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THE FRANKLIN INSTITUTE LABORATORIES
CHEMISTRY DIVISION


6 DIFFUSION IN ORGANIC CRYSTALS

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SYNOPSIS


 This report describes the determination of the self-diffusion coefficient in anthracene crystals as a function of temperature and crystal orientation.

Thermodynamic quantities associated with the diffusion process, ~~have been~~ evaluated and are discussed.

The origin of an unusually long tail of diffusant concentration is considered in terms of a secondary fast diffusion process.

Errors introduced by the experimental procedure are estimated.

I. INTRODUCTION

 The method of investigating self-diffusion in anthracene single crystals and the established experimental techniques were described in the previous reports. The major part of the effort in this period was spent on the determination of the self-diffusion coefficient in two directions in the anthracene crystal lattice, i.e. perpendicular to the ab and ac planes. The reasons for choosing these two directions will be discussed in a later section. Along with the measurements of diffusivities, some improvements on the sectioning technique have been achieved. Difficulties in leveling the specimens for sectioning by microtome have been minimized. Experimental errors due to this procedure are estimated.

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In the past three months four diffusion measurements in each crystal direction at different temperatures were completed. From these measurements, the activation energy, frequency factor and entropy change for self-diffusion in anthracene have been estimated.

II. EXPERIMENTAL RESULTS

Diffusivities perpendicular to the ab and ac planes of anthracene crystals have been measured at temperatures from 140°C to 196°C. Typical diffusion concentration profiles are shown in figure 1. The activity 'tail' at greater penetration depth was found in all the experiments. This tail was similar to that reported by Sherwood and Thomson⁽¹⁾. The magnitude of the tail was usually in the order of one per cent of the surface concentration and is somewhat larger than that found by the previous investigators. Examinations on the profile of the tail activity are being carried out. Possible reasons for its occurrence will be discussed in the next section.

All the diffusion coefficients presented in this report were obtained from the slope of the initial straightline portion of the penetration plot according to Gaussian distribution. Values of the diffusivities along with the corresponding temperatures are tabulated in Table 1. The diffusion coefficients were plotted against the reciprocal temperatures on a semilogarithmic scale. Straight lines with slopes of 12,140 and 12,800 were fitted to the data for diffusion perpendicular to the ab and ac planes respectively, shown in figure 2.

TABLE 1

<u>Temp °C</u>	<u>Orientation of Cryst. Perpendicular to plane</u>	<u>Diffusivities $\frac{D}{cm^2/sec} \times 10^{12}$</u>	<u>$\frac{1}{T^{\circ}K}$</u>
196	ab	160	2.14
196	ac	110	2.14
182	ab	42	2.20
172	ac	32	2.24
151	ab	8.7	2.36
151	ac	6.4	2.36
140	ab	5 ~ 8	2.42
140	ac	2.5 ~ 4.2	2.42

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The values of the corresponding activation energies and frequency factors are estimated as 24.2 Kcal/mol. and 29 cm²/sec for ab crystals and 25.4 Kcal/mol and 81 cm²/sec for ac crystals.

These plots satisfy the Arrhenius empirical relation for the diffusion process. Thus the diffusivities for self-diffusion in anthracene single crystals perpendicular to ab and ac planes can be respectively expressed as a function of temperature as:

$$D (\parallel ab) = 29 \exp \left(- \frac{24,200}{RT} \right)$$

$$D (\parallel ac) = 81 \exp \left(- \frac{25,400}{RT} \right)$$

when R is the gas constant and T the absolute temperature.

III. DISCUSSION

General theories for understanding the physical meaning of the activation energy, frequency factor and diffusivity in solids and for their correlations have been established in terms of atom jumps for inorganic crystals. Similar treatment has been considered for the organic molecular crystals, despite the fact that the difference in bond nature may cause great changes in the magnitude of the parameters. Through the common thermodynamical and statistical mechanical procedures, the final form of frequency factor, D_0 , can be expressed as

$$D_0 = \gamma a^2 \nu \exp \left(\frac{\Delta S}{R} \right) \quad (1)$$

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where γ is a geometric factor; a , the molecule jumping distance; ν , the lattice vibration frequency; R , the gas constant and ΔS the entropy change in the diffusion process.

For many crystal structures, γ is nearly unity. The average Debye vibrational frequency for anthracene can be estimated as 1.7×10^{12} per second. Taking 11×10^{-8} cm and 6×10^{-8} cm as the jumping distances in the two diffusion directions, the entropy change ΔS can be calculated from equation (1) using the experimental values of D_0 . In the present investigation, the values of ΔS are 19 cal/mole/deg. and 14 cal/mole/deg. respectively. These entropies are considerably larger than typical entropies obtained for diffusion in inorganic crystals. However, no significance can be attached to this in view of the difference in nature of the various crystals.

Diffusion mechanisms can not be specified solely based on this kind of calculation, because the diffusion processes of different mechanism should obey the same kinetics from which equation (1) was derived. On the other hand, from a consideration of the relation between the size of the molecules and the crystal lattice one may say that a vacancy mechanism is likely for anthracene self-diffusion.

The nature and the magnitude of intermolecular forces for such a material as anthracene are not nearly as well known as for ionic crystals or simple metals. Nor are sufficient experimental data available, such as precise elastic constants, from which intermolecular potential functions can be calculated. Consequently, correlations

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between the activation energy and the frequency factor can not be theoretically evaluated in order to justify the experimental measurements at the present time.

A discrepancy between the present measurements and the data reported by Sherwood and Thomson⁽¹⁾ should, however, be mentioned. They obtained the activation energy for self-diffusion in anthracene, perpendicular to the ab plane, as 42 Kcal/mole and the frequency factor as 6×10^{10} cm²/sec against our values of 24 Kcal/mole and 29 cm²/sec. respectively. There are two possibilities which may cause such a discrepancy.

(1) It is our opinion that the thick sections taken by the previous investigators for sectioning the crystals and the small number of experimental points in their concentration profiles are likely to lead to errors. In their high temperature measurements, the concentration profiles very likely extend deeply into the region of tail activity thus giving rise to larger apparent diffusivities.

(2) The two groups of investigators most likely used different grades of crystals. It is thus possible that the discrepancy merely reflects the difference in perfection of the different grades of crystals. More perfect crystals are currently being investigated in this laboratory in order to clarify this situation.

The origin of the unusually long tail of diffusant concentration in the penetration profile is not clear at the present time. However, two possibilities which have been considered are

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discussed below.

(1) The radioactive anthracene may contain traces of radioactive starting material or species intermediate in the synthesis. It is possible such individual species diffuse through anthracene lattice faster than the anthracene molecules, because the former molecules are smaller in size and lighter in weight. However, chromatographic examination has shown that the chemical impurities in the radioactive anthracene are less than 10 part per million. As compared with the magnitude of the tail of the concentration profile, it is unlikely that those impurities should yield a tail of about a percent of its surface concentration.

(2) It is known that, in general, the structure of an organic crystal is usually not as perfect as that of an ionic crystal or a simple metal. Diffusion through small angle boundaries and line imperfections or simply by falling through the holes and cracks that are usually present in organic crystals can possibly produce a tail activity in the concentration profile. In order to elucidate this possibility, experiments to isolate these anomalous diffusion processes and studies on more perfect crystals are being carried out.

Because diffusion is a structure sensitive process, anisotropic effect on diffusivities in most of the organic crystals should be expected. In a medium where diffusion is anisotropic, the diffusion constant is actually a multiple order tensor relating to the vectors concentration gradient, and diffusion flux, which may not be

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mutually parallel. If the third and higher orders are neglected, for a monoclinic system like anthracene crystals, thirteen diffusion coefficients are necessary to describe the diffusion process. We do not intend to measure all these self-diffusion coefficients along various crystallographic directions at the present time. Yet, in order to know if the anisotropic effect is detectable by the experimental technique, specimens with two orientations have been investigated.

Diffusion perpendicular to the ac plane has been measured because the b axis is twofold symmetrical. Diffusivity along this axis can be easily assessed by applying a concentration gradient perpendicular to the ac plane. This is one of the principal axes for diffusion in the crystal system of anthracene. The reason for investigating the diffusion process perpendicular to the ab plane is simply because it is the cleavage plane of the anthracene crystal and specimens of this kind can be easily prepared. Moreover, the only information available for diffusion in organic crystals is on self-diffusion of anthracene perpendicular to the ab plane. In order to establish a reliable experimental technique for a diffusion study in organic crystals, it is advisable to assess diffusion in this direction of anthracene so that we may compare the result with data available in the literature. The direction perpendicular to the ab plane is a crystallographic direction of high order index. It is about 14° , 20° and 35° of $[101]$, $[112]$ and $[001]$ respectively. Strictly from a geometrical point of view, one may say that the molecular jumps in the

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[101] direction should be more effective than jumps in other directions in contributing to the diffusivity perpendicular to the ab plane. However, the probability of a [101] jump occurring may not be as great as that of a [001] jump because of the difference in energy barriers of the two types of molecular jump. It is difficult to make an exclusive judgement on types of molecular jump which the diffusivity perpendicular to the ab plane may represent. However, regardless of these considerations the jumping distance for diffusion perpendicular to the ab plane is certainly greater than that in the direction perpendicular to the ac plane. Thus, from the experimental results, it appears that the anisotropy of diffusion in this crystal system is mainly due to the difference in distances of molecular jump.

IV. EXPERIMENTAL ERRORS

Assuming that each section has a thickness d and the misalignment distance from the planes of equal radioactivity is S , Shirn, Wajda and Huntington⁽²⁾ derived an expression for an estimation of the effect of misalignment on the diffusion coefficient. For specimens of circular cross section, the measured diffusivity D_m , can be expressed as

$$D_m = \frac{D}{1 - \frac{4d^2 + 3S^2}{96 Dt}} \quad (2)$$

where D is the exact diffusion coefficient and t is the diffusion time. For most of the experiments, the typical value of $D_m t$ is in the order of 1×10^4 square microns and S is about 30 microns. If d is always kept as 10 microns, the maximum difference between D_m and D can be estimated through equation (2) as about 1.4% of D_m .

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(10)
by

P. J. Reucrofts
~~P. J. Reucrofts~~
~~Sr. Res. Scientist~~



C. H. Lee
~~C. H. Lee~~
~~Sr. Res. Scientist~~

H. K. Kevorkian
~~H. K. Kevorkian~~ *and*
~~Res. Scientist III~~

M. M. Labes
~~M. M. Labes~~
~~Director~~
~~Chemistry Division~~

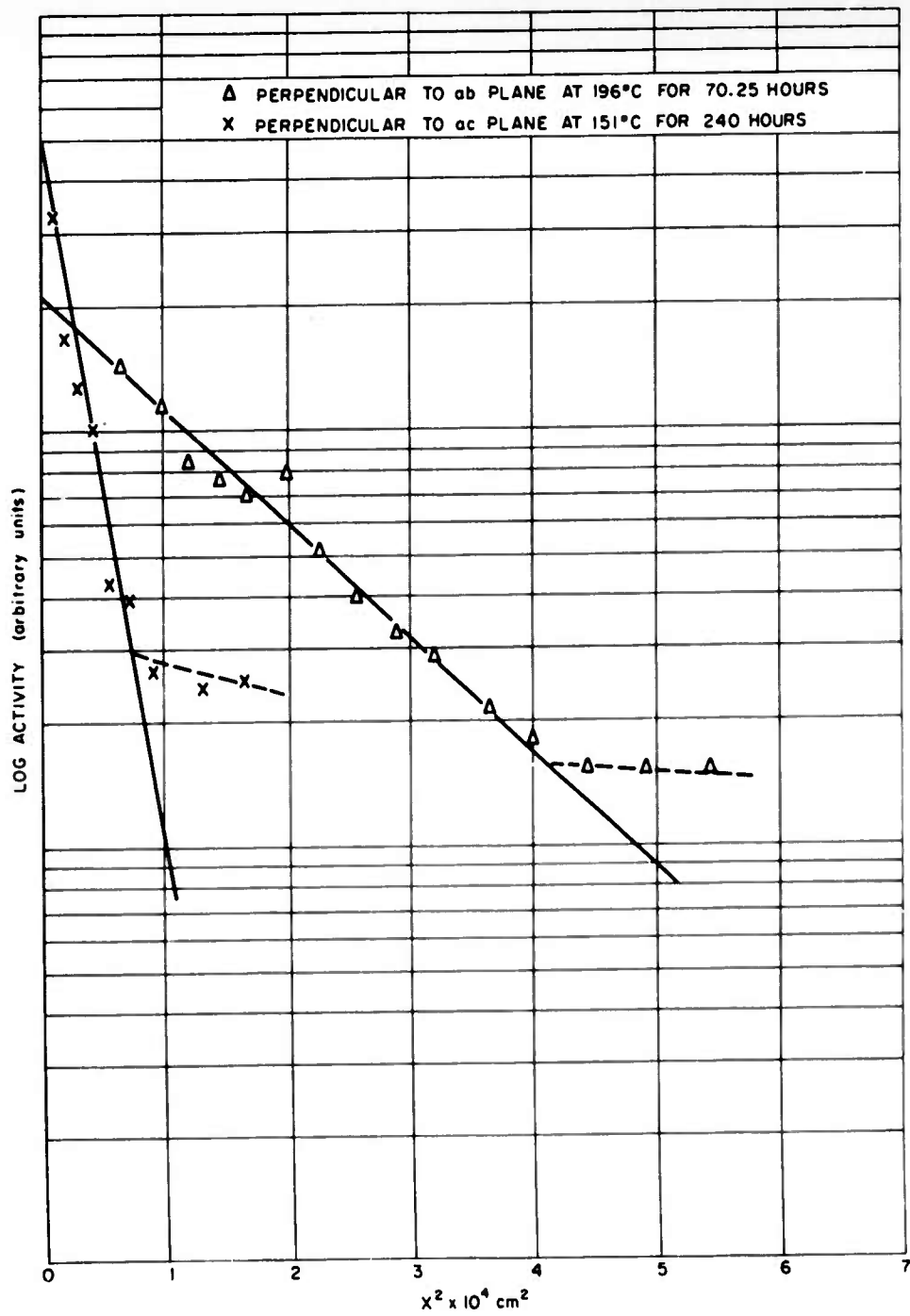


FIG. 1. CONCENTRATION PROFILE FOR SELF-DIFFUSION IN ANTHRACENE

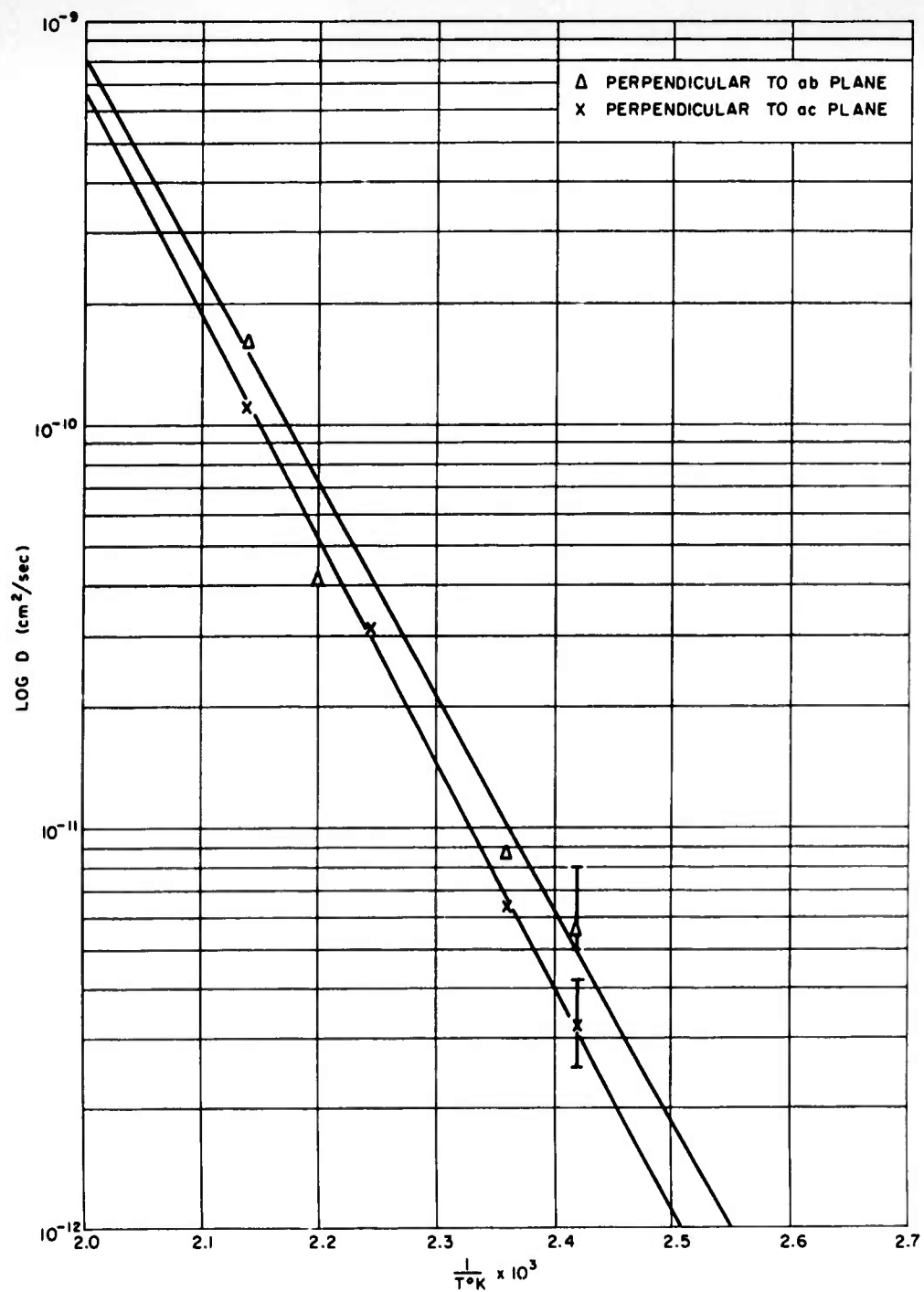


FIG. 2. TEMPERATURE DEPENDENCE OF SELF-DIFFUSION IN ANTHRACENE

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