

[CONTRIBUTION FROM THE BELL TELEPHONE LABORATORIES, INC.]

Kinetics of Hydrothermal Quartz Crystallization¹

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A study is reported of the growth rate of the basal (0001), major (10 $\bar{1}$ 1), minor (01 $\bar{1}$ 1) and prism (10 $\bar{1}$ 0) faces of quartz in 0.50 *m* NaOH under hydrothermal conditions. These rates are correlated with newly determined solubilities in the same system in an effort to find the rate-determining step and to calculate the pertinent thermodynamic data for the activated state. The principal findings are as follows: (1) The logarithm of the rate was found to be a nearly linear function of the reciprocal of the absolute temperature. (2) The rate was found to be linearly dependent on Δt , the temperature difference, between the growing and dissolving regions. (3) The rate was found to be almost linearly dependent on the per cent. fill and the perfection of material grown on the basal plane increased as the rate increased, when this rate increase was brought about by increasing the per cent. fill at 400°. Good quality material could be grown at rates in excess of 0.20 in./day. (4) The logarithm of the solubility was found to be linearly dependent on the reciprocal of the absolute temperature at constant fill and the heat of solution of quartz was found to be 1300 cal./mole at 80% fill. (5) The rate equation $R = k\alpha\Delta S$ where R is the rate of linear extension of a particular face, k is the velocity constant, ΔS is the supersaturation and α a constant was verified under a variety of conditions, and the energy of activation and the frequency factor were calculated. (6) The rate was found to be independent of the area of the growing surface provided the ratio of the area of the dissolving surface to the growing surface was greater than five. (7) The rate-determining step was found to occur probably at the interface: saturated solution-growing crystal.

Introduction

The application of a high temperature high pressure aqueous solvent to increase the solubility of a difficultly soluble material to a point where it can be crystallized on a seed without appreciable self-nucleation has been used with varying degrees of success since the nineteenth century. This technique, usually called hydrothermal crystallization, has been applied to the preparation of quartz by many investigators, notably Spezia,² Nacken,³ Hale,⁴ Brown⁵ and Walker.⁶ However, little quantitative information on the effect of parameters such as temperature, per cent. fill and temperature differential and virtually no data on the relationship of growth rate to supersaturation and solubility are available. This study reports a series of measurements of the linear velocity of crystallization made as a function of several parameters and the correlation of these rates with some newly determined solubilities of quartz. From these measurements an attempt to deduce the rate-determining step is made and the energies of activation and the frequency factor are calculated.

The system studied was H₂O–Na₂O–SiO₂ under conditions of constant relatively low Na₂O concentration and in a pressure–temperature range where quartz was the stable solid phase.

Experimental

Welded closure high pressure vessels of the sort described by Walker⁶ one inch in internal diameter by one foot in internal length were placed in ovens capable of producing any desired bottom temperature and any desired difference in temperature between dissolving and growing zones of the vessel. The oven was essentially of the design described by Walker.⁶ Seed crystals of the desired orientation and of known dimensions were cut from X-ray oriented specimens of natural Brazilian quartz and suspended in the upper or

growth region comprising about two-thirds of the autoclave volume and small particles of Brazilian quartz (size such as to pass U.S. sieve size #3 but not #4) were placed in the lower or nutrient region. Between the two regions there was placed a perforated metal disc or baffle which had been previously found in this laboratory to aid in decreasing the growth rate differences between the several crystals in the growth region. The autoclave was filled to the desired fraction or per cent. of fill of its free volume in every case with 0.50 *m* NaOH and closed. The autoclave then was placed in a furnace and maintained under predetermined conditions of bottom temperature, top temperature and temperature differential (Δt).

Temperatures were measured by strapped external chromel–alumel thermocouples. Temperature probes with extremely small thermal masses⁷ were used to measure the internal temperatures at various levels in a commercial Aminco⁷ delta ring seal vessel of similar geometry under conditions of fill and external temperature identical with the welded closure vessels. It was found that the external temperature could be related to the internal temperature quite readily and that at certain levels the internal and external temperatures were nearly identical. The temperatures reported in this study then are time averaged internal temperatures as determined by correcting external temperature readings with the data obtained by probing a vessel of geometry similar to the welded closure vessel. The vessels were maintained at predetermined temperatures for from several days to several weeks. Temperature fluctuations were seldom more than $\pm 3^\circ$ and warm up and cool down times were kept to a minimum. Probing furthermore showed that with a perforated metal disc or baffle whose open area was 10% of the cross-section of the vessel separating the dissolving and growth zones, the temperature within each zone was relatively uniform along the length of the vessel and the temperature drop took place almost entirely in a region extending from about two inches below to two inches above the baffle. The holes in the baffle consisted of one $\frac{3}{16}$ in. in the center and four $\frac{1}{8}$ in. holes drilled at the edge. Part of the open area was contributed by a $\frac{1}{16}$ in. annular space between the periphery of the baffle and the wall of the vessel. A baffle of this design was used throughout all the runs.

At the conclusion of the growth cycle the grown crystals were removed, their dimensions redetermined and the rate of linear extension calculated. The crystals were inspected in an oil-bath of suitable index of refraction for macroscopic perfection. The faces investigated were the basal plane (0001), the z -minor rhombohedral (01 $\bar{1}$ 1), the major rhombohedral (10 $\bar{1}$ 1) and the prism (10 $\bar{1}$ 0).

For the determination of the solubility of quartz under hydrothermal conditions a weight loss method similar in some respects to that employed by Morey⁸ was used. The

(1) Presented in part before the Physical and Inorganic Chemistry Division of the American Chemical Society Meeting, San Francisco, April, 1958.

(2) G. Spezia, *Accad. Sci. di Torino*, **44**, 95 (1908).

(3) R. Nacken, Captured German Report RDRDC/13/18, (February 28, 1946).

(4) D. R. Hale, *Science*, **107**, 393 (1948).

(5) C. S. Brown, R. C. Kell, L. A. Thomas, N. Wooster and W. A. Wooster, *Nature*, **167**, 940 (1951).

(6) A. C. Walker and E. Buehler, *Scientific Monthly*, **69**, 148 (1949).

(7) American Instrument Co., Silver Spring, Md. Thermocouple Assemblies Cat. Nos. 45-7623, 45-7626. Probes of special length were made to order. Delta ring autoclaves were made to order.

(8) G. W. Morey and J. M. Hesselgesser, *Am. J. Science*, Bowen Volume, B61 (1952).

data of Morey⁸ and of Kennedy⁹ were not applicable in the Na₂O concentration range of interest in our growth studies. The autoclave was of the same welded closure design as that used for the measurement of growth rates.

The hydrothermal autoclave containing NaOH solution of the appropriate per cent. fill was placed in a ceramic tube which was wound with nichrome wire to maintain a uniform temperature along its length. The solute, previously weighed plates of Brazilian quartz, was suspended on a frame in the autoclave and chromel-alumel thermocouples attached to a controller were strapped along the vessel. The tube with a bomb inside was placed in a horizontal position on a frame in the center of a metal box. Vermiculite insulation was poured into the box so that the tube was insulated from all sides. The metal box was fixed to a mechanism which gently rocked the box forward and backward at about 30° from the horizontal position. The apparatus described was capable of maintaining the whole length of the autoclave isothermal within ± 2° at any predetermined temperature.

Operating temperatures were reached as quickly as possible (ca. 4 hr.) and care was taken to avoid any over-shooting of the desired temperature. At the termination of a run, approximately three days after the bomb reached operating temperature, the power was turned off and the bomb was removed from the assembly and immediately quenched in cold water. The autoclave was then opened and the quartz sections dried and then accurately weighed to determine their loss. Suitable tests to insure that equilibrium had been attained were made.

Results of the Rate Studies

The parameters of principal importance in the growth process were found to be the orientation of the seed plate, the temperature of the growth region, the temperature difference (Δt) between nutrient and growth zone, the per cent. fill and the ratio of the area of the dissolving surface to the growing surface. Each of these parameters was studied by making a series of runs in which it was varied while all the others were held constant.

It was found that the fastest growing face under all conditions was the basal plane. The order of rates under all conditions was basal rate > minor rate > major rate >> prism rate.¹⁰ The rate on the prism face was generally so low as to preclude deduction of its quantitative dependence on external parameters.

Figure 1 shows the growth rate as a function of per cent. fill for major, minor and basal plates where the temperature of the growing zone was 385°, the temperature differential (Δt) between growing and dissolving zones was about 30° and the solution added was 0.50 *m* NaOH. The striking feature of Fig. 1 is that in the case of growth on the basal plane as the rate increased the macroscopic perfection also increased. Basal plane growth under most conditions of high rate is subject to macroscopic channel like voids roughly parallel to the *c*-axis. This imperfection has been called "crevice flawing" and is unexplained.¹¹ However, crevice flawing, and indeed almost all other crystalline imperfections, always have been found to increase as the growth rate increases. In contrast, as can be seen from Fig. 1 at a growth

(9) G. C. Kennedy, *Economic Geology*, **45** (7), 629 (1950).

(10) The growth rates as quoted in this paper are consistent with the general practice in hydrothermal quartz growth. That is they are the rates of linear extension normal to a plate of the specified orientation. For the calculation of the thermodynamic quantities for a surface of a particular orientation the rates were divided by two.

(11) Jacob M. Jost, *Quart. Progr. Rep.*, Contract No. DA36-039-sc-64589, Dept. of Army and Signal Corps, Clevite Research Center (Nov. 1955).

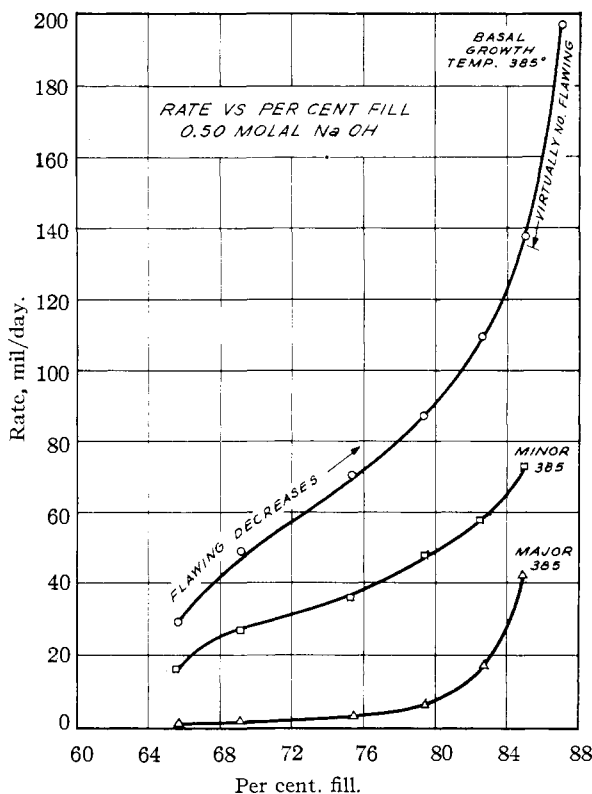


Fig. 1.—Rate vs. per cent. fill 0.50 *m* NaOH.

temperature of 385° as the per cent. fill is increased the rate increases and the flawing decreases until at 87% and a rate of 200 mil./day virtually flawless quartz can be grown. The rate in itself is surprisingly high for crystallization from a solvent and almost begins to approach the rates observed in melt systems. These unusually high rates together with high perfection are contrary to ordinary experience in crystal growth from a solvent and perhaps suggest a change in mechanism or in rate-determining step to a situation more like growth from a melt. The dependence of rate on per cent. fill at other temperatures was found to be generally similar.

If all parameters except temperature are held constant at say 80% fill, 0.50 *m* NaOH and 30° Δt and the growth rate data for the basal plane at growth temperatures of 310, 320, 330, 340, 375 and 400° are plotted as in Fig. 2 it is found that the logarithm of the growth rate is a linear function of the reciprocal of the absolute temperature, that is the data fit the empirical equation

$$\frac{d \ln (R)}{dT} = \frac{C}{RT^2} \quad (1)$$

where R is the rate, R is the gas constant and C is a constant. A similar relationship was found for the basal plane at 85% fill and 70% fill and probably holds true for the minor and major surfaces at 83.4%.

A study of the dependence of the rate on the area of the quartz surface available in the dissolving region was made by maintaining all other parameters constant while the surface area and number of seed plates was increased. It was found

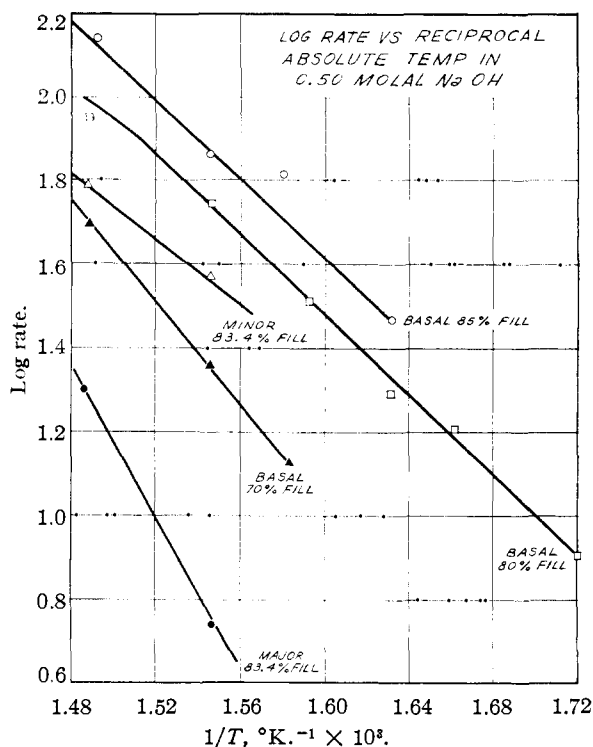


Fig. 2.—Log rate vs. reciprocal absolute temp. in 0.50 *m* NaOH.

that no changes in rate occurred at even the highest values for the surface area of the seeds provided the nutrient was the conventional small particle (#3 mesh) quartz ordinarily used in growth studies. However, when the nutrient was replaced with large lumps it was found that the rate fell off under all conditions where the ratio: area or dissolving surface/area of growing surface was less than five. Under these conditions the rate was dependent on the area of the dissolving surface.

Figure 3 shows that the dependence of rate on Δt at 85% was nearly linear and also indicates a method whereby extremely high rates may be obtained without inordinate pressures. The stability of NaOH solutions allows extremely high temperature differentials without self-nucleation. Rates as high as 100 mil./day were obtained with a Δt of 50° at 85% fill and 347° growth temperature while the pressure was below 27,000 p.s.i. as measured by a Bourdon gauge. A similar nearly linear dependence of rate on Δt was observed at 80% fill.

Results of Solubility Studies.—Solubility data for quartz in 0.50 *m* NaOH at 80% fill obtained by the loss weight method described above show, as can be seen in Fig. 4, that for a constant Δt , ΔS , the supersaturation is nearly constant and independent of temperature. Furthermore, as shown in Fig. 5 the temperature dependence of solubility at 80% fill obeys the van't Hoff expression for a constant volume system

$$\frac{d \ln s}{dT} = \frac{\Delta E}{RT^2} \quad (2)$$

where s is the solubility in moles per 1000 g. solvent and ΔE is the heat of solution. From the slope of

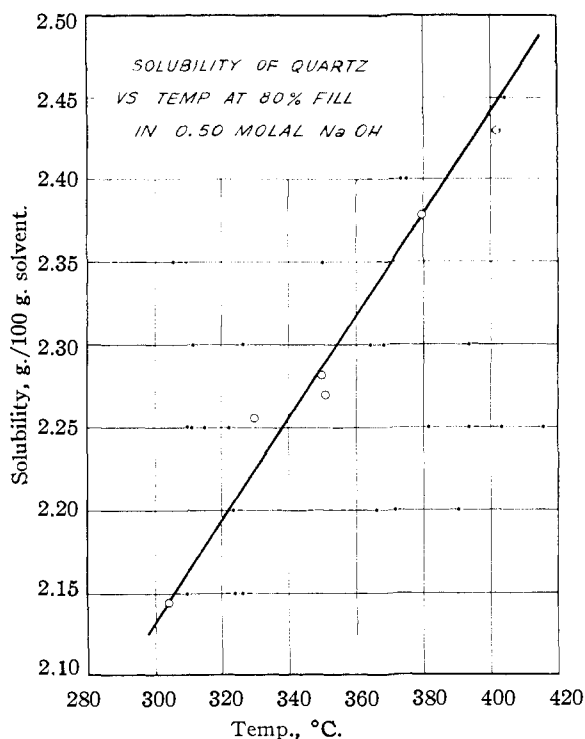


Fig. 3.—Solubility of quartz vs. temperature at 80% fill in 0.50 *m* NaOH.

Fig. 5 the heat of solution of quartz in 0.50 *m* NaOH at 80% fill was found to be 1,300 cal./mole and nearly independent of temperature between 300 and 400°. A study of quenched runs also showed that only one fluid phase was present under all the conditions where solubilities were measured.

Discussion

The dependence of the rate on the orientation of the seed was as would be expected from a consideration of the prevalence of the faces in natural quartz. The basal plane never occurs in nature and the size of the faces in typical natural crystals is prism > major > minor.

Understanding of the dependence of the rate on per cent. fill awaits a detailed determination of the solubility as a function of fill.

For a unimolecular hydrothermal crystallization one might expect that

$$\frac{dc}{dt} = k\Delta S \quad (3)$$

where dc/dt is the rate of deposition on a particular face in mole/sec. cm.³, k is the velocity constant in sec.⁻¹ and ΔS is the supersaturation, that is, the difference in solubility, $S - S_0$, between the dissolving and growth zones of the vessel. If we define α as a conversion factor such that

$$R/\alpha = \frac{dc}{dt} \quad (4)$$

then

$$R = k\alpha\Delta S \quad (5)$$

It would be expected that the temperature dependence of the crystallization rate constant k

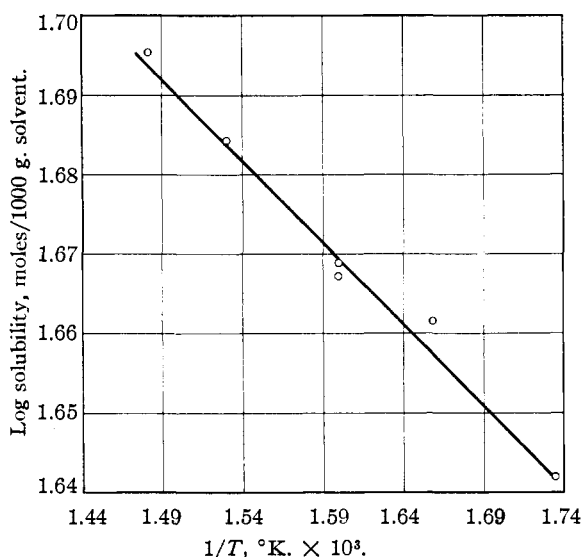


Fig. 4.—Solubility of quartz in 0.50 m NaOH at 80% fill.

would obey the Arrhenius relationship

$$\frac{d \ln k}{dT} = \frac{\Delta E_a}{RT^2} \quad (6)$$

where ΔE_a is the energy of activation for the rate-determining step. Combining eq. 5 and eq. 6

$$d \ln \frac{\alpha}{\alpha \Delta S} = \frac{\Delta E_a}{RT^2} \quad (7)$$

Equation 1 is then seen to be a special case of eq. 7 for the condition where ΔS is a constant. That is, eq. 1 would be expected to be obeyed at constant fill and constant Δt since ΔS has been shown to be constant and independent of temperature under these conditions. From eq. 7 one would then ex-

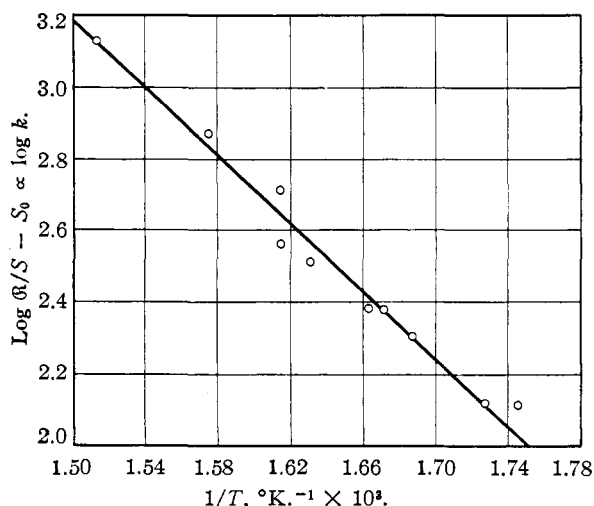


Fig. 5.—Velocity constant as a function of temperature 80% fill, basal plane, 0.50 m NaOH.

pect that $\ln (\alpha/\Delta S)$ would be a linear function of $1/T$ and Fig. 6 made with the solubility data of Fig. 4 and the rate data of Fig. 2 shows this to be true at 80% fill for the basal plane. From the slope of this curve the energy of activation was found to be 22,000 cal./mole. The energy of activation

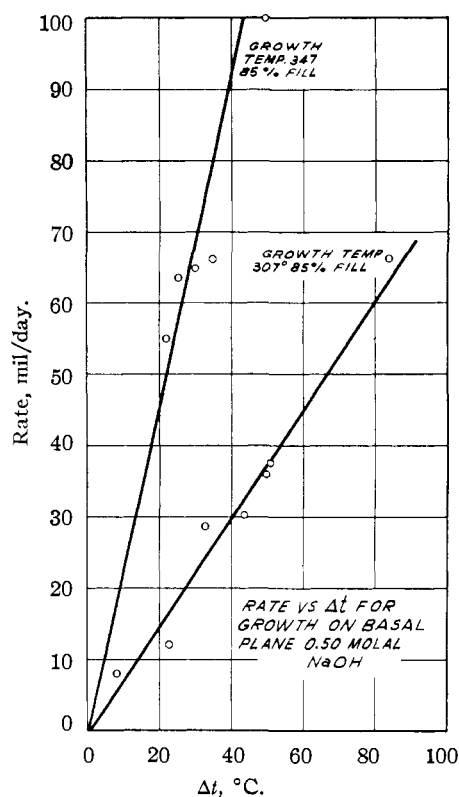


Fig. 6.—Rate vs. Δt for growth on basal plane 0.50 m NaOH.

as found from Fig. 2 for 80% fill was 19,900 cal./mole. The excellent agreement lends additional validity to eq. 5. Similarly the energy of activation for the minor face was found to be 14,400 cal./mole at 83.4% fill and for the major face 40,000 cal./mole at 83.4% fill. Since the energies of activation for the major and minor surfaces and the basal at 70% fill can be calculated with only two points, these values should perhaps be considered only tentative. The data of Fig. 2 also showed the energies of activation for the basal plane to be within experimental error nearly the same at 80 and 85% fill. Further support of eq. 5 is given by Fig. 3 which shows the linear dependence of α on Δt at 85% fill as would be required by eq. 5 if ΔS were linear with Δt . Although solubility data for 85% fill are not available, one is probably justified in assuming that as at 80% ΔS is linear with Δt as shown in Fig. 4.

The velocity constant k is related to the frequency factor A by the equation

$$k = A^{-E_a/RT} \quad (8)$$

By the use of eq. 8, the rate for the basal plane at 80% fill and the basal plane energy of activation at 400°, the frequency factor can be estimated.

For a determination of k the value of α in eq. 5 must be determined. It can be shown that

$$\alpha = \beta \frac{V}{\gamma} \quad (9)$$

where β contains pure dimensional conversion constants and V/γ is the minimum value which the ratio of the volume of the growth zone to the area of the growing surface can assume.

The value of γ is the maximum surface area of quartz which can be placed within the growth zone without changing the kinetics of the growth process. It was shown above that the rate was independent of the surface area in the growth zone provided that surface area was less than one-fifth the surface area of the quartz in the dissolving zone. For calculations where γ was required it was taken to be one-fifth the estimated area of the small particle nutrient in the dissolving zone. Since in conventional hydrothermal experiments the ratio of surface area in the growth zone to surface area in the dissolving zone is much less than one-fifth, the dissolving step is not rate determining.

With the above data by the use of eq. 5 and the appropriate rate and supersaturation values k was calculated to be between 10^{-3} and 10^{-4} sec.⁻¹ for the basal plane at 80% fill and 400°. The frequency factor under these conditions from eq. 8 was found to be between 10^{11} and 10^{12} which compares sensibly with frequency factors of from 10^{12} to 10^{14} for most gaseous and many liquid unimolecular reactions. The calculation of frequency factors and velocity constants for other conditions and other faces awaits further solubility data.

The nature of the rate-determining step may profitably be considered further at this time. The surface area experiments assuredly eliminate dis-

solving as the rate-determining step under ordinary conditions. The dependence of rate on the temperature of the growth region and the apparent validity of eq. 5 seem to indicate that the step occurs at or near the interface: saturated solution-growing crystal and that the crystallization is probably first order and unimolecular but this is by no means an unequivocal conclusion. The fact that the Arrhenius relation and eq. 5 are obeyed is, of course, not sufficient proof that the mechanism is simple. In crystal growth from solution it is generally assumed that both volume diffusion of solute and surface migration of adsorbed molecules can contribute to the observed rate. The differences in rates for the various faces observed in this study suggest the importance of surface migration but do not exclude diffusion. The possibility that transport is rate determining under certain conditions is being investigated by systematic variation of the baffle which in this work was held constant at 10% open area.

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[CONTRIBUTION FROM THE CHANDLER LABORATORY OF COLUMBIA UNIVERSITY]

Photochemical Space Intermittency. A Proposal for Measuring Diffusion Coefficients of Reactive Free Radicals

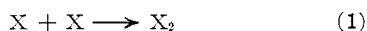
BY RICHARD M. NOYES¹

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If photochemically produced radicals are destroyed by a second-order process and if a cell is illuminated with a pattern of light and dark areas, the average concentration of radicals in space is dependent not only upon the total incident illumination but also upon the sizes of individual light areas. This space intermittent effect is similar to the familiar use of a rotating sector to produce light intermittent in time, and it permits measurement of the average distance a radical diffuses during its lifetime. If quantum yields and rate constants are known for a particular system, it would be possible to measure diffusion coefficients of highly reactive short lived radical intermediates. These diffusion coefficients cannot be determined by conventional methods, but precise values would contribute greatly to a detailed theory of molecular behavior in liquids.

Introduction

Let the equation



represent a reaction between two identical chemical species in solution. If the species are so reactive that the rate is determined by their diffusion together, and if the average age of the species is sufficiently great (about 10^{-8} second under most conditions), Smoluchowski² has shown that the rate constant for reaction 1 in liter/mole sec. is given by

$$k = \frac{4\pi\rho DN}{1000} \quad (2)$$

where

- ρ = encounter diameter of X in cm.
- D = diffusion coefficient of X in cm.²/sec.
- N = Avogadro's number

If both k and D were measured independently for a particular diffusion controlled reaction, sub-

stitution into equation 2 should indicate a value of ρ identical with the van der Waals diameter of X. However, the derivation of equation 2 is based on an application of Fick's laws of diffusion to a system of molecular dimensions. Because this application involves certain assumptions of undetermined reliability, an exact test of equation 2 is desirable.

(a) Equation 2 assumes X species can be treated as spherically symmetrical in their interactions with each other. This assumption is almost certainly valid for iodine atoms in solution but is not strictly valid for polyatomic species.

(b) The derivation assumes that individual diffusive displacements are small compared to ρ . If the magnitudes of these displacements are significant, equation 2 becomes³

$$k = \frac{12\pi\rho^2 DN}{1000(3\rho + \sigma)} \quad (3)$$

where σ is the root-mean-square distance for diffu-

(1) Department of Chemistry, University of Oregon, Eugene, Ore.

(2) M. v. Smoluchowski. *Z. physik. Chem.*, **92**, 129 (1917).

(3) R. M. Noyes. *This Journal*, **78**, 5486 (1956).