The kinetics of crystallization of potassium bromide from aqueous solution

K. RIDGWAY AND M. E. AULTON

Department of Pharmaceutics, The School of Pharmacy, University of London, Brunswick Square, London, W.C.1, U.K.

The densities of aqueous solutions of potassium bromide have been determined as a function of concentration and temperature up to saturation at temperatures between 10 and 50°. The saturation line and nucleation were studied, over the same temperature range, in a circulatory crystallizer with continuous concentration monitoring. Small quantities of seed crystals were grown under different degrees of supersaturation and at different temperatures, so that the mass transfer coefficients and the activation energy for deposition from solution could be measured. The activation energy of the crystallization process was 100·9 kJ mol⁻¹, indicating that the rate-determining step was the incorporation of KBr on to the crystal lattice. Rapidly-grown crystals might thus be expected to be softer, and this proved to be so.

Crystallization rates, particularly of pharmaceutically interesting materials from solution, have not been extensively studied, although the crystallization process is widely used in their manufacture. Rate data are relatively scarce yet are needed to test theories of deposition rate limitation, which may be governed by diffusion, viscosity or energy of incorporation into the crystal lattice: such data are also useful in crystallizer design.

Potassium bromide is used in the photographic industry, in pharmacy and in spectroscopy; it therefore seemed that measurements of the rate of growth of potassium bromide crystals from aqueous solution would be of some industrial interest. In addition, since the alkali halides have a simple crystal structure, it appeared likely that any lattice defects would produce macroscopic effects more easily observable than proved to be the case with aspirin crystals. Whereas the effect of growth rate upon crystal hardness could not be demonstrated with certainty for aspirin (Glasby & Ridgway, 1968), with potassium bromide it was felt that rapid growth rates might lead to lattice imperfections giving crystals with a measurably lower hardness. No data were found in the literature for the crystallization of potassium bromide beyond some solubility data for aqueous solutions (Linke, 1965).

APPARATUS AND METHODS

The continuously circulating crystallizer was of the type designed by Mullin & Garside (1968) (cf. Glasby & Ridgway, 1968); a small fluidized bed of seed crystals is held in a rising stream of supersaturated solution. The solution is heated to remove nuclei, then cooled to give the required supersaturation. Its concentration is monitored by continuous density measurement. A subsidiary heater prevented crystal deposition in the density meter sampling line; the meter compensator easily dealt with the 5° temperature rise so caused. Calibration was by using solutions of known density.

Material

The circulating solution was made from potassium bromide (B.D.H. Analar); used without further purification; the solution was filtered before pouring it into the crystallizer. Seed crystals were hand-picked from small batches recrystallized from water.

Density and solubility

Densities of solutions of known concentration were measured at temperatures between 50° and either 10° or the spontaneous nucleation temperature, whichever was the higher. The temperature was controlled, using a contact thermometer, to $\pm 0.05°$ at 5° intervals over the range covered, and was maintained for at least 30 min at the appropriate temperature before the density determination was made. The range of concentration was 5 to 45% by weight of potassium bromide, the density being between 1·01 and 1·41 g cm^{-3}.

The saturation line between 10 and 50° ranges from 37 to 45 wt % of potassium bromide, and this composition range was examined in greater detail, using solutions increasing in concentration by 1 wt % increments, to give information about saturation and nucleation behaviour. The solution was brought to the correct strength in the crystallizer and cooled to a temperature of about 10° above the saturation temperature, which was already known approximately. The solution was then allowed to cool very slowly, density and temperature being recorded continuously, until nucleation occurred. This could be observed visually, and corresponded to the maximum recorded density. Crystals formed and the system was maintained at this constant temperature until there had been no density change, and hence no growth, for at least 1 h. This was considered to be saturation, reached from the supersaturated side. Saturation was then approached from the reverse direction. Most of the crystals that had been formed were removed, and the remainder were redissolved by heating. The solution was then re-cooled to just below the saturation temperature of the *original* solution. Thus the solution is now *un*saturated because of the amount of potassium bromide that has been removed. When a steady state had been reached, this amount of bromide was replaced and the system left until the density ceased increasing, i.e., saturation had been reached from the unsaturated region by dissolution.

Crystal growth

The solution temperature was adjusted to 10° above the previously determined growth temperature, and the concentration also adjusted until the solution condition lay on the correct (extrapolated) density line for the required growth conditions. Solution was then circulated, cooled to the growth temperature, and allowed to stabilize for about 30 min, when it was ready for seeding.

Seed crystals were prepared by slow evaporation of an aqueous solution of potassium bromide at room temperature. They were removed from the solution when of the correct size, washed with acetone, dried and sieved into standard sieve fractions. The best cubic crystals were hand-picked under a binocular microscope and re-sieved, about 200 mg being used for a crystallization run. The small quantity is dictated, partly by the labour of obtaining good seed crystals, and partly so that the depletion of potassium bromide in solution in the crystallizer shall be small.

In a typical case, 200 mg were deposited on the seeds from the total of several kg in the circulating solution, so that the concentration driving force could be regarded as constant during a run.

The weighed quantity of seed crystals was allowed to remain in the crystallizer for a measured time under defined conditions, and was then removed, drained, washed with acetone, dried, and sieved using a set of 2 inch diameter sieves (Endecott Ltd.): the fractions were then weighed. Knowing the initial and final size distributions, and the weight of potassium bromide deposited, the coefficient of mass transfer operative during the run could be calculated.

The surface area on which the deposition occurred was found by determining the mean side length of a number of good cubic crystals by a projection microscope. For potassium bromide, which crystallizes in the cubic system, the dimensions of the unit cell are 0.328 nm; it has a density of 2.75 g cm^{-3} at $20°$.

Surface hardness

Crystals from each batch were mounted on the stage of a pneumatic micro-indentation apparatus (Research Equipment (London) Ltd.), which gave a curve from which the Brinell hardness could be obtained by a technique described earlier (Ridgway, Aulton & Rosser, 1970).

RESULTS AND DISCUSSION

A summary of the experimental results is given in Table 1. The densities of aqueous solutions of potassium bromide at various concentrations are shown as a function of temperature in Fig. 1. More extensive determinations were made in the immediate neighbourhood of the saturation line to establish its position as accurately

Table 1. *Deposition rate of potassium bromide crystals from solution*

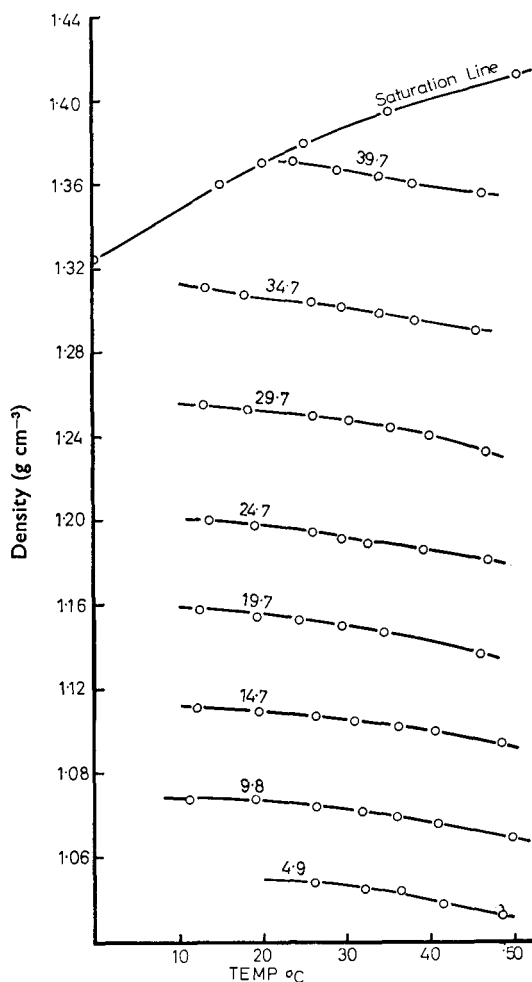| Tempera-ture °C	Run	Growth concen-tration % w/w	Super-saturation ΔC % w/w	Percentage of super-saturation at growth	Weight of crystals (g) Initial	Final	Surface area of crystals (mm²) Initial	Final	Deposition rate ng mm⁻² s⁻¹	Mass transfer coeffi-cient ng mm⁻² s⁻¹ (%w/w)⁻¹	Brinell hardness number kgmm⁻²
21·05	Saturation	(39·987)	(0)	(0)					—	3·90	
	21A	40·183	0·196	27	0·2914	0·3225	1620	2530	0·225		0·301
	21B	40·256	0·269	37	0·2101	0·2330	1345	1500	0·422		0·270
	21C	40·322	0·336	47	0·2354	0·2804	1016	1192	0·744		0·466
	21D	40·412	0·425	59	0·2057	0·3201	1480	1990	3·033		0·310
	21E	40·438	0·451	63	0·1957	0·4245	996	1737	93		0·216
	Nucleation	(40·70)	(0·72)	(100)					—		
29·97	Saturation	(41·982)	(0)	(0)					—	16·20	
	30A	42·233	0·251	38	0·2338	0·2575	1223	1385	0·698		0·354
	30B	42·302	0·320	49	0·6413	0·8494	2643	3193	2·328		0·268
	30C	42·369	0·387	59	0·3035	0·4758	1655	2632	2·542		0·432
	30D	42·435	0·453	69	0·3356	0·6395	1438	2285	15·2		0·151
	Nucleation	(42·64)	(0·66)	(100)					—		
40·00	Saturation	(43·584)	(0)	(0)					—	41·75	
	40A	43·719	0·135	35	0·1631	0·1808	928	982	1·45		0·282
	40B	43·815	0·231	60	0·1015	0·1494	515	755	4·15		0·396
	40C	43·877	0·293	76	0·3139	0·8314	1606	3825	7·25		0·321
	40D	43·918	0·334	86	0·2917	0·5828	1729	2444	454		0·164
	Nucleation	(43·97)	(0·39)	(100)					—		
47·57	Saturation	(44·545)	(0)	(0)					—	131·0	
	47A	44·695	0·150	39	0·2267	0·2775	1200	1369	2·60		0·481
	47B	44·753	0·208	54	0·1642	0·2570	779	1102	3·81		0·424
	47C	44·809	0·264	69	0·6329	1·1009	1317	3415	17·5		0·339
	47D	44·869	0·322	84	0·2406	3·1192	1451	6607	185		0·227
	Nucleation	(44·93)	(0·39)	(100)					—		

FIG. 1. Densities of aqueous solutions of potassium bromide of various concentrations, as a function of temperature. The numbers are the wt % KBr in the solution. The saturation line is plotted from published data (Linke, 1965).

as possible, and also the position of the nucleation line or limit of metastability, above which any solution will nucleate spontaneously under the working conditions of the crystallizer (Fig. 2). Since nucleation is a function of the degree and duration of agitation in the solution and of the presence of solid impurities which could act as nuclei, the scatter of the points defining nucleation is greater than that of the points defining the solubility line. The square points in pairs, one open and one filled, are the results obtained by approaching saturation from above and below respectively; these pairs bracket the saturation line closely.

In Fig. 3, a growth-rate determination is followed through in the form of a histo-gram. This series is for one of the higher temperature runs at which growth is rapid. In some of the slower runs, the change in sieve analysis was small, although the overall weight change was readily measured. This is why the weight rather than size change has been measured in most runs, and used to calculate the mass transfer coefficient. The median size increases as growth proceeds, although the range of
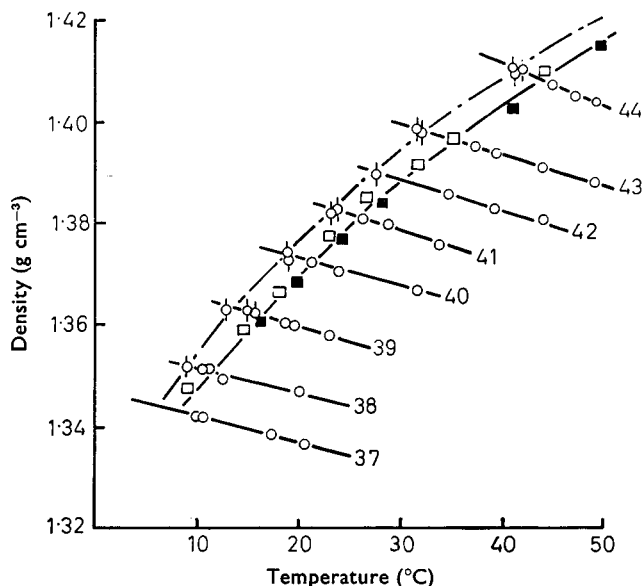
Fɪɢ. 2. The solubility line for potassium bromide in water, obtained by approaching the saturation condition from above and from below, the line being drawn between the points obtained by the two methods. □ approach from the supersaturated solution. ■ approach from the unsaturated solution. ○ density–temperature lines: the numbers on these lines refer to the wt % of KBr contained. Points with a vertical line through them indicate that nucleation occurred.

size does not broaden. In industrial practice, specific measures are taken to classify the product by size and to overcome any tendency of the size range to increase. This increase occurs (a) because of nucleation and attrition, both of which cause small crystals to form and (b) because large crystals tend to segregate to the bottom of a bed and meet incoming strong liquor, and thus grow even larger. In the circulating crystallizer used in this work, both effects appear to be absent. Any nuclei or small particles formed are removed from the crystal cage; also, the bed is small and well-mixed, so that there is no segregation of larger crystals within the cage.

The amount of potassium bromide deposited on the seed crystals is given in Fig. 4 for four temperatures and a range of supersaturations. After an initial short period of fast deposition in some cases all these plots of deposition against time are linear. This effect is usually ascribed (Mullin, 1961) to the fact that the seed crystal surface is microscopically rough and cracked due to attrition and storage: cracks are healed during the initial deposition, but the area for deposition is higher until this healing has taken place.

From the weight deposited plots of Fig. 4, the graphs of Fig. 5 are obtainable, where the data for each temperature are reduced to a single line, the slope of which is the mass transfer coefficient. This is the amount deposited on unit area of crystal surface in unit time, divided by the concentration difference causing the deposition. The slope of the lines increases with temperature, and all are approximately linear. They do not start from the origin, suggesting that a finite supersaturation is needed to start growth; such behaviour has been observed in other systems (Mullin, Amatavivadhana & Chakravorty, 1970), who showed that a degree of supersaturation was required in several salt-water systems to start growth. In dissolution, however,
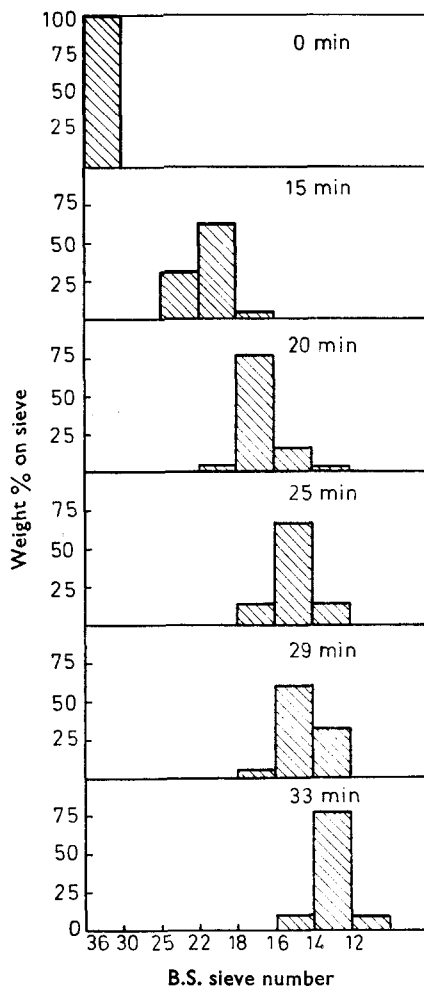
FIG. 3. Histogram showing the change of size distribution as growth proceeds.

it seems that the smallest reduction of concentration below the equilibrium solubility will cause the solid phase to dissolve. It is this effect which makes it necessary to approach the solubility line from both sides in order to fix its position. In this present work, at high supersaturations, the linearity of deposition with concentration driving force breaks down abruptly, since, even below the spontaneous nucleation point, growth occurred by rapid deposition of fresh small parasitic crystals on the seeds. Their surface became roughened, the deposition rate increased by a factor of 10–100 times, and the resultant crystals would have been regarded industrially as of very poor quality.

Mass transfer coefficients obtained from the slopes of the linear portions of the lines in Fig. 5 are strongly dependent upon the temperature. The dependence is of the Arrhenius form, so that a straight line is obtained in Fig. 6, where the logarithm of the mass transfer coefficient is plotted against the reciprocal of the absolute temperature: the slope of the line is -5260. The Arrhenius equation is
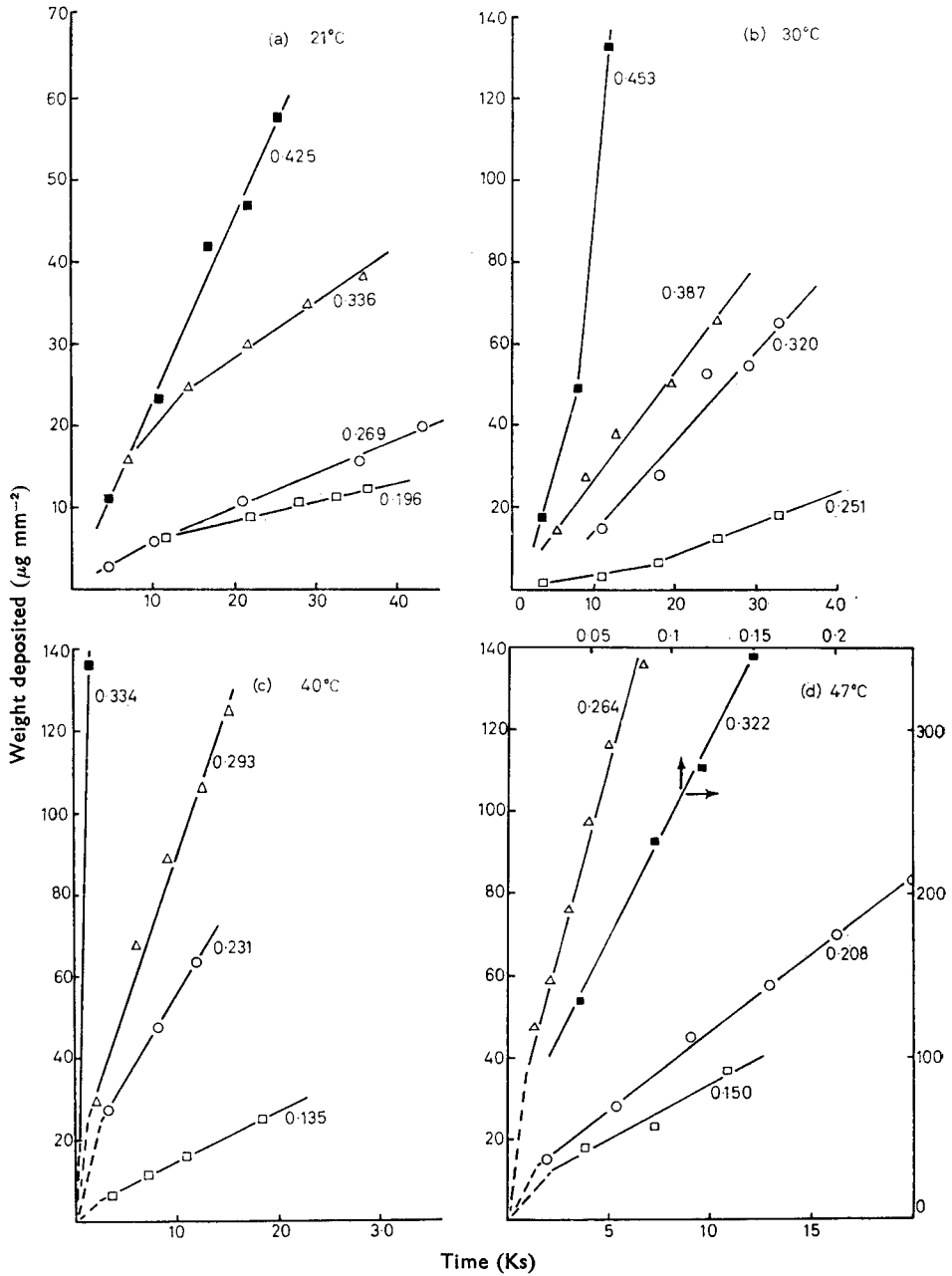
$$k = A \exp(-E/RT)$$

FIG. 4. The weight of potassium bromide deposited per unit area of crystal surface as a function of time, for four temperatures as indicated. The supersaturation, expressed as $\Delta C =$ (actual wt % concentration)—(saturated solution wt % concentration) is marked on each growth line.
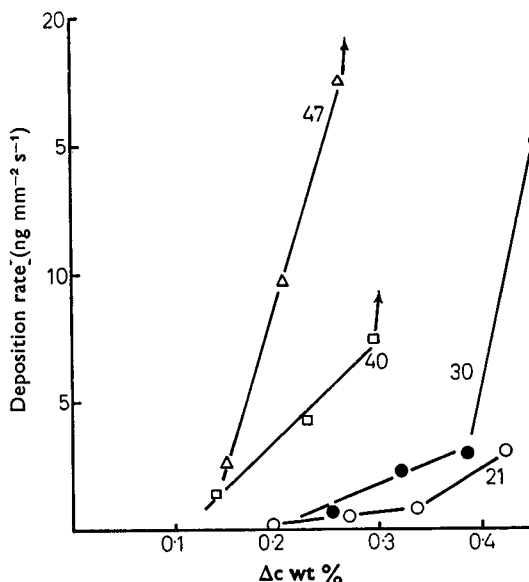
FIG. 5. The deposition rate of potassium bromide as a function of supersaturation at four temperatures. The initial portion of each graph is approximately a straight line, but a sudden rapid increase in deposition rate occurs at higher values of ΔC; the points are indicated, but the measured deposition rates are off the diagram at the scale used to show the other growth rates; their values are recorded in Table 1.

where k is a rate, A is a constant, E the activation energy for the rate process, R the gas constant and T the absolute temperature. Thus,

$$\log k = \frac{-E}{2 \cdot 303 \, RT} + \log A$$

and the slope of the Arrhenius plot is $\dfrac{-E}{2 \cdot 303 \, R}$: hence the activation energy is

$100 \cdot 9$ kJ mol^{-1}. This may be compared with the value of $92 \cdot 1$ kJ mol^{-1} at $0°$ obtained by van Hook (1944) for the crystallization of sucrose from water, and with $91 \cdot 2$ kJ mol^{-1} obtained by Glasby & Ridgway (1968) for the crystallization of aspirin from ethanol. It is apparent from this value that the rate-controlling step is the incorporation of a molecule or ion-pair into the crystal lattice, and not the rate of diffusion to the crystal surface. Activation energies for diffusion are normally much lower, $20 \cdot 9$ kJ mol^{-1} being quoted for sodium chloride between 50 and $70°$ (Rumford & Bain, 1960). These authors' value for the activation energy of a diffusion-controlled crystallization agrees with van Hook's estimate of $27 \cdot 2$ kJ mol^{-1}, for sucrose, at the same elevated temperature. Rumford & Bain also suggested that below $50°$ the surface reaction step becomes controlling; no activation energies were published, however, for this region.

In the fluidized-bed crystallizer used in the present work, particularly with solutions of low viscosity, diffusion is rapid as boundary layers are thin. The viscosity of the solutions from which potassium bromide was deposited was about $1 \cdot 1$ cP despite the high concentration of the salt.

Fig. 7 suggests that there is a decrease in hardness with increase in rate of growth; rapidly grown crystals would be expected to contain more imperfections, built in
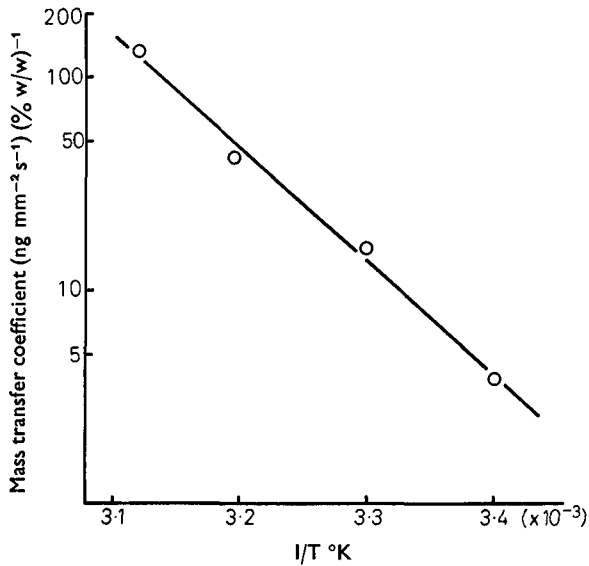
FIG. 6. Arrhenius-type plot of log k against 1/T. The line has a slope of −5260, giving an activation energy for the deposition process of 100·9 kT mol⁻¹.

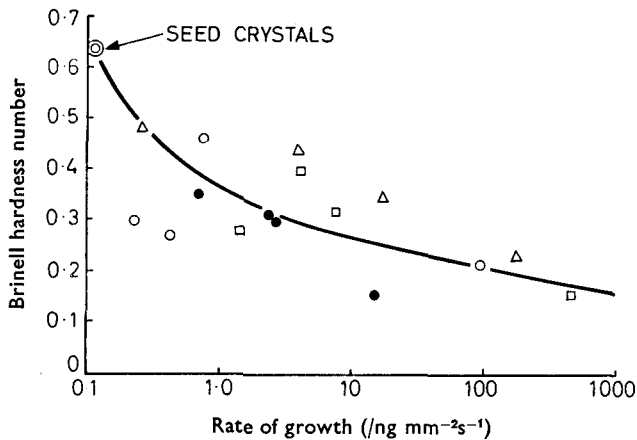FIG. 7. Hardness as a function of growth rate. The symbols represent the growth temperatures as follows: ○ 21°, ● 30°, □ 40°, △ 47°.

during their deposition, and so, to be softer. The plot of hardness against the rate of growth for crystals made in the concentration range where the mass transfer coefficient was constant, gave an indication of the trend: the variability of the crystals within a batch, added to the experimental errors of hardness measurement, made it impossible to draw a line, but the trend towards softer crystals at higher growth rates is not in doubt; seed crystals moreover were harder than any grown in the circulatory crystallizer.

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