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Nucleation of crystals of sparingly soluble salts

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NUCLEATION OF CRYSTALS OF SPARINGLY SOLUBLE SALTS

by

Louis Milton Brown

A Dissertation Submitted to the
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I. INTRODUCTION

A. Statement of Purpose

The separation of a new phase from an already existing phase is a phenomenon in which scientists have maintained interest for many years. Of more particular interest is the initiation of this second phase, a process generally referred to as nucleation. In this work only the nucleation of crystals of sparingly soluble salts shall be considered although other nucleation processes may be discussed in reviewing the existing theories.

It is the purpose of this thesis, not only to discuss the existing theories of nucleation, but to present the development of a new theory which purports to overcome the inconsistencies and difficulties of the others. In addition the theory will be treated with data obtained from experiments with three different sparingly soluble salts. Finally, suggestions will be made concerning future work necessary in order to obtain a complete picture of nucleation and in particular of nucleus size.

B. Review of the Literature

1. Theory of Volmer

The "classical" general theory of nucleation is that developed by Volmer[1] and, as shall be seen, it has been used and extended by many others. The basic assumption of this theory is that all phase transitions have a basic similarity in character, namely, the appearance of the new phase in microscopic amounts without alteration of the macroscopic state parameters. This indicates that in all cases the nucleus formation is governed by local variation of these parameters in small domains. These local variations are called fluctuations.

Let w be the fraction of the time a given part, with mass m, of a system finds itself in a state different from the equilibrium state of the rest of system. If $m \Delta s$ is the entropy decrease due to this fluctuation, then

$$w = e^{-m \Delta S/k} ,$$

where k is the Boltzman constant. This is a form of the Boltzman equation $s = k \ln w$.

In general, it may be shown that to form a new phase by an isothermal reversible process work must be done on the system. This work A_K is

$$A_K = \frac{\sigma a_K}{3}$$

where is the interfacial tension between phase I and phase II, and a_k is the area of the nucleus.

The probability that a mass m, part of a relatively large phase I, forms a nucleus of phase II by a reversible process is, except for a factor,

$$w = e^{-A_k/kT} \quad .$$

If Z is the number of times per second such an agglomerate of mass m is formed, then the probability w' per unit time, that a nucleus of mass m is present is

$$w' = Z\, e^{-A_k/kT} \quad .$$

Let J' be the frequency of formation of such nuclei per unit time and τ their mean life time, then

$$w' = J'\tau$$

and

$$J' = \frac{Z}{\tau}\, e^{-A_k/kT} \quad .$$

The above equations apply to reversible formation of nuclei. Since a particle so formed has equal probabilities of gaining or losing a molecule, the rate of formation of nuclei which continue to grow, J, is then

$$J = \frac{J'}{2} = \frac{Z}{2\tau}\, e^{-A_k/kT} \quad .$$

Note that it is assumed that phase II is formed with negligibly small changes in the state parameters of phase I. Note also that if the nucleus consists of N_k fold ions or molecules, no assumption of an N_k fold collision has been made. Further, the flux J is the maximum flux since it is based on the minimum work.

Since J depends on the rate of nucleus formation and since experimentally it is difficult to separate nucleus formation and nucleus growth, the quantity J is difficult to evaluate. Dehlinger and Wertz[2] investigated the spontaneous nucleus formation in supersaturated solutions of alum by determining the times before precipitation started. They were unable to apply the theory of Volmer to their data and suggested an explanation based on negative diffusion. Neumann and Miess[3] reinterpreted the results of Dehlinger and Wertz and showed them to be in good agreement with the theory.

Van Hook[4,5,6] has studied the precipitation of silver chromate from both aqueous solutions and gelatin media. Although he assumes a fluctuation mechanism for the production of nuclei, he shows that the rate of nucleation is first order in ion product of the reactants.

In addition to determining the rate of nucleation, it is desired to find the number of ions or molecules predicted by the theory under consideration or extensions of it[7,8,9]. The Kelvin - J. J. Thompson equation relates the supersaturation pressure of a vapor to the radius of the spherical drop with which it will be in equilibrium. It can be easily shown that for salts in aqueous solution the equation is[10]

$$i \frac{RT}{M} \ln \frac{S_r}{S} = \frac{2\sigma}{dr}$$

where M is the molecular weight, d is the density of the crystals, i is the van't Hoff factor, σ is the interfacial tension between the crystal and the solution.

Van Hook[5] obtained a value of 10^8 to 10^9 molecules per seed crystal of silver chromate which he calls an order of size far in excess of that usually conceived as composing the elementary seed. La Mer and Dinegar[10] have calculated values $r = 50$ Å for AgCl and $r = 100$ Å for $BaSO_4$. This indicates that the number of molecules per nuclei is of the order of 10^4.

Another method suggested for determining the radius of crystal nuclei has been developed by Gopal[11] from the early suggestions of Jones and Partington[12]. The equation which was developed is

$$(T_s - T) = \frac{2\sigma M}{d\lambda} \cdot \frac{T_s}{r}$$

where T_s is the saturation temperature, T the temperature of spontaneous crystallization, and λ the molecular heat of solution. The other quantities have their previous significance. Typical calculations[13] using this equation also give $r = 100$ Å as an order of magnitude.

It should be pointed out that the radii determined for crystal nuclei are about ten times the values calculated for liquid nuclei in vapor-liquid transitions. This is explained qualitatively[10] and theoretically[9] as being due to solute-solvent interaction. The solvent, in effect, is a catalyst that lowers the necessary free energy of transformation by making possible larger size embryos.

The concept of interfacial tension becomes somewhat vague when it is applied to particles of the order of ten molecules[14] thick. Moreover, in the case of spherical drops in content with vapor, it has been shown that the magnitude of the surface tension seems to depend on the curvature of the surface.[15,16,17] Perhaps the interfacial tension between crystals and solution is also dependent upon size of the crystals.

2. Recent theories

More recent theories of nucleation have been based on kinetic studies of precipitation processes. Duke, Bever, and Diehl[18] showed that the experimental curve for the precipitation of barium sulfate could be explained if the nuclei were assumed to be ion pairs and if the growth equation

$$\frac{dP}{dt} = k\ S\ [Ba^{++}]\ [SO_4^{=}]$$

were assumed. In this equation P is the number of moles of precipitate, k the specific rate constant and S the surface area of the precipitate. The data and method of interpretation of it are admittedly insensitive to the size of the nucleus; however, the paper presents a new concept of nucleation of crystals. For this reason, it is valuable in this discussion.

The recent work of Christiansen and Nielsen[19,20,21,22] is quite significant in that their theory of nucleation also is based on the kinetics of precipitation. Since the theory predicts that the nucleus consists of a small number of ions and since it resembles somewhat the theory to be presented here, a more detailed discussion is worthwhile.

It should be stated that the above authors discuss the initiation of crystallization in terms of the formation of crystal germs instead of nuclei.[20] This is done to distinguish their initial particles from those of La Mer,[10] Frenkel[7] and others who speak of nuclei as having a hundred or more particles as discussed earlier. In this work we shall still consider these "germs" as nuclei since they are the means by which crystals start in supersaturated solutions of sparingly soluble salts.

Christiansen and Nielsen[19] studied the kinetics of barium sulfate and silver chromate precipitations by determining the time necessary for the formation of the first visible precipitate. The data was obtained in three ways. First, for the higher concentrations of reagents a flow method based on Roughton's principle[23] was used. The place and thus the time of the occurrence of the first visible precipitate could be observed. Intermediate times were observed in the flow apparatus by stopping the flow and noting the time of the appearance of the first visible precipitate. Note that the outlet tube in the flow apparatus had a bore of about 2 mm. Finally, longer times were determined by mixing the reagents in a beaker. These times were taken to mean the times of appearance of a certain constant fraction of the precipitate.

These authors expressed their results in the form of the equation

$$t \cdot C_o^{p-1} = k$$

where t is the time of precipitation, C_o the original molar concentration taken as the $\underline{i}$ th root of the ionic product, if one molecule dissociates into $\underline{i}$ ions, and p and k are constants. For barium sulfate, p was found to be 7 or 8; for silver chromate, p = 5, and from data of Jensen[24] on calcium fluoride, p = 8 or 9.

Christiansen and Neilsen[20] refer to La Mer[25] in stating that the rate of growth of nuclei in a supersaturated solution is proportional to the instantaneous concentration of reactants to a low power. Since they have shown that the velocities of precipitation are proportional to the concentrations in powers from 6 to 9, they conclude, therefore, that the rate determining step in precipitation must be the process of nucleation. Moreover, the powers to which the instantaneous concentrations appear in the rate equation must denote the number of ions in the nucleus.

Since the results are not sufficiently accurate in some cases so that there are two possible values, the decision is made on the assumption that the nuclei are electroneutral. This gives a nucleus for barium sulfate of 4 barium ions and 4 sulfate ions, for silver chromate of 4 silver and 2 chromate ions, and for calcium fluoride of 3 calcium ions and 6 fluoride ions.

The equation

$$t\, C_o^{p-1} = k$$

has also been developed theoretically by these authors.[21] This is done by considering the probability of forming ion "clusters" up to the nucleus size by a series of equilibrium steps distinguishing nuclei from clusters by assuming that the probability of gaining an ion by the nuclei is much greater than that of losing an ion. Reactions between two clusters to form a cluster of a higher order are neglected.

Finally, Christiansen[22] and Nielsen have taken these earlier results and the data to Tovborg Jensen,[24] and have attempted to extend the theory to include the growth process. Showing that even though the assumption that the nucleation is complete before growth starts is a good approximation, it is concluded that both processes must be considered.

The shape of an experimental curve for the precipitation of calcium fluoride suggested that the growth process is autocatalytic. Hence, it is assumed that the rate of growth is dependent on the surface area of the crystals. Note the same assumption in the work of Duke, et al.[18]

Considering these assumptions, these authors have developed two interdependent differential equations. The equation

$$\frac{dX}{dt} = k_x\,(1-XN)^9$$

is the new equation for nucleation of calcium fluoride where $X = C/C_o$, the ratio of the instantaneous concentration to the initial concentration, N is the number of molecules per crystal, and k_x is proportional to ${C_o}^8$. The growth equation is

$$\frac{dN^{1/3}}{dt} = k_n\,(1-XN)^3$$

where k_n is proportional to ${C_o}^3$. Notice that a third order rate equation is assumed. This infers that the growth process is first order in calcium ions and second order in fluoride ions.

When a theoretical curve, calculated from these equations, was made to closely approximate the growth part of the experimental curve, the deviation over the upper portions of the curves was quite marked. Likewise, when the nucleation curve, the initial portion, was fitted, there was no correlation at all with the lower portion. This indicates inconsistencies in the theory.

As has been seen from the discussion to this point, the size of the nucleus considered necessary to begin separation of a sparingly soluble salt from its supersaturated solution has decreased from several hundred molecules to a few ions. It is interesting to note that La Mer, who has reported a nucleus size for barium sulfate which approximates 100 molecules,[10] has reinterpreted his data in light of the theory of Christiansen and Nielsen.[22] Using both sets of data, La Mer concludes that there are seven ions in the nucleus instead of eight; however, the important point is that La Mer, who once discussed molecules in terms of hundreds of molecules, now believes only a few ions are involved in the formation of nuclei.

II. THEORY

As has been shown in the preceding section, recent work has led to the conclusion that a comparatively small number of ions is involved in the nuclei of barium sulfate,[18,20,22] silver chromate,[20] and calcium fluoride[20] crystals. The question arises concerning the forces holding a small nucleus together--particularly one composed of relatively large ions in aqueous solution;[26,27] it seems likely that the same sort of forces which cause the crystal to be insoluble are involved in nucleus formation. Thus, the nucleus should be considered to be a complex of ions or molecules held together in solution by short-range forces in addition to any coulombic forces present. It is noteworthy that electrolytic solution theory would predict, on the basis of coulombic forces alone, that tetraphenylarsonium perchlorate crystals would be highly soluble.

Since a large number of crystals are formed when sparingly soluble salts are precipitated from solution, one should be able to apply ordinary statistics to the nucleation process; thus ordinary rate laws are assumed to hold. The rate equation for nucleation is

$$\frac{dN}{dt} = k_1 \; A^n \, B^m, \qquad (1)$$

where N is the number of particles or potential particles; A and B, the concentrations of the ions of which the crystal will be composed; t, the time; n and m, the number of ions of the kind indicated comprising the nucleus. Note that N is not the number of nuclei.

The equation for nucleus growth is

$$\frac{dP}{dt} = k_2 \, S \, A^{n'} \, B^{m'} \tag{2}$$

where P is the amount of precipitate formed, S is the surface area or the number of sites available to ions on the growing crystalloid; t, the time and k_2, the rate constant. Combining the two equations yields

$$\frac{dN}{dP} = \frac{k_1 \, A^{n-n'} B^{m-m'}}{k_2 S} \quad . \tag{3}$$

S may be expressed in terms of N and P as follows: the volume of the precipitate, $\frac{PM}{\rho}$, where M is molecular weight and ρ, the density, divided by V_p, the volume of a particle, gives the number of particles, N. The surface per particle is $V_p{}^{2/3}$, providing the particles are all the same size, and the total surface is then

$$S = \frac{P^{2/3} M^{2/3} N^{1/3}}{\rho^{2/3}} \quad . \tag{4}$$

Substituting in equation (3) above, we obtain

$$\frac{dN}{dP} = \frac{k_1 \, A^{n-n'} B^{m-m'} \rho^{2/3}}{k_2 \, P^{2/3} M^{2/3} N^{1/3}} \quad . \tag{5}$$

Integration yields

$$N^{4/3} = \frac{4k_1 \; A_o^{n-n'} B_o^{m-m'} \; \rho^{2/3} P^{1/3}}{k_2 \; M^{2/3}} \qquad (6)$$

in the region where an insignificant amount of precipitation has occurred; that is, before a significant change in the original concentrations of A and B has occurred. It is assumed that the number of particles is fixed in this region; that is, the formation of nuclei cannot compete with nucleus growth even while the crystals are very small.

The equation describing the point where nucleation ceases to compete effectively with nucleus growth is

$$\frac{dN}{dP} = C = \frac{k_1 \; A_o^{n-n'} B_o^{m-m'} \; \rho^{2/3}}{k_2 \; P^{2/3} N^{1/3} M^{2/3}} \quad . \qquad (7)$$

C is the value approached by $\frac{dN}{dP}$ after which nucleus formation becomes insignificant. Since C contains both the surface or number of sites available and also the concentration of the ions, C should be constant for a given substance and a given mechanism of nucleation and growth. Solving (7) for $P^{1/3}$ and substituting in equation (6), we obtain

$$N = \frac{2 \times 2^{1/3} \; k_1 \rho^{2/3}}{k_2 \; M^{2/3} C^{1/3}} \; A_o^{(n-n)} B_o^{(m-m')} \; . \qquad (8)$$

Equation (8) can be rewritten in the much simpler form

$$N = K \; A_o^{(n-n')} B_o^{(m-m')} \qquad (9)$$

where

$$K = \frac{2 \times 2^{1/3} k_1 \rho^{2/3}}{k_2 M^{2/3} C^{1/3}} \quad .$$

It is quite evident that this theory can be tested easily if it is written in the logarithmic form, so that

$$\log N = \log K + (n-n') \log A_o + (m-m') \log B_o \ . \quad (10)$$

If the number of crystals, N, is determined in several different precipitations of a given compound while the initial cation concentration A_o has varying values and the anion concentration B_o is the same in each case, then plot of log N versus log A_o should give a slope of (n-n'). Similarly the plot of log N versus log B_o, under conditions of constant A_o, should give a slope of (m-m'). In both cases the temperature must not be allowed to vary since K is a function of temperature.

A second way to test the above theory is by determining the variation in the number of crystals obtained when the precipitation is carried out at several temperatures. The concentrations must be the same in each case.

If it is assumed that the exponents of A_o and B_o do not change with temperature, then the rate constants k_1 and k_2 are the only quantities which are temperature dependent. Equation (8) can be rewritten as a function of k_1 and k_2 giving the simplified equation

$$N = \frac{k_1}{k_2} \quad K' \tag{11}$$

where

$$K' = \frac{2 \times 2^{1/3} \rho^{2/3} A_o^{(n-n')} B_o^{(m-m')}}{N^{2/3}\, C^{1/3}} \quad .$$

If it is assumed that the activation energies of the two competitive processes, nucleation and growth, are invariant with temperature, the equation

$$\frac{d \log \frac{k_1}{k_2}}{d\, 1/K^o} = \frac{-(\Delta H_1 - \Delta H_2)}{2.3\ N} \tag{12}$$

is easily derived. In this equation, ΔH_1 and ΔH_2, are the energies of activations of nucleation and growth respectively, and K^o is the temperature in degrees Kelvin.

By letting $\Delta H_{diff} = \Delta H_1 - \Delta H_2$ and substituting from equation (11) into equation (12) we find that

$$\frac{d \log N}{d\, 1/K^o} = -\, 2/3\, \frac{\Delta H_{diff}}{2.3\ R} \quad . \tag{13}$$

Thus a plot of log N vs. $1/K^o$ should yield a straight line. From the slope of that line ΔH_{diff} can be calculated from equation (13).

The theory presented above considers nucleation as a process which is competitive with the growth of the nuclei. Two methods of testing the theory experimentally are outlined. In the following section, experiments which have been designed and carried out to test the theory are described.

III. INVESTIGATION

A. Choice of Reagents

The study was begun with tetraphenylarsonium permanganate.[28] This precipitant was chosen because it was felt that the principal binding forces within the crystal are ionic in nature and because sufficient numbers of crystals are produced so that the data can be treated statistically and thermodynamically. In addition, the size and shapes of the crystals are such that they may be readily photomicrographed and measured. However, it was soon apparent that part of the permanganate was decomposing during the precipitation; although freshly filtered permanganate solutions were used, manganese dioxide was found on the microscope slides when the run had been completed.

Even though many data were obtained with tetraphenylarsonium permanganate, it was felt to be unreliable except to confirm results otherwise obtained. In light of this , a similar salt, tetraphenylarsonium perchlorate was chosen to confirm initial results and continue the investigation. The sizes and shapes of the crystals of this salt are comparable to those of tetraphenalarsonium permanganate; so that, the same experimental procedure was used in both cases.

In addition to the two above mentioned salts, it seemed desirous to test the theory with an unsymmetrical salt, i.e., a divalent cation and mono-valent anion or vice versa. An attempt was made to find a divalent anion which would form a suitable precipitate with the tetraphenylarsonium cation. Of all of those tried only persulfate, dichromate, thiosulfate, molybdate gave a precipitate at relatively low concentrations and none of these proved satisfactory for continued study.

The nickel glyoxime derivatives were then considered as possibilities. Dimethylglyoxime, heptoxime and nioxime was chosen for investigation. The principal reason for the choice being that nickel nioxime is considerably less soluble than the other two thus giving a wider concentration range, at lower concentrations, with which to work. Nickel nioxime, which is better characterized by the name cyclohexanonedioxime[29], is a chelate compound and has a structure similar to that for nickel dimethyglyoxime.

B. Experimental Method

The stock solutions of tetraphenylarsonium chloride, and nioxime were prepared by weight. Those of perchloric acid and nickel chloride were prepared from previously standardized solutions, while the stock solution of potassium permanganate was prepared in the usual way, i.e., boiling dissolved permanganate, filtering, and finally standardizing with ethylenediamine ferrous sulfate. All stock solutions were approximately .01M and all other solutions were prepared from these by dilution.

Each precipitation, or run as it shall be called, was carried out as described below. A volume of 50 ml. of each reagent of the desired concentration was poured into a 150 ml. beaker and placed in a water bath set at a chosen constant temperature. After thermal equilibrium was established, the solutions were mixed by pouring the first into the second which was being stirred vigorously with a mechanical stirrer. After approximately five seconds, stirring was then stopped, the stirrer removed, and the beaker covered allowing precipitation to continue without disturbance.

As was expected, reaction times were shorter for runs made at higher concentrations and lower temperatures. The time for each run was determined by experiment or by interpolation from other runs. Although each run was terminated as soon after completion as possible, experiments have shown that the crystals involved are of such size that no effects due to aging could be detected after a period of three days.

At least two runs were made at each set of conditions. The order of mixing, pouring the first reagent into the second or the second into the first, was varied in order to avoid the effects of localization. If localization effects were evident, more runs were made in order to minimize the error.

C. Estimation of the Number of Crystals

Every run for each of the three precipitants was treated in the above way; however, the method for determining the number of crystals per liter of solution was different in the case of nickel nioxime. That method will be described separately.

In the runs of tetraphenylarsonium permanganate and tetraphenylarsonium perchlorate the crystals were removed from solution by centrifugation. After rinsing with distilled water, the crystals were placed on microscope slides to be observed qualitatively with the aid of the microscope and to be photographed. All photomicrographs were taken at 250 magnifications on 4" x 5" Kodak contrast process ortho film. After the negatives were developed, the length and width of all crystals on each were measured. Measurements were made with a clear plastic millimeter scale, and with the aid of a viewer which consisted of a box with a frosted plate glass top and containing a fluorescent light. The number of crystals, from 16 to 150, which were measured from any one run depended on the size of the crystals and the placement on the negative.

The average volume per crystal for a given run was estimated by multiplying the average length by the square of the average width. It was felt this was the best estimation possible and that the approximation is reasonably accurate in view of the size and shapes of the crystals. An equally good approximation would be the average of the length times width squared for each crystal on a negative. This was, in fact, done in a few cases. The results were in quite close agreement; hence, the simpler approximation was used throughout.

As has been pointed out earlier, before an estimation of the number of crystals per liter for any given run could be made, the density of the crystals must be known. These densities were determined experimentally by dispersing the crystals in solutions of toluene in carbon tetrachloride until the solution was found which kept the crystals suspended for a period greater than two days. The density of that solution, as determined by a Westfall balance, was taken as the density of the compound.

The number of crystals per liter of reaction mixture was easily calculated after the average volume per crystal, v, and the density, ρ, had been estimated. If P is the moles of precipitate and M the molecular weight, then the number of crystals per liter, N, is calculated by

$$N = \frac{P \times M}{\rho\, v} \quad . \tag{14}$$

The method for determing the number of crystals per liter for runs with nickel nioxime varied greatly from the above procedure. The reasons for this are several. The nickel nioxime crystals formed in these runs were either needle-like or starshaped or a mixture of the two. Because of this, the volume could not be approximated as before. The method described below is much simpler and provides an easy method to test the postulated theories. When precipitation was complete, determined as before and by the Tyndall effect, an aliquot was removed with a .1 ml. pipette graduated in .01 ml., and .01 ml. was placed on a clean microscope slide. The crystals contained on the slide were then counted with the aid of a Bausch and Lomb binocular eyepiece microscope with a movable stage. The microscope objective was selected so that it magnified about 100 times. With the field of the microscope limited, the counting was accomplished by sweeping back and forth across the slide working from one end of the slide to the other. The actual counting was done with the aid of a Veeder hand tally counter.

Three slides were prepared from each run, and after the first few runs only one of these was counted. The errors in preparing the slides proved to be about 10 per cent of the number of crystals on the side. Since the deviation in the number of crystals per liter for two runs of the same concentrations was greater, that error, 10 per cent, was neglected. For some runs for which the number of crystals on the slides was less than 300, two to ten hundreths of a milliliter was placed on the slides to be counted in order to increase the accuracy. The number of crystals per liter of solution was determined, after counting, by the appropriate conversion factor, usually 10^5.

D. Dependence of the Number of Crystals on Concentration

In order to rigorously test the theory, it was necessary to carry out two series of runs for each precipitant studied. In the case of tetraphenylarsonium permanganate the concentration of the reagent which was being held constant was 5×10^{-5} molar initially. The initial concentration of the other reagent varied from 10^{-4} molar to 5×10^{-3} molar. Similarly with tetraphenylarsonium perchlorate one reagent was held constant at 10^{-4} molar and the other varied up to 5×10^{-3} molar. Because of its lower solubility, the lower concentration was 5×10^{-6} molar and 10^{-5} molar for nickel and nioxime concentration being held constant respectively. The upper limit of the concentration range in this case was 10^{-4} molar for nioxime and 5×10^{-5} for nickel chloride.

Results from the effect of the variation of temperature on the number of nickel nioxime crystals indicated need for making a series of runs keeping the concentration present in excess constant and varying the reagent which had the lower concentration. Two such series of runs were made. In the first, the nickel concentration was 5×10^{-5} molar and the nioxime concentration varied from 5×10^{-6} molar to 2×10^{-5} molar. Another concentration series was made in which the nioxime concentration was initially 2.5×10^{-5} molar in each run, and the nickel concentration was varied from 1.25×10^{-6} molar to 1×10^{-5} molar.

All runs described above were carried out at 25° C; therefore, it was considered important to investigate the effect of varying the concentration at another temperature. This was done with tetraphenylarsonium perchlorate at 0° C using an ice bath to maintain a constant temperature. Only one series of runs was made, that being a variation of the perchlorate concentration from 2×10^{-4} molar to

5×10^{-4} molar while as before the tetraphenylarsonium chloride was 10^{-4} at the start of precipitation. The concentration range was limited because of the decrease in size of the crystals and increased difficulty in measuring.

E. Dependance of the Number of Crystals on Temperature

An investigation into the effect of temperature on the number of crystals produced at a given initial concentration was necessary to learn something of the heats of activation of the processes. In this connection two series of runs were made with each precipitant. In every case the concentrations were held constant with one or the other of the reagents in excess as follows: the concentrations for tetraphenylarsonium permanganate were 5×10^{-5} molar and 5×10^{-4} molar initially; the higher concentration being first potassium permanganate and then, in the second series, tetraphenylarsonium chloride. With tetraphenylarsonium perchlorate the concentrations used were 10^{-4} molar and 10^{-3} molar. One series with nickel nioxime was run with 10^{-5} molar nioxime and 4×10^{-5} molar nickel chloride; the other used 2×10^{-5} molar nioxime and 5×10^{-6} molar nickel chloride.

The temperatures in each case covered a range from 0° C to 40° C. All temperatures were controlled with a constant temperature water bath which was accurate to ± .05° C, excepting 0° C and approximately 13° C. Crushed ice in a four liter Dewar flask was used to maintain 0° C, and running tap water in a Dewar flask gave a temperature of about 13° C which was constant to ± 0.1° C.

F. Dependence of Number of Crystals on Ionic Strength

With the concentrations in each case 1×10^{-4} molar tetraphenylarsonium and 1×10^{-3} molar perchlorate, the effect of varying ionic strength was determined. From an approximately 2 molar stock solution of sodium chloride, reaction mixtures were prepared so that the reaction would be carried out in solutions of from 0 to 1.2 molar sodium chloride. Both reagent solutions had the same sodium chloride concentration before mixing.

G. Dependence of Number of Crystals on Stirring

Since each run was begun by pouring the solutions together and stirring vigorously with a mechanical stirrer for a brief period, it was desired to determine whether the amount and type of stirring used influenced the results obtained. Two types of experiments were designed, one to investigate the effect of the time of stirring, and the other to determine the effect of the rate of stirring. The experiments are qualitative only.

In the first experiments, the runs were stirred vigorously and at the same rate from one to twenty minutes, the stirring stopped, and the reaction allowed to proceed in a covered beaker. In every run the concentrations were 10^{-3} molar perchlorate and 10^{-4} molar tetraphenylarsonium chloride.

In the other experiments on the effects of stirring, each run was stirred continuously until precipitation was complete. The rate of stirring was regulated by means of a variac, so that each run was made with successively faster rates of stirring. The concentrations of the reagents in these runs were the same as stated above.

IV. RESULTS

The results of the experimental investigation are given below. The results obtained with each of the three different compounds are reported separately in order to facilitate later discussion. For quick reference the results are summarized in Table 16 at the end of this section.

A. Tetraphenylarsonium Permanganate

1. Variation of concentration

Table 1 gives data showing the variation of the number of crystals as the concentration of permanganate is increased in successive runs from 1×10^{-4} molar to 5×10^{-3} molar. In each case the tetraphenylarsonium permanganate concentration is 5×10^{-5}. In this table C is the concentration of permanganate,   is the average volume per crystal as measured from the photomicrographs, and N is the number of crystals per liter of reaction mixture. The volume, υ, is converted to N by equation (14).

Figure 1 is a plot of log N vs. log C as found in Table 1.

From Figure 1 it can be seen quite clearly that, even though the points are quite scattered, a straight line

Table 1

Variation of the number of tetraphenylarsonium permanganate crystals with concentration of potassium permanganate

$C \times 10^4$ moles/l	ν (mm^3)	$N \times 10^{-6}$	-log C	log N
1.0	58.8	7.80	4.00	6.89
1.0	59.6	7.73	4.00	6.89
2.0	26.3	17.5	3.70	7.24
2.5	32.6	14.7	3.60	7.15
2.5	23.3	19.8	3.60	7.30
3.0	13.4	34.4	3.52	7.54
4.0	20.0	23.0	3.40	7.36
5.0	4.48	103	3.30	8.01
5.0	2.88	160	3.30	8.20
5.0	6.27	73.5	3.30	7.87
10.0	2.54	181	3.00	8.26
20.0	1.53	301	2.70	8.48
25.0	1.27	363	2.60	8.56
25.0	1.25	369	2.60	8.57
30.0	0.81	669	2.52	8.83
40.0	0.29	1590	2.40	9.20
50.0	0.079	5380	2.30	9.77
50.0	0.51	904	2.30	8.96
50.0	0.24	1920	2.30	9.28

5×10^{-5} molar $(C_6H_5)_4$ AsCl

fits the data. As previously stated, the slope of the line gives the value for the exponent of A_o in equation (8). The slope is 1.17 indicating that one more permanganate ion is involved in nucleation than in the growth of tetraphenylarsonium crystals.

Data showing the variation of the number of crystals with varying concentrations of tetraphenylarsonium ions are

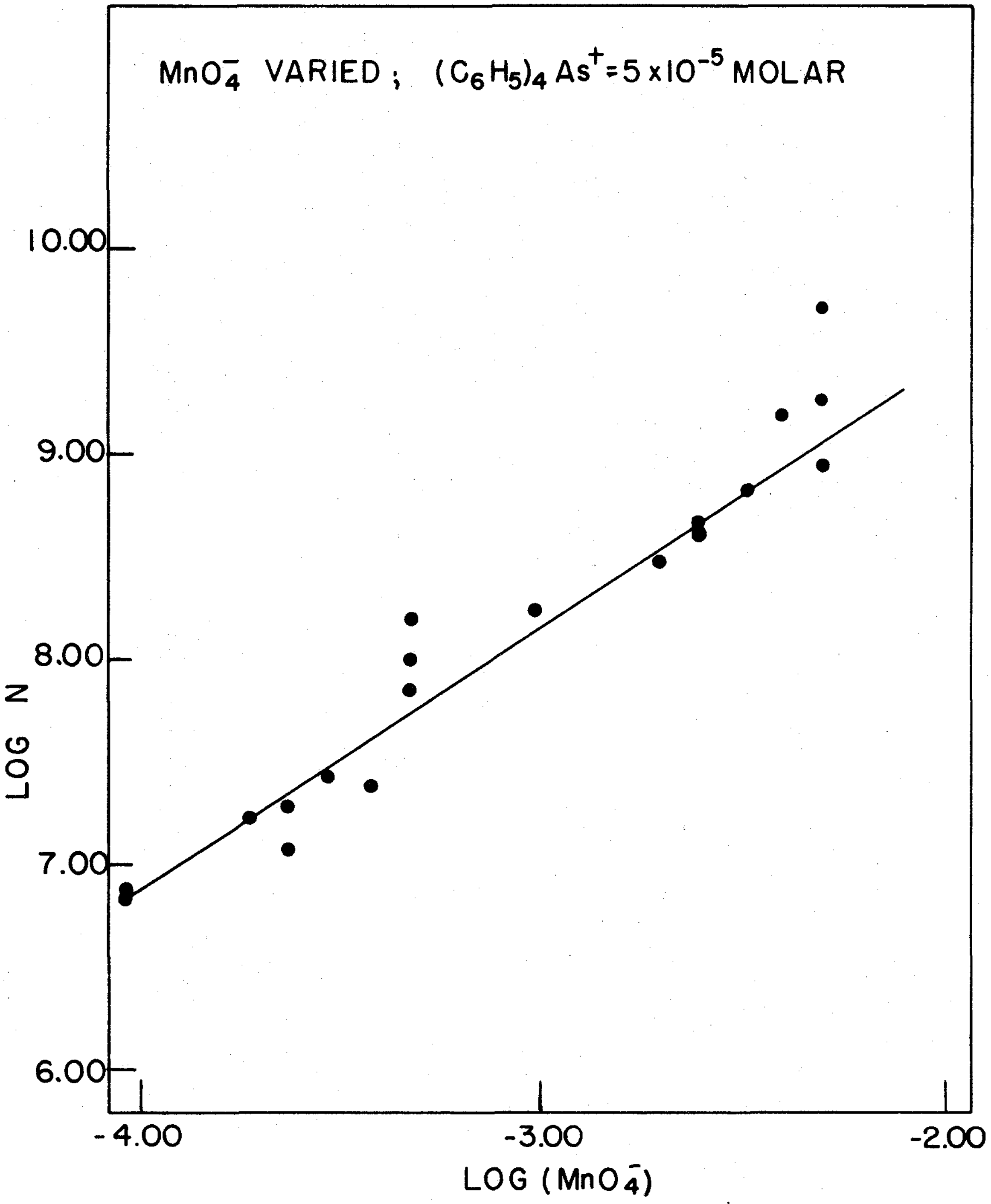

Figure 1. Variation of number of tetraphenylarsonium permanganate crystals with concentration of potassium permanganate

found in Table 2. In this case C is the concentration of tetraphenylarsonium chloride at the beginning of precipitation. The other quantities are defined as before. Only the average values for all the runs which were carried out under a given set of conditions are tabulated. In every run the initial concentration of potassium permanganate was 5 x 10^{-5} molar. The data found in Table 2 are plotted

Table 2

Variation of the number of tetraphenylarsonium permanganate crystals with concentration of tetraphenylarsonium chloride

$C \times 10^4$	$\nu (mm^3)$	$N \times 10^{-6}$	-log C	log N
1	929	0.496	4.00	5.70
3	498	0.926	3.52	5.99
5	78.4	5.88	3.30	6.77
25	8.58	53.7	2.60	7.83
50	3.04	152	2.30	8.18

$KMnO_4$ = 5 x 10^{-5} molar

in Figure 2. The slope of the straight line shown is 1.60. Since (m-m') must be an integer, this indicates that (m-m') is probably two.

2. Variation of temperature

Table 3, the data of which are plotted in Figure 3, shows the variation of the number of crystals with tempera-

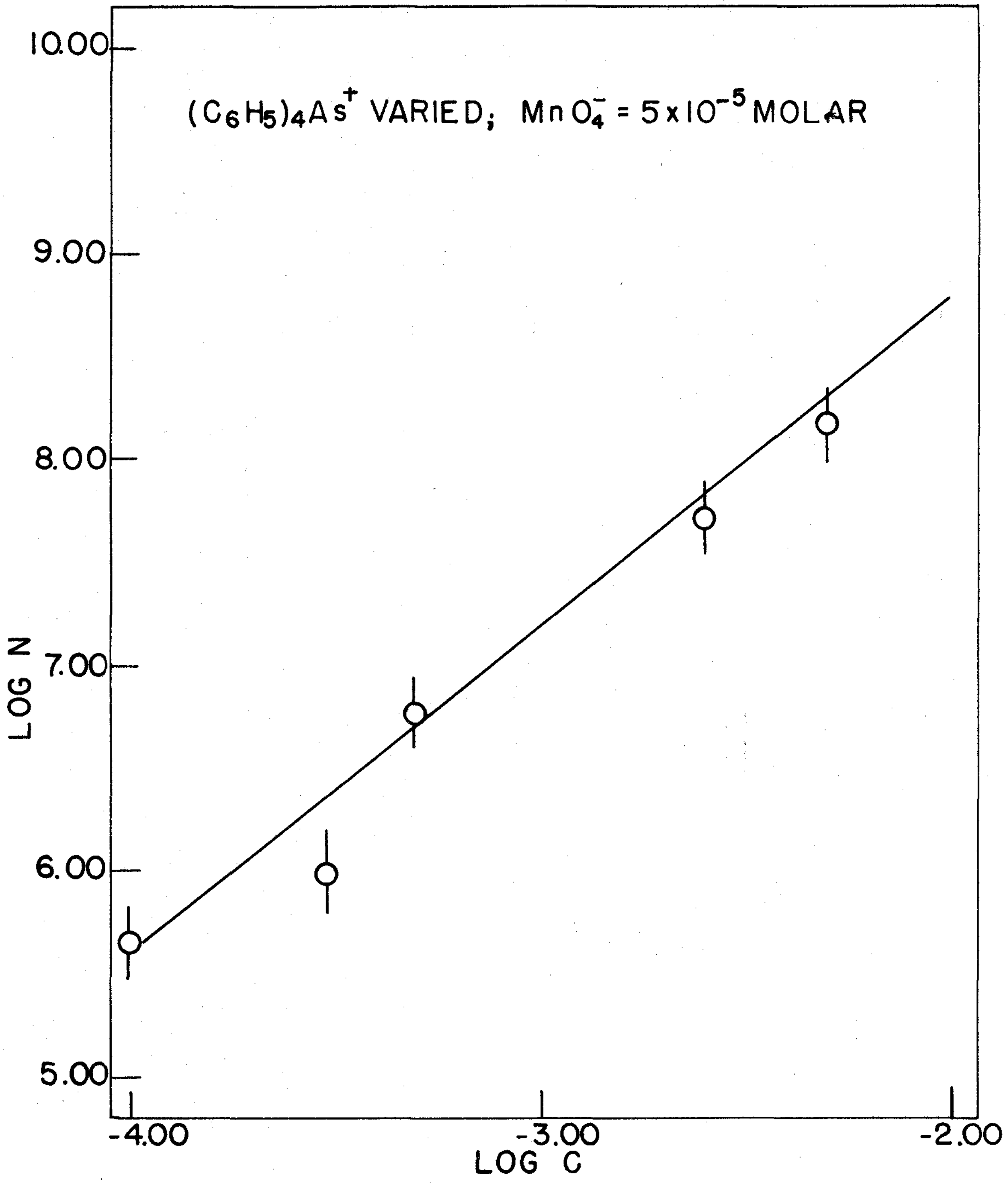

Figure 2. Variation of number of tetraphenylarsonium permanganate crystals with concentration of tetraphenylarsonium chloride

ture. According to equation (13), a plot of log N vs. log $^1/K_o$ should be a straight line with a slope of $-2/3 \frac{\Delta H_{diff}}{2.3 R}$. From this slope, ΔH_{diff}, the difference in the activation energies of the processes of nucleation and growth of crystals. For each run represented by data in Table 3 the reaction mixture was initially 5×10^{-4}

Table 3

Variation of the number of tetraphenylarsonium permanganate crystals with temperature

Temp. °C	ν(mm^3)	N x 10^{-7}	$^1/K^o$ x 10^3	log N
0.0	1.36	36.6	3.66	8.56
11.5	3.50	13.4	3.51	8.13
20.0	4.36	10.7	3.41	8.03
25.0	4.54	8.22	3.36	7.91
30.0	10.17	4.53	3.30	7.66
40.0	43.36	1.06	3.13	7.03

5×10^{-4} molar $KMnO_4$; 5×10^{-5} molar $(C_6H_5)_4$ AsCl

molar potassium permanganate and 5×10^{-5} molar tetraphenylarsonium chloride.

The slope of the line given in Table 3 is 3.03×10^3 from which a value of -21 k cal/mole is obtained for ΔH_{diff}.

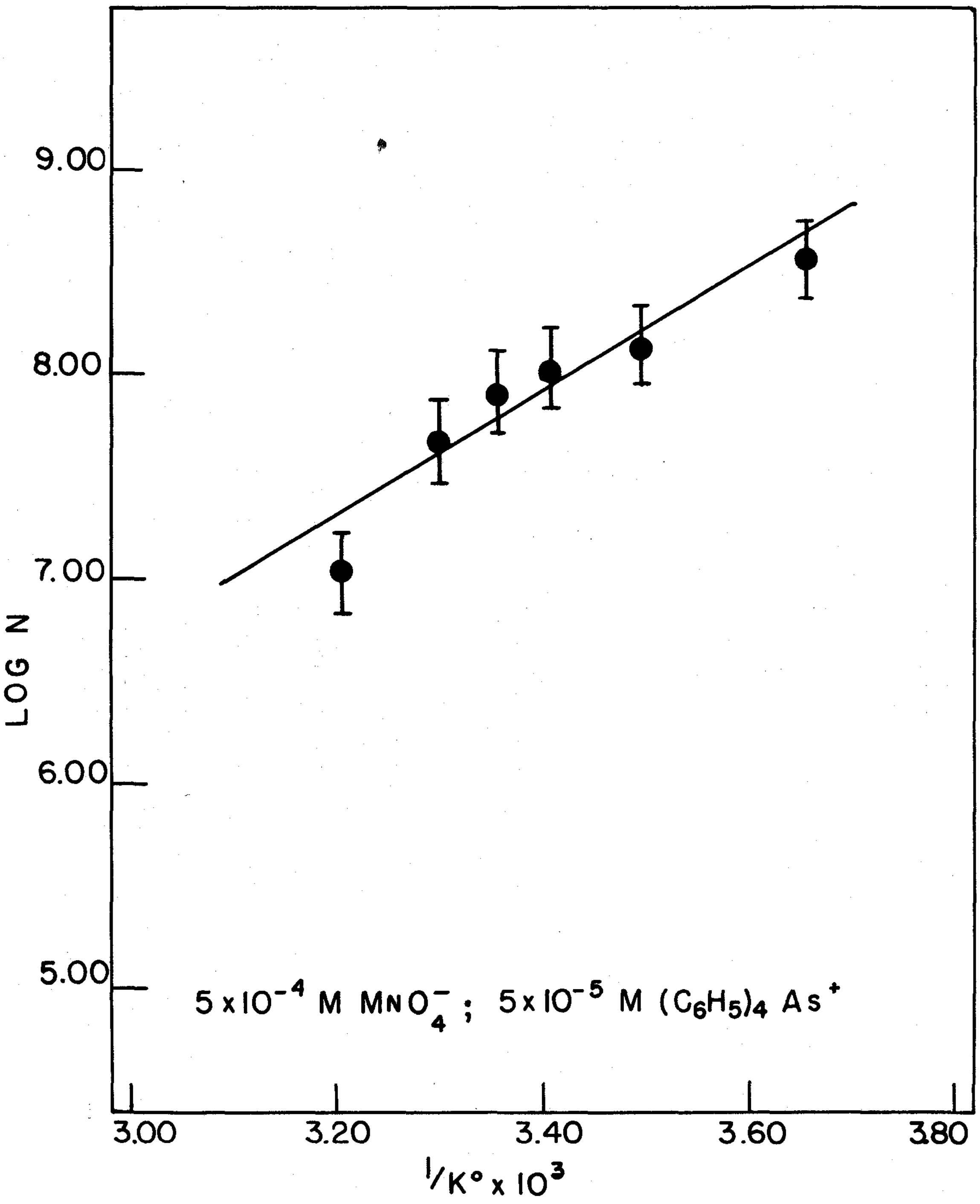

Figure 3. Variation of number of tetraphenylarsonium permanganate crystals with temperature

B. Tetraphenylarsonium Perchlorate

The results obtained experiments with tetraphenylarsonium perchlorate are much more complete than those concerning tetraphenylarsonium permanganate for reasons already discussed. These results are given in Figures 4 through 11 and Tables 4 through 9.

1. Variation of concentration

Figure 4 consists of photomicrographs (250X) precipitated at 5×10^{-4} molar tetraphenylarsonium chloride and four different concentrations of perchloric acid as shown. These are a part of the crystals which were measured to obtain the data tabulated in Table 4 and plotted as the upper curve in Figure 5.

The lower line in Figure 5 shows the variation of the number of crystals with concentration of tetraphenylarsonium chloride. The data for this line are given in Table 5. The two parallel lines were drawn so that $(n-n') = 2 = (m-m')$. The data fit these theoretical lines quite nicely.

Each of the runs of Tables 4 and 5 was made at a constant temperature of 25° C.

As was stated in the section on experimental procedure, it was desired to know whether the concentration effect was the same at two different temperatures, i.e., 25° C misprint

Table 4

Variation of number of tetraphenylarsonium perchlorate crystals with concentration of perchloric acid

$C \times 10^4$	v (mm^3)	$N \times 10^{-5}$	$-\log C$	$\log N$
3	938	5.32	3.48	5.73
5	84.7	55.8	3.26	6.75
10	21.8	215	3.00	7.33
25	14.6	322	2.56	7.51
50	1.95	1950	2.26	8.29

1×10^{-4} molar $(C_6H_5)_4$ AsCl

Table 5

Variation of number of tetraphenylarsonium perchlorate crystals with concentration of tetraphenylarsonium chloride

$C \times 10^4$	v (mm^3)	$N \times 10^{-5}$	$-\log C$	$\log N$
3	3020	1.56	3.52	5.19
5	582	8.70	3.30	5.94
10	436	11.6	3.00	6.06
25	32.2	20.1	2.60	7.30
50	12.6	37.3	2.30	7.57

1×10^{-4} molar $HClO_4$

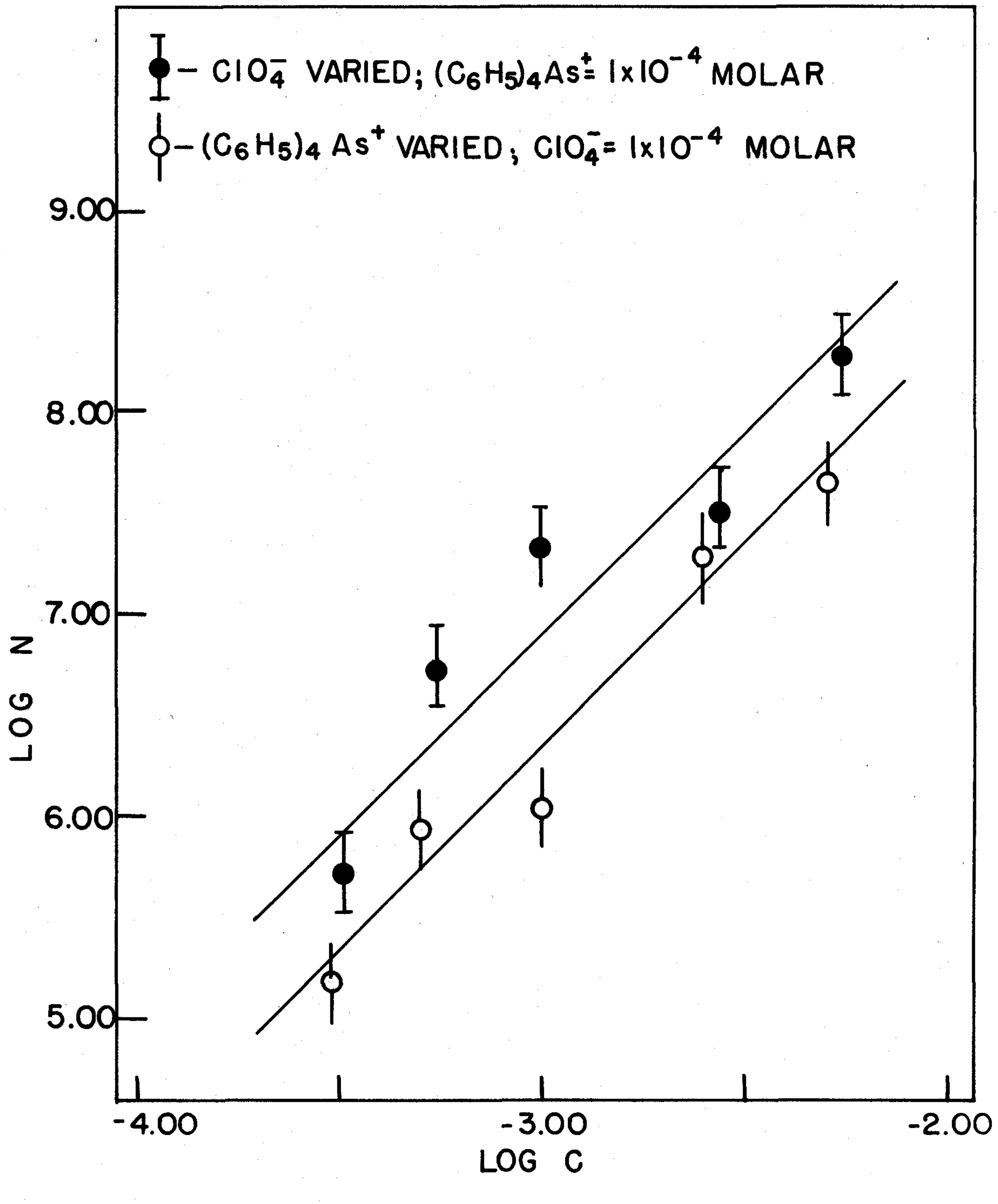

Figure 5. Variation of number of tetraphenylarsonium perchlorate crystals with concentration of the reagent present in excess

and 0° C. Table 6 and Figure 6 show respectively the data and graph of the data for the variation of the number of crystals with concentration of tetraphenylarsonium chloride. The perchloric acid concentration was 1×10^{-4} molar in each run.

Table 6

Variation of number of tetraphenylarsonium perchlorate crystals with concentration of tetraphenylarsonium chloride at 0° C

$C \times 10^4$	$\nu(mm^3)$	$N \times 10^{-7}$	$-\log C$	$\log N$
2	20.8	2.37	3.70	7.37
3.5	11.4	4.14	3.46	7.62
5	8.1	5.94	3.30	7.78
10	4.75	11.2	3.00	8.05
15	.861	57.5	2.82	7.78

1×10^{-4} molar $HClO_4$

While the agreement is not good, a straight line, with a slope of two, fits the curve if equal weight is given to each point. It should be pointed out that if the uppermost point in Figure 6 is disregarded, the remaining points fit a straight line with slope = 1.

2. Variation of temperature

Figure 7 shows pictures of crystals from typical runs when temperature was the changing parameter as indicated.

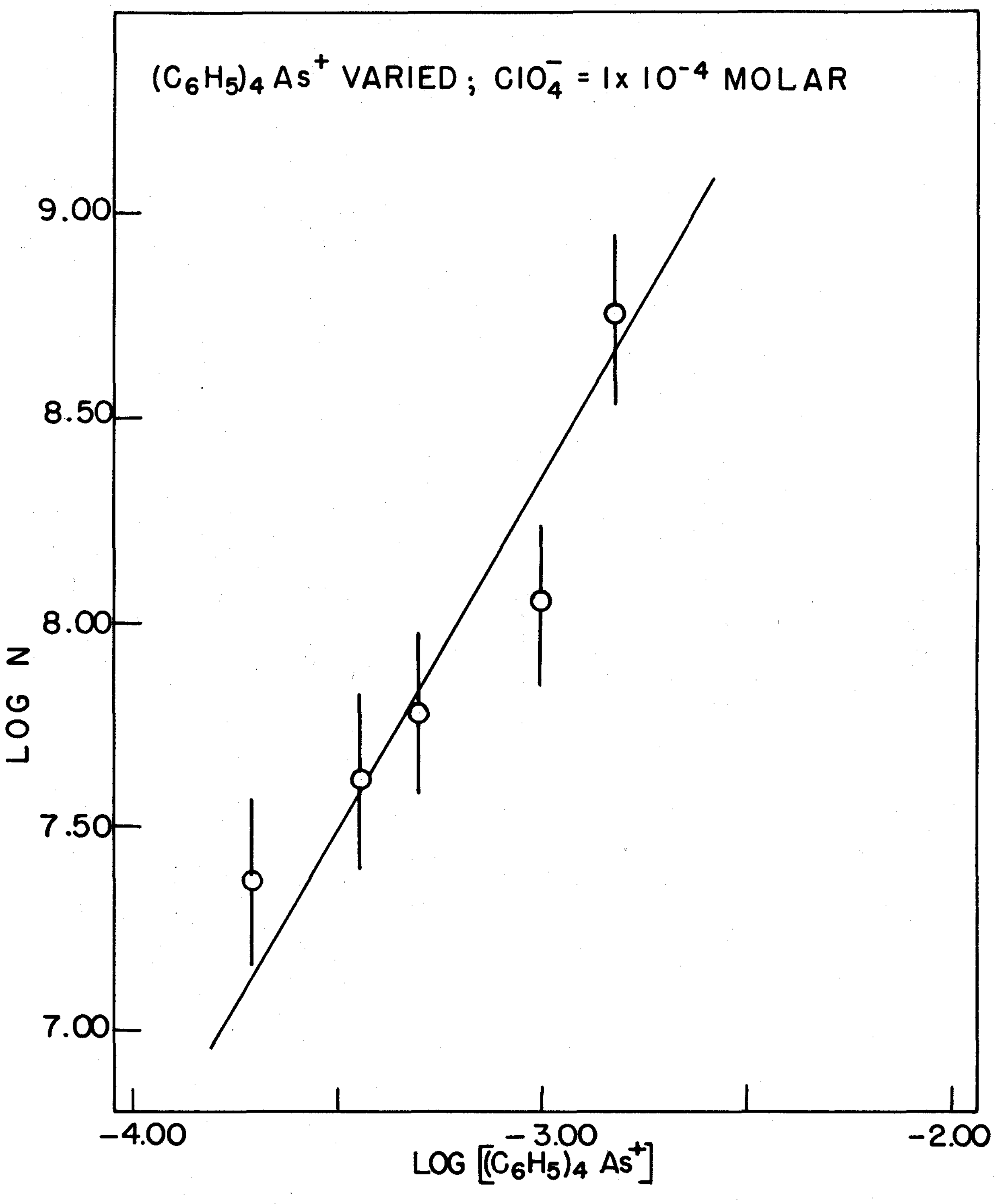

Figure 6. Variation of number of tetraphenylarsonium perchlorate crystals with concentration of tetraphenylarsonium chloride at 0° C

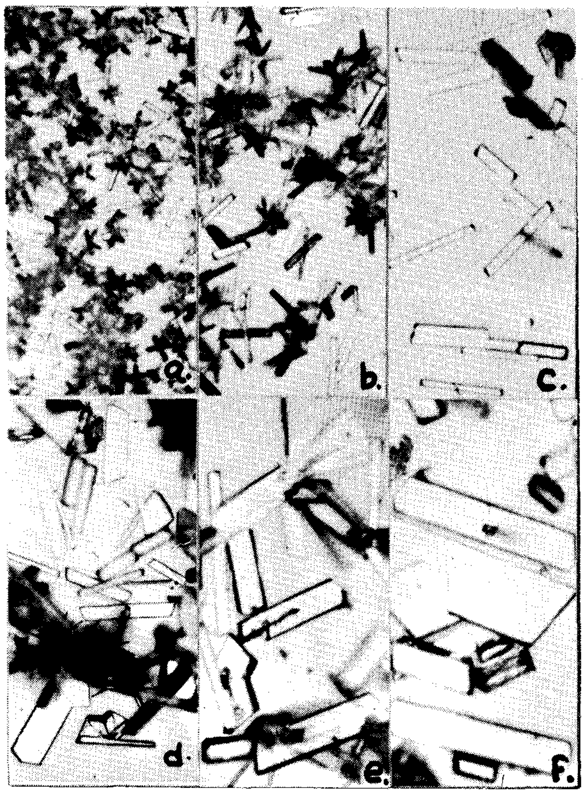

Figure 7

Variation of crystal size with temperature

Precipitated with 1x10^{-4}M $(C_6H_5)_4AsCl$ and 1x10^{-3}M $HClO_4$.

a. 0°C   c. 20°C   e. 30°C
b. 12°C   d. 25°C   f. 40°C

The data taken from these and other similar photomicrographs are tabulated in Table 7 and plotted as the upper curve in Figure 8. In the runs represented by these data, perchlorate ions were present in excess as shown.

In like manner, the temperature effect on the number of crystals when tetraphenylarsonium ions are in excess is shown by the data in Table 8. These data are plotted as the lower line in Figure 8.

From the slopes of the lines as drawn in Figure 8 and with the aid of equation (13), $\Delta H_{diff} = -22.1$ k cal/mole, when perchlorate ions are present in excess. When tetraphenylarsonium ions are present in excess, the result is $\Delta H_{diff} = -36.4$ k cal/mole.

3. Variation of ionic strength

If the ionic strength of a precipitating mixture is increased in successive runs, the number of crystals per liter of mixture decreases. This is shown in Table 9 and Figure 9 where the ionic strength was varied by addition of sodium chloride.

The line drawn through the points in Figure 9 is merely an indication of the results. Qualitatively the number of crystals decreases with increasing ionic strength. The reasons for this will be discussed in the following section.

Table 7

Variation of the number of tetraphenylarsonium perchlorate crystals with temperature when perchloric acid is present in excess

Temp. (°C)	ν(mm^3)	N x 10^6	$1/K°$ x 10^3	log N
0.0	2.01	234	3.66	8.37
12.0	5.17	90.9	3.51	7.96
16.0	7.09	66.3	3.46	7.82
20.0	15.2	31.0	3.41	7.49
25.0	18.5	25.4	3.36	7.40
30.0	27.2	17.3	3.30	7.24
40.0	118	4.00	3.19	6.60

1 x 10^{-3} molar $HClO_4$; 1 x 10^{-4} molar $(C_6H_5)_4$ AsCl

Table 8

Variation of the number of tetraphenylarsonium perchlorate crystals with temperature when tetraphenylarsonium chloride is present in excess

Temp. (°C)	ν(mm^3)	N x 10^5	$1/K°$ x 10^3	log N
0.0	4.20	1120	3.66	8.04
12.0	17.5	268	3.51	7.43
20.0	86.2	54.6	3.41	6.74
25.0	436	10.8	3.36	6.03
30.0	600	7.83	3.30	5.89
40.0	1317	3.57	3.19	5.52

1 x 10^{-4} molar $HClO_4$; 1 x 10^{-3} molar $(C_6H_5)_4$ AsCl

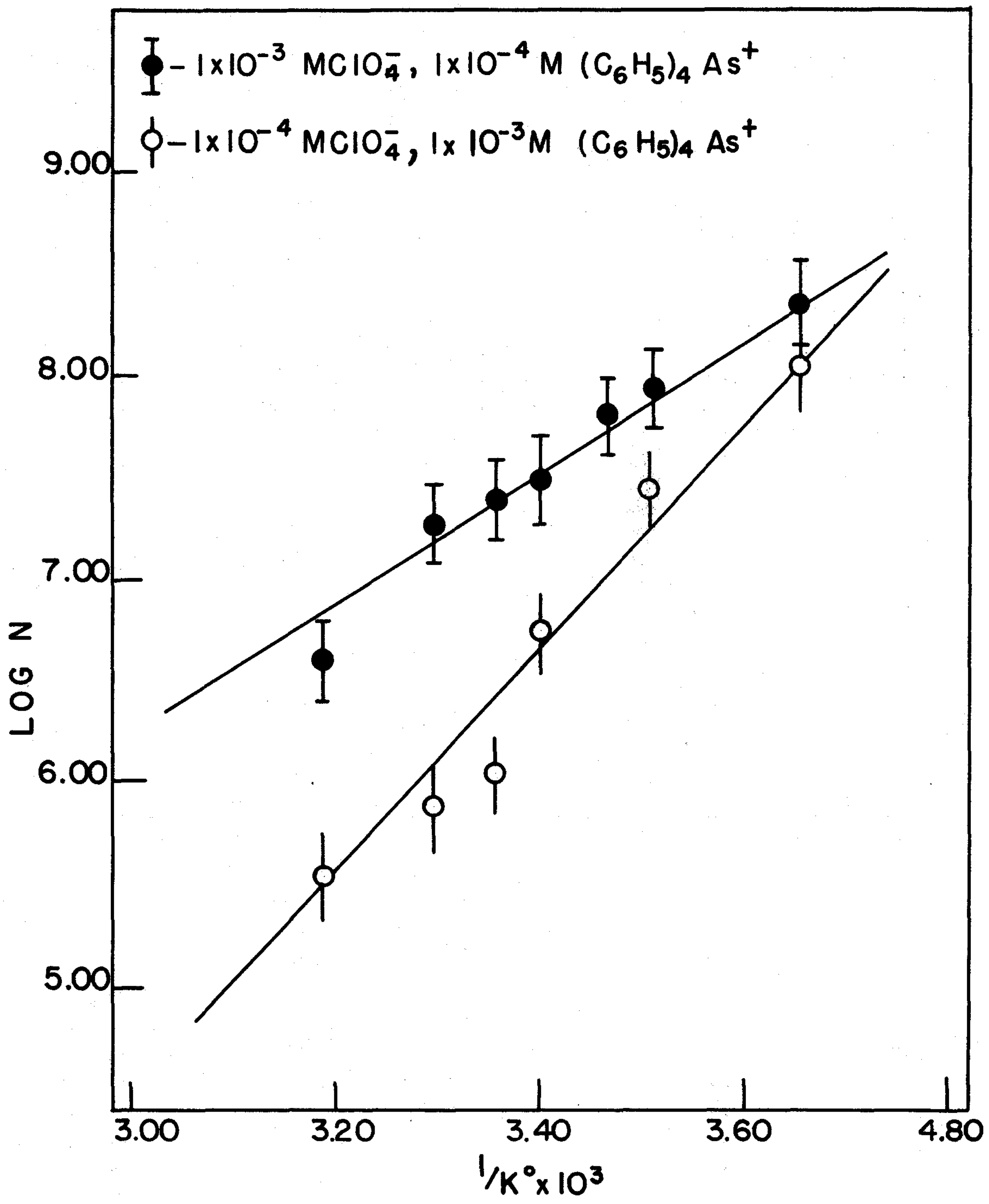

Figure 8. Variation of number of tetraphenylarsonium perchlorate crystals with temperature

Table 9

Variation of the number of tetraphenylarsonium perchlorate crystals with increasing ionic strength

Total Concn.	v(mm^3)	N x 10^{-6}	$\sqrt{\mu}$	log N
.001	18.4	25.8	0.05	7.41
.411	132	3.62	0.65	6.56
.821	170	2.77	0.91	6.44
1.231	138	3.41	1.11	6.53
1.401	295	1.59	1.17	6.20

1 x 10^{-3} molar $HClO_4$; 1 x 10^{-4} molar $(C_6H_5)_4$ AsCl

4. Variation of stirring

The effect of stirring has been investigated qualitatively, with both rate and time of stirring being studied. Figure 10 shows photomicrographs of crystals obtained from runs made with three different rates of stirring. These rates were maintained throughout the run. Qualitative results show that the crystal size varies inversely as the rate of stirring.

The crystal size also varies inversely with the time of stirring as is seen in Figure 11. In the runs from which these crystals were taken, the rate of stirring was the same as in Figure 10, photograph c. The times were as indicated. In both Figure 10 and Figure 11 the concentrations of tetraphenylarsonium chloride and perchloric

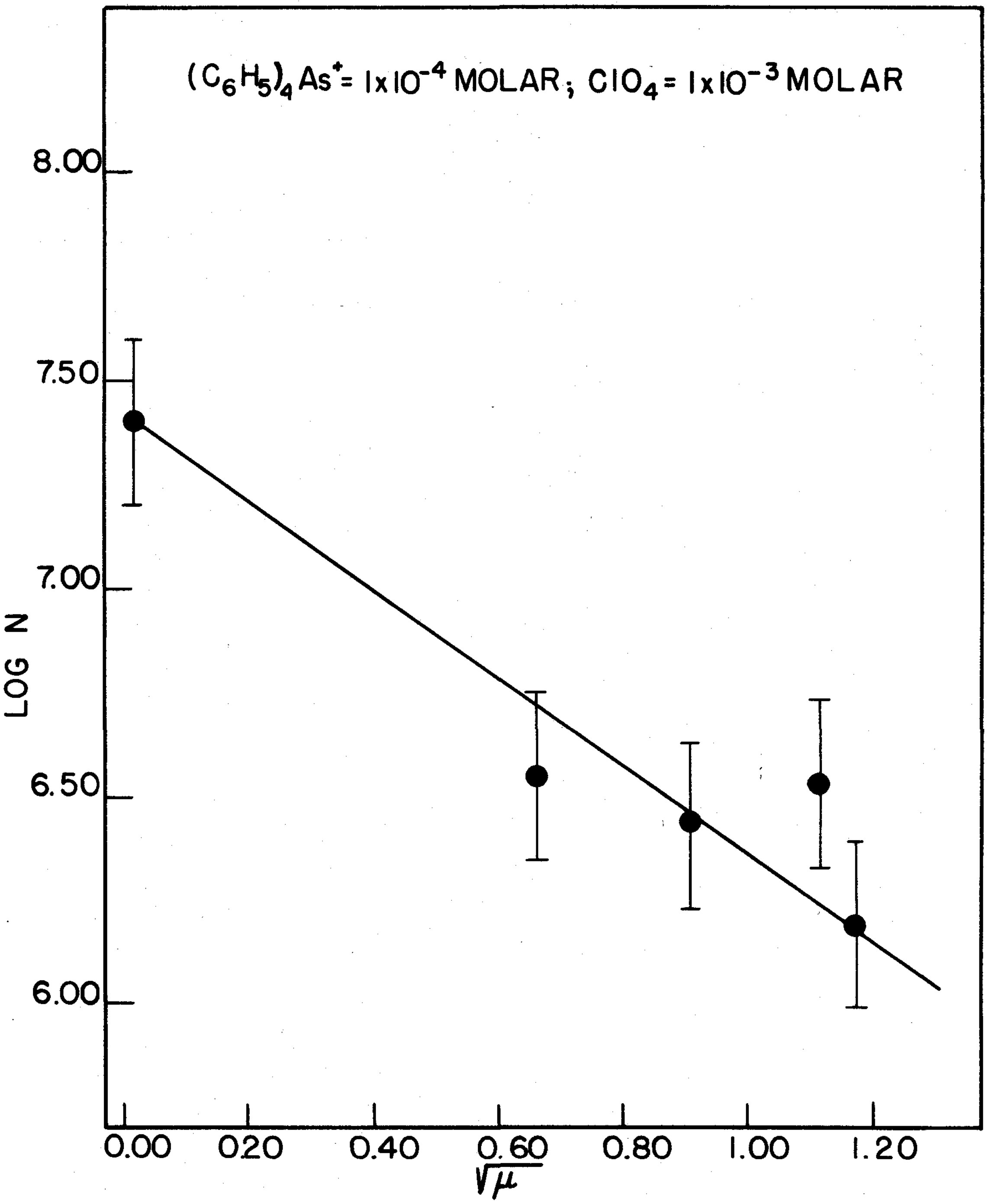

Figure 9. Variation of number of tetraphenylarsonium perchlorate crystals with increasing ionic strength

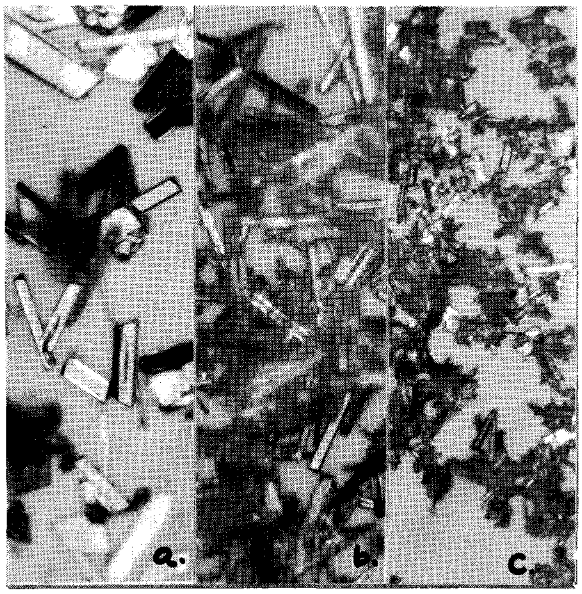

Figure 10

Variation of crystal size with rate of stirring

a. Moderate stirring

b. Rapid stirring with
no turbulence from
air steams

c. Very rapid with turbulence from air steams

All crystal precipitated with 1x10^{-4}(C_6H_5)$_4$AsCl and 1x10^{-3} $HClO_4$. All photomicrographs taken at 250X. For crystal with only initial stirring at these size concentrations see Figure 4 or Figure 7.

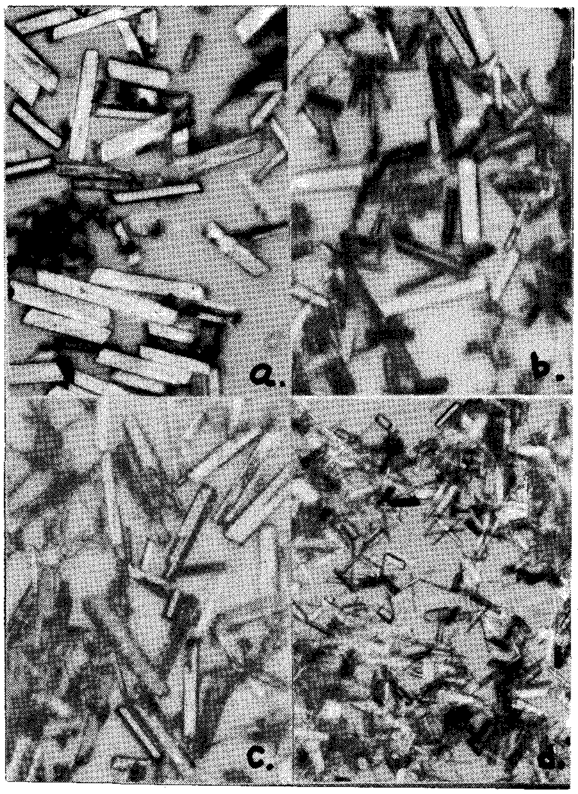

Figure 11

Variation of crystal size with time of stirring

Rate constant and same as
Figure 10.

a. 5 min. c. 15 min.

b. 10 min. d. 20 min.

All crystal precipitated with 1x10^{-4}(C_6H_5)$_4$AsCl and 1x10^{-3} $HClO_4$. All photomicrographs taken at 250X. For crystal with only initial stirring at these same concentrations see Figure 4 or Figure 7.

acid were 1 x 10^{-4} molar and 1 x 10^{-3} molar respectively.

5. Determination of densities

In order to convert the volume per crystal, v, to the number of crystals per liter of reaction mixture, N, it was necessary to determine the density of the crystals. This conversion was accomplished by use of equation (14). Since that data for the precipitation of nickel nioxime was obtained by direct counting of the crystals, only the densities of tetraphenylarsonium perchlorate and permanganate were determined. For tetraphenylarsonium permanganate $\rho = 1.580$ and for tetraphenylarsonium perchlorate $\rho = 1.549$.

C. Nickel Nioxime

The results obtained when the theory was tested using nickel nioxime are given in Tables 10 to 15 and Figures 12 to 14. It should be remembered that all the results given previous to these are obtained by estimating the number of crystals per liter of reaction mixture from a measurement of the average volume per crystal. In all the data given below, this value, N, is estimated by direct count of 0.01 ml. of the reaction mixture.

1. Variation of concentration

Table 10 and the solid points in Figure 12 show the variation of the number of nickel nioxime crystals with concentration of nioxime. In the runs which these data represent, nioxime is present in excess. These points agree closely with the straight line whose slope is 2 which has been drawn through them.

Table 10

Variation of number of crystals with concentration of nioxime when that reagent is in excess

$C \times 10^6$	$N \times 10^{-5}$	$-\log C$	$\log N$
5	160	5.30	7.20
10	320	5.00	7.51
20	850	4.70	7.93
30	2300	4.52	3.36
40	3100	4.40	3.49
50	5300	4.30	3.72

5×10^{-6} molar $NiCl_2$

According to the data found in Table 11 and plotted as open circles in Figure 12, there is no variation in the number of nickel nioxime crystals with nickel concentration when nickel is present in excess. This indicates that $(n-n') = o$, i.e., the same numbers of nickel ions are involved in both nucleation and growth of nickel

Table 11

Variation of number of nickel nioxime crystals with concentration of nickel ions when that reagent is present in excess

$C \times 10^5$	$N \times 10^{-5}$	$-\log C$	$\log N$
1	899	5.00	7.95
2	1175	4.70	8.07
3	981	4.52	7.99
4	852	4.40	7.93
5	940	4.30	7.97
10	795	4.00	7.90

1×10^{-5} molar nioxime

nioxime crystals when nickel is present in excess.

When the concentration of one reagent is kept constant at some high value and a series of runs is made varying the reagent with the smaller concentration, different results are obtained. Table 12 and the solid points in Figure 13 show the same results, $m-m' = 2$, when nickel is present in excess and the nioxime concentration is varied; however, when nioxime is present in excess and the nickel concentration is varied, it is found that $n-n' = 1.60 \approx 2$. This is shown by the data in Table 13 and the graph of the open circles in Figure 13. The dependence of $n-n'$ on the reagent present in excess indicates that either nucleation or growth or both processes depend on the excess reagent.

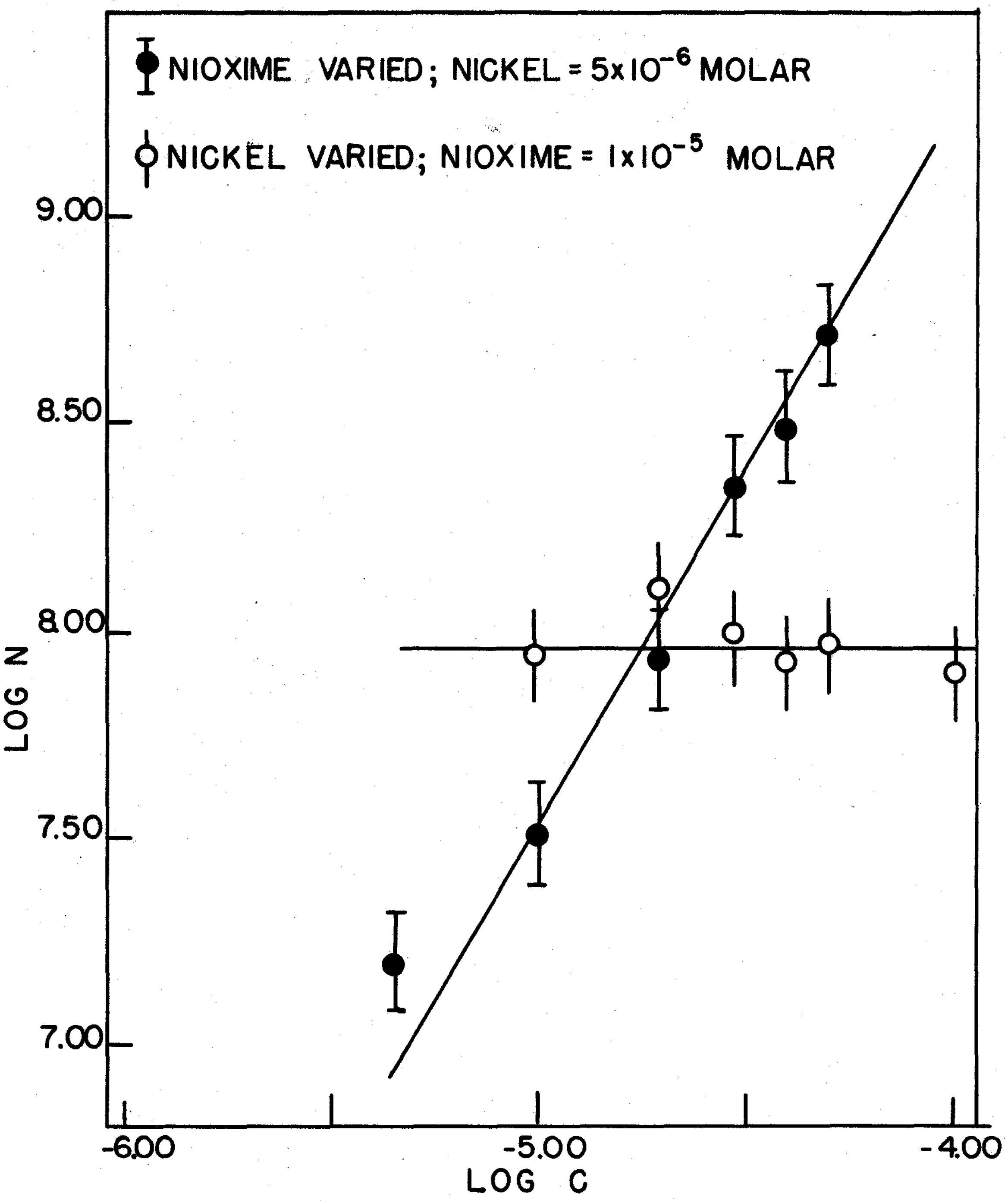

Figure 12. Variation of number of nickel nioxime crystals with concentration of the reagent present in excess

Table 12

Variation of number of nickel nioxime crystals with concentration of nioxime when nickel chloride is present in excess

$C \times 10^6$	$N \times 10^{-5}$	-log C	log N
4	155	5.40	7.19
5	325	5.30	7.51
10	912	5.00	7.96
15	2267	4.83	8.36
20	5843	4.70	8.77

5×10^{-5} molar $NiCl_2$

Table 13

Variation of number of nickel nioxime crystals with concentration of nickel chloride when nioxime is present in excess

$C \times 10^6$	$N \times 10^{-5}$	-log C	log N
1.25	190	5.90	7.27
2.5	436	5.60	7.64
5.0	1464	5.30	8.17
10.0	4303	5.00	8.63

2.5×10^{-5} molar nioxime

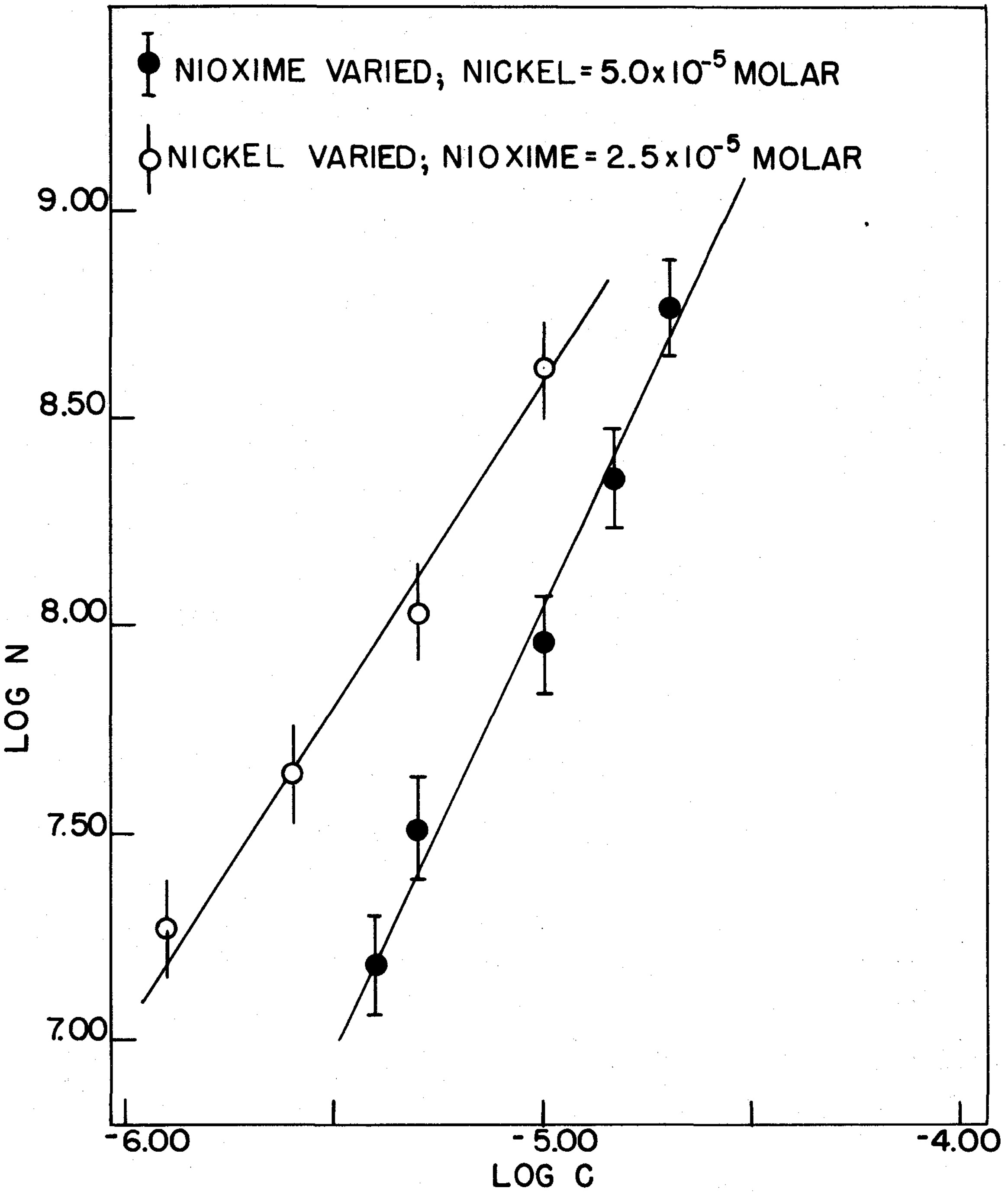

Figure 13. Variation of number of nickel nioxime crystals with concentration of the more dilute reagent

2. Variation of temperature

There is a marked difference in the effect the temperature has on the precipitation of nickel nioxime which depends on the reagent present in excess. This is shown by the two sets of data tabulated in Tables 14 and 15 and plotted in Figure 14. The data from Table 14 are plotted as solid points in Figure 14. In each run which these data represent, the nioxime concentration was four times that of the nickel chloride which was 5×10^{-6} molar.

When the nickel concentration is a fourfold excess over the 1×10^{-5} molar nioxime, the temperature effect is much greater as shown by Table 15 and the open points in Figure 14.

The ΔH_{diff} values are calculated according to equation (13). When nickel chloride is in excess $\Delta H_{diff} =$ 21.1 k cal/mole and when nioxime is in excess, $\Delta H_{diff} =$ -2.8 k cal/mole using the slopes of the lines as drawn.

D. Tabulation of Results

All of the principal results given in this section are compiled for easy reference in Table 16. These results will be discussed in light of the theory which has been presented.

In Table 16, which contains all the results given in

Table 14

Variation of number of nickel nioxime crystals with temperature when nioxime is present in excess

Temp. °C	$N \times 10^{-5}$	$1/K^{o} \times 10^{3}$	log N
0.0	911	3.66	7.96
14.0	619	3.49	7.79
20.0	691	3.41	7.84
25.0	825	3.38	7.92
30.0	513	3.30	7.71

5×10^{-6} molar $NiCl_2$; 2×10^{-5} molar nioxime

Table 15

Variation of number of nickel nioxime crystals with temperature when nickel is present in excess

Temp. °C	$N \times 10^{-5}$	$1/K^{o} \times 10^{3}$	log N
13.5	2636	3.48	8.42
20.0	1685	3.41	8.23
25.0	981	3.38	7.99
30.0	721	3.30	7.86
40.0	407	3.19	7.61

4×10^{-5} molar $NiCl_2$; 1×10^{-5} molar nioxime

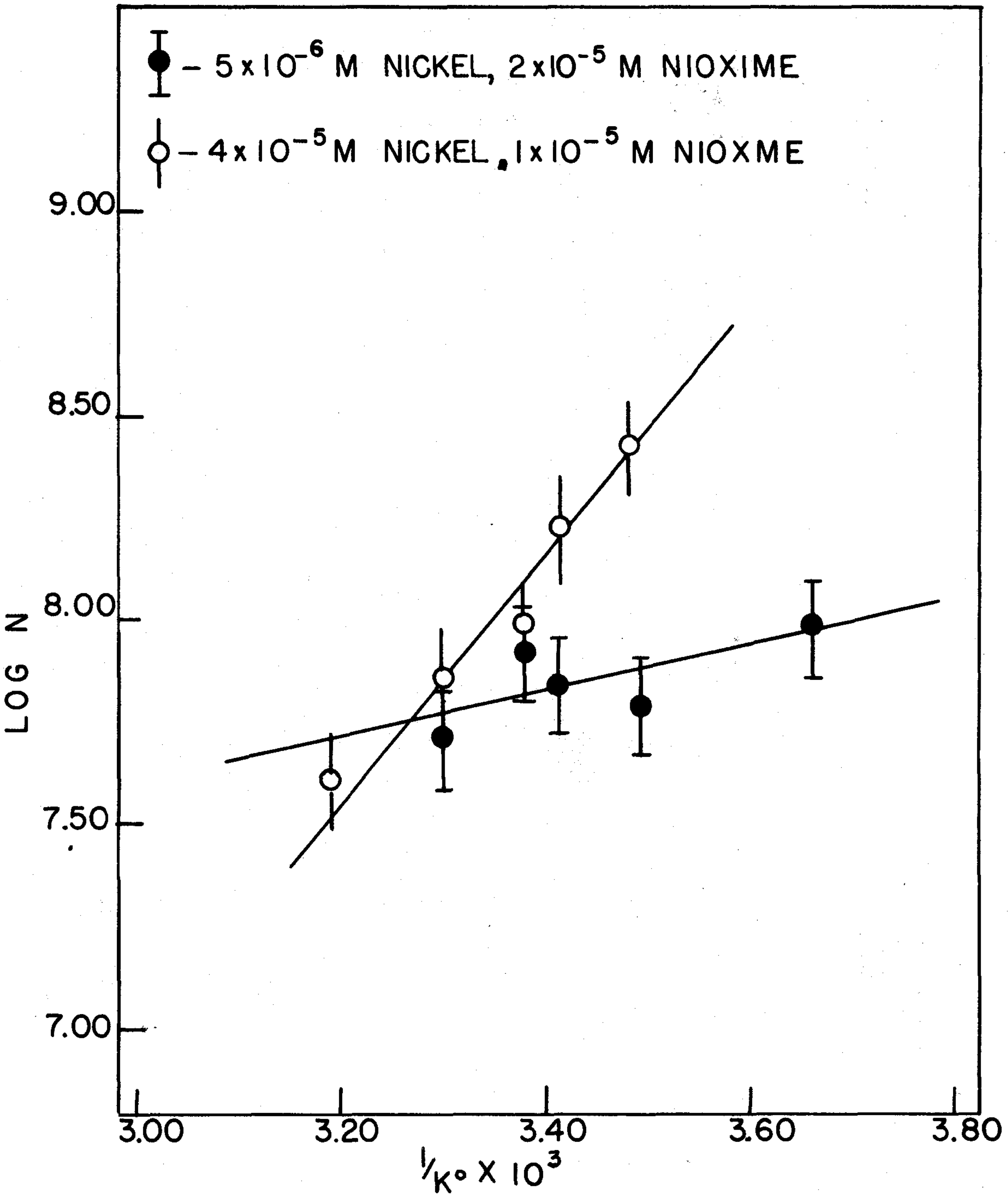

Figure 14. Variation of number of nickel nioxime crystals with temperature

Table 16

Tabulation of results obtained from data on all three compounds

	Compound		
Quantity	$(C_6H_5)_4AsMnO_4$	$(C_6H_5)_4AsClO_4$	$Ni(Niox)_2$
$(n-n')_A$[a]	----	----	0
$(n-n')_B$	2 (1.60)[b]	2[c]	2 (1.60)
$(m-m')_A$	1 (1.17)	2	2
$(m-m')_B$	----	----	2
$(\Delta H_{diff})_A$	----	-36.4 kcal	-21.1 kcal
$(\Delta H_{diff})_B$	-21.0 kcal	-22.1 kcal	- 2.8 kcal
ρ	1.580 gm/cm^3	1.549 gm/cm^3	

[a] Subscripts indicate whether the excess reagent is the one furnishing cations (A) or anions (B).

[b] Values in parentheses represent the values actually obtained when they differ substantially from the integer.

[c] This value was obtained at both 25° C and 0° C. All other values for n-n' or m-m' were obtained at 25° C.

this section, each quantity has the same meaning as previously defined, namely: n-n' and m-m' are the exponents of the cation, A, and anion, B, respectively as found in equation (8). The difference of the heats of activation of the nucleation and growth processes has been defined as ΔH_{diff}, and ρ is the density of the crystals. The subscripts denote the reagent present in excess when the result was obtained. The cation and anion reagents are indicated by the subscripts A and B respectively.

The results given in Table 16 will be discussed in light of the theory which was presented in the preceding section.

V. DISCUSSION

A. Discussion of Theory

Before the results can be interpreted, certain assumptions which have been made in the development of the theory should be discussed. The first is that nucleation of sparingly soluble salts follow the rate law

$$\frac{dN}{dt} = k_1 A^n B^m \quad . \tag{1}$$

This is best considered to be a series of fast second order equilibrium steps forming ionic agglomerates of intermediate size followed by the rate determining step which is the addition of a final particle to form the nucleus. If, as an example, we assume that a given salt AB has as its nucleus in the precipitation process the ion quadruplet A_2B_2, then the formation of nuclei is shown schematically by the equations

$$A + B \underset{K_1}{\overset{\text{fast}}{\rightleftharpoons}} AB$$

$$AB + A \underset{K_2}{\overset{\text{fast}}{\rightleftharpoons}} A_2B$$

$$A_2B + B \xrightarrow{k_1} A_2B_2 \text{ (nuclei).}$$

These equations, when treated kinetically, give equation (1). Christiansen and Nielsen[21] derived this same equation for the formation of nuclei. The mechanism is analogous to that assumed in Volmer's theory[1] except that in the latter a great many more particles are involved.

Christiansen and Nielsen[22] suggest that the rate of growth of crystal nuclei is dependent on the ion concentrations to some low power and upon the surface area of the precipitate; however, the growth equation developed by them does not directly contain the surface area. Equation (2), which is

$$\frac{dP}{dt} = k_2 \, S \, [A]^{m'} [B]^{n'} \quad , \tag{2}$$

does contain the total surface area of precipitate, S. La Mer and Dinegar[10,25] have shown that the number of particles in dilute solution is set by the original concentration in the saturated solution. In this case, it is believed to be the result of the factor S in the rate equation rather then a large difference in reaction order between nucleation and growth.

The assumption that the growth law is dependent on A and B to low powers, i.e., that m' and n' are small, has been shown to be valid by several workers.[4,10,22] Although the assumption is good, the actual size of the nuclei of sparingly soluble salts cannot be determined until the correct growth law for each is known.

Another assumption is that the number of particles, N, is fixed in the region where an insignificant amount of precipitation has occurred. Turkevich, Stevenson and Hiller,[30] who treat nucleation and growth as being separable processes, report the nucleation is essentially complete before as much as five per cent of the reactants have been used. If this assumption is true, then it is a fact that at some point in the precipitation, i.e., when

$$\frac{dN}{dP} = C \quad ,$$

nucleation no longer competes with growth. This does not exclude the formation of nuclei after C is reached, but the nuclei which are formed after that are not likely to grow into crystals.

B. Discussion of Results

1. Test of the theory

The data on the precipitation of tetraphenylarsonium permanganate are not as reliable as those for the other salts, because of apparent side reactions. Although this is true, the data still give certain valid results. According to equation (10), the plot of log N vs. log C should be a straight line if the theory is correct. Figure 1 is the graph of log N vs. log MnO_4^- which shows a point for each run made. Even though these points are somewhat scattered, they fit the straight line quite nicely. In addition, the value $(m-m')_3 = 1$ is reasonable and of the order expected by the theory.

The second test of the theory is found in equation (13) which predicts that a graph of log N vs. $^1/_{K^o}$ will be a straight line. In addition, since nucleation is considered to be a higher order reaction than growth of the nuclei, the slope of this straight line graph should be positive. These two predictions are substantiated by Figure 3.

Because of the result of Figure 1, i.e., that log N vs. log C yields a straight line, fewer runs were necessary in all other series of runs where a concentration was the variable. This was true because only the slope of the line to the nearest integer was needed in the results.

2. Variations of concentrations

The results of the concentration variation of both reagents for each precipitate are best seen in Table 16. No definite conclusions can be drawn concerning the size of the nuclei of tetraphenylarsonium permanganate and tetraphenylarsonium perchlorate unless we assume that the precipitation mechanism is independent of the precipitating reagent present in excess. However, the results are very important, for they show conclusively that only a small number of ions form the nuclei of crystals of sparingly soluble salts.

More complete results have been obtained in studying the precipitation of nickel nioxime. These results show that n-n' and m-m' have different values when nickel is present in excess than when nioxime is present in excess. This leads to the conclusion that either one or both of the processes, nucleation and growth, is different in the two cases. If a reasonable growth law is assumed, it is possible to obtain the size and composition of the nucleus. Table 17 shows several assumed growth laws and the nucleus for each when the indicated reagent is in excess.

The first growth equation in each case is based on the fact that the reagent present in excess may be zero order in the growth step. The third growth law is that assumed by Christiansen and Nielsen.[22] The second is merely intermediate to the others. For every other postulated growth law a corresponding nucleation equation could be written.

It is important to notice that none of the nucleation rate laws would predict a stoichiometric ration of nickel to nioxime. This is contrary to the arguments of Christiansen and Nielsen.[21] La Mer, in reinterpreting his data for

Table 17

Sizes of nuclei of nickel nioxime associated with each assumed growth law

Assumed Growth Rate Law	Nucleation Rate Law
A. Nickel in excess: $(n-n')_A = 0$, $(m-m')_A = 2$	
1. $\frac{dP}{dt} = k_2 [Niox]$	$\frac{dN}{dt} = k_1 [Niox]^3$
2. $\frac{dP}{dt} = k_2 [Ni^{++}][Niox]$	$\frac{dN}{dt} = k_1 [Ni^{++}][Niox]^3$
3. $\frac{dP}{dt} = k_2 [Ni^{++}][Niox]^2$	$\frac{dN}{dt} = k_1 [Ni][Niox]^4$
B. Nioxime in excess: $(n-n')_B = 2$, $(m-m')_B = 2$	
1. $\frac{dP}{dt} = k_2 [Ni^{++}]$	$\frac{dN}{dt} = k_1 [Ni^{++}]^3 [Niox]^2$
2. $\frac{dP}{dt} = k_2 [Ni^{++}][Niox]$	$\frac{dN}{dt} = k_1 [Ni^{++}]^3 [Niox]^3$
3. $\frac{dP}{dt} = k_2 [Ni^{++}][Niox]^2$	$\frac{dN}{dt} = k_1 [Ni^{++}]^3 [Niox]^4$

barium sulfate,[10] according to their theory, obtained a value of 7 for the total number of ions in the nucleus. This would give a charged nucleus which might be either $Ba_3(SO_4)_4^{=}$ or $Ba_4(SO_4)_3^{++}$. These theoretical arguments based entirely upon electrostatic forces should not necessarily apply to chelate compounds such as nickel nioxime.

3. Variation of temperature

The variations of the number of crystals with increasing temperature is exactly that predicted by the theory. Not only is the graph of log N vs. $^{1}/_{K^{o}}$ a straight line, but the slope is positive. This indicates that the heat of activation for the nucleation process is more negative than that for the growth process. The effect is just what would be predicted from the fact that the nucleation process is of greater total order than the growth process.

The results obtained from Figures 8 and 14 show that for both tetraphenylarsonium perchlorate and nickel nioxime the value of ΔH_{diff} depends on which precipitating reagent is in excess. This fact supports the results already discussed, namely, that (m-m') and (n-n') depend on the reagent in excess. From the fact that ΔH_{diff} is only -2.8 kcal when nioxime is in excess, it appears reasonable to predict that the nucleation mechanism is very similar to the growth mechanism. This observation is seemingly not true at least for the postulated mechanisms of Table 17.

4. Variation of ionic strength

The results from the variation of the number of crystals with increasing ionic strength are qualitative. This effect can be explained, however, on the basis of the competitive rate equations for nucleation and growth. Since the nucleation rate has a higher total order than the growth rate, i.e., $(m-m')_B = 2$, the nucleation rate would be more retarded than the growth rate because of the affect of increasing ionic strength. If the nucleation rate were decreased relative to the growth rate, fewer crystals would be predicted. This is the qualitative result which has been observed.

5. Variation of stirring

The experiments on rate of stirring and the length of stirring time were designed to determine whether or not the rapid stirring at the beginning of each run had any detrimental effects. Figure 10 shows that the size of the crystals is not affected when the reaction mixture is stirred throughout the precipitation unless the stirring is very rapid. This effect of rapid stirring is great if it is accompanied by much turbulence and air bubbles and might be caused by these air bubbles, and dust particles carried by them, acting as crystal nuclei, thus increasing the number of crystals formed.

If the above conclusion is so, it would then be expected that the number of crystals would be increased if turbulent stirring were continued only until completion of nucleation. Figure 11 indicates that this rapid stirring has only a slight effect until the reaction has proceeded 15 or 20 minutes. Surely nucleation is complete before half of the reaction time has passed.

The most reasonable explanation which has been postulated is that the effects of stirring during precipitation are entirely mechanical. This can be thought of as the breaking up of the crystals by eddy currents and air bubbles when they reach a certain size. Each of these pieces then grow to a well defined crystal. This argument is supported by the fact that in Figure 10c., in which run turbulent stirring was continued throughout precipitation, many crystals with broken edges can be seen.

The fact that the above explanation may or may not be correct does not alter the result originally sought. These experiments have shown conclusively that the five seconds of turbulent stirring at the beginning of each run could not have affected the results in any way.

C. Discussion of Errors

Essentially all the errors in this work are confined to the estimation of the number of crystals. Errors in the concentrations of reagents and in the temperature of the water baths are negligible compared to the other errors.

The greatest error, caused by a combination of several factors, was the reproducibility of the number of crystals when the precipitations were carried out under identical conditions. Usually the deviation from the average number of crystals was about 25 per cent; however, in some cases the deviation would be as much as 100 per cent or 150 per cent. In these cases the error was attributed to localization effects though it may have been due to other causes.

The errors in estimating the number of crystals in precipitating tetraphenylarsonium permanganate and tetraphenylarsonium perchlorate are, in addition to the above, the result of measuring and estimating the average volume per crystal. Since the crystals were measured from photomicrographs with a plastic millimeter scale, the measurements were accurate to 0.1 mm. This, of course, gave a greater percentage error for small crystals than for larger ones. A second error in determining the average volume was caused by the fact that only a few large crystals could be located on the photograph. The average volume calculated from these few may not have been accurate. The calculation of the volume per crystal from the equation $v = lw^2$ is not correct though it is a good approximation as previously discussed. All of these errors together work in such a way that the average error per run should be about constant as indicated by the vertical lines in all the graphs involving these compounds.

Since the number of crystals in each run with nickel nioxime was estimated by direct count, the errors in measuring were eliminated. Other errors must be considered. The error of measuring 0.01 ml. from a graduated 0.1 ml. pipette may be as much as 10 per cent. In fact, this error together with errors of counting the crystals under the microscope, was found to be about 10 per cent as determined by counting several aliquots from the same solution. As before, the vertical lines on the graphs concerning nickel nioxime indicate an average error.

As can be seen from the above discussion and from the scatter of points on the various graphs, the method used in obtaining the data for nickel nioxime has distinct advantages over the method used for the first compounds studied. This method is to be recommended for any future studies of this nature.

D. Suggestions for Extension of Work

The mechanism of nucleation cannot be determined completely until the orders of the ions in the growth equation are known. Because the results for nickel nioxime contained in this work are the most complete, it is suggested that the growth of nickel nioxime crystals be studied. The results of that study should be compared with the postulated mechanisms listed in Table 17.

Conductance methods for determining the rate of precipitation[24] probably would not be satisfactory for use with nickel nioxime. A more promising method is to follow the reaction by means of a Sargent Model V Oscillometer. This instrument measures a combination of dielectric constant and high frequency conductance.[31] The scale reading of this instrument has been shown to be a linear function of concentration within a limited concentration range. Qualitative experiments indicate that this concentration range can be shifted by placing a metal slug in the center of the oscillator coil.

In addition to studying the growth mechanism for nickel nioxime, the theory which has been set forth here should be tested with other sparingly soluble salts. Perhaps barium sulfate and silver chromate should be studied, so that this theory can be compared more closely with that of Christiansen and Nielsen. It would be of interest also to study other salts which have highly charged cations or anions such as ferric ferrocyanide.

VI. CONCLUSIONS

1. Nucleation and growth are competitive processes and nucleation cannot be studied separately.

2. The size of the nuclei of crystals of sparingly soluble salts is equal to the kinetic order of the reacting ions in the nucleation rate equation. These nuclei contain only a small number of ions.

3. The difference in the exponents of a given ion in the rate equation for nucleation and growth can be determined by estimating the number of crystals produced when the precipitation is carried out at several concentrations of that ion. The slope, or the integer nearest the slope, is equal to this difference in exponents.

4. The difference in exponents, as found above, is independent of the temperature at which they are determined.

5. The actual size of the nucleus cannot be determined without knowing the mechanism of growth. Assuming reasonable growth mechanisms, nucleus sizes have been predicted for nickel nioxime.

6. Determination of the number of crystals produced by the same initial concentrations at several different temperatures permits the calculation of ΔH_{diff}, the difference in activation energies of the nucleation and growth

processes.

7. That the value of ΔH_{diff} depends on which precipitating ion is in excess is true for tetraphenylarsonium perchlorate and nickel nioxime. This indicates that either the nucleation process or the growth process or both depends upon which reagent is in excess. The results obtained from the variation of the reagent concentrations in the precipitation of nickel nioxime substantiate this conclusion for that compound.

8. The number of crystals produced in a given precipitation is dependent on the ionic strength of that reaction mixture. Fewer crystals are formed at a higher total concentration of ions. This is the effect predicted by the theory.

9. Both rate of stirring and the time of stirring have an effect on the size of the crystals produced, but the effect is considered to be a mechanical breaking of small crystals.

10. The methods used for determining the number of crystals produced in a precipitation reaction are inaccurate; however, the accuracy is such that the slopes of the lines of log N vs. log C could be determined to the nearest integer. The method used to determine the number of crystals of nickel nioxime is much simpler and more

accurate than that used for the other salts.

11. Additional data are needed to test the theory more completely. The growth mechanism of nickel nioxime should be studied to determine the actual sizes of its crystal nuclei. Other compounds, particularly those which have higher charged ions, should be studied to substantiate the results reported in this work.

VII. SUMMARY

Volmer[1] considered the crystal nucleus to be the agglomerate of ions or molecules of just sufficient size to be stable in a separate phase in contact with solution of a given degree of supersaturation. By using reasonable values of interfacial tensions, it is calculated that crystal nuclei consist of one-hundred or more molecules.

Recent work, based on the kinetics of precipitation, has led to the conclusion that a very small number of ions is involved in the nucleus of silver chromate,[20] calcium fluoride,[20] and barium sulfate.[18,20,22] In every investigation to the present time, nucleation has been treated as a process totally separable from the growth process. This assumption is based on the association of nucleation with the induction period in precipitation reactions.

In this work the formation of crystal nuclei is considered to be a process competitive with growth of these nuclei. The size of the nucleus is defined by the kinetic order in ions or molecules of the nucleation reaction. The relative rates of nucleation and growth are estimated by counting the number of crystals obtained from a given supersaturated solution. Effects of variation in degree of supersaturation on the number of crystals obtained allows a determination of the number of each kind of ion per nucleus providing a growth rate is known or assumed. Variation of the number of crystals with temperature allows determination of the relative activation energies for nucleation and growth.

The theory outlined above has been tested with three different compounds: tetraphenylarsonium permanganate, tetraphenylarsonium perchlorate and nickel nioxime. These results are summarized in Table 16. The results for nickel nioxime are the most complete, and they show that either the nucleation mechanism, or the growth mechanism, or both, is dependent on which precipitating reagent is in excess. The values of ΔH_{diff} obtained from experiments with tetraphenylarsonium perchlorate indicate that the above fact is also true for that salt. The results obtained from data concerning tetraphenylarsonium permanganate are not considered reliable because of evidence of side reactions during the precipitations.

The method of estimating the number of crystals produced in precipitations of nickel nioxime was different from that used for the other two salts.

In runs producing the tetraphenylarsonium salts, the number of crystals per liter was found from the average volume per crystal. With nickel nioxime, N was found by direct count of the crystals in an aliquot of reaction mixture. The latter procedure is much better, for it eliminates many errors which occur in the former.

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