

AN INVESTIGATION OF THE VELOCITY  
OF FREEZING OF SUPER COOLED NITROBENZENE

by

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## INTRODUCTION

While the kinetic theory of the solid and gaseous phases of materials are fairly well developed, little is known about the kinetics of the liquid phase. The study of the velocity of the interface between the liquid and solid in a freezing undercooled liquid was undertaken to yield information on this subject.

When a sample of liquid is placed in a long tube and undercooled, it is observed that after freezing is initiated, the freezing front moves down the tube with a finite and reproducible velocity. The velocity is directly dependent on the degree of undercooling.

In this experiment an attempt is made to develop the relationship between the velocity and the temperature of the liquid. The results were compared to a similar experiment by Barter (1) with benzene and with the theory. An empirical equation is proposed which fits the data.

## EQUIPMENT AND PROCEDURE

The sample holder was a closed pyrex glass tube with a concentric well at the top to be used to initiate freezing. Nitrobenzene was vacuum distilled into the sample tube through a side arm attached to the top of the sample tube.

The sample was placed in a cooling bath of methanol which was held in a transparent Dewar Flask. This container was in the form of a Dewar Flask to prevent frosting and to ensure efficient cooling. The outside diameters of the tubes making up the Dewar flask were 51 mm and 32 mm. Plate I shows the construction of the sample holder and bath.

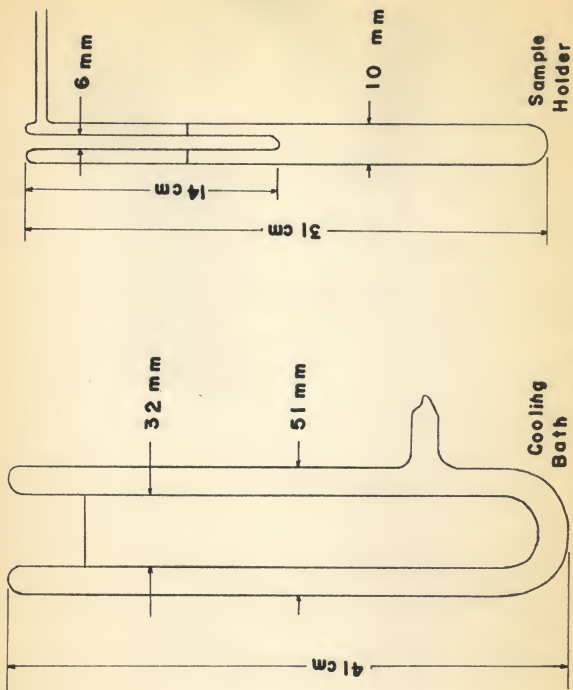
The bath was cooled by passing air through copper coils placed in liquid air and then through a copper U-tube which was placed in the cooling bath.

EXPLANATION OF PLATE I

Fig. 1 Cooling Bath  
A. Methanol

Fig. 2 Sample Tube  
B. Nitro benzene

PLATE I



The temperature of the sample was varied by adjusting the rate of the flow of air.

The temperature of the bath was measured using a copper-constantan thermocouple with the reference junction in a water-ice mixture, and a Rubicon potentiometer. The other junction was sheathed in glass and placed in the cooling bath. A stirring apparatus was used to eliminate temperature differences in the bath. The pressure was maintained at 720 mm of Hg by attaching the side arm of the sample tube to a mercury manometer and an air reservoir.

A millimeter scale was attached to the outside of the cooling bath parallel to the sample tube. The position of the freezing interface and the reading of a stopwatch were recorded on Kodak Plus X Reversal movie film using a Filmo 70 Bell and Howell movie camera set at 12.5 frames per second and placed 2.7 feet from the sample.

Using a slide projector the film was projected on a screen so that the image appeared about 1.5 times as large as the actual size of the apparatus. Readings were taken of the position of the freezing front. Readings of time were taken from the film from a timing device which was placed near the sample and scale so that all would appear in the picture.

The position was then plotted against the time to obtain the velocity. In almost all cases, the points fell extremely close to a straight line. The slope of this line gave the velocity in each particular case. The data are shown in Table I.

#### DISCUSSION

Turnbull (8) develops a theory of phase boundary migration for a one component system where the effects due to density are ignored: consider the case of a liquid ( $L$ ) to solid ( $S$ ) transition at a supercooled temperature of  $(T - T_0)$  where  $T_0$  is the normal freezing point temperature. In order to

Table I. Temperatures in Millivolts and Corresponding Temperatures in Degrees Centigrade and Corresponding Velocities in Centimeters Per Second \*

Temperature	Temperature	Velocity
- .289	- 7.5	6.3
- .169	- 4.5	2.7
- .115	- 3.0	1.3
- .236	- 6.3	4.7
- .198	- 5.2	2.78
- .123	- 3.2	1.71
- .132	- 3.5	1.85
- .187	- 4.9	3.10
- .272	- 7.2	6.2
- .070	- 1.8	0.94
- .206	- 5.4	3.7
- .305	- 8.1	6.45
- .311	- 8.2	6.8
- .327	- 8.7	7.3
- .210	- 5.5	3.3
- .247	- 6.5	3.3
- .324	- 8.5	6.7
- .351	- 9.2	7.5
- .050	- 1.3	0.7
- .039	- 0.9	0.59
- .224	- 5.9	4.4
- .054	- 1.5	0.83
- .252	- 6.6	5.8
- .219	- 5.8	4.8
- .259	- 6.8	5.35
- .088	- 2.5	0.93
- .278	- 7.3	6.8
- .059	- 1.6	0.67
- .236	- 6.2	4.00
- .151	- 4.0	2.45
- .260	- 7.1	5.9
- .141	- 3.7	2.06
- .041	- 1.0	0.65
- .323	- 8.7	6.96
- .138	- 3.3	1.73
- .268	- 7.0	5.93
- .111	- 2.9	1.62

\* Temperature in degrees corresponding to that in millivolts for a copper constantan thermocouple was determined from data by Dike (2).

cross the interface from the liquid to the solid a molecule must acquire an activation energy  $\Delta G$ . The frequency of transfer is

$$\nu_{LS} = \nu_0 \exp(-\Delta G/kT)$$

where  $\nu_0$  is the frequency of molecules striking the barrier.

If  $\Delta G'$  is the difference in Gibbs potentials per molecule between liquid and solid, the frequency of transfer in the opposite direction is

$$\nu_{SL} = \nu_0 \exp[-(\Delta G + \Delta G')/kT].$$

The net frequency of transfer across the phase boundary is

$$\nu = \nu_{LS} - \nu_{SL}$$

and the velocity of migration of this boundary is proportional to  $\nu$ .  
Then

$$V = C \exp(-\Delta G/kT) [1 - \exp(-\Delta G'/kT)].$$

Frenkel (4) indicates that the rate of change in phase must be inversely, proportional to the viscosity. If this is also true of the velocity of crystallization, and if  $\Delta G$  is assigned the value of the activation energy associated with diffusion, Turnbull's (8) expression becomes:

$$V = \frac{C}{\eta} F(T)$$

where

$$F(T) = 1 - \exp(-\Delta G'/kT).$$



If  $\Delta G'$  can be written as

$$\Delta G' = g(T - T_0) = \sum_{m=1}^{\infty} C_m (T - T_0)^m$$

(where  $C_0 = 0$  in order that  $\Delta G' = 0$  at  $T = T_0$ ), then  $F(T)$  can be written as a Taylor's expansion around  $T_0$

where

$$F(T) = 1 - \exp(-g/kT).$$

The coefficients of  $F(T)$  become:

$$F(T_0) = 0, \quad F'(T_0) = \frac{g'}{kT_0}$$

$$F''(T_0) = \left[ \frac{g''}{kT_0} - \frac{2g'}{kT_0^2} - \left( \frac{g'}{kT_0} \right)^2 \right]$$

$$F'''(T_0) = \left[ \frac{g'''}{kT_0} - \frac{3g''}{kT_0^2} + \frac{6g'}{kT_0^3} + \frac{6g'^2}{kT_0^3} - \frac{3g'g''}{k^2T_0^2} + \left( \frac{g'}{kT_0} \right)^3 \right]$$

$$\begin{aligned} F^{IV}(T_0) = & \left[ \frac{g^{IV}}{kT_0} - \frac{4g'''}{kT_0^2} + \frac{12g''}{kT_0^3} - \frac{24g'}{kT_0^4} - \frac{3g''^2}{kT_0^2} \right. \\ & - \frac{4g'g'''}{k^2T_0^2} + \frac{18g'g''}{k^2T_0^3} - \frac{36g'^2}{k^2T_0^4} + \frac{6g'^2g''}{k^3T_0^3} - \frac{12g'^3}{k^2T_0^4} \\ & \left. - \left( \frac{g'}{kT_0} \right)^4 \right]. \end{aligned}$$

If  $g'$  is the only important derivative of  $g$  then

$$F'(T_0) = \frac{g'}{kT_0}, \quad F''(T_0) = -\frac{2F'(T_0)}{T_0} - F'(T_0)^2$$

$$F'''(T_0) = \frac{6F'(T_0)}{T_0^2} + \frac{6kF'(T_0)^2}{T_0} + F'(T_0)^3$$

$$F^{IV}(T_0) = -\frac{24F'(T_0)}{T_0^3} - \frac{36F'(T_0)^2}{T_0^2} - \frac{12kF'(T_0)^3}{T_0} - F'(T_0)^4$$

If  $g''$  is the only important derivative of  $g$  then

$$F'(T_0) = 0 \quad F''(T_0) = \frac{g''}{kT_0}$$

$$F'''(T_0) = -\frac{3F''(T_0)}{T_0}$$

$$F^{IV}(T_0) = \frac{12F''(T_0)}{T_0^2} - 3F''(T_0)^2$$

If  $g'''$  is the only important derivative of  $g$  then

$$F'(T_0) = 0 \quad F''(T_0) = 0$$

$$F'''(T_0) = \frac{g'''}{kT_0}$$

$$F^{IV}(T_0) = -\frac{4F'''(T_0)}{T_0}$$

and so on.

If  $\Delta G'$  is written as

$$\Delta G' = \Delta H + P\Delta V,$$

where  $R$  is the Helmholtz free energy,  $P$  is the pressure and  $\Delta V$  is the change in volume from liquid to solid, then it is seen that

$$\begin{aligned} g &= \Delta G' = -kT \ln f_L + kT \ln f_S + P\Delta V \\ &= kT (\ln f_S - \ln f_L) + P\Delta V \end{aligned}$$

Where  $f_L$  and  $f_S$  are the partition functions for the respective states.

Then if  $P\Delta V$  is considered constant

$$\begin{aligned} g' &= kT \left( \frac{\frac{\partial f_S}{\partial T}}{f_S} - \frac{\frac{\partial f_L}{\partial T}}{f_L} \right) + k (\ln f_S - \ln f_L) \\ &= kT \left( \frac{\frac{\partial^2 f_S}{\partial T^2}}{f_S} - \left( \frac{\frac{\partial f_S}{\partial T}}{f_S} \right)^2 - \frac{\frac{\partial^2 f_S}{\partial T^2}}{f_L} + \left( \frac{\frac{\partial f_L}{\partial T}}{f_L} \right)^2 \right) \\ &\quad + 2k \left( \frac{\frac{\partial f_S}{\partial T}}{f_S} - \frac{\frac{\partial f_L}{\partial T}}{f_L} \right) \end{aligned}$$

and so forth.

Eyring (4), treating the liquid as if some of the molecules had solid-like degrees of freedom, and some molecules had gas-like degrees of freedom, has successfully calculated some thermodynamic properties of some liquids.

If  $\frac{V_S}{N}$  is the volume per molecule in the solid phase, and  $\frac{V_L}{N}$  is the volume per molecule in the liquid phase then

$$N \frac{\left( \frac{V_L}{N} - \frac{V_S}{N} \right)}{\frac{V_L}{N}} = \frac{N(V_L - V_S)}{V_L}$$

is the percentage of molecules of the liquid which have gas-like degrees of freedom, and

$$N - \frac{N(V_L - V_S)}{V_L} = N \frac{V_S}{V_L}$$

is the percentage of molecules of the liquid which have solid degrees of freedom.

Using this approach, the partition function for a substance such as benzene or nitrobenzene is, for the solid

$$f_s = \left[ (1 - \exp(-\theta/T))^{-3} \right]^N \left[ \sum_i^3 (1 - \exp(-\frac{h\nu_i}{kT})) \right]^N \times f_{vib}.$$

and for the liquid (including free rotation):

$$f_L = \left[ (1 - \exp(-\theta/T))^{-3} \right]^{\frac{NV_L}{V_L}} \left[ \sum_i^3 (1 - \exp(-\frac{h\nu_i}{kT})) \right]^{\frac{NV_L}{V_L}} \\ \times \left[ \exp\left(\frac{E_s}{RT}\right) (1 + m_h \exp(-\frac{G}{m_h RT})) \right]^{\frac{NV_L}{V_L}} \left( \frac{\pi}{ABC} \left( \frac{kT}{hC} \right)^3 \right)^{\frac{N}{2}} \\ \times \left[ \frac{(2\pi mkT)^{3/2}}{h^3} \exp \frac{V_L}{N} \right]^{\frac{N(V_L - V_s)}{V_L}} \times f_{vib}.$$

Where  $E_s$  is the energy of sublimation at the melting point,  $\theta$  is the Einstein characteristic temperature at the melting point,  $m_h$  is the number of equilibrium sites accessible to a molecule besides its most stable position.  $\frac{G}{m_h}$  is the strain energy stored in the system as the molecule shifts to one of the  $m_h$  sites. The frequency of vibration in the lattice is  $\nu$ , and  $A, B, C$  are the rotator constants of the molecule, for example  $A = \frac{h}{8\pi^2 I_A}$  where  $I_A$  is the moment of inertia around the  $A$  axis.

Then

$$\begin{aligned}
 q &= NkT \left[ -3 \ln(1 - \exp(-\theta_T)) + \ln \sum_i \left( 1 - \exp\left(-\frac{h\nu}{kT}\right) \right) \right. \\
 &\quad + \frac{3V_s}{V_L} \ln(1 - \exp(-\theta_T)) - \frac{V_s}{V_L} \ln \sum_i \left( 1 - \exp\left(-\frac{h\nu}{kT}\right) \right) - \frac{V_s}{V_L} \frac{E_s}{RT} \\
 &\quad - \frac{V_s}{V_L} \ln\left(1 + m_h \exp\left(\frac{-q}{m_h RT}\right)\right) - \frac{1}{2} \left( \ln \frac{\pi}{ABC} + 3 \ln \frac{kT}{hC} \right) \\
 &\quad \left. - \frac{(V_L - V_s)}{V_L} \left( \frac{3}{2} \ln(2\pi m kT) + 3 \ln h + 1 + \ln V_L - \ln N \right) \right] \\
 &\quad + P \Delta V
 \end{aligned}$$

since the vibrational terms are assumed to be the same. By straight forward differentiation with respect to  $T$  on obtains;

$$\begin{aligned}
 q' &= NkT \left\{ \frac{3\theta_T \exp(-\theta_T)}{T^2(1 - \exp(-\theta_T))} - \frac{\frac{3}{T} \frac{h\nu}{kT^2} \exp(-\frac{h\nu}{kT})}{\sum_i (1 - \exp(-\frac{h\nu}{kT}))} \right. \\
 &\quad - \frac{3V_s}{V_L} \frac{\theta_T \exp(-\theta_T)}{T^2(1 - \exp(-\theta_T))} + \frac{V_s}{V_L} \frac{\frac{3}{T} \frac{h\nu}{kT^2} \exp(-\frac{h\nu}{kT})}{\sum_i (1 - \exp(-\frac{h\nu}{kT}))} + \frac{V_s}{V_L} \frac{E_s}{RT^2} \\
 &\quad \left. - \frac{V_s}{V_L} \frac{q \exp(-\frac{q}{m_h RT})}{RT^2(1 + m_h \exp(\frac{q}{m_h RT}))} - \frac{3}{2} \frac{1}{T} - \frac{3}{2} \frac{(V_L - V_s)}{V_L T} \right\} \\
 &\quad + Nk \left\{ -3 \ln(1 - \exp(-\theta_T)) + \ln \sum_i \left( 1 - \exp\left(-\frac{h\nu}{kT}\right) \right) \right. \\
 &\quad + \frac{3V_s}{V_L} \ln(1 - \exp(-\theta_T)) - \frac{V_s}{V_L} \ln \sum_i \left( 1 - \exp\left(-\frac{h\nu}{kT}\right) \right) - \frac{V_s}{V_L} \frac{E_s}{RT} \\
 &\quad - \frac{V_s}{V_L} \ln\left(1 + m_h \exp\left(\frac{-q}{m_h RT}\right)\right) - \frac{1}{2} \left( \ln \frac{\pi}{ABC} + 3 \ln \frac{kT}{hC} \right) \\
 &\quad \left. - \frac{(V_L - V_s)}{V_L} \left( \frac{3}{2} \ln(2\pi m kT) - 3 \ln h + 1 + \ln V_L - \ln N \right) \right\}
 \end{aligned}$$

and

$$\begin{aligned}
q'' = & 2Nk \left\{ \frac{3\theta \exp(-\theta/T)}{T^2(1 - \exp(-\theta/T))} - \frac{\frac{3}{2} \frac{h\nu}{kT^2} \exp(-\frac{h\nu}{kT})}{\frac{3}{2}(1 - \exp(-\frac{h\nu}{kT}))} \right. \\
& - \frac{3V_s}{V_L} \frac{\theta \exp(-\theta/T)}{T^2(1 - \exp(-\theta/T))} + \frac{V_s}{V_L} \frac{\frac{3}{2} \frac{h\nu}{kT^2} \exp(-\frac{h\nu}{kT})}{\frac{3}{2}(1 - \exp(-\frac{h\nu}{kT}))} \\
& + \frac{V_s}{V_L} \frac{E_s}{RT^2} - \frac{V_s}{V_L} \frac{d \exp(-\frac{d}{m_h RT})}{RT^2(1 + m_h \exp(-\frac{d}{m_h RT}))} - \frac{3}{2T} - \frac{3(V_L - V_s)}{2V_L T} \Big\} \\
& + NkT \left\{ \frac{3\theta^2 \exp(-\theta/T)}{T^4(1 - \exp(-\theta/T))} - \frac{6\theta T (\exp(-\frac{\theta}{T}) - \exp(-\frac{2\theta}{T})) - 3\theta^2 \exp(-\frac{2\theta}{T})}{T^4(1 - \exp(-\theta/T))^2} \right. \\
& - \frac{\frac{3}{2} [(\frac{h\nu}{kT})^2 - \frac{2h\nu}{kT^3}] \exp(-\frac{h\nu}{kT})}{\frac{3}{2}(1 - \exp(-\frac{h\nu}{kT}))} + \frac{(\frac{3}{2} \frac{h\nu}{kT^2} \exp(-\frac{h\nu}{kT}))^2}{(\frac{3}{2}(1 - \exp(-\frac{h\nu}{kT}))^2} \\
& - \frac{3V_s}{V_L} \frac{\theta^2 \exp(-\frac{\theta}{T})}{T^4(1 - \exp(-\frac{\theta}{T}))} + \frac{V_s}{V_L} \frac{6\theta T (\exp(-\frac{\theta}{T}) - \exp(-\frac{2\theta}{T})) - 3\theta^2 \exp(-\frac{2\theta}{T})}{T^4(1 - \exp(-\theta/T))^2} \\
& + \frac{V_s}{V_L} \frac{\frac{3}{2} [(\frac{h\nu}{kT})^2 - \frac{2h\nu}{kT^3}] \exp(-\frac{h\nu}{kT})}{\frac{3}{2}(1 - \exp(-\frac{h\nu}{kT}))} - \frac{V_s}{V_L} \frac{(\frac{3}{2} \frac{h\nu}{kT^2} \exp(-\frac{h\nu}{kT}))^2}{(\frac{3}{2}(1 - \exp(-\frac{h\nu}{kT}))^2} \\
& - \frac{2V_s}{V_L} \frac{E_s}{RT^3} - \frac{V_s}{V_L} \frac{q^2 \exp(-\frac{q}{m_h RT})}{R^2 T^4(1 + m_h \exp(-\frac{q}{m_h RT}))} \\
& + \frac{V_s}{V_L} \frac{2RTq (\exp(-\frac{q}{m_h RT}) + m_h \exp(-\frac{2q}{m_h RT})) + q^2 \exp(-\frac{2q}{m_h RT})}{R^2 T^4(1 + m_h \exp(-\frac{q}{m_h RT}))^2} \\
& + \frac{3}{2T^2} + \frac{3(V_L - V_s)}{2V_L T^2} \Big\}
\end{aligned}$$

Expressing the coefficients of  $F(T)$  as functions of the coefficients of  $g$  gives

$$\begin{aligned}
 F'(T_0) &= \frac{C_1}{k T_0}, \quad F''(T_0) = \left[ \frac{2C_1}{k T_0} - \frac{2C_1}{k T_0^2} - \left( \frac{C_1}{k T_0} \right)^2 \right] \\
 F'''(T_0) &= \left[ \frac{6C_2}{k T_0} - \frac{6C_2}{k T_0^2} + \frac{6C_1}{k T_0^3} + \frac{6C_1}{k T_0^2} + \frac{C_1^2}{k T_0^3} - \frac{6C_1 C_2}{k^2 T_0^2} + \left( \frac{C_1}{k T_0} \right)^3 \right] \\
 F^{IV}(T_0) &= \left[ \frac{24C_4}{k T_0} - \frac{24C_4}{k T_0^2} + \frac{24C_2}{k T_0^3} - \frac{24C_1}{k T_0^4} - \frac{12C_2}{k^2 T_0^2} - \frac{24C_1 C_2}{k^2 T_0^2} + \frac{36C_1 C_2}{k^2 T_0^3} \right. \\
 &\quad \left. - \frac{36C_1^2}{k^2 T_0^2} + \frac{12C_1^2 C_2}{k^3 T_0^3} - \frac{12C_1^3}{k^2 T_0^4} - \left( \frac{C_1}{k T_0} \right)^4 \right].
 \end{aligned}$$

Barter (1) shows that  $F(T)$  for benzene is of the form

$$F(T) = \frac{F''(T_0)}{2!} (T - T_0)^2 + \frac{F'''(T_0)}{3!} (T - T_0)^3$$

The following are values of constants appearing in the partition function for benzene as given by Eyring.

$$\begin{aligned}
 T_0 &= 278.6^\circ \text{K} \\
 E_s &= 10,383.8 \text{ cal} \\
 V_s &= 77.00 \text{ ml} \\
 V_L &= 87.28 \text{ ml} \\
 K &= 1.38047 \times 10^{-16} \text{ erg/deg} \\
 h &= 6.624 \times 10^{-27} \text{ erg sec} \\
 N &= 6.0228 \times 10^{23} \text{ molecules/mole} \\
 R &= 8.31 \times 10^7 \text{ erg/mole deg} \\
 A_{SC} &= 283 \\
 n_h &= 2.67 \\
 q &= .12 \\
 \Theta &= 80.24^\circ \text{K} \\
 \Theta' &= 55.2^\circ \text{K} \\
 \nu &= 9 \times 10^{12} \text{ CPS} \\
 B &= 0.17165 \text{ cm}^{-1}
 \end{aligned}$$

$\Theta$  is the Debye temperature of solid, and  $\Theta'$  is the Debye temperature of the liquid.

These values give

$$g' = C_1 = -73.5 \times 10^7, \quad g'' = 2C_2 = .05 \times 10^7$$

This yields

$$F'(T_0) = -192 \times 10^{21} = -192 \times 10^{18}$$

$$\frac{F''(T_0)}{2} = -36800 \times 10^{36}$$



It can be seen from the form of the expressions for  $g$ ,  $g'$  and  $g''$  that the values for higher order derivatives of  $g$  become progressively less important for any given set of constants. Since  $(T-T_0)$  and  $C_1$  are negative, and  $C_2$  is by far the most dominant term, Eyring's theory will give a series of terms of alternating sign. As the series is of the form  $A\Delta T - A^2\Delta T^2 + A^3\Delta T^3 - \dots$  and  $A$  is equal to  $-192 \times 10^{18}$ , it can be seen that this form does not agree at all with empirical results. If  $C_1$  is positive all terms are negative resulting in negative velocities.

### RESULTS

The velocity of crystallization of nitrobenzene was plotted as a function of temperature as shown in Plate II. Barter (1) found a similar plot for benzene as shown in Plate III. Barter obtained an empirical equation for benzene in the form

$$V = \frac{A}{\eta} (B\Delta T^2 + \Delta T^3)$$

where (if  $\Delta T = T - T_0$ )

$$A = -0.0123 \quad B = -3.99$$

and  $\eta$  is the viscosity.

By extrapolating viscosity-temperature values obtained from the Handbook of Chemistry and Physics (6) a plot was obtained of  $V\eta$  versus  $\Delta T^3$ . This is shown in Plate IV. Using these values and obtaining a best fit to the original data an empirical equation for nitrobenzene was found of the form

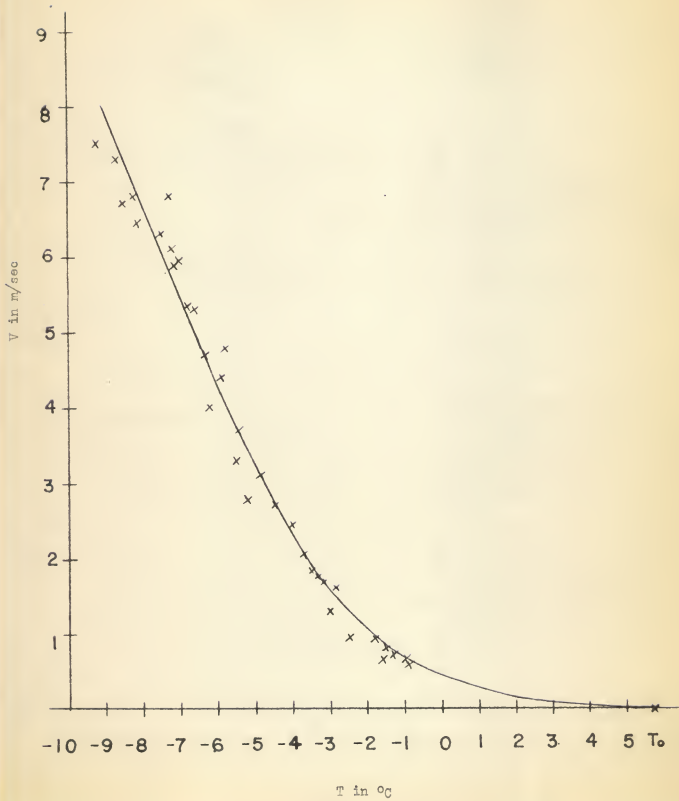
$$V = \frac{A}{\eta} (B\Delta T^3 + \Delta T^4)$$



EXPLANATION OF PLATE II

Plot of velocity of crystallization of  
Nitrobenzene versus temperature

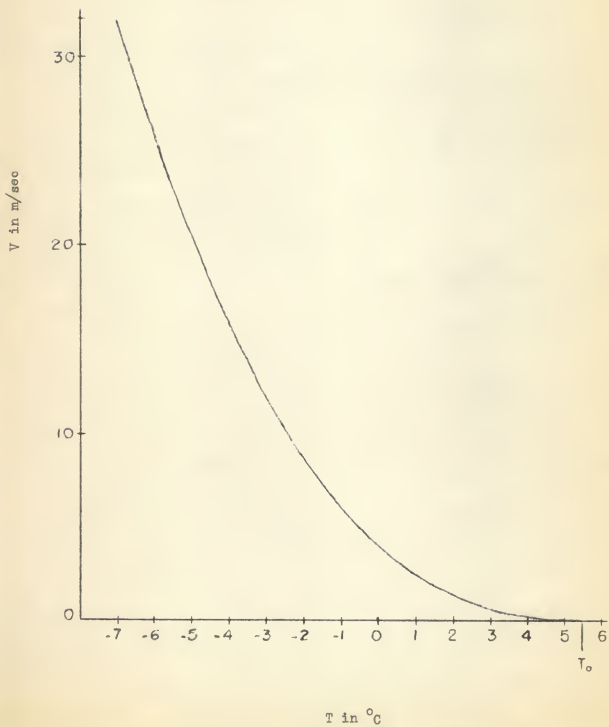
## PLATE II



EXPLANATION OF PLATE III

Plot of velocity of crystallization of  
Benzene versus temperature, obtained by Barter

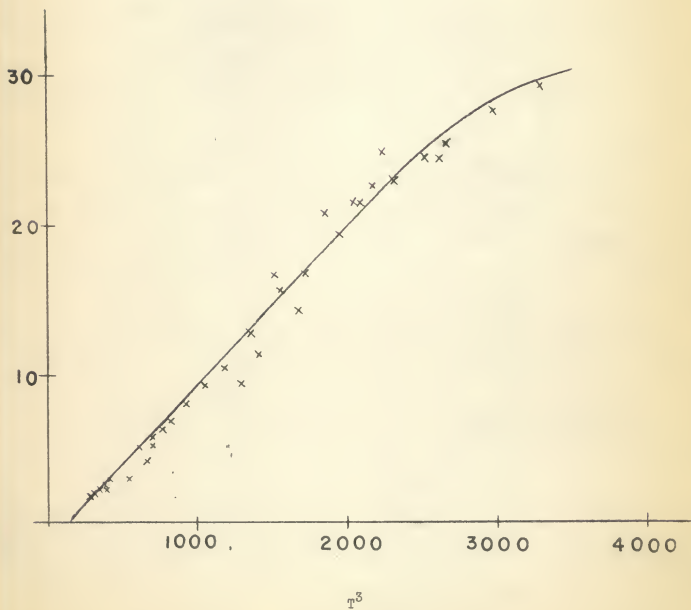
## PLATE III



EXPLANATION OF PLATE IV

A plot of  $V\eta$  versus  $\Delta T^{\circ}$  for benzene.  
Values of  $\eta$  were determined by an extrapolation  
of values from the Handbook of Chemistry and Physics.

## PLATE IV



where

$$A = .000387$$

and

$$B = -11.6$$

This is shown in Plate V. As can be seen by comparing the plots for benzene and nitrobenzene, the freezing velocity for nitrobenzene approaches zero faster as  $T$  approaches  $T_0$ . This leads to difficulty in measuring the velocity for temperatures close to  $T_0$ . Not only is it difficult to start freezing and keep the sample at an equilibrium temperature, but the freezing front is poorly defined and the contrast is not great on the film. In some instances it was difficult to see the freezing front directly, much less on the film. It is for these reasons that no readings taken corresponding to supercooling to a temperature greater than zero.

#### CONCLUSION

The combination of Turnbull's expression with Eyring's partition function does not produce agreement with the empirical results. There are several places from which this discrepancy might arise.

First, the expression involving the relationship between the frequency of transfer of a molecule from one phase to another to the activation free energy developed by Turnbull might be incorrect. Turnbull assumes there is only one average free energy in each state or only one barrier. However the activation energy could depend on the orientation of the molecules. That is,

EXPLANATION OF PLATE V

Plot of velocity of crystallization of  
benzene versus temperature using expression

$$V = \frac{A}{\eta} (B\Delta T^3 + \Delta T^4)$$

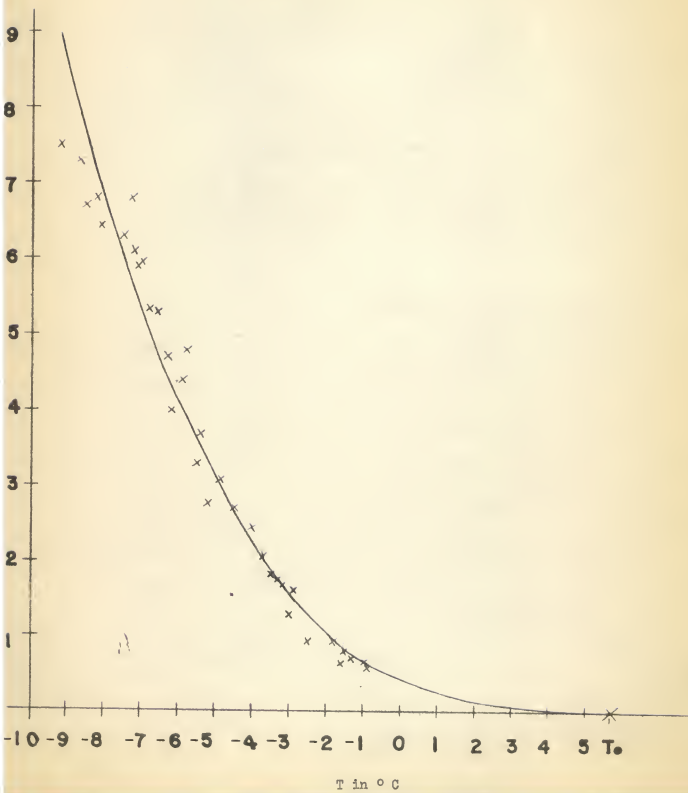
where

$$A = .000387$$

$$B = -11.6$$



## PLATE V



there may be a rotation barrier. In fact there might be a great number of barriers which could not be easily represented as a single average barrier.

Second, in taking the derivatives of  $\Delta G = \Delta F + P\Delta V$  with respect to  $T$ ,  $P\Delta V$  was assumed to be constant, or at least the change in  $P\Delta V$  was assumed negligible when compared to the derivatives of  $\Delta F$ . This assumption appears to be well justified in this experiment.

The third possible source of the discrepancy between the theoretical and empirical results is Eyring's partition function.

Thus last appears to be the most likely source of difficulty since Turnbull's expression seems reasonable and the higher derivatives of  $\Delta V$  diminish much faster than the derivatives of  $\Delta F$ .

Therefore it seems likely that although Eyring's treatment of a liquid as a mixture of molecules with gas-like degrees of freedom and molecules with solid-like degrees of freedom, while accurate enough to yield many thermodynamic properties, is not sufficiently accurate to give correct values for the velocity of crystallization.

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AN INVESTIGATION OF THE VELOCITY  
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by

JOHN RAYMOND SMITH

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AN ABSTRACT OF A THESIS

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A sample of nitrobenzene was supercooled to various temperatures and freezing initiated. The velocity of the freezing front was recorded using a movie camera set at 12.5 frames per second. Readings of velocity were taken from the film and plotted against the temperature. These results were compared with a similar experiment on benzene.

A relationship between velocity and temperature was derived using reaction rate theory and a proposed model of the liquid phase. The values obtained did not agree with empirical results. An empirical equation was obtained:

$$V = \frac{.000387}{\eta} (-11.6 \Delta T^3 + \Delta T^4)$$