accelerated protons and helium ions was increased.[21]

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

The Kinetics of Precipitate Formation: Barium Sulfate[1]

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In the early stage of precipitation, the reaction is limited by nucleation and the slow growth of the newly-formed crystals. The sharp termination of the induction period arises from the autoinductive nature of the growth process. Autoinduction arises because the rate of growth is kinetically dependent upon the surface, and, as growth proceeds, the surface increases causing the rate of growth to increase. The precipitation process is interpreted as being initially controlled by the nucleation reaction and finally controlled by the growth reaction. During the first part of the induction period, only a few crystals are present and they grow so slowly that precipitation does not appear to take place. Near the end of the induction period, the "oldest" crystals attain considerable surface area and begin to grow rapidly. At the end of the induction period these crystals begin to reduce the concentration of the solution so rapidly that the smaller crystals are never able to reach a comparable size. After the "oldest" crystals begin to grow rapidly, they dominate the further precipitation and the precipitate approaches homogeneity with respect to crystal size. Theoretical equations based on these concepts have been derived and are well supported by experimental data. The first part of the precipitation process is represented by a relationship which takes into account the simultaneous nucleation and growth reactions. The equation fits the experimental data very well for times up to approximately twice the length of the induction period. For the remainder of the precipitation process the nucleation reaction is considered to be negligible and the rate equation involves only the growth reaction operating on a respective fixed number of particles. From consideration of the equations, and the experimentally determined constants, it has been found that the number of crystals is constant in the activity range examined.

Introduction

In the course of precipitate formation from very dilute solutions, two stages are observed: the induction period and the growth period. In the induction period, metastable systems of relatively great supersaturations may exist for considerable lengths of time without producing a visible precipitate. The induction period is terminated rather abruptly by the appearance of the precipitate. The growth stage follows during which precipitation occurs relatively rapidly, the particles grow, and the supersaturation is relieved.

From the standpoint of reaction mechanism, precipitate formation is considered to be a two-step process, the steps being nucleation and growth. The nucleation step involves the buildup of clusters, clusters being those entities which are part of the mother phase and which tend to dissociate. The nucleation step is culminated as the entities attain a critical size, beyond which the stability pattern is reversed and the particles tend to grow. The entities which have attained the critical size are called nuclei and are a new phase. The growth stage involves their development.

The empirical equation

$$I = \lambda C_0^{-n} \qquad (1)$$

has been fitted to the induction period data of many slightly soluble salts by some investigators.[2-6] In equation 1, I is the induction period, C_0 is the initial molar concentration, λ and n are constants. Christiansen and Nielsen[7] proposed that n was related to the order of the nucleation reaction. LaMer[8] has discussed this proposal with respect to the data of LaMer and Dinegar.[9] Duke[10] as well as Turnbull[11] proposed that the nucleation process takes place only during mixing and that growth of these first nuclei is responsible for the induction period and growth behavior. Christiansen and Nielsen[12] derived equations treating the nucleation and growth processes separately and fitted their equations to the data of Tovborg Jensen.[3] Large deviation from the theoretical curve during the first part of the precipitation process was attributed to the invalidity of the assumption that the crystals were of the same age.

Processes in the Induction Period.—The rate of growth of a single crystal may be represented by

$$\frac{\mathrm{d}a}{\mathrm{d}t} = -k(C_0 - C)^{2/3} \times a^q \qquad (2a)$$

where a is mean ionic activity, $\sqrt{(\mathrm{Ba}^{++})(\mathrm{SO}_4^{=})}$, at time t, C_0 and C are molar concentrations of barium sulfate available for precipitation at the initial time and at time t, respectively, and k and q are constants. The term in the parentheses is in molar concentration units since it relates mass to

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[1] Material in this paper has been taken from the Ph.D. thesis of J. D. O'Rourke and was presented before the Colloid Division at the 124th Meeting of the American Chemical Society in Chicago, Sept. 1953.

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surface; the corresponding shape factor is incorporated in k. The rate constant is also incorporated in k. It is assumed that the rate of change of mean ionic activity is proportional to some power, q, of the mean ionic activity, as well as the surface of the particle. During the induction period and until shortly after its termination the value of a^q is nearly constant; also, during this period the value of the activity coefficient at C will be substantially the same as that of C_0. The integral equation for growth of a single particle from time τ then becomes

$$\int_{a_0}^{a}(a_0 - a)^{-2/3}\,\mathrm{d}a = -\frac{k\alpha^q}{\gamma^{2/3}}\int_{\tau}^{t}\mathrm{d}t, \text{ or}$$

$$(a_0 - a) = \frac{k^3a^{3q}}{27\gamma^2}(t - \tau)^3 \quad (2b)$$

It is assumed that nuclei are formed at all times after mixing and that the rate of formation of these nuclei is given by

$$\frac{\mathrm{d}\nu}{\mathrm{d}t} = Ka^p \quad (3a)$$

in which ν is the number of particles and p is a constant. Again, because the concentration during the induction period and shortly after its termination is essentially constant, the rate of particle formation may be considered constant. The number of particles formed in the interval $\tau \leq t \leq (\tau + \mathrm{d}\tau)$ is expressed as

$$\mathrm{d}\nu = Ka^p\,\mathrm{d}\tau \quad (3b)$$

The expression for change in activity caused by the condensation taking place on all the particles formed in this interval is from (2b) and (3b)

$$(a_0 - a) = \frac{k^3a^{3q}}{27\gamma^2}(t - \tau)^3 \times ka^p\,\mathrm{d}\tau \quad (4)$$

The time of nucleus formation, τ, may vary from time of mixing to the time t, thus, the decrease in activity due to formation and growth of all crystals up to time t is given by

$$(a_0 - a) = \int_0^t \frac{Kk^3a^{(3q+p)}}{27\gamma^2}(t - \tau)^3\mathrm{d}\tau, \text{ or}$$

$$(a_0 - a) = \frac{Kk^3a^{3q+p}}{108\gamma^2} \times t^4 \quad (5)$$

When $(a_0 - a)$ is the smallest detectable change in activity, t is the induction period, I. Equation 5 should hold only for a short time after the termination of the induction period, as the activity term $a^{(3q+p)}$, does not remain constant beyond this time.

Theory of the Growth Period.—It is probable that soon after the induction period the growth reaction so predominates the precipitation process that contributions from nucleation may be neglected. Accordingly, equation 2 represents the reaction rate during this period. Two modifications are necessary, however: (1) the back reaction becomes important in the latter part of the period and is taken into account by using the term $(a - a_s)$ instead of a, where $a_s = \sqrt{K_{\text{s.p.}}} = 10^{-5}$; (2) the number of growing particles must be considered. Since large particles grow so much faster than small particles, the contribution of the smaller particles may be neglected. Further, if the large particles sharing the greatest load of the growth reaction constitute only a small fraction of the total number of particles, the former may be assumed to be approximately homogeneous with respect to size. If their advantage is maintained throughout the growth process, the number of particles involved in growth may be assumed to be constant. Accordingly, the growth equation becomes

$$\frac{\mathrm{d}a}{\mathrm{d}t} = -k\nu^{1/3}(C_0 - C)^{2/3}(a - a_s)^q \quad (6)$$

The fractional power of the number of particles arises from the dependence of the surface on the number of particles present in the solution. The volume per particle is represented by $(C_0 - C)/\nu$, so that the surface per particle varies with $[(C_0 - C)/\nu]^{2/3}$, and the total surface area of the precipitate is $\nu[(C_0 - C)/\nu]^{2/3}$, or $\nu^{1/3}(C_0 - C)^{2/3}$.

The direct integration of equation 6 leads to an equation which cannot be handled easily. Numerical integration by the method of Gauss[13] provides a solution from the experimental data. The concentrations appearing in the surface term must be replaced by activities in order to apply the method of Gauss to the data. The error in assuming that the term $(a_0 - a)^{2/3}$ is representative of the surface is small.

Experimental

The reactant concentration was followed conductometrically using an Industrial Instruments conductivity bridge, Model R.C. Solutions of the individual reactants were prepared from 0.01 M stock solutions of C.P. barium chloride and C.P. sodium sulfate. The reaction mixtures were prepared by pouring together the two reactant solutions and mixing rapidly. Reactants and the reaction mixtures were maintained within 0.05° for each run. Time was measured from the instant of mixing. In order to avoid, as completely as possible, any effect of heterogeneity at the moment of mixing, the barium and sulfate solutions were made as dilute as possible before mixing.

The conductance cells and beakers were cleaned with a freshly prepared sulfuric acid–potassium dichromate cleaning solution after each run. The cleaning solution was left in the glassware for at least 30 minutes before it was rinsed out. After the conductance cells were thoroughly rinsed, they were filled with distilled water and allowed to stand for over an hour, the water being changed several times during this period. Bright platinum electrodes were used in preference to platinized electrodes in order to reduce the adsorption of the cleaning solution to a minimum.

It was found that the cleaning solution was easily saturated with barium sulfate and it was necessary to prepare a new cleaning solution quite often. Also, the glassware was given a preliminary washing with distilled water before adding the cleaning solution. This avoided adding barium chloride to the sulfuric acid–dichromate solution.

The following equation was used to determine the decrease in the concentration of barium sulfate

$$C = 1000\Delta\kappa/2\Lambda$$

where κ is specific conductance and Λ is equivalent conductance. The value of the equivalent conductance, Λ, was found by use of the Onsager equation[14]

$$\Lambda = \Lambda_0 - (0.6476\Lambda_0 + 85.18)\cdot 2\sqrt{2C}$$

Activities were determined using coefficients calculated from the Debye–Hückel equation with 4.5 Å. as the distance of closest approach of the ions.[15]

The length of the induction period was determined by ex-

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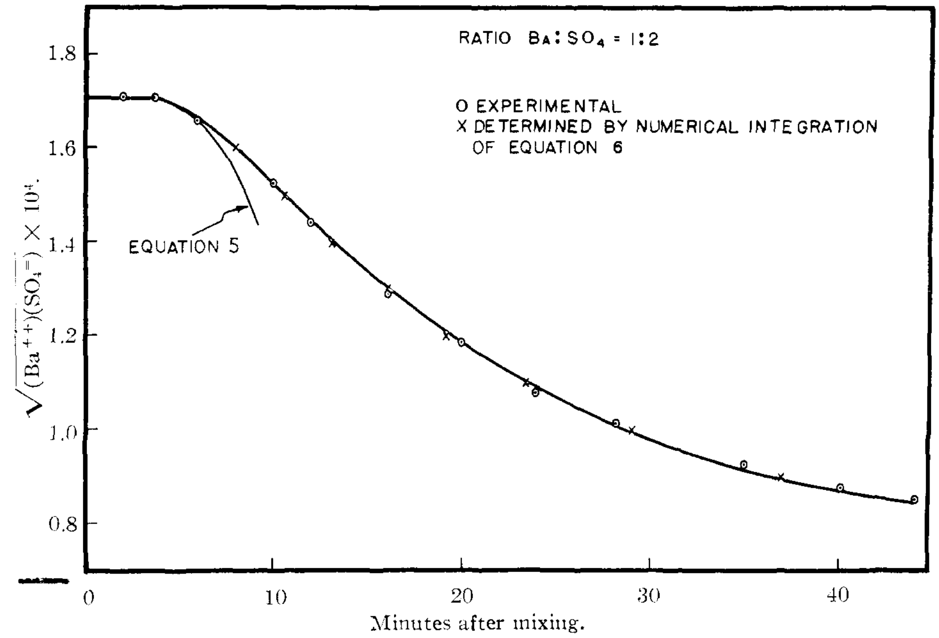

Fig. 1.

trapolating the precipitation curve to the original concentration using only the first few measurements taken after precipitation had been detected.

Evaluation of Constants.—The value of $(3q + p)/4$ may be determined experimentally by observing the dependence of the length of the induction period on the activity. Equation 5 may be rewritten as

$$I = \left[\frac{(a_0 - a)108\gamma^2}{k^3K} \times a^{-(3q + p)}\right]^{1/4} \qquad (7)$$

The first detectable decrease in activity $(a_0 - a)$ is assumed to be constant, hence

$$\log (I) = {}^1\!/_4 \log \frac{(a_0 - a)108\gamma^2}{k^3K} - \frac{3q + p}{4} \log (a) \qquad (8)$$

Equation 8 was treated as a linear regression with log (I) as the dependent variable and log (a) as the independent variable. The regression was tested for linearity at the 95% level by an analysis-of-variance technique, assuming the activity coefficient was constant in the activity range investigated, 0.9×10^{-4} to 1.7×10^{-4}. The standard error of estimate of log (I) was 0.02; hence, the small variation in the activity coefficient should have no appreciable effect upon the value of $(3q + p)/4$.

Values of $(3q + p)/4$ found at various temperatures are all approximately 4.0. Since $(3q + p)/4$ does not appear to vary with temperature, it may be assumed that the precipitation mechanism is independent of temperature.

The value of q was determined by fitting the experimental data from the growth period to equation 6 and substituting in various integral values for q. In all cases, four was the only value which would fit the experimental data from shortly after the termination of the induction period to the end of the precipitation process. Since q is four, the rate of nucleation must depend upon the fourth power of the mean ionic activity also.

By fitting equation 5 to the first part of the precipitation curve the value of k^3K may be determined. Figure 1 illustrates the fit of equations 5 and 6 to experimental data. Values of $k\nu^{1/3}$ and K/ν found from equations 5 and 6 are compiled in Table I.

The variation in the last two columns in Table I appears to be random and uncorrelated with activity of reactants.

TABLE I

RATE CONSTANTS, NUMBER OF NUCLEI AND IONIC ACTIVITIES

k = growth rate constant (including certain geometric factors) K = nucleation rate constant; ν = number of crystals per liter.

Initial mean ionic activity	$(Ba^{++})_0$: $(SO_4^{=})_0$ ratio	$k\nu^{1/3}$	K/ν
2.33×10^{-4}	1:2	8.6×10^{17}	1.12
2.33×10^{-4}	2:1	8.6×10^{17}	0.63
1.71×10^{-4}	1:2	13.5×10^{17}	.60
1.60×10^{-4}	1:1	12.9×10^{17}	.45
1.49×10^{-4}	1:1	19.3×10^{17}	1.31
0.89×10^{-4}	1:1	11.4×10^{17}	2.20

This suggests that the number of crystals, ν, is constant over the activity range studied. If the number of crystals varied with changing concentration, then these values would vary accordingly. The explanation of the constancy of the number of crystals rests upon the dependence of the rate of nucleation and the length of the induction period upon the mean ionic activity. If the activity is doubled, the rate of nucleation increases 16 times. However, the time during which the nucleation process is effective is decreased 16-fold because the rate of growth is so great at the end of the induction period that the rate of nucleation is no longer a factor. Thus, at the end of the induction period, the number of crystals should remain constant regardless of the initial concentration. As a consequence of this, the final size of the particles should increase with concentration. This behavior has been experimentally observed for precipitations from very dilute solutions by Von Weimarn (The First Precipitation Law)[16] and Fisher.[17]

Since the activity dependence of the rate of nucleation is the same as growth, there is a possibility that the growth process involves a mechanism similar to that of the nucleation mechanism.

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