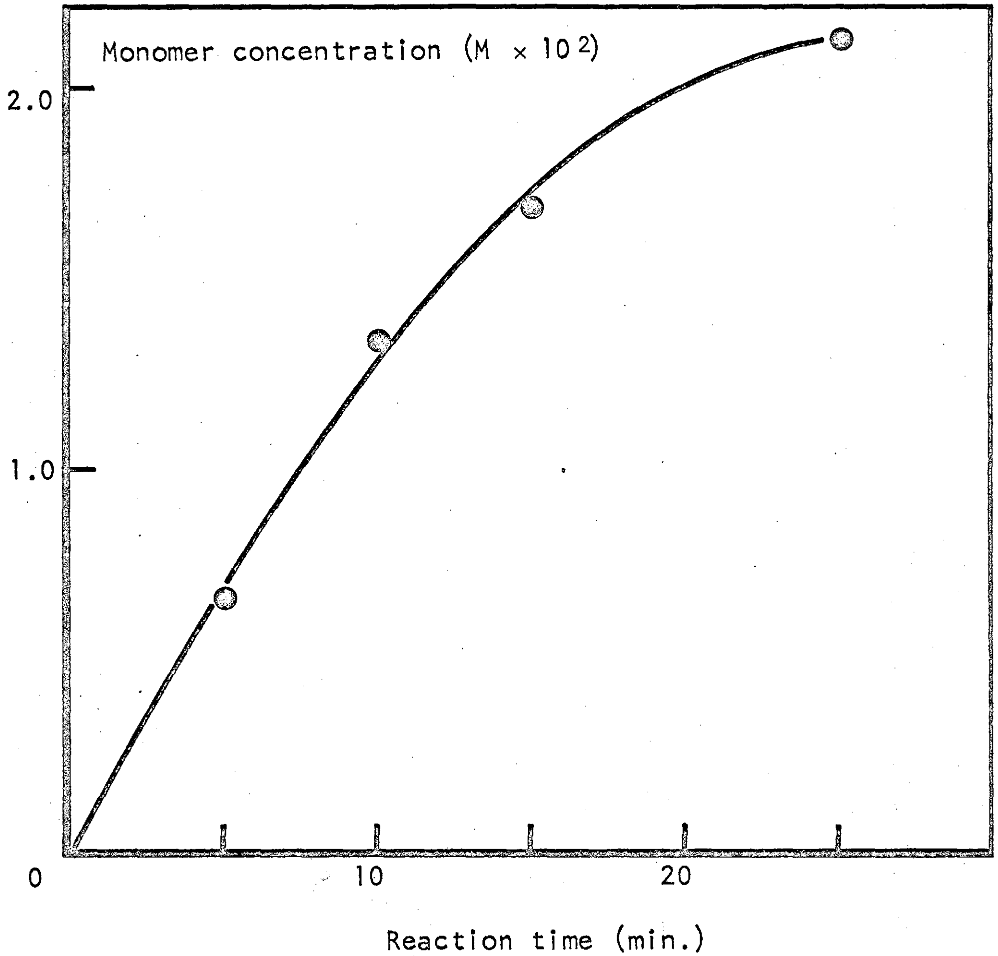

Monomer concentration (M × 10 2)
2.0
1.0
0
10
20
Reaction time (min.)

TABLE 25

RESULTS OF THE CALCULATION OF PARAMETERS FOR THE Ni(II) AND Pd(II) CHELATES, ASSUMING LOG A = 30 cm^{-3} sec^{-1}

Compound	Solubility[a] (M)	S	γ (ergs cm^{-2})	r* (Å)	n*
$Pd(C_7H_{11}N_2O_2)_2$	3.5×10^{-4}	21	23	16	38
$Pd(C_6H_9N_2O_2)_2$[b]	2.3×10^{-5}	249	36	12	19
$Ni(C_6H_9N_2O_2)_2$	1.7×10^{-4}	88	34	12	25
$Ni(C_7H_{11}N_2O_2)_2$	2.4×10^{-4}	46	29	14	30

---

[a] See Table 3 for reaction conditions.

[b] In a short communication[37] on the nucleation of $Pd(C_6H_9N_2O_2)_2$, the values of S, γ and r* were given as 1000, 47 ergs cm^{-2} and 11 Å, respectively. These values were based on a solubility of 1×10^{-5} M, which was determined spectrophotometrically, and a median crystallization time of 11.5 minutes, which was determined by a method different from the one employed here. The present values were adopted because they were considered more reliable.

$$\log J = \log A - \frac{16\pi\ \gamma^3 \nu^2}{3\ (2.3kT)^3 (\log S)^2} \tag{16}$$

that a plot of log J versus $(\log S)^{-2}$ should yield a straight line with an intercept equal to log A. The results of such plots for the four compounds studied are shown in Figures 23 through 26.

From the intercepts and the slopes of the lines obtained, the values of log A, γ, n^* and r^* were calculated. The results are shown in Table 26. It can be seen that there are large discrepancies between the nucleation parameters of Table 25 and those of Table 26. Since the experimental values of log A were more than 20 orders of magnitude lower than the theoretical values, the use of the latter in calculating the values of Table 25 should be seriously questioned.

The method of calculation which yielded the values of Table 26 was more reasonable, but the unusually low magnitudes of the values obtained indicate that they, too, are questionable. The reason for this is that, although the straight line obtained supports the functional relationship found in equation (16), it does not necessarily imply that the presently accepted mathematical expression for ΔG_n^* is correct. As mentioned in the Introduction, the correct method of calculating ΔG_n^* is being debated at the present time. Also, it was mentioned that similar discrepancies between the theoretical and experimental values of A have been reported by Dunning et al[24,25] and by Melia and Moffitt[23]. Dunning has attributed the discrepancy to the large entropy change which occurs during the phase transformation. This entropy change has been neglected in the calculation of ΔG_n^*. A similar argument can be employed to explain the results of the present studies since, due to the structural complexity

FIGURE 23. <u>Log J</u> Versus <u>$(\text{Log S})^{-2}$</u> for $Pd(C_7H_{11}N_2O_2)_2$

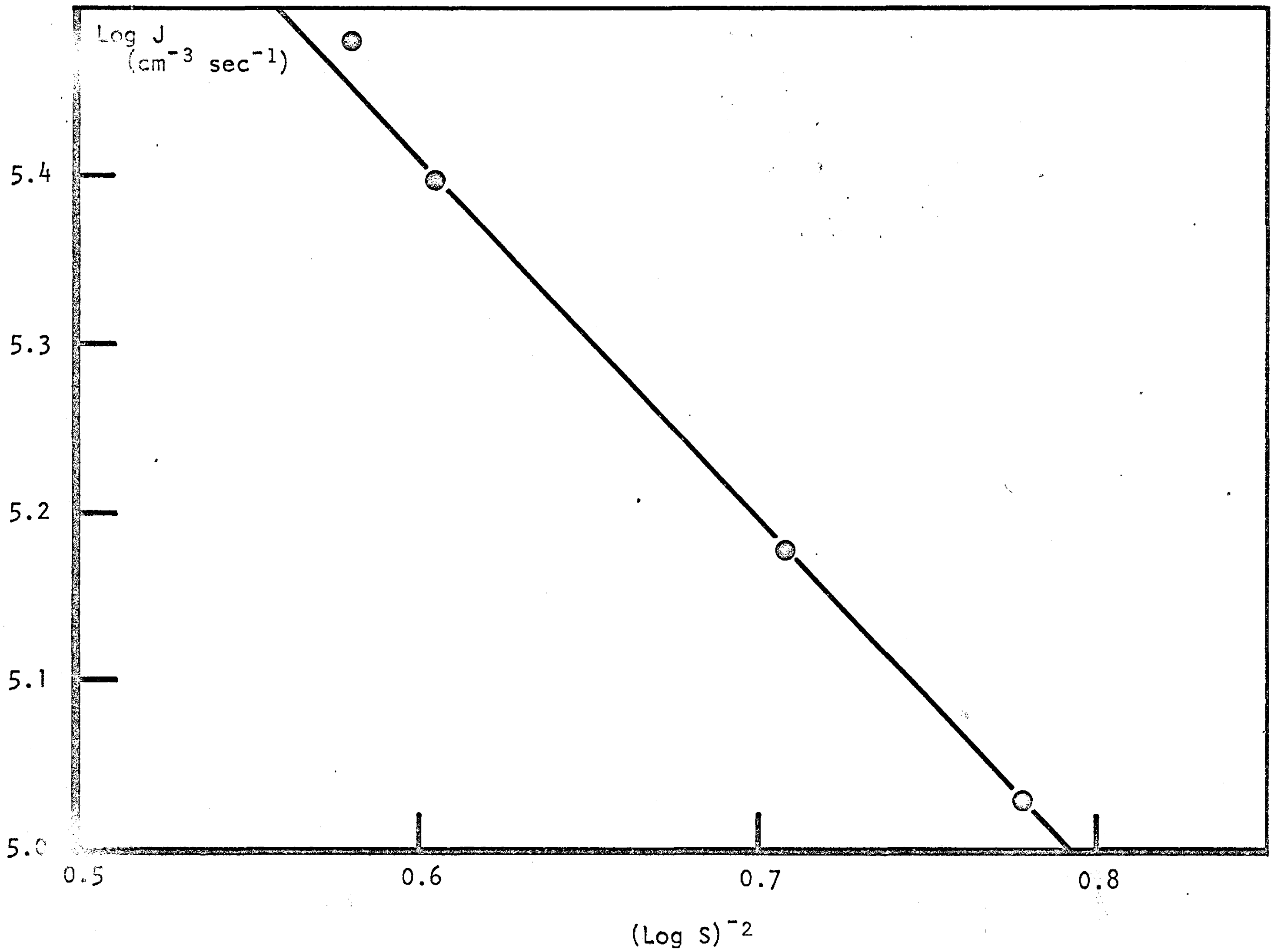

Log J
(cm^{-3} sec^{-1})
5.4
5.3
5.2
5.1
5.0
0.5
0.6
0.7
0.8
(Log S)$^{-2}$

FIGURE 24. Log J Versus $(\text{Log S})^{-2}$ for $Pd(C_6H_9N_2O_2)_2$

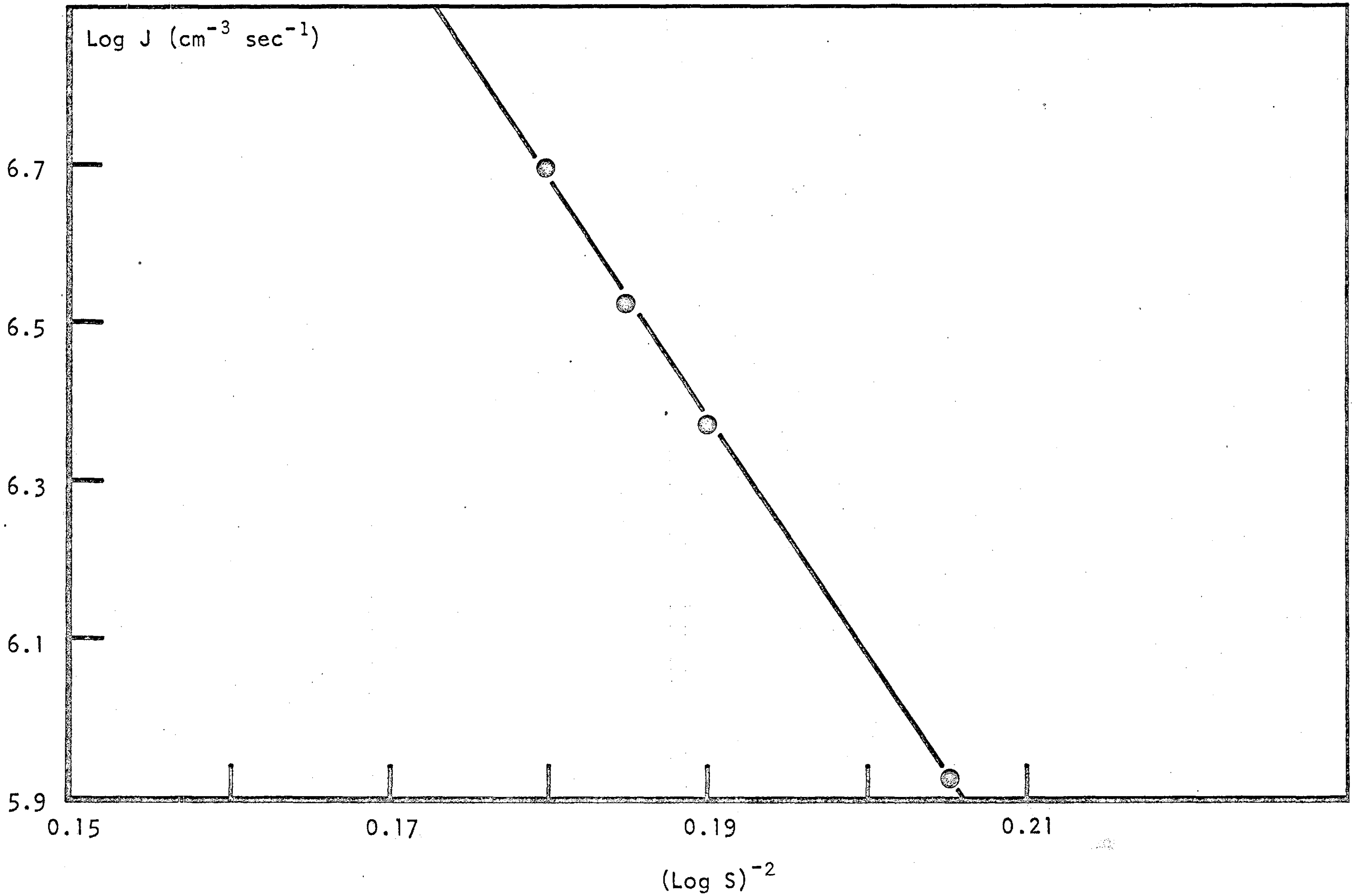

Log J (cm^{-3} sec^{-1})
6.7
6.5
6.3
6.1
5.9
0.15
0.17
0.19
0.21
(Log S)$^{-2}$

FIGURE 25. Log J Versus $(\text{Log } S)^{-2}$ for $Ni(C_6H_9N_2O_2)_2$

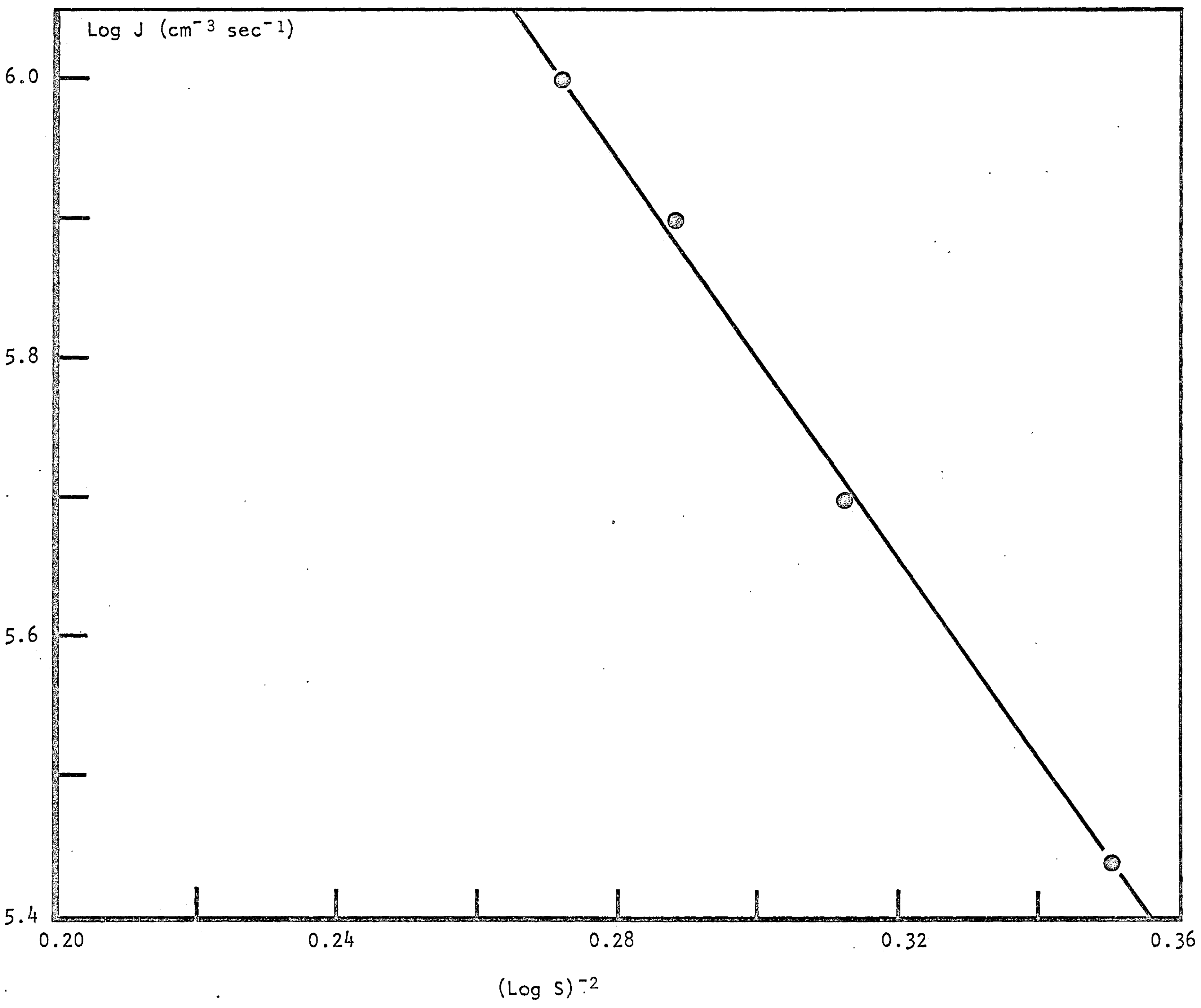

Log J (cm^{-3} sec^{-1})
6.0
5.8
5.6
5.4
0.20
0.24
0.28
0.32
0.36
(Log S)$^{-2}$

FIGURE 26. Log J Versus (Log S)$^{-2}$ for Ni$(C_7H_{11}N_2O_2)_2$

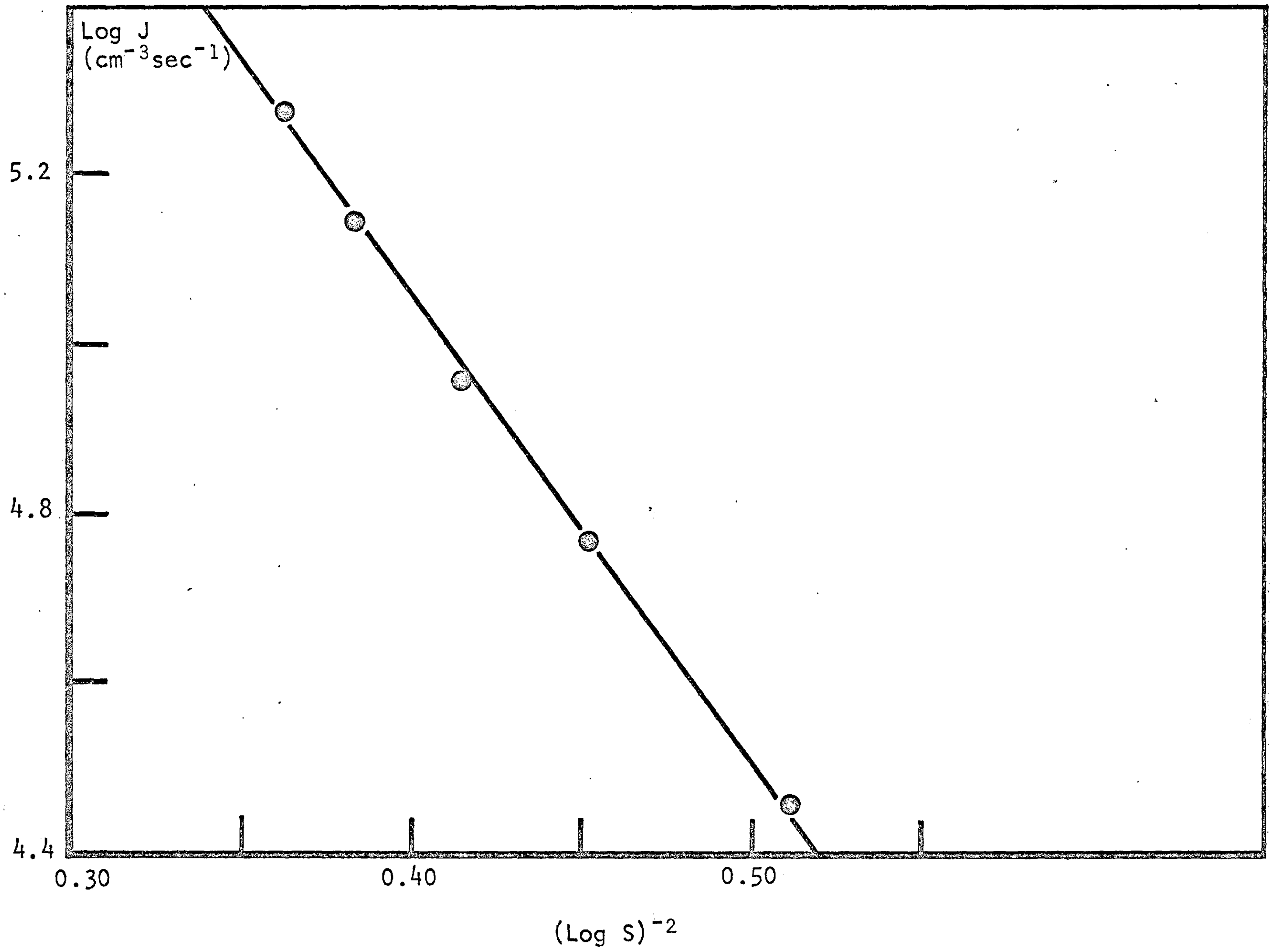

Log J
(cm^{-3}sec^{-1})
5.2
4.8
4.4
0.30
0.40
0.50
(Log S)$^{-2}$

TABLE 26

EXPERIMENTAL VALUES OF A, γ, r* AND n* FOR THE Ni(II) and Pd(II) CHELATES

Compound	Log A	γ (ergs cm^{-2})	r* (Å)	n*
$Pd(C_7H_{11}N_2O_2)_2$	6.7	8.6	6	2
$Pd(C_6H_9N_2O_2)_2$	12.0	17.1	6	2
$Ni(C_6H_9N_2O_2)_2$	8.0	14.6	5	2
$Ni(C_7H_{11}N_2O_2)_2$	7.3	12.8	6	2

of the compounds studied, the activation of the molecules for interface transfer must be accompanied by a large entropy decrease.

IV.C. Studies on the Nucleation from Solution of Some Soluble Inorganic Salts

During the course of the preliminary investigation it was observed that droplets of distilled water dispersed in silicone oil gradually decreased in volume and finally disappeared. At the time this was objectionable; consequently, all subsequent work was carried out with mineral oils. Later it was thought that this contraction of the droplets could be used as the basis of a new method of producing supersaturation in droplets.

To test the idea a saturated solution of potassium dichromate was dispersed in silicone oil as described in Section III.C.2. The Nessler cup was then placed in a desiccator containing phosphorus pentoxide. Periodically, the dispersion was removed from the desiccator and photomicrographs were taken. Polarizers were found to be unnecessary for the detection of crystallization and were not employed. As expected, the droplets gradually decreased in volume and finally crystallized.

The type of crystallization observed in these droplets appeared to be different from that observed with the metal chelates. With the latter, a small crystal suddenly appeared, usually at the edge of the droplet, and gradually increased in size. With potassium dichromate, however, the whole droplet instantly turned black at the moment of crystallization. Figure 27 shows one photograph taken immediately after the preparation of the dispersion and another taken after all the droplets

FIGURE 27. Photographs Taken During Studies on Nucleation of $K_2Cr_2O_7$:

(a) immediately after the preparation of the dispersion;

(b) after all the droplets had crystallized.

had crystallized. It can be seen in the photographs that one of the droplets exhibited the first type of crystallization described above.

The data from these experiments were collected by projecting the 35 mm slides onto a calibrated screen and measuring the diameters, d_1 and d_2, of the initial and crystallized droplets, respectively. Those data obtained with potassium dichromate are shown in Table 27.

From the data it was found that the value of d_2/d_1 was independent of the initial droplet volume. This is shown in Figure 28. For this reason, the relative frequency of crystallization as a function of d_2/d_1 was calculated without regard to droplet size. The results are shown in Table 27 and plotted in Figure 29. From this plot the probability of crystallization versus d_2/d_1 was calculated. The results are shown in Figure 30.

In order to determine the values of the nucleation rate at various levels of supersaturation it was necessary to study the rate at which the supersaturation was increasing in the droplets. Because this rate increased with decreasing droplet size, the study was carried out with droplets of average size only (135 μ in diameter). The study showed that the droplet diameter decreased linearly with time. Lines corresponding to different droplets had slightly different slopes. Therefore, the line representing the majority of the droplets was selected for analysis purposes. The plot is shown in Figure 31. This linear relationship can be expressed as

$$d = -0.0634\ t + 135. \tag{65}$$

The values of t corresponding to any value of d_2/d_1 were obtained by substituting the appropriate value of d_2 for d in equation (65). The

TABLE 27

RESULTS OF DROPLET EXPERIMENTS ON THE NUCLEATION OF POTASSIUM DICHROMATE

d_2/d_1	Number of crystallized drops	Relative frequency of crystallization
0.545-0.536	3	3.3
0.535-0.526	2	2.2
0.525-0.516	0	0
0.515-0.506	3	3.3
0.505-0.496	7	7.6
0.495-0.486	12	13.1
0.485-0.476	17	18.5
0.475-0.466	40	43.5
0.465-0.456	73	79.4
0.455-0.446	92	100.0
0.445-0.436	66	71.8
0.435-0.426	28	30.4
0.425-0.416	0	0

FIGURE 28. Median d_2/d_1 Versus Log d_1 for $K_2Cr_2O_7$

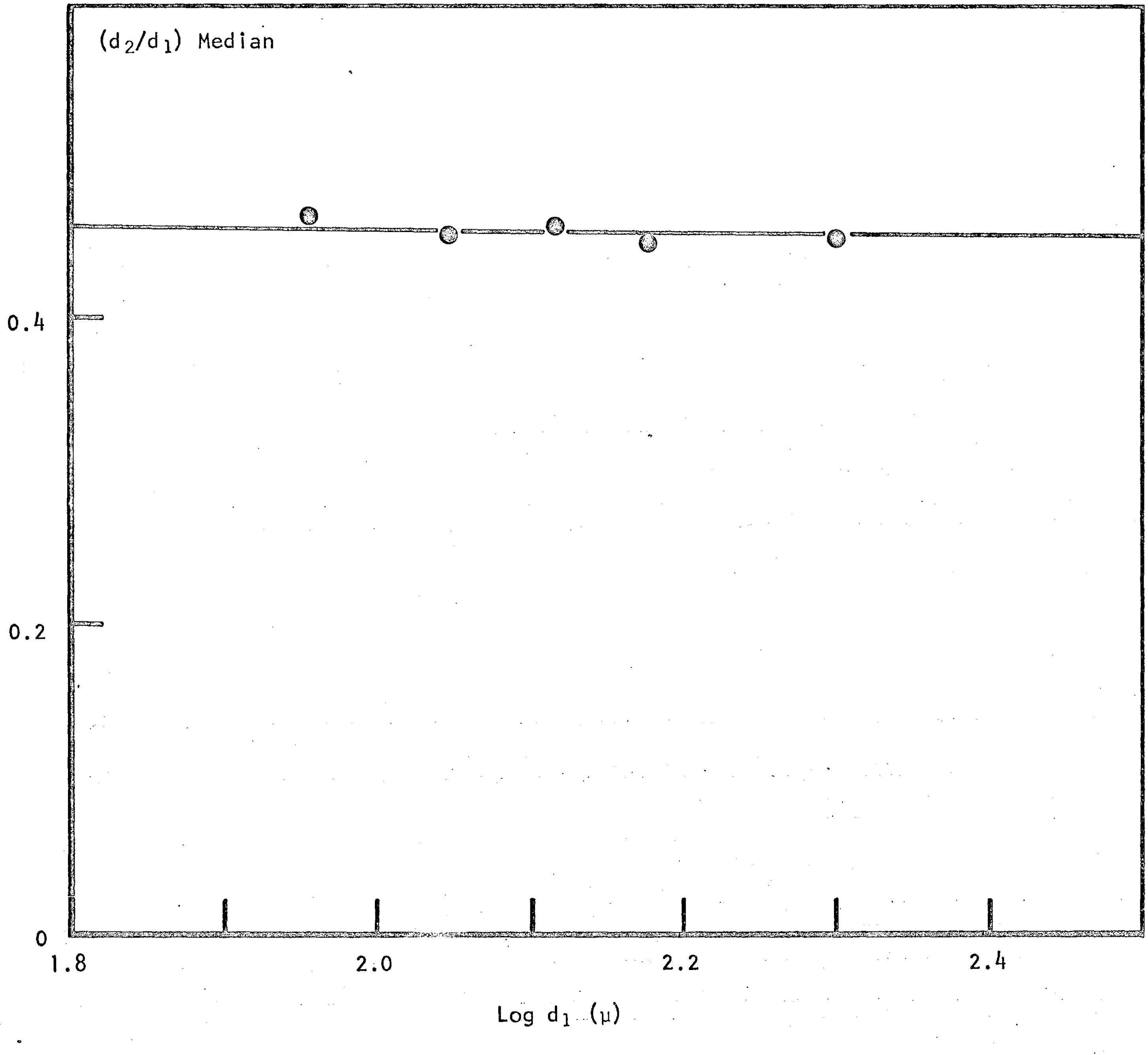

(d2/d1) Median
0.4
0.2
0
1.8
2.0
2.2
2.4
Log d1 (μ)

FIGURE 29. Relative Frequency of Crystallization Versus d_2/d_1 for $K_2Cr_2O_7$

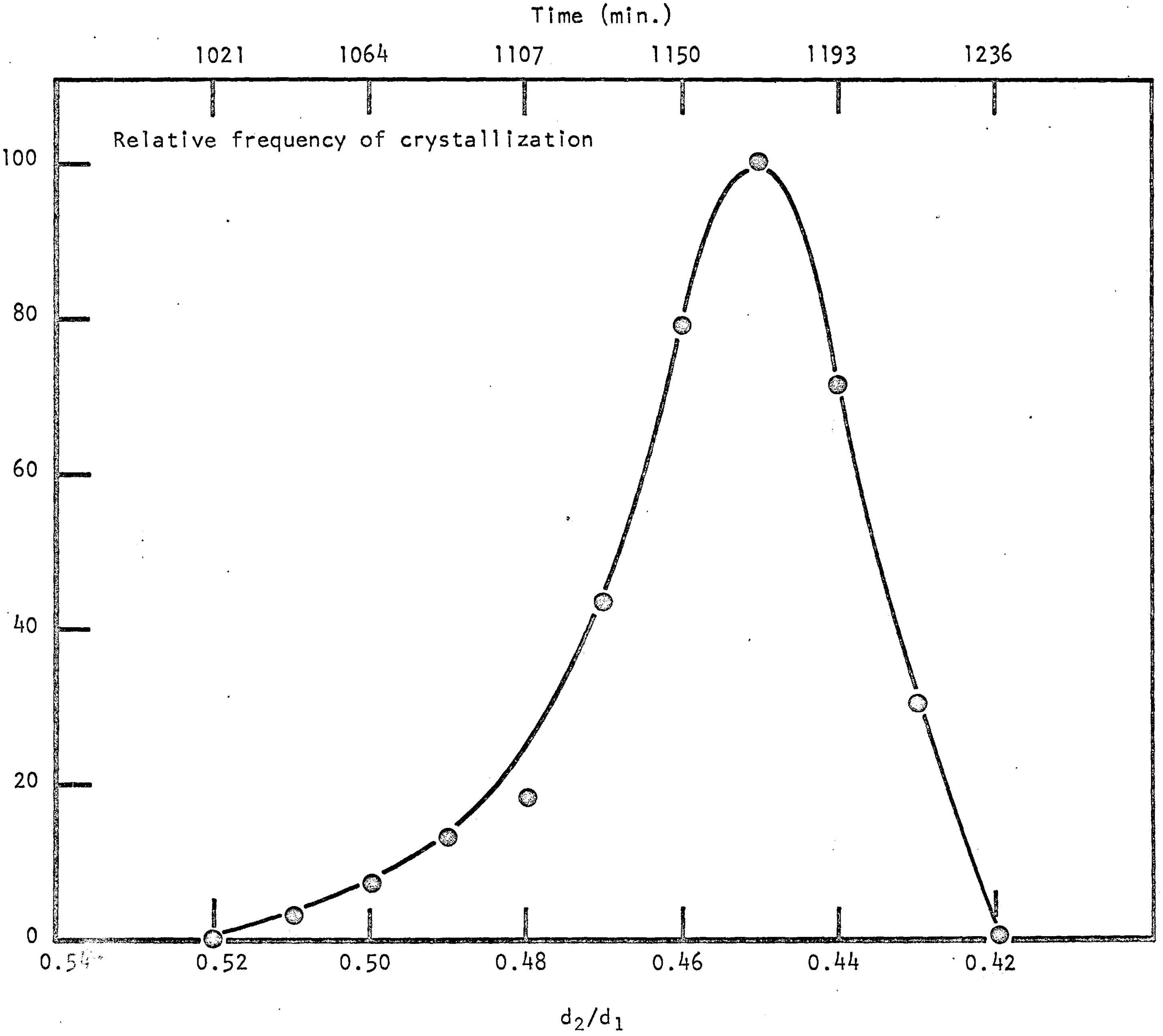
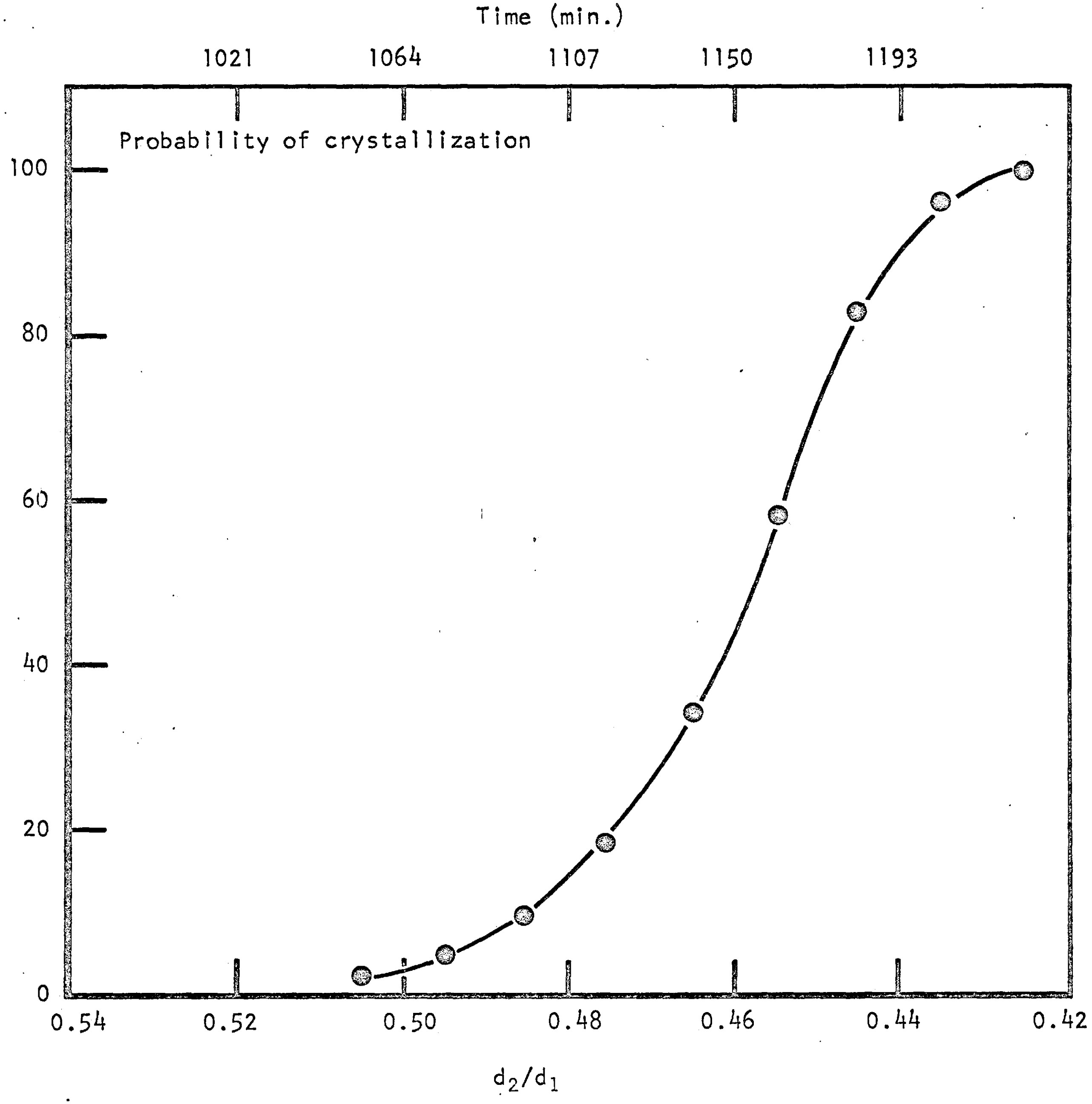
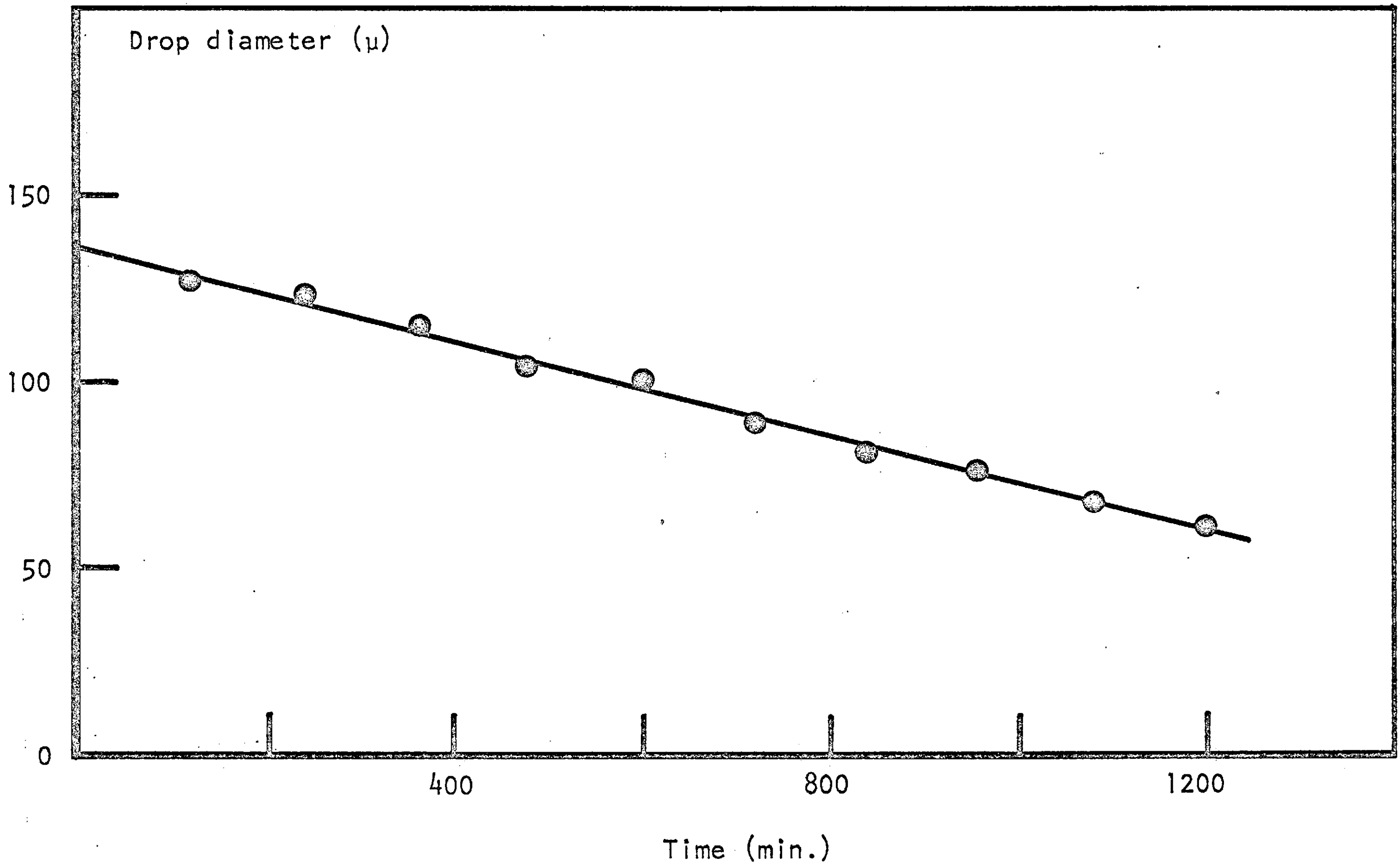

Time (min.)
1021
1064
1107
1150
1193
1236
Relative frequency of crystallization
100
80
60
40
20
0
0.54
0.52
0.50
0.48
0.46
0.44
0.42
d_2/d_1

FIGURE 30. Probability of Crystallization Versus d_2/d_1 for $K_2Cr_2O_7$



Time (min.)
1021
1064
1107
1150
1193
Probability of crystallization
100
80
60
40
20
0
0.54
0.52
0.50
0.48
0.46
0.44
0.42
d_2/d_1

FIGURE 31. Drop Diameter Versus Time for $K_2Cr_2O_7$


Drop diameter (μ)
150
100
50
0
400
800
1200
Time (min.)

results are shown in Table 28. These results enabled the d_2/d_1 axis of Figure 30 to be substituted by a time axis. The values of the nucleation rate versus time were then calculated as already described for the metal chelates. The results are shown in Table 29.

To assess the validity of the classical nucleation theory, the value of the pre-exponential term was determined as previously described for the metal chelates. With potassium dichromate, the values of S were determined with the aid of equation (56). The results of the calculations are shown in Table 29 and the plot of log J versus $(\log S)^{-2}$ is shown in Figure 32.

From the plot of Figure 32 a value of $\log A = 5.6$ was obtained. As with the metal chelates, this result is considerably lower than expected. With potassium chromate, however, this low value of the pre-exponential term is very difficult to explain on the basis of a large entropy decrease. As already mentioned, most experiments on nucleation from solution have yielded values of A of the same order of magnitude as those found in the present studies. Therefore, the evidence is now very strong that equation (16), with $A = 10^{30}$ cm^{-3} sec^{-1}, is inadequate to describe nucleation from solution.

The new method of producing supersaturation discussed above was employed in nucleation studies of several other inorganic salts. With some of these compounds it was found that contraction of the droplets did not occur unless the dispersion was heated. With others, most of the droplets crystallized as described previously for the metal chelates. This type of crystallization invariably occurred at much lower supersaturations than the instant, whole droplet crystallization observed

TABLE 28

RESULTS OF THE CALCULATIONS TO CONVERT d_2/d_1 SCALE INTO A TIME SCALE

d_2/d_1	Time (min.)
0.52	1021
0.50	1064
0.48	1107
0.46	1150
0.44	1193
0.42	1236

TABLE 29

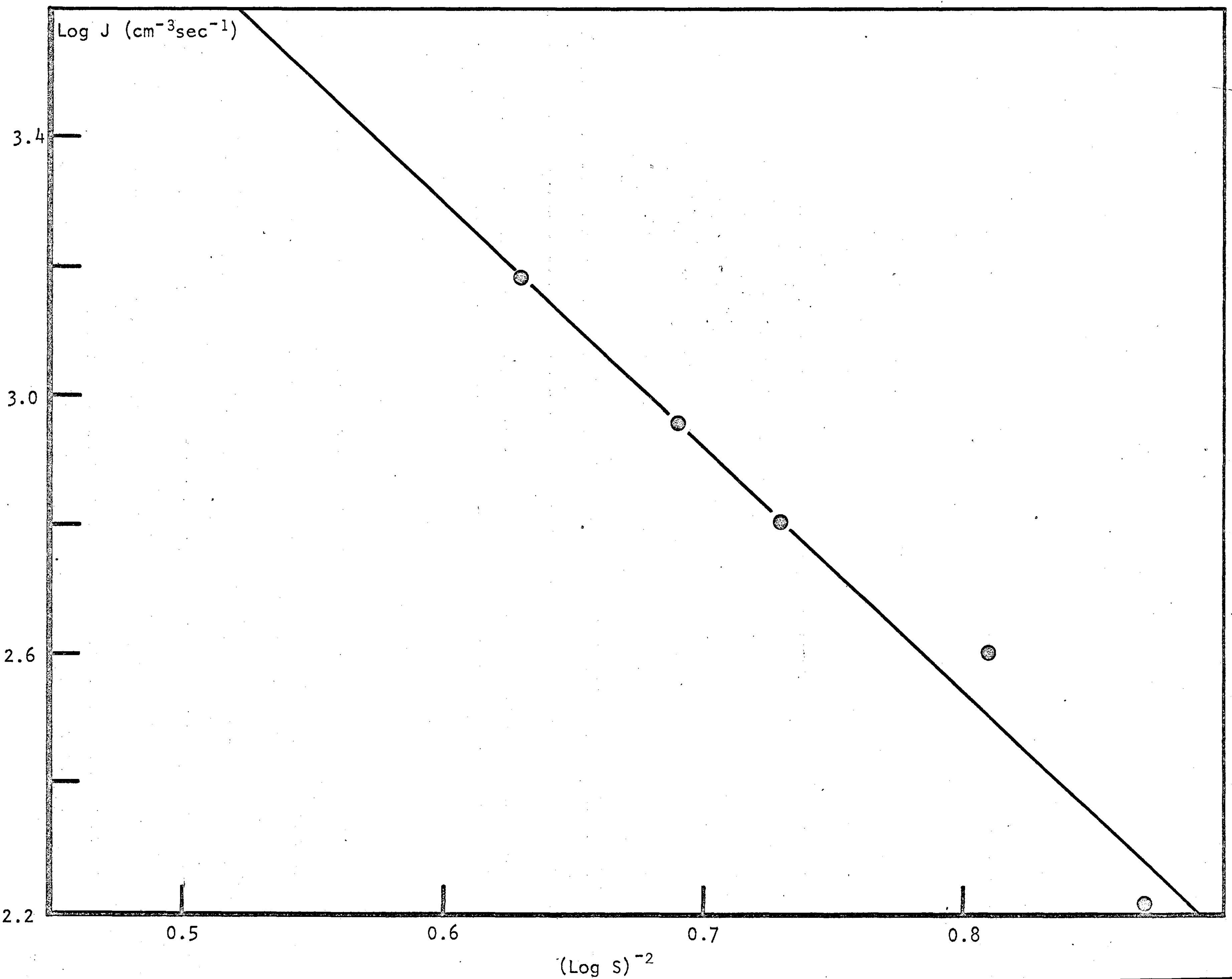
RESULTS OF THE CALCULATION OF THE NUCLEATION RATE OF $K_2Cr_2O_7$[a] VERSUS TIME

d_2/d_1	dP/dt (sec^{-1})	J ($cm^{-3}sec^{-1}$)	S
0.50	1.82×10^{-5}	1.61×10^{2}	11.8
0.49	4.46×10^{-5}	3.95×10^{2}	12.9
0.48	7.03×10^{-5}	6.22×10^{2}	14.4
0.47	10.4×10^{-5}	9.20×10^{2}	16.1
0.46	17.1×10^{-5}	15.1×10^{2}	18.3

---

[a] Solubility of potassium dichromate at 22°C: 11.5%; density of saturated solution: 1.07 g cm^{-3}.

FIGURE 32. Log J Versus $(\text{Log S})^{-2}$ for $K_2Cr_2O_7$


Log J (cm^{-3}sec^{-1})
3.4
3.0
2.6
2.2
0.5
0.6
0.7
0.8
(Log S)$^{-2}$

with potassium dichromate. It is common practice in nucleation studies to associate homogeneous nucleation with the highest supersaturation obtainable with any given substance. Therefore, in applying this method, only data associated with whole droplet crystallization were considered. Because the droplet populations studied in these experiments were not sufficiently large to enable the type of analysis described for potassium dichromate, the mean values of d_2/d_1 obtained were used to calculate S, γ, n* and r*. A summary of the results obtained is shown in Table 30.

Previous nucleation studies from aqueous solution have failed to produce any correlation between the values of the nucleation parameters and any of the macroscopic properties of the substances studied. In these experiments it was found empirically that if the negative of the logarithm of the mole fraction solubility was plotted versus the logarithm of the supersaturation ratio, a straight line was obtained. The plot is shown in Figure 33. Such a plot would be expected if there existed a linear relationship between the free energy of solution and the free energy of activation for nucleation. This plot is useful because, as mentioned in Section II.E., it can be used in conjunction with the monograms to estimate the values of the nucleation parameters for various substances. A limitation to this is that, presumably, the structures and properties of the substances considered should be similar to those of the substances involved in the correlation.

IV.D. Errors

Because of uncertainties in the experimental data and in the equations employed in the calculations, the results of the experiments

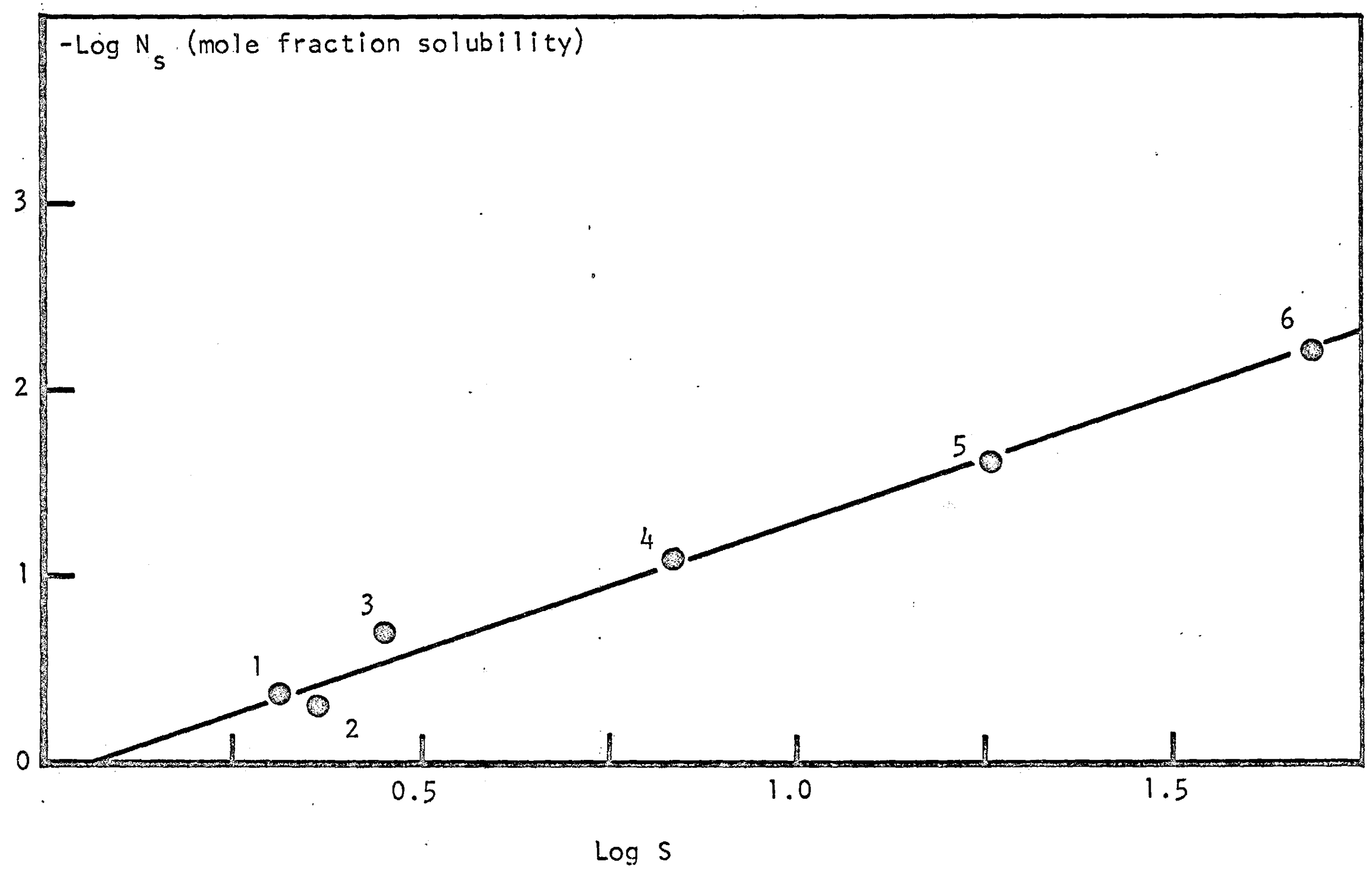
TABLE 30

SUMMARY OF THE RESULTS OF NUCLEATION STUDIES ON INORGANIC SALTS

Substance	d_2/d_1	S	γ (ergs cm^{-2})	n*	r* (Å)
NH_4SCN	0.886	2.07	37	151	12.1
NH_4NO_3	0.862	2.33	47	141	10.5
NH_4Cl	0.757	2.82	66	107	9.0
$(NH_4)_2Cr_2O_7$	0.630	6.85	58	58	9.6
$K_2Cr_2O_7$	0.456	18.6	82	43	8.6
$(NH_4)_2C_2O_4 \cdot H_2O$	0.371	49.0	129	29	6.4

FIGURE 33. Negative Log Mole Fraction Solubility Versus Log S for Soluble Inorganic Salts

1.	NH_4SCN	4.	$(NH_4)_2Cr_2O_7$
2.	NH_4NO_3	5.	$K_2Cr_2O_7$
3.	$NH_4C\ell$	6.	$(NH_4)_2C_2O_4 \cdot H_2O$


-Log N_s (mole fraction solubility)
3
2
1
0
0.5
1.0
1.5
Log S
1
2
3
4
5
6

described herein may be in error. The assumptions and approximations associated with equations (16) through (21) have already been described in the Introduction. There were relatively few sources of experimental error in the studies with the inorganic salts. Because of their complexity, however, the experiments with the metal chelates were subject to a considerable number of uncertainties. The main sources of experimental error can be described as follows.

It was assumed that the time interval from nucleation to crystal detection was the same for all droplets. Further, it was sometimes difficult to determine the time (or slide) at which the crystal was first detectable. It was estimated that, because of the large number of droplets observed, these uncertainties did not affect significantly the results obtained.

The measurements of the droplet diameters were estimated to be accurate to about ±2 μ.

In the determination of the concentration of monomers in the droplets it was assumed that the rates of formation per unit volume, of monomers and precipitate, were equal.

Although the solvent systems used for the solubility determinations were not identical to those in the droplets, the solubility of the metal chelate in both media was assumed to be the same.

In contrast to the uncertainties described above for the experiments with the metal chelates, the only significant source of error with the inorganic salts was the measurement of the droplet diameters. This error was minimized by using relatively large droplets.

In summary, it was estimated that the combined experimental error in these experiments was small compared with the error due to uncertainties in the equations used in the calculations.

SUMMARY

1. Two new methods were devised for producing supersaturation in droplets. In the first method the solute was gradually generated within the droplet at constant volume. The second method maintained the amount of solute constant while gradually reducing the volume of the droplet.

2. The solute generation method was applied successfully to isothermal nucleation studies on sparingly soluble metal chelates.

3. The droplet contraction method was applied successfully to isothermal nucleation studies on soluble inorganic salts.

4. With the solute generation method, a linear relationship between the median supersaturation ratio and the logarithm of the droplet volume was found.

5. With the droplet contraction method, the median supersaturation ratio was found to be independent of the logarithm of the droplet volume.

6. A linear plot of log J versus $(\log S)^{-2}$ was obtained for all compounds studied. This result supports the functional relationship predicted by the classical nucleation theory [equation (16)].

7. Values of the pre-exponential factor of the order of 10^6-10^{12} $cm^{-3}sec^{-1}$ were obtained for all compounds studied. These were compared with the theoretical value of 10^{24}-10^{30} $cm^{-3}sec^{-1}$.

8. As a result of the discrepancy between the theoretically predicted and experimentally determined values of A, the validity of the theoretical expression for ΔG_n^* was questioned. It was pointed out that if the expression for ΔG_n^* contained an additional term which varied with

supersaturation, then this term would have to be included along with $(\log S)^{-2}$ as the independent variable. It was concluded that agreement with equation (16) should not be expected in nucleation experiments from solution until ionic and solvent effects, as well as entropy effects, were incorporated into the theory.

9. The negative of the logarithm of the mole fraction solubility was found to be linearly related to the logarithm of the supersaturation ratio.

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