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AN APPLICATION OF EYRING'S THEORY TO
CRYSTALLIZATION KINETICS OF POLYPHENYLS

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ABSTRACT

The Eyring-type theory developed by Kirwan and Pigford for the interfacial kinetics of crystal growth was applied to predict the rate of crystal growth for o- and m-terphenyls, and 1:3:5:-Tri- α -naphthylbenzene (ToNB). The predicted values agree well with experimentally measured data for m-terphenyl. The agreement between the computed values and reported literature data was good for o-terphenyl for undercooling below 12° C. An order of magnitude prediction was obtained for ToNB at undercooling below 40° C.

INTRODUCTION

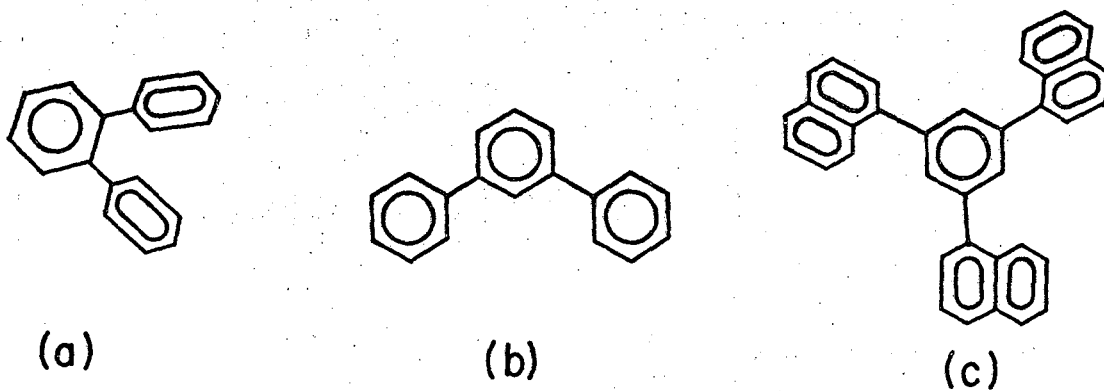
Growth of crystals from their melts and from solutions continues to be more of an art than a science, even though crystalline products have been prepared for centuries. This is especially true for organic substances because nowhere have their structures in the liquid and solid states received as much attention as the comparatively simpler metals. Yet the advance of methods for using crystallization phenomena in the purification of organic compounds requires that an understanding be developed for the rate processes which govern both the velocity of growth and the purity of the crystals which are formed.

It is known that crystal growth occurs by the attachment of molecules to the crystal surface. Furthermore it is intuitively obvious that such attachment will require that the approaching molecules be oriented in the right direction if they are to fit into vacant sites in the crystal lattice. Moreover, the molecules which are ready to attach themselves must break their bonds with their neighbors in the liquid. Finally, the concentration on the crystal face of vacancies suitable for the attachment of new molecules may be low, the more perfect surfaces offering fewer sites for attack.

Although several proposals have been made for the quantitative analysis of these factors none has seemed as promising as the combination of a kinetic theory which follows the ideas of Eyring (1941) with an estimate of surface defect structures according to Frank (1948, 1951). Such analyses have been made by Hillig and Turnbull (1956) and by Kirwan and Pigford (1969). Results have been somewhat promising but the expressions for growth rates obtained along such lines have not yet been tested in a definitive way.

A few more complicated organic compounds, such as polyphenyls, become very viscous when their melts are cooled. In fact, cooling may easily occur many degrees below the equilibrium freezing points of these substances because nucleation and growth of the solid phase are so slow.

Such substances apparently form highly oriented, multiple links between neighboring molecules, even in the liquid state, such temperature-dependent structures resulting in high liquid viscosity.



XBL6911-6203

Fig. 1. Units of molecular structure of polyphenyls
(a) o-terphenyl, M.W. = 230.31, (b) m-terphenyl, M.W. = 230.31
(c) 1:3:5-tri- α -naphthylbenzene, M.W. = 456.

Recently, growth rates and liquid viscosities for o-terphenyl have been reported by Greet (1967). This compound has a large, positive entropy of activation for viscous flow, indicating the presence of entangled structures in the liquid. It should be useful to compare predicted and observed growth rates for this substance to test the theories. Also, new data are reported here on the growth rates of an isomeric substance, m-terphenyl, which does not form so viscous a liquid and which, if the theories are right, should crystallize more quickly. In addition, data are available from Magill and Plazek (1967) on the growth rates of a still more complex structure, 1:3:5-Tri- α -naphthylbenzene, providing a third set of data for which the rate theory comparison should be significant. Figure 1 shows the structures of the three compounds.

In the following the Eyring-type theory will be reviewed, especially the adaptation of it by Kirwan and Pigford (1969), and its application to data on the more complex organic molecules will be made. The aim is to test certain hypotheses concerning the estimation of the thermodynamic properties of the crystallization activated state, especially the suggestion of Kirwan and Pigford (1969) that the molecule which is ready to attach itself to the crystal lattice has less entropy than the molecule which is ready to flow, the difference being about equal to the entropy of fusion.

AN ABSOLUTE RATE THEORY OF CRYSTAL GROWTH

Following the developments of Hillig and Turnbull (1956) and of Clifton (1957), the net molar flux of material onto the crystal interface is given by

$$N = f (\lambda_L \rho_L k^F - \lambda_S \rho_S k^R) = f \lambda_S \rho_S (k^F - k^R) , \quad (1)$$

where the terms in the parentheses represent the forward rate owing to the liquid molar concentration ρ_L and the reverse rate at which the solid dissolves owing to the concentration ρ_S . Each process shifts the interface by a small molecular spacing λ . The second equality follows from the assumption that the molecular spacings are inversely proportional to the densities. The fraction f represents the small fractional part of the surface to which arriving molecules can attach themselves. The complete theory comprises estimates of both the rate coefficients and the surface fraction in terms of thermodynamic and other pure component properties.

Following Eyring (1941) the forward rate constant becomes

$$k^F = \chi \left(\frac{kT}{h} \right) \exp \left(- \frac{\Delta H_C^\ddagger}{RT} \right) \exp \left(\frac{\Delta S_C^\ddagger}{R} \right), \quad (2)$$

where the quantities in the "frequency factor", kT/h have their usual meaning and where $\Delta S_C^\ddagger = S_C^\ddagger - S_L$ and $\Delta H_C^\ddagger = H_C^\ddagger - H_L$ represent the excess of the standard entropy and standard enthalpy of the molecule which is activated for attachment to the crystal over the standard state values for the liquid. χ is the transmission coefficient to allow for the possibility that not every activated complex is converted into one of the reaction products in which one is interested. A similar equation, based on the same activated standard state, applies to the reverse coefficient, k^R . It is simply related to Eq. (2) by

$$k^R = k^F \exp \left(\frac{-\Delta \mu^0}{RT} \right), \quad (3)$$

where $\Delta\mu^0 = \mu_L^0 - \mu_S^0$ is the difference between the standard-state chemical potentials of the phases. At the melting point of the pure substance, T_m , the chemical potentials are equal; their rate of change with respect to temperature depends on the entropy, so that $\Delta\mu^0 \sim \Delta S_f (T_m - T) = \Delta S_f \cdot \Delta T$ where ΔS_f is the entropy of fusion.

Estimation of f depends on the surface mechanism for attachment of molecules to the solid. Here we follow the proposal of Frank (1948, 1951) that many crystals grow by attachment of molecules to the spiral steps of screw-shaped dislocations on the surface. The value of f then is equal to the distance on the surface between adjacent arms of the spiral divided into the width on the surface of a single molecule. Assuming that the spiral is Archimidean in shape we obtain

$$f = \frac{\lambda_S}{4\pi r_c} \quad (4)$$

where r_c is the radius of curvature of the tip of the spiral. If we assume that this tip is of such size that is just neutrally stable, we may equate r_c to the thermodynamically calculated size of the critical two-dimensional nucleus,

$$r_c = \frac{\sigma}{\rho_S \Delta\mu^0} \sim \frac{\sigma}{\rho_S \Delta S_f \Delta T} \quad (5)$$

where σ is the excess surface free energy in the interface per unit of surface area. We obtain this value from the correlation of Turnbull (1958), according to whom, for non-metals and organic compounds,

$$\sigma = 0.3 \left(\frac{\Delta H_f}{N^{1/3} V_S^{2/3}} \right), \quad (6)$$

where ΔH_f is the enthalpy of fusion, N is Avogadro's number, and $V_S = \rho_S^{-1}$ is the molar volume of the solid.

Combining Eqs. (1) through (6) we develop the equation from which we intend to predict the crystal growth rate,

$$V = \left(\frac{\Delta T}{1.2\pi T_m} \right) \left(\chi \frac{kT}{h} \right) \lambda_S [1 - \exp(-\frac{\Delta\mu^0}{RT})] \exp(-\frac{\Delta H_C^\ddagger}{RT}) \exp(\frac{\Delta S_C^\ddagger}{R}), \quad (7)$$

where we have introduced the growth velocity, $V = N/\rho_S$, and $\lambda_S = (V_S/N)^{1/3}$. The first factor on the right of Eq. (7) is the surface fraction, f . Note that V depends on the amount of undercooling of the melt through the effect of ΔT both on f and on $\Delta\mu^0$. Thus, for this particular mechanism, the growth velocity varies more rapidly than in proportion to the undercooling. For many conditions $\Delta\mu^0$ is much smaller than RT for the third parenthesis in Eq. (7) to be approximated by the first term in its Taylor series, giving

$$V = \left(\frac{1}{1.2\pi} \right) \left(\frac{kT}{h} \right) \left(\frac{\lambda_S}{R} \right) \left(\frac{\Delta T}{T_m} \right)^2 \exp(-\frac{\Delta H_C^\ddagger}{RT}) \exp(\frac{\Delta S_C^\ddagger}{R}), \quad (7a)$$

showing that V is approximately proportional to the square of the undercooling. Comparison of the exponent on ΔT , determined from experimentally observed growth velocities, with the expected value according to Eq. (7a) has often been interpreted as a test of the postulate that growth occurs

by the screw dislocation mechanism (Hillig and Turnbull, 1956). Obviously, however, the equation will be of little use generally unless ways are found for the estimation of the entropy and enthalpy of the crystallization-activated state.

A plausible guess of the activation quantities was made by Hillig and Turnbull (1956) who suggested that the values appropriate for crystallization be assumed equal to those for viscous flow. The latter are likely to be available or, if not, they can be measured rather easily. Following this line of thought one may multiply Eq. (7) by the similar Eyring equation for the viscosity of the liquid (Glasstone, Laidler and Eyring, 1941),

$$\eta = \left(\frac{Nh}{V_L}\right) \exp\left(\frac{\Delta H_V^\ddagger}{RT}\right) \exp\left(-\frac{\Delta S_V^\ddagger}{R}\right), \quad (8)$$

where the subscript V now refers to the activation quantities for viscous flow. From Eqs. (7) and (8), the product of the growth velocity and the liquid viscosity is given by

$$v\eta = \left(\frac{1}{1.2\pi}\right) \left(\frac{\Delta T}{T_m}\right) \left(\chi \frac{NkT}{V_L}\right) \lambda_S [1 - \exp(-\frac{\Delta\mu^0}{RT})] \exp\left(\frac{\Delta H_V^\ddagger - \Delta H_C^\ddagger}{RT}\right) \exp\left(\frac{\Delta S_C^\ddagger - \Delta S_V^\ddagger}{R}\right), \quad (9)$$

or, for small undercooling, ΔT , Eq. (9) can be further simplified to

$$v\eta = \left(\frac{1}{1.2\pi}\right) \left(\frac{\chi\lambda_S \Delta H_f}{V_L}\right) \left(\frac{\Delta T}{T_m}\right)^2 \exp\left(\frac{\Delta H_V^\ddagger - \Delta H_C^\ddagger}{RT}\right) \exp\left(\frac{\Delta S_C^\ddagger - \Delta S_V^\ddagger}{R}\right), \quad (9a)$$

where ΔH_f will be expressed in erg/mole $^{\circ}\text{K}$ if poise units are used for η . Furthermore, if one would assume that the activated state is the same for the two processes the two exponential factors would vanish. Then, at fixed thermal driving force and temperature, the growth velocity would vary from one substance to another in inverse proportion to the liquid viscosity. For some substances, especially those with rather complex molecular structure, the viscosity can become very large at low temperatures. If such substances can be cooled far below their freezing points the rates at which they freeze may be small in spite of the very large ΔT .

Kirwan and Pigford (1969) suggested, however, that this simplest assumption about the properties of the molecule which is ready to attach itself to a crystal lattice may be too crude. After all, many molecules require very specific orientation if they are to fit into steps in the crystal. Some orientation may be needed for viscous flow but it seems very likely that the requirements are not nearly so stringent as for crystal growth. As an estimate of the difference of the entropies of the two standard states it was suggested that

$$\Delta S_C^\ddagger = \Delta S_V^\ddagger - (\Delta S_f - R) . \quad (10)$$

This assumes that the entropy of the crystallization-activated molecule falls about as far below the entropy of the flow-activated molecule as the solid entropy falls below that of the liquid. The extra term, R , is an estimate of the entropy of fusion of a spherical molecule, which requires no orientation.

There appears to be no comparable way of guessing at the enthalpy of the activated state, just as there is seldom a way to estimate the activation energy of an ordinary chemical reaction. It seems very possible that ΔH_V^\ddagger could differ appreciably from ΔH_C^\ddagger because a somewhat different sequence of events is required for attachment to the solid and for flow. For the latter, not only must the molecule become so energetic that it is able to "jump", i.e. to break the bonds by which it is attached to its neighbors in the liquid but, in addition, a hole must occur in the liquid nearby. For crystallization, however, there is no energy requirement to "make a hole" for the crystal face itself offers a site for completion of the attachment reaction. Thus, the energy of activation for viscous flow can be subdivided into two different parts:

$$\Delta H_V^\ddagger = \Delta H_{V,j}^\ddagger + \Delta H_{V,h}^\ddagger, \quad (11)$$

or, to indicate the corresponding quantities which can be measured experimentally,

$$\Delta H_V^\ddagger = \left. \frac{\partial \ln(V_L \eta)}{\partial (1/T)} \right|_P = \left. \frac{\partial \ln(V_L \eta)}{\partial (1/T)} \right|_{V_L} + \frac{\partial V_L}{\partial (1/T)} \bigg|_P \cdot \left. \frac{\partial \ln(V_L \eta)}{\partial V_L} \right|_T. \quad (12)$$

Thus, when in a very few cases the isothermal dependence of liquid viscosity on liquid density is known, the two parts of the right side of Eq. (11) can be found separately. It seems very likely that only the activation enthalpy needed to cause a molecule to jump away from its surroundings is sufficient for the crystallization rate equation, i.e., the first term

on the right of Eq. (12)--a number which may be smaller than the total activation energy for viscosity.

In a few cases where data were available it was possible for Whitaker and Pigford (1958) to compute $\Delta H_{V,j}^\ddagger$, and to compare it with ΔH_V^\ddagger . They found that the ratio of the quantities depends on the nature of the molecule involved, including its tendency to form a hydrogen-bonded structure in the liquid. Thus for alcohols they found $(\Delta H_{V,j}^\ddagger / \Delta H_V^\ddagger) \sim 0.6$; for hydrocarbons like benzene and carbon tetrachloride the value was about 0.3. Thus it is difficult to estimate the term involving ΔH_C^\ddagger in Eq. (7) or (9); except for the simplest substances. In most cases it will be necessary to find the difference between the two activation enthalpies from one measured growth rate. Afterwards, other growth rates can be estimated from Eqs. (7), (9) and (10).

The final equation, based on introducing the assumption about entropy expressed in Eq. (10) into Eq. (9), is

$$V\eta = \left(\frac{e}{1.2\pi}\right) \lambda_s \left(\chi \frac{NkT}{V_L T}\right) (\Delta T) \left[1 - \exp\left(-\frac{\Delta\mu^0}{RT}\right)\right] \exp\left(-\frac{\Delta S_f}{R}\right) \exp\left(\frac{\Delta H_V^\ddagger - \Delta H_C^\ddagger}{RT}\right). \quad (13)$$

The first purely numerical factor in Eq. (13) is equal to 0.72. For many conditions the first exponential factor can be approximated by $(\Delta S_f \Delta T / RT)$, as noted earlier. Since for most organic substances $\Delta H_V^\ddagger > \Delta H_C^\ddagger$, the last exponential factor usually exceeds unity.

Table I. Growth Rate Data and Physical Properties of Polyphenyls and Phosphorus

Compound	Equilibrium Thermodynamic Properties			Derived Properties from Viscosity				Rate-Derived Properties from Crystal Growth Rate			
	T_m	ΔS_f	ΔH_{vap}	T	η	ΔS_V^\ddagger	ΔH_V^\ddagger	V	ΔS_C^\ddagger	ΔH_C^\ddagger	$\Delta H_C^\ddagger / \Delta H_V^\ddagger$
	°C	cal/mole	°K kcal/m	°C	poise	cal/m°K	kcal/m	cm/sec	cal/m°K	kcal/m	
o-terphenyl ^g	55.5	13.4	14.84 ^a	50	0.50	24.0	14.0	3.3×10^{-4}	-260.0	-71.0	-5.1
		± 0.2	15.77 ^b	40	1.30	48.0	22.0	2.3×10^{-3}	26.0	17.0	0.77
				30	5.42	77.0	31.0	1.6×10^{-3}	51.0	26.0	0.84
				20	40.50	108.0	40.0	5.2×10^{-4}	79.3	34.0	0.85
				10	6.1×10^2	142.0	50.0	1.0×10^{-4}	114.0	42.0	0.84
m-terphenyl	85.61 ^c	12.3	15.97 ^d	84	0.057	5.0	7.5	2.5×10^{-4}	-5.3 ⁱ	6.0	0.80
	87.0 ± 0.1		16.84 ^e								
T α NB ^h	199.0	21.2	27.90 ^f	195	0.48	14.92	17.09	1.7×10^{-7}	-627.3	-274.5	-16.10
				190	0.63	21.65	20.22	1.6×10^{-5}	-355.9	-148.6	-7.33
				185	0.83	28.60	23.42	4.4×10^{-5}	-78.3	-20.0	-0.85

ave.
= 0.82

(continued)

Table I. continued

Compound	Equilibrium Thermodynamic Properties			Derived Properties from Viscosity				Rate-Derived Properties from Crystal Growth Rate				
	T_m	ΔS_f	ΔH_{vap}	T	η	ΔS_V^\ddagger	ΔH_V^\ddagger	V	ΔS_C^\ddagger	ΔH_C^\ddagger	$\Delta H_C^\ddagger / \Delta H_V^\ddagger$	
	°C	cal/mole°K	kcal/m	°C	poise	cal/m°K	kcal/m	cm/sec	cal/m°K	kcal/m		
				160	6.45	67.06	40.55	4.5×10^{-5}	47.45	37.1	0.92	
				140	222.0	103.0	55.74	8.2×10^{-6}	68.5	46.0	0.83	
				120	5.3×10^3	144.5	72.48	5.8×10^{-7}	93.0	55.7	0.77	
				100	1.5×10^6	192.9	91.02	1.1×10^{-8}	121.2	66.6	0.73	
											ave.	
											= 0.81	
phosphorus ^j	44.3	1.984		37.9	1.84	-2.6	2.62	23.4	9.1	3.06		
				35.1	1.90	-2.7	2.60	45.5	9.7	3.24		
				33.4	1.95	-2.8	2.59	63.0	10.1	3.36		
				33.2	1.99	-2.9	2.57	79.0	10.5	3.44		
				29.8	2.05	-3.0	2.55	102.0	10.9	3.61		
				29.3	2.06	-3.1	2.55	108.0	11.1	3.64		
				25.8	2.16	-3.3	2.51	153.0	11.9	3.89		
				25.0	2.26	-3.4	2.50	161.0	12.1	3.95		
				23.0	2.19	-3.4	2.49	181.0	12.5	4.07		

(continued)

Table I. continued

Compound	Equilibrium Thermodynamic Properties			Derived Properties from Viscosity				Rate-Derived Properties from Crystal Growth Rate			
	T_m	ΔS_f	ΔH_{vap}	T	η	ΔS_V	ΔH_V	v	ΔS_C^\ddagger	ΔH_C^\ddagger	$\Delta H_C^\ddagger / \Delta H_V^\ddagger$
	°C	cal/mole	°K kcal/m	°C	poise	cal/m°K	kcal/m	cm/sec	cal/m°K	kcal/m	
phosphorus ^j				22.0	2.30	-3.5	2.47	210.0	12.9	4.17	
				21.4	2.32	-3.6	2.47	210.0	13.0	4.21	

Note: m-terphenyl data, except for viscosity, obtained from this work.

^aFor temperature range from 280 to 340° C.

^bFor temperature range from 220 to 280° C.

^cMeasured value, this work.

^dFor temperature range from 330 to 380° C.

^eFor temperature range from 260 to 330° C.

^fFor temperature range from 430 to 530° C.

^gData of Greet (1967).

^hData of Magill and Plazek (1967).

ⁱComputed from Eq. (10).

^jData of Hildebrand and Rotariu (1951).

EXPERIMENTAL DATA FOR m-TERPHENYL

For m-terphenyl the viscosity data and the melt specific volume via Batshinski relationship are measured by Andrew and Ubbelohde (1955). The molar volume of solid is taken as 200.4 cc/g mole (Andrew and Ubbelohde, 1955). The latent heat of fusion is taken to be as equal to that of o-terphenyl. The sample of m-terphenyl was obtained from Eastman Kodak Co. and used for the growth experiment after it was purified by zone refiner. The melting point was measured to be 85.61° C. The measurement by Andrew and Ubbelohde was 87.0 ± 0.1° C (1955). Experimental procedures are described in detail elsewhere (Cheng and Pigford, 1969).

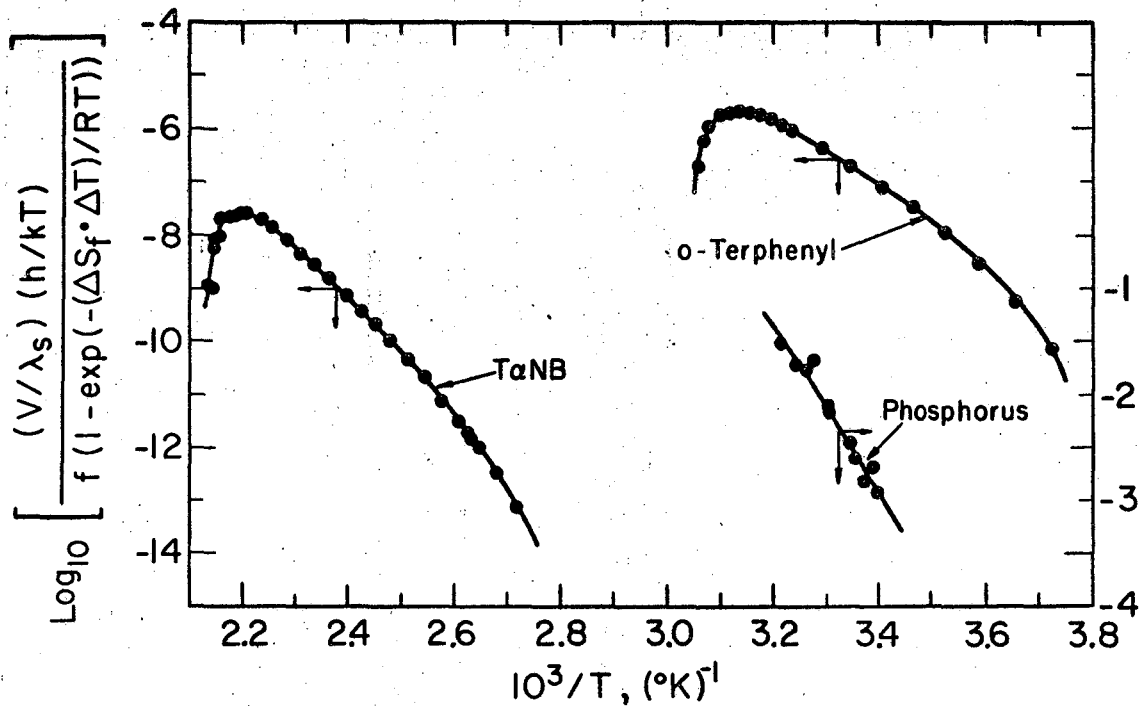
The experimentally measured rates of growth are plotted in terms of $(\Delta T)^2$ in Fig. 3. The predicted values of growth rate at various undercoolings, using Eq. (9) with the assumption of $\Delta H_C^\ddagger = 0.76 \Delta H_V^\ddagger$ and ΔS_C^\ddagger calculated from Eq. (10), are also plotted in Fig. 3. It appears that Eq. (9) does result in a reasonable prediction of the growth rate for m-terphenyl for a limited temperature range of experiment.

DISCUSSION

In Table I all the pertinent physical properties of the pure substances are listed, along with the calculated values of the two enthalpies and the two entropies of activation for each compound. At the higher temperatures for o-terphenyl and ToNB the values derived from crystal growth rates differ sharply from those from viscosity, and correspondingly, the lines shown on Fig. 2 change their courses sharply except for phosphorus. This suggests that in the range of small undercooling these polyphenyl compounds crystallize by a different mechanism than at lower

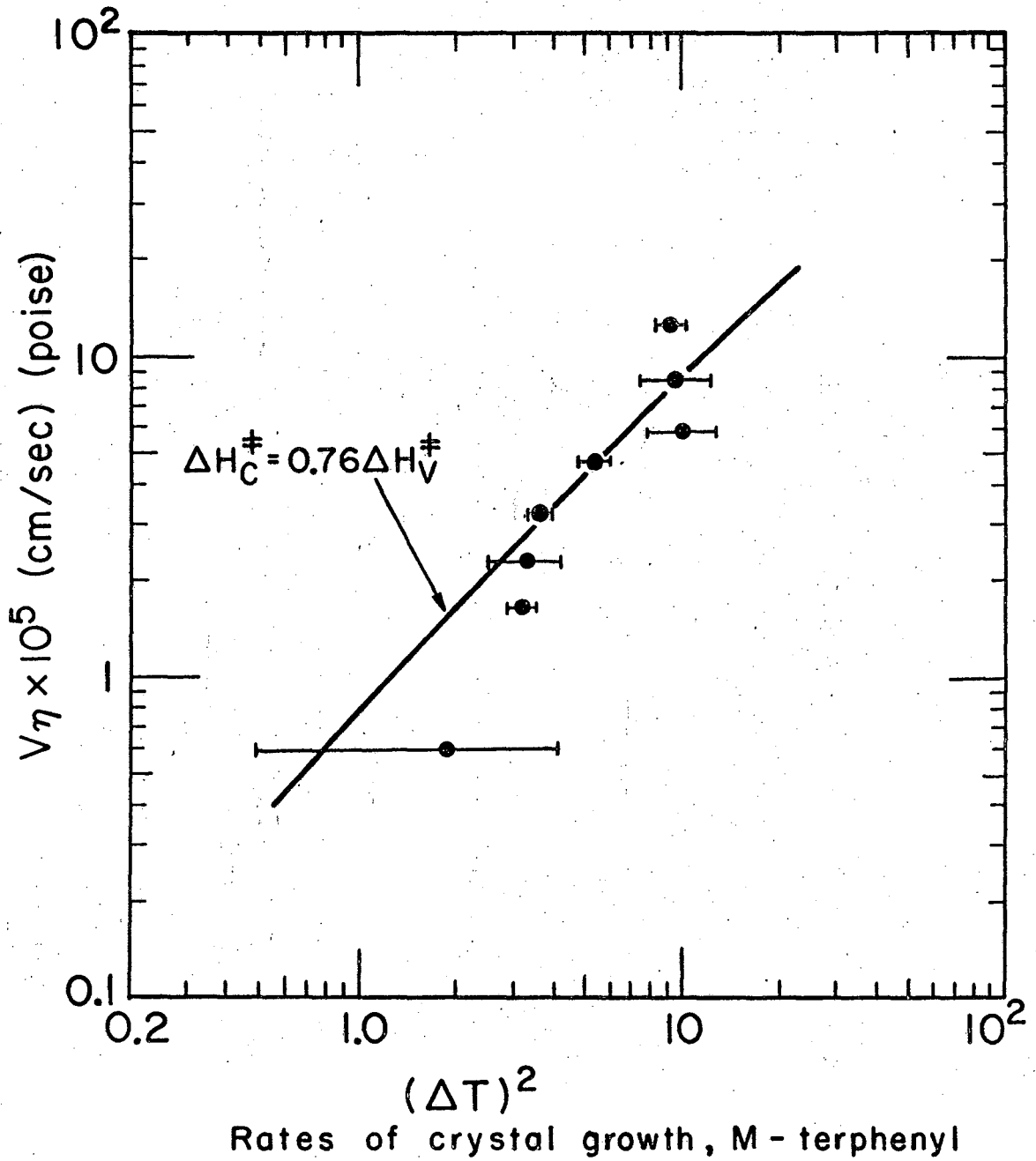
temperatures, where the lines are nearly straight. At the lower temperatures the ratio $\Delta H_C^\ddagger / \Delta H_V^\ddagger$, is smaller than unity, as expected. Over most of the temperature ranges the ratio is about 0.81, which agrees with the value 0.80 found from the new m-terphenyl data after assuming that Eq. (10) gives the right entropy of activation. For the other three compounds the entropy of activation can be computed directly from the observed growth rates using Eq. (7), i.e. based on slopes of the curves in Fig. 2. Inspection of the table shows that the difference between ΔS_V^\ddagger and ΔS_C^\ddagger is greater than the entropy of fusion for o-terphenyl and ToNB, in contrast with Eq. (10). In fact, the difference is occasionally about twice the entropy of fusion. For phosphorus (Hildebrand and Rotariu, 1951) not only ΔH_C^\ddagger is larger than ΔH_V^\ddagger but also the large positive values of ΔS_C^\ddagger are to compare with the negative values of ΔS_V^\ddagger . Apparently Eq. (10) does not hold for these three compounds.

In order to test the theory further, we have arbitrarily taken $\Delta H_C^\ddagger = 0.89 \Delta H_V^\ddagger$ and have ΔS_C^\ddagger computed from Eq. (10). Thus, the predicted values of growth rate, V , using Eq. (9) are plotted in Fig. 4 for o-terphenyl and in Fig. 5 for ToNB. For o-terphenyl it yields a reasonable agreement with the reported data at ΔT below 12° C. However the predicted values are higher than the literature values at ΔT greater than 12° C and ΔT below 3° C. For ToNB the agreement between the experimental data and the predicted values is rather poor. A larger value of ΔH_C^\ddagger for o-terphenyl than for m-terphenyl regardless the similarity of their molecular structures arises from the fact that the large interlocked molecules of o-terphenyl apparently require a larger activation enthalpy for jumping in viscous flow.



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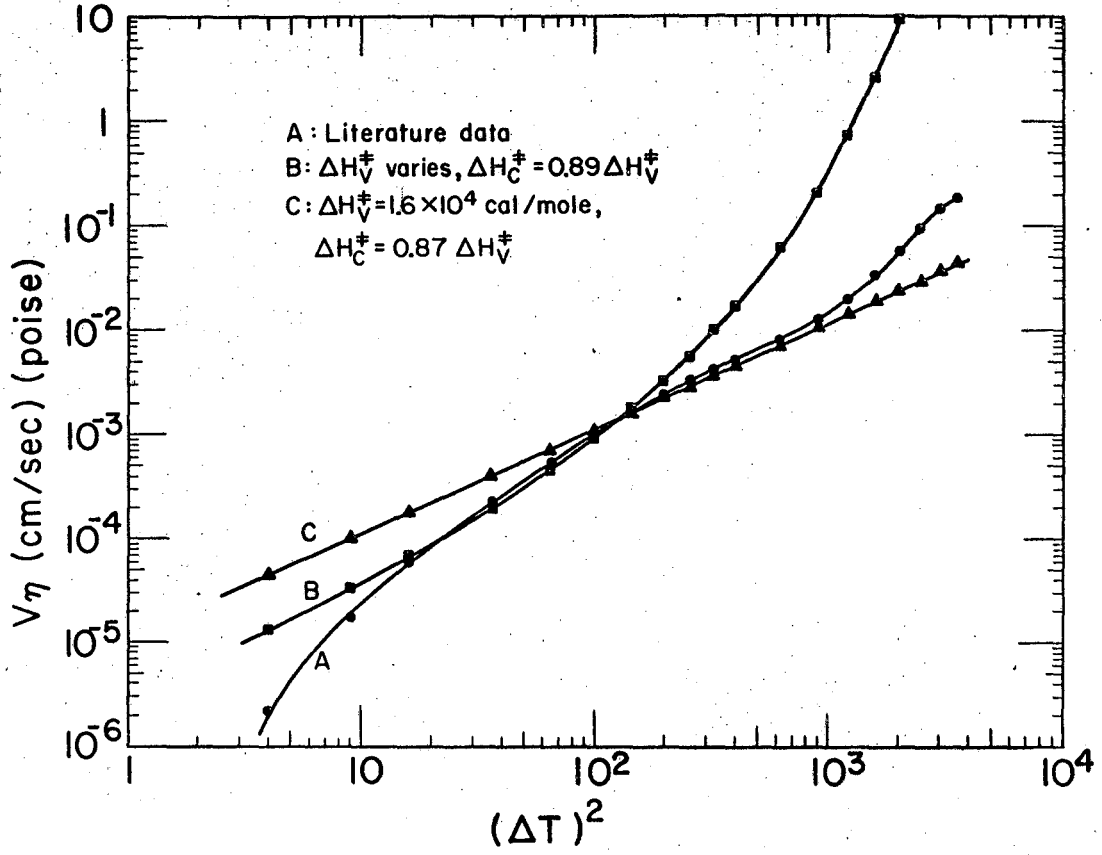
Fig. 2. Reduced growth rates of pure compounds in undercooled liquids.



Rates of crystal growth, M - terphenyl

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Fig. 3



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Fig. 4. Comparison of predicted growth rates and literature values, o-terphenyl.

A greater deviation occurs at lower temperature end (larger ΔT) is due to a large increase in the difference of $(\Delta H_V^\ddagger - \Delta H_C^\ddagger)$. For most metals and substances whose molecular structures are simple the difference is constant under the assumption that ΔH_C^\ddagger can be approximated as equal to $\Delta H_{V,j}^\ddagger$, which is a fraction of ΔH_V^\ddagger . Indeed this is the case for most of the experimental data used by Kirwan and Pigford (1969) for the test of the theory they developed. However this is not so for polyphenyls where the difference of two activation enthalpy varies approximately five times in the range of experimental data reported in the literature.

Curves C's in both Figs. 4 and 5 are the predicted growth rate, V , computed using Eq. (10) for ΔS_C^\ddagger and ΔH_V^\ddagger obtained from the slope of the best straight line fit of $\log \eta$ -vs- $(1/T)$ at freezing point (Andrew and Ubbelohde, 1955). The deviation at lower ΔT are even greater while a reasonable agreement between the literature data and the predicted values at large undercooling may be fortuitous, because the screw dislocation mechanism may not be operable there due to the change of the morphology of the growing crystal.

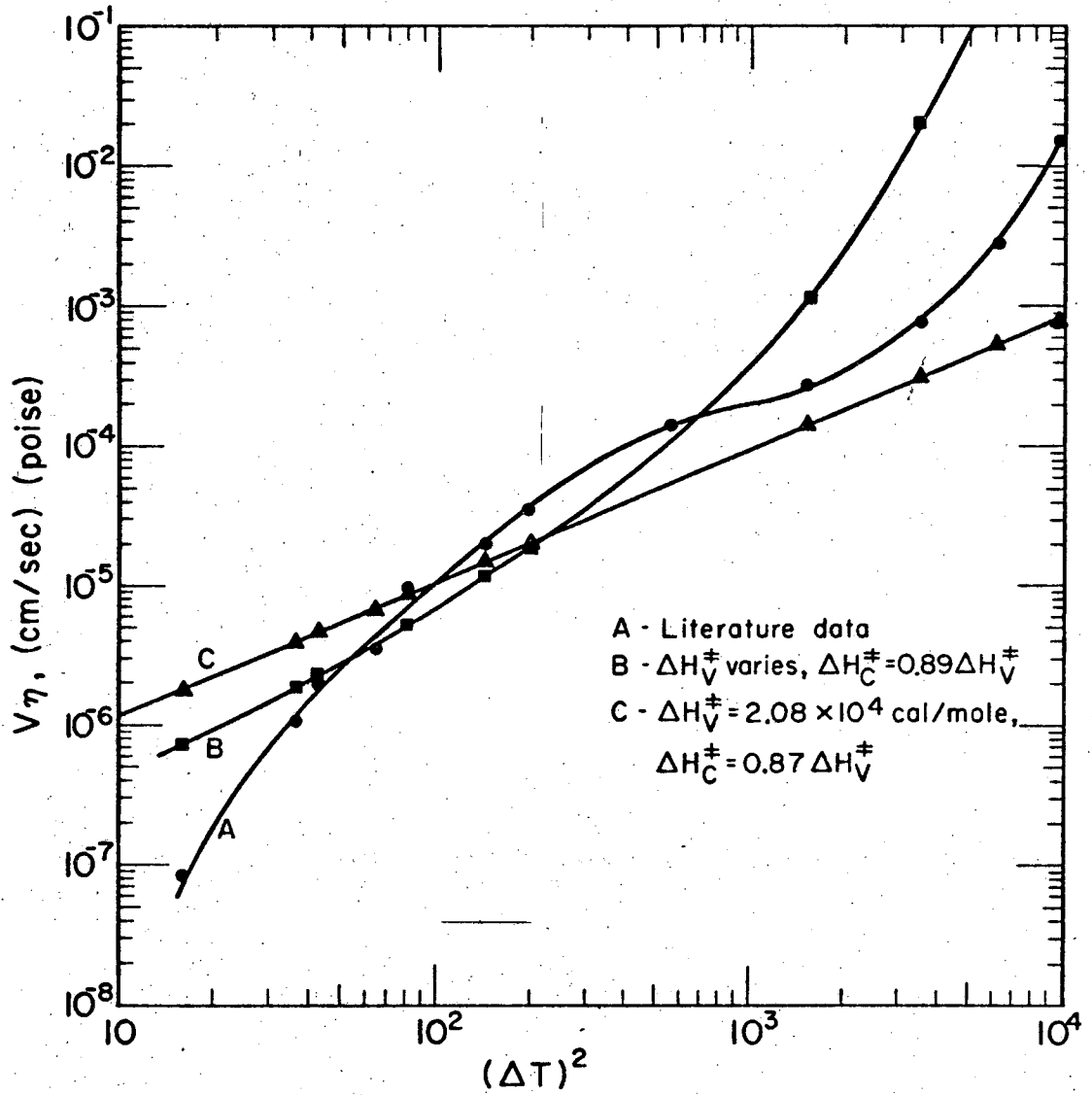
Entropy effect may be a possible explanation to the deviations both at small and large undercoolings between the literature data and the computed values. Both the number of molecules present at the interface and their orientations in the right directions have significant effects on the kinetics of crystallization. For substances whose molecules interlock significantly in the melt such as o-terphenyl and TcNB the molecular orientation effect for the transformation from liquid to solid may be greater than $(\Delta S_f - R)$. If the predicted values of V would have to fit

the literature data with $\Delta H_C^\ddagger = 0.89 \Delta H_V^\ddagger$, the ΔS_C^\ddagger should have values as plotted in Figs. 6 and 7 for both polyphenyl compounds. The deviation of this ΔS_C^\ddagger from that of estimated with Eq. (10) is considerable at large undercooling.

Both literature data for growth rates pass through a maximum value at temperature, T_{\max} about 175° C for TqNB and around 40° C for o-terphenyl. Analysis done by Greet (1967) for o-terphenyl and by Magill and Plazek (1967) for TqNB indicated that the exponential relationship equivalent to growth by surface nucleation described their experimental results best for the temperature above T_{\max} . This is in accord with what we had suggested earlier that apparently these polyphenyl compounds crystallize by a different growth mechanism in the range of small undercooling.

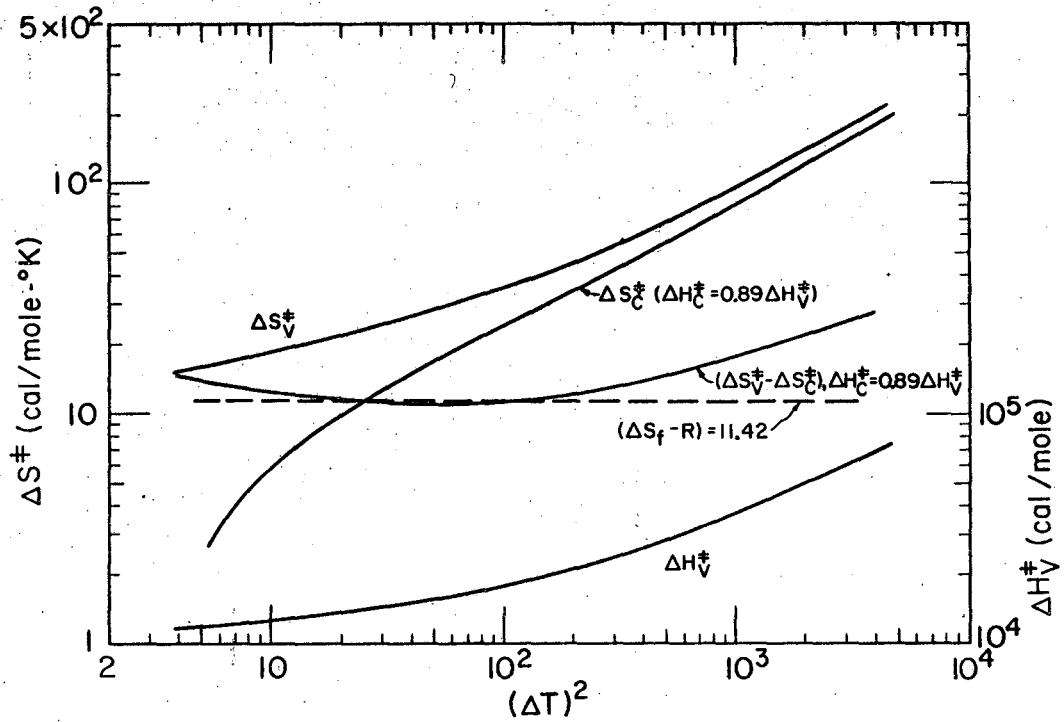
Although the hypothesis concerning the estimation of activation entropy for crystallization, ΔS_C^\ddagger by Eq. (10) has failed to hold for three compounds, except for m-terphenyl, tested here, there is no reason to doubt that Eq. (9) has its practical use in predicting the rates of crystal growth for a wider range of undercooling from one measured growth rate. In spite of the questionable model built in terms of macroscopic activated-state properties to represent the molecular transport phenomena and an idealized surface structure of the solid-liquid interface which is derived from the screw dislocation concept, thus, we have seen that Eq. (9), with some knowledge about transport process in the melt, appears to be capable in predicting the growth rate within an order of magnitude.

The kinetic rate formula expressed in terms of ART in the functional relationship as shown in Eq. (1) has an advantage in separating the surface



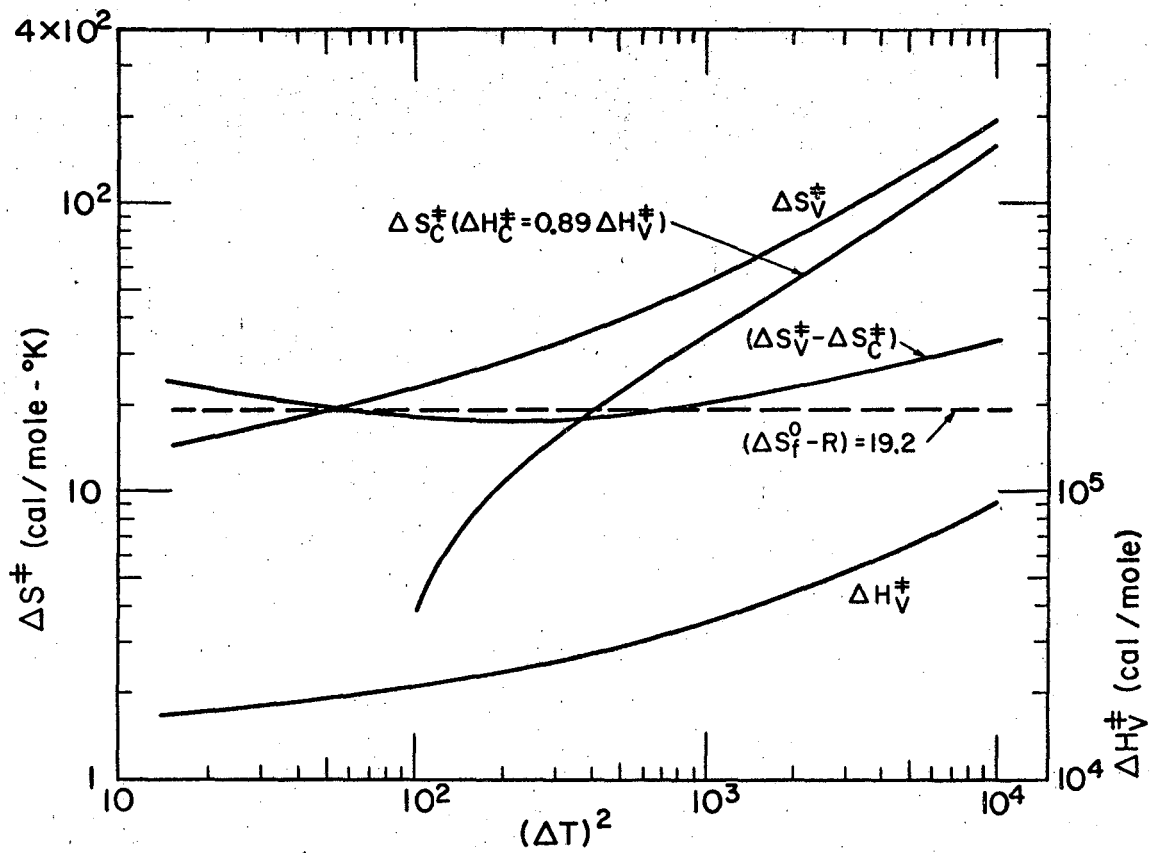
XBL6911-6180

Fig. 5. Comparison of predicted growth rates and literature values, ToNB.



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Fig. 6. Derived activated-state properties from viscosity and from crystal growth rate, o-terphenyl.



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Fig. 7. Derived activated-state properties from viscosity and from crystal growth rate, ToNB.

condition and the transport terms which include the activation energy of jumping molecules and the free energy for the phase transformation. It is hoped in the future that better understanding on the liquid structure and possibility in predicting the surface structure in contact with the melt quantitatively will greatly improve the technology of crystallization and increase the knowledge in science of crystal growth so that the best condition in growing a specific crystal can be determined from the physical properties of the substances.

CONCLUSIONS

The Eyring-type of kinetic rate expression developed by Kirwan and Pigford, using screw dislocation concept for surface step density and the knowledge of the difference in the activated states for crystallization and that for viscous flow, is applied in predicting the growth rate of polyphenyls-o- and m-terphenyls and ToNB.

The predicted values of growth rate agree well with the experimental data for m-terphenyl when $\Delta H_C^\ddagger = 0.76 \Delta H_V^\ddagger$ is used. For o-terphenyl the agreement between the computed values and the literature data is good for undercooling below 12° C but deviations magnify at larger undercooling when $\Delta H_C^\ddagger = 0.89 \Delta H_V^\ddagger$ is used. The predicted values do not fit as well with the reported data for ToNB but an order of magnitude estimate is obtained for undercooling below 20° C. Values of ΔS_C^\ddagger estimated from Eq. (10) are used for these predictions although Eq. (10) itself does not seem to hold for three compounds tested here.

Until the quantitative knowledge about the crystal morphology in relation to the surface step density and about the liquid structure are

further advanced the present Eyring-type theories based on the macroscopic properties provide simple models for practical purposes.

ACKNOWLEDGMENTS

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NOTATION

f = surface step density

h = Planck's constant, 6.6252×10^{-27} erg/sec

H = molar enthalpy, cal/g mole

k = interfacial rate constant, sec^{-1} , or Boltzmann's constant,
 1.38045×10^{-16} erg/°K

N = crystallization flux, mole/sq cm-sec, or Avogadro's number,
 6.0232×10^{23} mole⁻¹

r_c = critical radius of two-dimensional nucleus, cm

R = gas constant, cal/g mole °K

S = molar entropy, cal/g mole °K

T = temperature, °C or °K

V = freezing velocity, cm/sec, or molar volume, cc/g mole

GREEK LETTERS

η = viscosity, poise

λ = interatomic spacing, cm

μ = chemical potential, cal/g mole

ρ = molar density, g mole/cc

σ = interfacial surface free energy, cal/sq cm

χ = transmission coefficient

SUPERSCRIPTS

F = forward process

O = standard state property

R = reverse process

= activated state property

SUBSCRIPTS

C = crystallization activated state property

f = fusion process

h = hole formation process

j = jumping process

L = liquid state property

m = melting process

P = constant pressure condition

S = solid state property

T = constant temperature condition

V = viscous flow activated state property, or constant volume condition

vap = vaporization process

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