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Correlation between the Transition Temperature and the Rotational Potential Barrier in Plastic Crystals

Hideaki Chihara and Yoshikata Koga*
Department of Chemistry, Osaka University, Toyonaka
* *Department of Chemistry, University of British Columbia, Vancouver 8, B. C., Canada*

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A linear retationship was found between the transition temperature of plastic crystals and potential energy barrier hindering molecular rotation determined below or above the transition point, with the slope of the line 7.5 ***R*** and 4.1 ***R***, respectively, where ***R*** is the gas constant. Consideration of the distribution of molecules between the librational and the rotational states showed that the transition starts to occur cooperatively when the fraction of the rotating molecules reaches a value of 1/60 and concludes with a value of 1/3. The model gives the entropies of transition which reasonably agree with the observed values.

Many of the phase transitions in molecular solids are the result of a further acquisition of the degree or degrees of freedom of motion at the transition point. In the case of globular molecules, the additional degrees of freedom are considered to be of rotational or orientational origin.[1] In fact, a previous paper[2] demonstrated an approximately linear relationship between the transition temperature and the height of the potential barrier hindering the molecular rotation in a few molecular crystals of this type. There, the values of the hindering potential was derived from the entropy evaluation and its procedure was subject to an assumption based on the corresponding state principle.

Meanwhile, more reliable values of the hindering potential barrier height have been accumulated by application of the nuclear magnetic resonance techniques; In particular the measurements of the spin-lattice relaxation time by the pulsed NMR methods have proved to give the more meaningful values for such a quantity than does the indirect thermodynamic reasoning.

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[1] J. Timmermans, *J. Phys. Chem. Solids*, **18**, 1 (1961).

[2] H. Chihara and T. Shinoda, This Bulletin, **37**, 125 (1964).

TABLE 1. TRANSITION TEMPERATURE (T_c), ENTROPY OF TRANSITION (ΔS_c), AND BARRIER TO ROTATION ($E^\dagger$) OF SOME PLASTIC CRYSTALS

No. in Fig. 1	Material	T_c	$E^\dagger$(kcal/mol)		$\Delta S_c/R$	
			Phase B	Phase A	Exptl	Calcd
1	CH_4	20.50	0.20[a]	—	0.38[e]	0.88
2	CD_4	26.9	0.53[a]	—	0.62[f]	1.49
3	CF_4	76.221	—	—	2.31[g]	2.29
4	H_2Se	82.3	1.4[b]	0.23[b]	1.88[h]	2.06
5	HCl	98.38	1.4[c]	—	1.45[h]	1.55
6	DCl	105.03	—	0.85[c]	1.52[i]	1.80
7	HI	125.68	1.74[c]	—	1.0[h]	1.79
8	DI	128.28	—	0.97[c]	1.51[i]	1.94
9	$C(CH_3)_4$	140.498	3.0[d]	1.0[d]	2.25[j]	2.44
10	$(CH_3)_2CCl_2$	188.1	—	2.2[d]	—	2.36
11	$(CH_3)_3CCl$	183	2.8[d]	1.5[d]	—	2.00
12	CCl_4	225.5	—	—	2.40[h]	2.38
13	Ar	83.81	1.28[k]	—	1.68[l]	—
14	Kr	115.78	1.77[k]	—	1.69[l]	—

a) Derived from G. A. DeWit, Ph. D. Thesis, University of British Columbia (1966).
b) J. H. Loehlim, P. G. Menaitt, and J. S. Waugh, *J. Chem. Phys.*, **44**, 3912 (1965).
c) D. J. Genin, D. E. O'Reilly, E. M. Peterson, and T. Tsang, *J. Chem. Phys.*, **48**, 4525 (1968).
d) E. O. Stejskal, D. E. Woessner, T. C. Furrar, and H. S. Gustowsky, *J. Chem. Phys.*, **31**, 55 (1959).
e) K. Clusius, and L. Popp, *Z. Physik. Chem.*, **B46**, 63 (1940).
f) J. H. Colwell, E. K. Gill, and J. A. Morrison, *J. Chem. Phys.*, **39**, 635 (1963).
g) H. Enokido, S. Shinoda, and Y. Mashiko, This Bulletin, **42**, 3415 (1969).
h) "Selected Values of Chemical Thermodynamic Properties," NBS Circular 500 (1952).
i) K. Clusius and G. Wolf, *Z. Naturforsch.*, **2a**, 495 (1947).
j) H. Enokido, T. Shinoda, and Y. Mashiko, This Bulletin, **42**, 84 (1969).
k) Enthalpy of vacancy formation; See Ref. 3.
l) Entropy of fusion; See Ref. 3.

In the present paper, we will put forward a revised relationship between the transition temperature and the potential barrier hindering the molecular rotation in solids and also discuss some of its ramifications which will help to understand the nature of the cooperative phenomena.

Potential Energy Barrier and Fraction of Rotating Molecules. Table 1 is a compilation of the experimental values of the barrier height for a number of plastic crystals. Where available, the value for both the high temperature phase and the low temperature phase are given. These barrier values are plotted against the transition temperatures in Fig. 1. Inert gas crystals, Ar and Kr, are also listed at the bottom of the Table, which are the plastic crystals that have no transition points; Their values refer to the triple points and the heats of vacancy formation.[3] The significance of these two points will be discussed in a later Section.

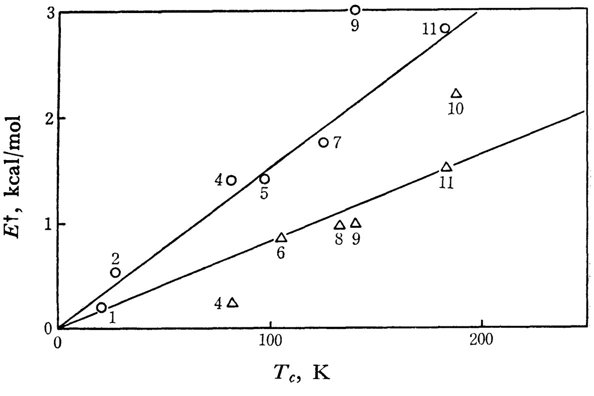

Fig. 1. Linear relationship between the transition temperature (T_c) and the potential energy barrier ($E^\dagger$) hindering molecular rotation: ○ Phase B, △ phase A. Numbers in the figure correspond to those given in Table 1.

It is seem from Fig. 1 that the points corresponding to the high-temperature phase (phase A) and those corresponding to the low-temperature phase (phase B) lie on the two separate straight lines. Both lines pass through the origin as pointed out earlier[2] and the lines are represented by the formula

$$E^\dagger = \alpha R T_c \qquad \begin{matrix} \alpha = 4.1 \text{ for phase A} \\ \alpha = 7.5 \text{ for phase B} \end{matrix} \qquad (1)$$

These relationships may be interpreted as showing that the phase transition takes place when the average thermal energy reaches a certain fraction of the potential barrier and the factor α at which it occurs does not depend on a particular compound.[4] However α depends on the direction in which the transition point is approached and there is a jump in its value at T_c. The jump occurs in a cooperative way but we shall focus our attention on its difference between the two

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[3] R. H. Beaumont, H. Chihara, and J. A. Morrison, *Proc. Phys. Soc.* (London), **78**, 1462 (1961).

[4] The compounds listed in Table 1 assume the face-centered cubic structure in phase A with exceptions of CCl_4 (rhombohedral), CF_4(unknown), and $(CH_3)_2CCl_2$ (unknown).

[5] G. B. Guthrie and J. P. McCullough, *J. Phys. Chem. Solids*, **18**, 53 (1961).

phases. Although the cooperative effect does not abruptly come into play at T_c, the transitions under consideration are very close to those of the first order. Therefore, we may extrapolate the properties of the phases A and B to T_c to examine what triggers the cooperative transition.

To evaluate the significance of Eq. (1), we shall take a simplified classical picture. It will be assumed that a crystal consists of two different species of molecules, 'rotational' and 'librational' (abbreviated as R and L, respectively), and that a quasi-chemical equilibrium

$$\mathrm{L} \rightleftarrows \mathrm{R} \tag{2}$$

is established between the two species, with the Helmholtz energy difference $A^\dagger$ given by

$$A^\dagger = E^\dagger - TS^\dagger\,. \tag{3}$$

$E^\dagger$ will be taken as the potential barrier height and

$$S^\dagger = S_\mathrm{R} - S_\mathrm{L} \tag{4}$$

The transition may now be looked upon as an abrupt displacement of the equilibrium (2) toward the right as T_c is approached from Phase B. This may be achieved by an increase in $S^\dagger$ and/or a decrease in $E^\dagger$ in a cooperative way.

In the present treatment, S_R was calculated in a conventional way from the knowledge of the geometry of molecules and S_L was obtained in the harmonic oscillator approximation from the appropriate values of $E^\dagger$ and the appropriate number of minima $(=4)$ of the potential function for both Phases A and B.

Such calculations yielded $S^\dagger/\boldsymbol{R}=3.2\pm0.6$, except for methanes, with a surprisingly small scatter from compound to compound and between the two phases. Therefore, the transitions are associated with a decrease in $E^\dagger$ (as shown in Eq. (1)) rather than with an increase in $S^\dagger$.

The fraction of rotating molecules or the equilibrium constant of the reaction (2) may be written as

$$N_\mathrm{R}/N_\mathrm{L} = \exp(-A^\dagger/\boldsymbol{R}T) = \exp(S^\dagger/\boldsymbol{R})\exp(-E^\dagger/\boldsymbol{R}T) \tag{5}$$

where N_R and N_L denote the number of 'rotational' and 'librational' molecules. Thus at $T=T_c$, Eq. (5) reads

$$N_\mathrm{R}{}^\mathrm{B}/N_\mathrm{L}{}^\mathrm{B} = (30\pm20)\exp(-7.5) \fallingdotseq 1/60 \tag{6}$$

for Phase B and

$$N_\mathrm{R}{}^\mathrm{A}/N_\mathrm{L}{}^\mathrm{A} = (30\pm20)\exp(-4.1) \fallingdotseq 1/2 \tag{7}$$

for Phase A.

This means that only one molecule out of 60 is 'rotating' in phase B, whereas as many as one-third of the molecules are in the 'rotational' state in Phase A at the transition temperature, *i.e.* the transition would be triggered by the fraction of molecules that amounts to 1.7% of the total or one-quarter $(1/60)^{1/3}$ of a one-dimensional extention of the molecular array.

Entropy of Transition

We shall now attempt to calculate the entropy of transition by use of Eqs. (6) and (7).

The entropy of either phase S is given by

$$S = \boldsymbol{k}T\left(\frac{\partial \ln Q}{\partial T}\right)_{V,N} + \boldsymbol{k}\ln Q \tag{8}$$

where Q is the partition function of the phase, which may be written, aside from the configurational part, as

$$Q = q^N \tag{9}$$

q being the molecular partition function,

$$\begin{aligned} q = \sum_{i=1}^{\infty}\exp(-E_i/\boldsymbol{k}T) &= \sum_{i}^{E_i\leq E^\dagger}\exp(-E_i/\boldsymbol{k}T) \\ &+ \sum_{i}^{E_i>E^\dagger}\exp(-E_i/\boldsymbol{k}T) \end{aligned} \tag{10}$$

the first sum in Eq. (8) corresponds to the 'librational' state and the second corresponds to the 'rotational' state. If q_L and q_R denote the corresponding partition functions, Eq. (8) can be rewritten as

$$q \fallingdotseq q_\mathrm{L} + [\exp(-E^\dagger/\boldsymbol{k}T)]q_\mathrm{R}. \tag{11}$$

The entropy of the molecules in the two states is given by

$$S_\mathrm{L} = \boldsymbol{R}T\left(\frac{\partial \ln q_\mathrm{L}}{\partial T}\right)_{V,N} + \boldsymbol{R}\ln q_\mathrm{L} \tag{12}$$

and

$$S_\mathrm{R} = \boldsymbol{R}T\left(\frac{\partial \ln q_\mathrm{R}}{\partial T}\right)_{V,N} + \boldsymbol{R}\ln q_\mathrm{R} \tag{13}$$

Therefore,

$$\begin{aligned} \frac{N_\mathrm{L}S_\mathrm{L}+N_\mathrm{R}S_\mathrm{R}}{N} = \frac{\boldsymbol{R}T}{N}\Bigg[N_\mathrm{L}\left(\frac{\partial \ln q_\mathrm{L}}{\partial T}\right)_{V,N} \\ + N_\mathrm{R}\left(\frac{\partial \ln q_\mathrm{R}}{\partial T}\right)_{\mathrm{V,N}}\Bigg] \\ + \frac{\boldsymbol{R}}{N}N_\mathrm{L}\ln q_\mathrm{L}+N_\mathrm{R}\ln q_\mathrm{R}) \end{aligned} \tag{14}$$

Now, since

$$\frac{q_\mathrm{L}}{q} = \frac{N_\mathrm{L}}{N} \quad \text{and} \quad \frac{q_\mathrm{R}\exp(-E^\dagger/\boldsymbol{k}T)}{q} = \frac{N_\mathrm{R}}{N} \tag{15}$$

we have

$$\begin{aligned} \ln q_\mathrm{L} &= \ln\frac{N_\mathrm{L}}{N} + \ln q \\ \ln q_\mathrm{R} &= \ln\frac{N_\mathrm{R}}{N} + \ln q + E^\dagger/\boldsymbol{k}T \end{aligned} \tag{16}$$

From Eqs. (8), (9), (14), and (16), the total entropy S is given by

$$S = \frac{N_\mathrm{L}}{N}S_\mathrm{L} + \frac{N_\mathrm{R}}{N}S_\mathrm{R} - \boldsymbol{R}\left(\frac{N_\mathrm{L}}{N}\ln\frac{N_\mathrm{L}}{N} + \frac{N_\mathrm{R}}{N}\ln\frac{N_\mathrm{R}}{N}\right) \tag{17}$$

The entropy of transition ΔS_c is defined by

$$\Delta S_c = S^\mathrm{A} - S^\mathrm{B} \tag{18}$$

where S^A and S^B desote the total entropies of the Phases A and B. $N_\mathrm{R}/N_\mathrm{L}$ values are given by Eqs. (6) and (7). Therefore the entropy of transition may be obtained simply from the knowledge of T_c and the geometry of molecules. The result is given in the last column of Table 1. General agreement with the observed entropy changes is satisfactory except for CH_4 and CD_4.

Discussion

It has been shown that the fraction of rotating molecules changes in a cooperative way from 1/61 in phase B to 1/3 in phase A at least in a class of compounds that undergoes 'rotational' transition. Further experimental evidence may be required to establish this as an empirical rule but it does seem that the intermolecular interaction of the cooperative nature extends as far as the second neighbors in phase B where the crystal field is rather 'hard,' whereas it extends only to the nearest neighbors in phase A in which the crystal field is rather 'soft' because of the large kinetic energy.

It is interesting in this connection to note that the fusion of argon and krypton is governed by the same principle; *i.e.* melting occurs when the fraction of vacancies reaches the same number 1/61, This equality in the number, however, may only be a fortuitous one in the sense that $S^{\dagger}/\boldsymbol{R}$ for both cases happened to be the same and this may have brought about the equality in $E^{\dagger}/\boldsymbol{R}T_c$. Therefore it seems extremely interesting to analyze various kind of phase changes in terms of such two-species model as is developed in the present treatment.

The molecular model adopted here is a crude one which neglects the detailed configurational considerations and deals with a uniform phase as a mixture of the two molecular species, nevertheless the good agreement of the calculated and observed entropies of transition suggests that it should serve a useful picture of such solids. It is certainly more realistic than interpreting the entropy in terms of increased uniform orientational degrees in phase A.[5)]

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