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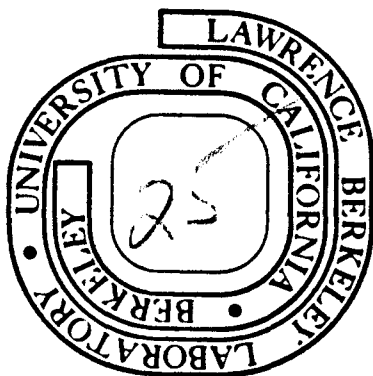
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KINETICS OF GRAPHITIZATION IN GLASSY CARBON

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ABSTRACT

The kinetics of graphitization has been studied using structure parameters d_{002} , L_c and L_a derived from wide angle x-ray diffraction measurements. For Glassy Carbon (GC) isochronally (two hours each) heat treated in the temperature range 1000-2800°C, the behavior of these parameters can be studied in three separate regions: (1) For heat treatment temperature (HTT) < 1500°C GC undergoes dehydrogenation, (2) For 1500°C < HTT < 2300°C the main process is stress relief, (3) For HTT > 2300°C graphitization takes place. The activation energy for graphitization in the third region has been determined to be $215 \pm$ Kcal/mole using the 'superposition technique'.

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INTRODUCTION

Glassy carbon (GC) is a non-graphitizing carbon characterized by a d_{002} always larger than that of graphite, i.e. $3.35\text{\AA}$ ⁰. High resolution electron microscopic studies¹ show that GC has an entangled lath like structure. By using selected area electron diffraction Whittaker et al² have found evidence of various allotropic forms of carbon in GC. Our work in this area has produce basically similar results. However, we believe that the material is homogeneous, and the 'allotropes' are artifacts of the sample preparation technique. Crushing the material leads to straightening of the laths and relief of shrinkage stresses built in during pyrolysis³. This explains why on heat treatment the alleged allotrope nuclei do not grow and why GC does not 'transform' into graphite. In the high resolution electron microscopy studies the specimens are thinned by ion milling and in these cases no allotropes have been reported.

However structural parameters of GC do change on heat treatment suggesting that one can study the "kinetics of graphitization". The interplanar separation d_{002} , the crystallite size in the layer plane L_a and in a plane normal to the layer L_c have been used extensively to characterize GC. These can be easily determined from XRD patterns. For GC it is extremely difficult to resolve higher order reflection due to overlapping (00 l) and (hk) bands. Thus strain broadening effects have remained in L_a and L_c . The actual crystallite sizes, on removing strain broadening, should be larger than those calculated using simple line broadening formulae.⁴

The most extensive study of kinetics in GC is "Tensile Creep Studies on GC" by Fischbach.⁵ An effective energy of 350 ± 40 Kcal/mole over the range 2500-2900°C was calculated from the creep data. No other estimate of an activation energy has been reported, to the authors' knowledge.

EXPERIMENTAL:

Wide angle x-ray diffraction was used to characterize the structure of heat treated glassy carbon samples.* The range of samples studied included isochronal heat treatments for two hours each at 1100°C and from 1300 to 2800°C in 100° increments. To study the kinetics of structural changes in GC, samples were heated at 1700, 2000, 2300, 2500 and 2700°C for various time intervals. The heat treatments of the GC samples were carried out in a graphite furnace. The GC samples (5.0 x 2.5 x 0.16) cms were placed in a cylindrical graphite crucible 7.6 cms x 6.3 cms size and surrounded with GC wool. An optical pyrometer calibrated for the temperature range 1000-3000°C was used to measure the temperature. The nomenclature for the heat treated samples is henceforth GC-HHT-time, e.g. GC-1500-2 means GC heat treated at 1500°C for two hours.

The x-ray data on 2.5 x 1.2 cms GC samples were obtained on a GE XRD-3 diffractometer. A 1° beam slit, MR Soller Slit and 0.1° receiving slit in reflection geometry were used in our experiments. This combination was decided upon to obtain sufficient intensity, usually quite low for GC samples, and because our experiments with varying slit sizes

*The GC plates (8"x2"x1/16") were bought from Polycarbon Co., Hollywood, CA.

showed that the effect of a large slit in distorting the diffraction pattern is mainly in the low angle ($2\theta < 15^\circ$) region. CuK_α radiation was used at 45KV, 40mA. Both a Ni filter and pulse height analyzer were used for improved monochromatization. For a few samples data were obtained in both point count and recorder modes. For the former, fixed counts of 10^4 were made at each value of 2θ . For the recorder mode the goniometer was scanned at $2^\circ/\text{min}$ and chart speed was adjusted so that the chart abscissae divisions corresponded to 0.1° (2θ) intervals. After applying all the corrections discussed below, the two sets of data were found to be equivalent, hence the recorder technique was used for the majority of samples.

Because of the large volume of voids in GC there is pronounced small angle x-ray scattering that persists at high angles. To obtain the true profile of (002) reflection it is necessary to subtract the small angle scattering intensity and make other corrections. The data were corrected by first subtracting the Compton background intensity and the small angle scattering intensity and dividing out the Lorentz-Polarization and atomic scattering factors. The data were then normalized to the maximum intensity value in each case. Three parameters were obtained from the intensity vs. $\sin \theta$ plots.

1. d_{002} - from the (002) peak position using $\lambda = 2d\sin\theta$
2. L_c - from the width at half maximum of the (002) peak using Scherrer's formula
$$L_c = \frac{0.45\lambda}{\Delta(\sin\theta_c)}$$
3. L_a - from the width at half maximum of the (10) band using Warren's formula,
$$L_a = \frac{0.92\lambda}{\Delta(\sin\theta_a)}$$

0 0 0 0 4 7 0 4 9 3 3
0 0 0 0 4 7 0 1 0 4 2

-4a

Because of the breadths of the maxima the peak position is difficult to determine precisely, even after all the corrections are made, but the d_{002} data are accurate to $\pm 0.005\text{\AA}$. The width at half maximum of the (10) band is difficult to determine because of interference from the superimposed 004 reflection. For this reason a parameter L_a was also

obtained in some cases using the width at 75% maximum of the (10) band.

The precisions of L_c , L_a data are $\pm 0.5^\circ$, $\pm 2^\circ$ respectively.

RESULTS - Isochronal Studies:

The variations of d_{002} , L_c and L_a for the isochronals are shown in Fig. 1. Three regions can be separated according to HTT variation of d_{002} . Below a HTT of 1500°C , d_{002} decreases with HTT. From 1500°C to 2300°C d_{002} is approximately constant at 3.44° . The third region is above 2300°C where d_{002} decreases with HTT. As seen in Fig. 1 both L_c and L_a increase as HTT increases, but the separation into three regions is not as striking as in the case of the d_{002} variation.

RESULTS - Kinetic Studies:

The "superposition technique"⁶ was used to study the kinetics of change in GC. This technique does not depend on the order of the kinetics. However it could be easily illustrated for a first order case. Briefly, if a property, P, follows first order kinetics,

$$P = P_f + (P_i - P_f) \exp(-kT)$$

where P_i , P_f are the initial and the final values of the property P.

For a thermally activated process the rate constant k is expected to follow,

$$k = k_o \cdot \exp(-\Delta H/RT) = k_o \cdot K(T)$$

Plotting the property vs $\ln t$, if a translation along the $\ln$ time axis superimposes curves for different HTT, then

$$\ln \frac{K(T)}{K(T_o)} = \ln t_o - \ln t = - \frac{\Delta H}{R} \left(\frac{1}{T} - \frac{1}{T_o} \right)$$

where the subscript "o" refers to an arbitrarily chosen reference curve of P vs $\ln t$. Hence a plot of such shifts along $\ln t$ needed to superimpose all the curves onto the reference curve against $1/T$ gives the apparent activation energy ΔH .

The plot of L_c vs $\ln t$ for five different HTT is shown in Fig. 2. The curves of 1700 and 2000°C are seen to be superimposable but do not overlap the higher HTT curves. This seems to confirm that they belong to a different region and the kinetics of this region is rather slow. The curves for the other 3 HTT's do overlap and taking L_c for GC 2700-2 as a reference point they can all be made to fall on one single curve as shown in Fig. 3. The plot of the shifts vs. $1/T$ shown in Fig. 4 gives an apparent activation energy 200 ± 30 Kcal/mole. The L'_a data could also be translated to obtain a composite plot shown in Fig. 5. The activation energy plot is shown in Fig. 6. The apparent activation energy is found to be 225 ± 30 Kcal/mole. Combining the two estimates the apparent activation energy is 215 ± 40 Kcal/mole. Although there is scatter in the data the variations in d_{002} and L_a were found to be consistent with the calculated activation energy.

DISCUSSION:

From the experimental data it is evident that the evolution of the structure of GC with HTT goes through three different stages. The three regions can be understood on the following basis. Up to the HTT of 1500°C, the material is going through a settling down process, and completion of dehydrogenation around 1500°C has been suggested⁷. We have recently done a preliminary study using a mass spectrometer and were able to

detect increasing amount of H_2 evolution as GC-1000-1 was heated up to 1150°C . The second region is characterized by a constant value of d_{002} at $3.44\text{\AA}$ corresponding to turbostratic carbons. We believe that the increase in L_c and L_a in this region is largely due to stress relief. Fischbach⁵ in his creep studies of GC has noted that as a result of shrinkage (approximately 40%) during pyrolysis, GC probably has high internal stresses which are relieve slightly with higher heat treatment temperatures (greater than 2000°C). Also while trying to intercalate GC with K in a gaseous atmosphere the material was reduced to a fine powder. The proposed explanation was the presence of intense frozen stresses in GC which were abruptly relieved.⁸ In our kinetic data the curves of L_c versus $\ln t$ for 1700°C and 2000°C HTT are seen to be similar to each other but qualitatively different from the curves for higher HTT. It should be possible to study stress relief in this region roughly below 2300°C although rather long times are required to get small changes.

In the third stage the structure slowly evolves toward the ideal graphite structure and limited graphitization takes place. But even at 2800°C the interlayer spacing of $3.40\text{\AA}$ is much larger than the ideal $3.35\text{\AA}$. It seems that this material is metastable in its disordered form and thermodynamic evidence for this is given in the work of Das and Huckle.⁹ The activation energy for structural change for $\text{HTT} > 2300^\circ\text{C}$ is found to be ~ 215 Kcal/mole. It should be pointed out that no attempt has been made to remove strain broadening effects in this region. If these are large, the effect would be to increase the estimate of the activation energy.

Kinetics of graphitization has been reviewed in detail by Fischbach.⁶ The activation energy values reported range from 90-270 Kcal/mole. For graphitizing carbons 260 Kcal/mole is the accepted value, and the mechanism is considered to be vacancy diffusion. Unfortunately, estimates of activation energy for vacancy diffusion vary considerably and no reliable direct measurement of self diffusion has been made. It is found that the activation energy obtained for GC in this study of L_c is less than that for graphitizing carbons.

It is difficult to reconcile our value of the activation energy of 215 ± 40 Kcal/mole with Fischbach's estimate of 350 ± 40 Kcal/mole⁵. It is possible that a strain broadening correction would change our estimate enough to account for the difference. It is also possible that there is more than one process involved and the creep studies measure a complex effective activation energy.

CONCLUSION:

Our results show that the kinetics of graphitization in GC can be studied in three different regions. These are identified by characteristic processes of dehydrogenation, stress relief, and graphitization. The estimate of activation energy in the third region ($HTT > 2300^\circ\text{C}$) is 215 ± 40 Kcal/mole.

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ACKNOWLEDGEMENT

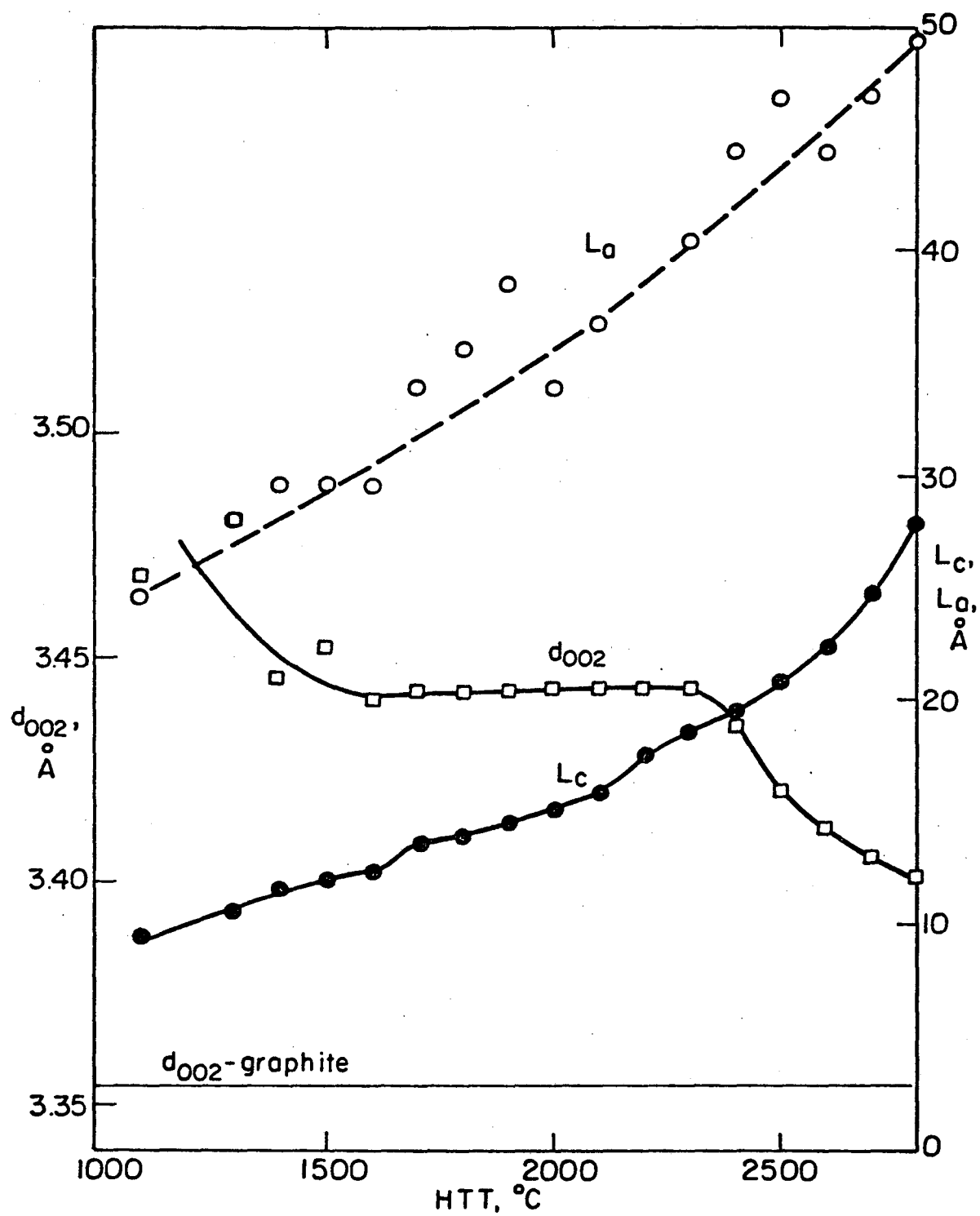
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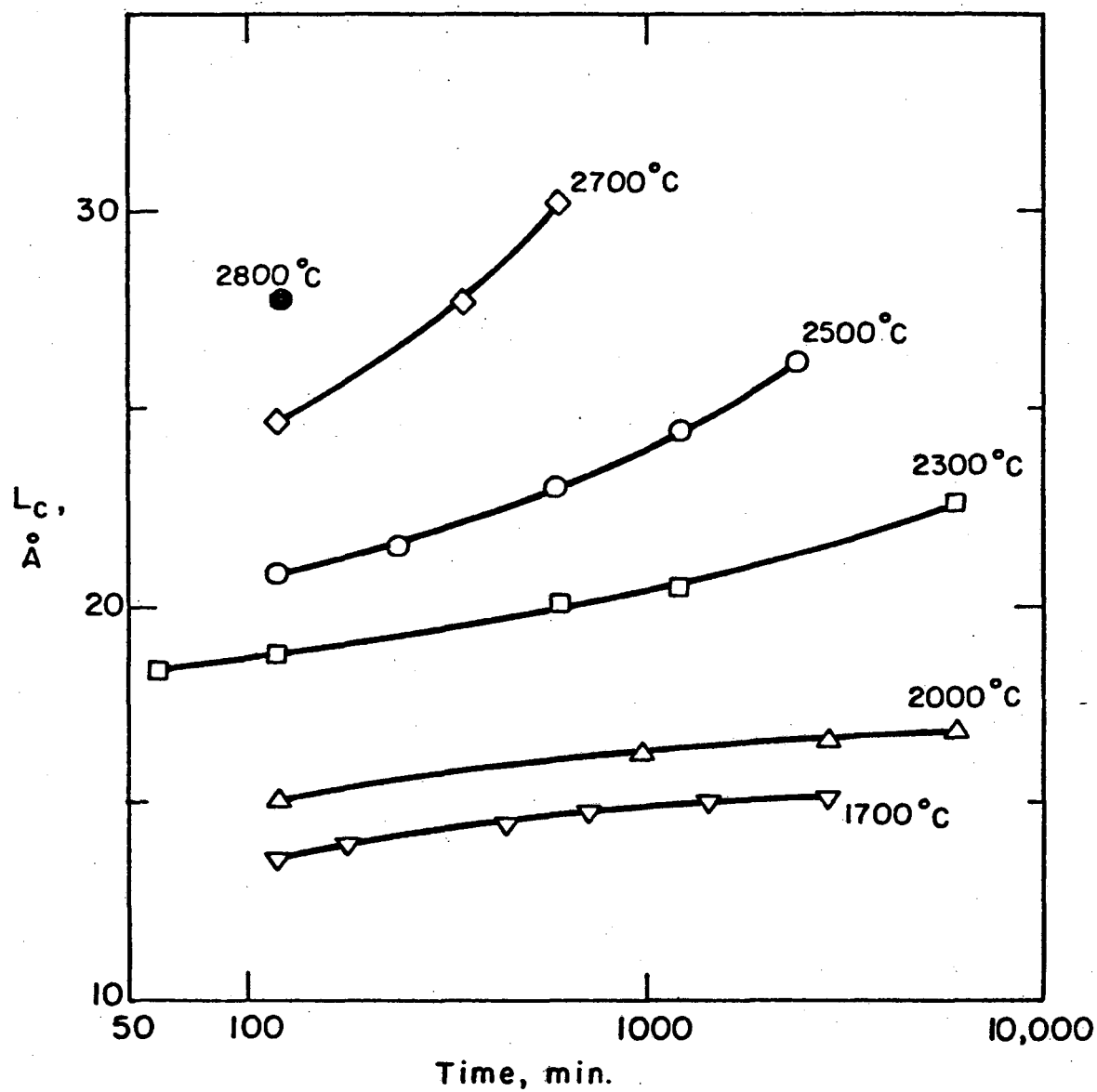
FIGURE CAPTIONS

- Fig. 1. Heat treatment temperature dependence of d_{002} , L_c and L_a for GC heat treated for two hours each.
- Fig. 2. Heat treatment temperature and time dependence of L_c .
- Fig. 3. Composite plot for L_c data using GC 2700 as reference.
- Fig. 4. Activation energy plot for L_c data.
- Fig. 5. Composite plots L'_a parameter.
- Fig. 6. Activation energy plot for L'_a .



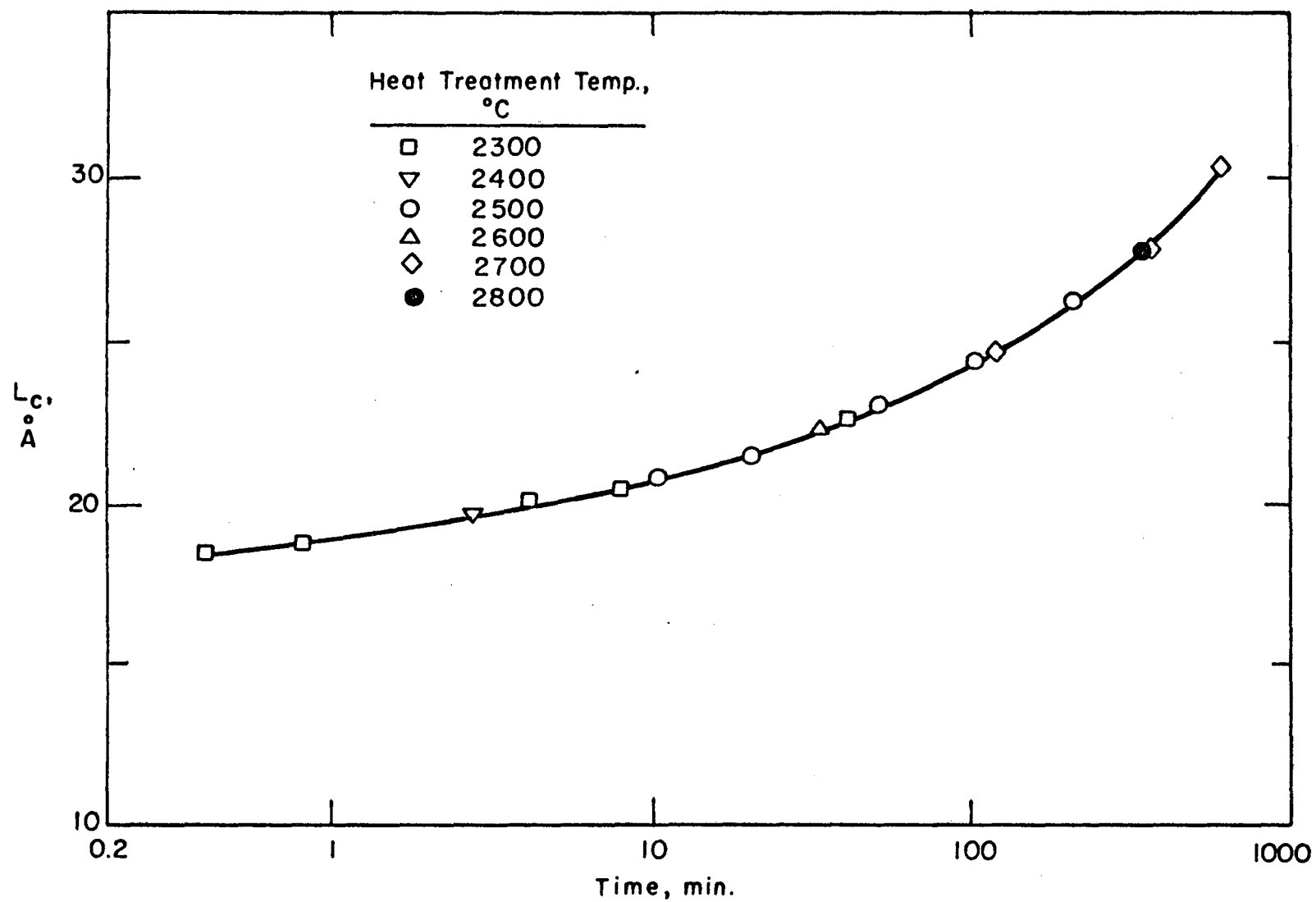
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Fig. 1



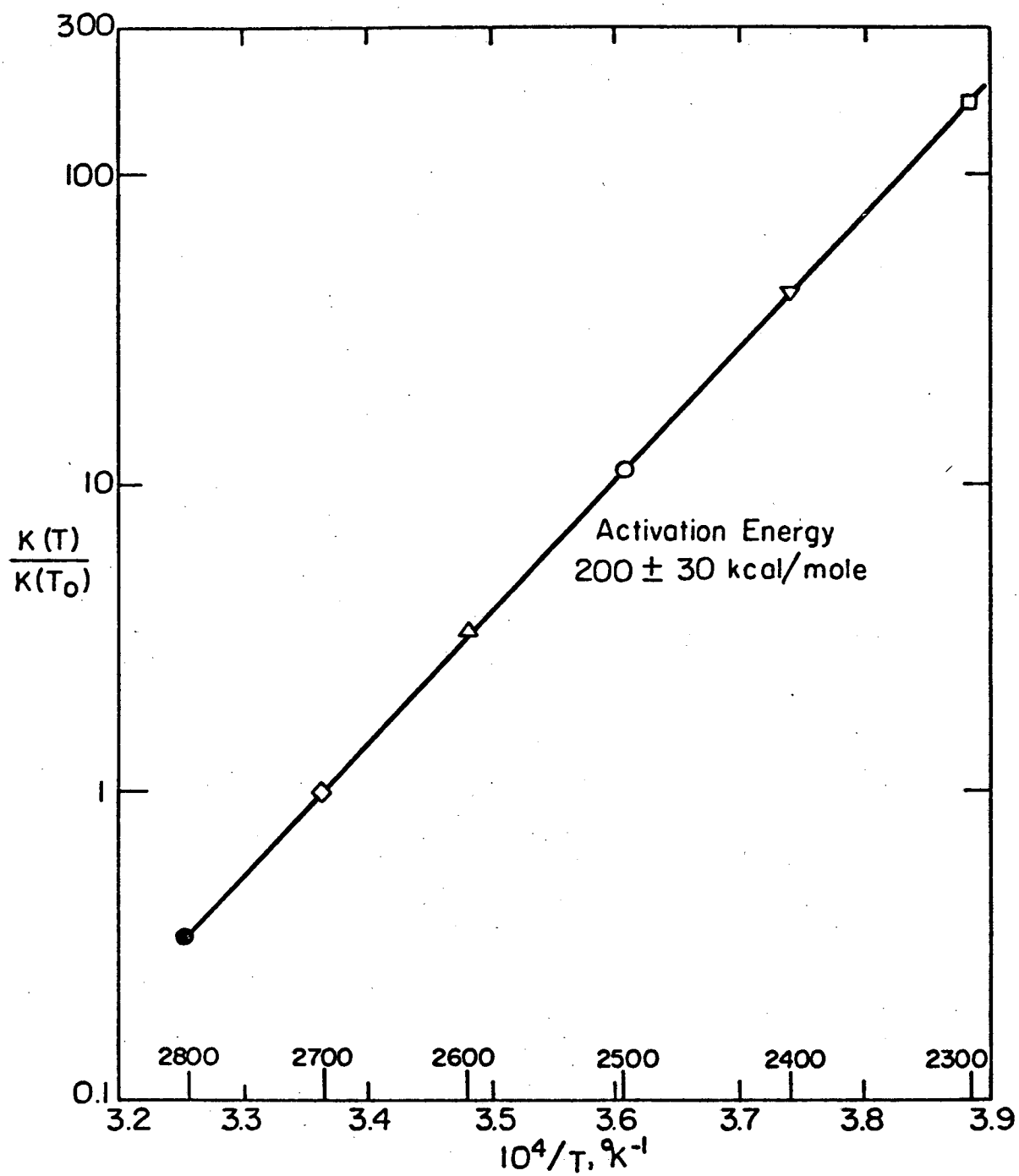
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Fig. 2



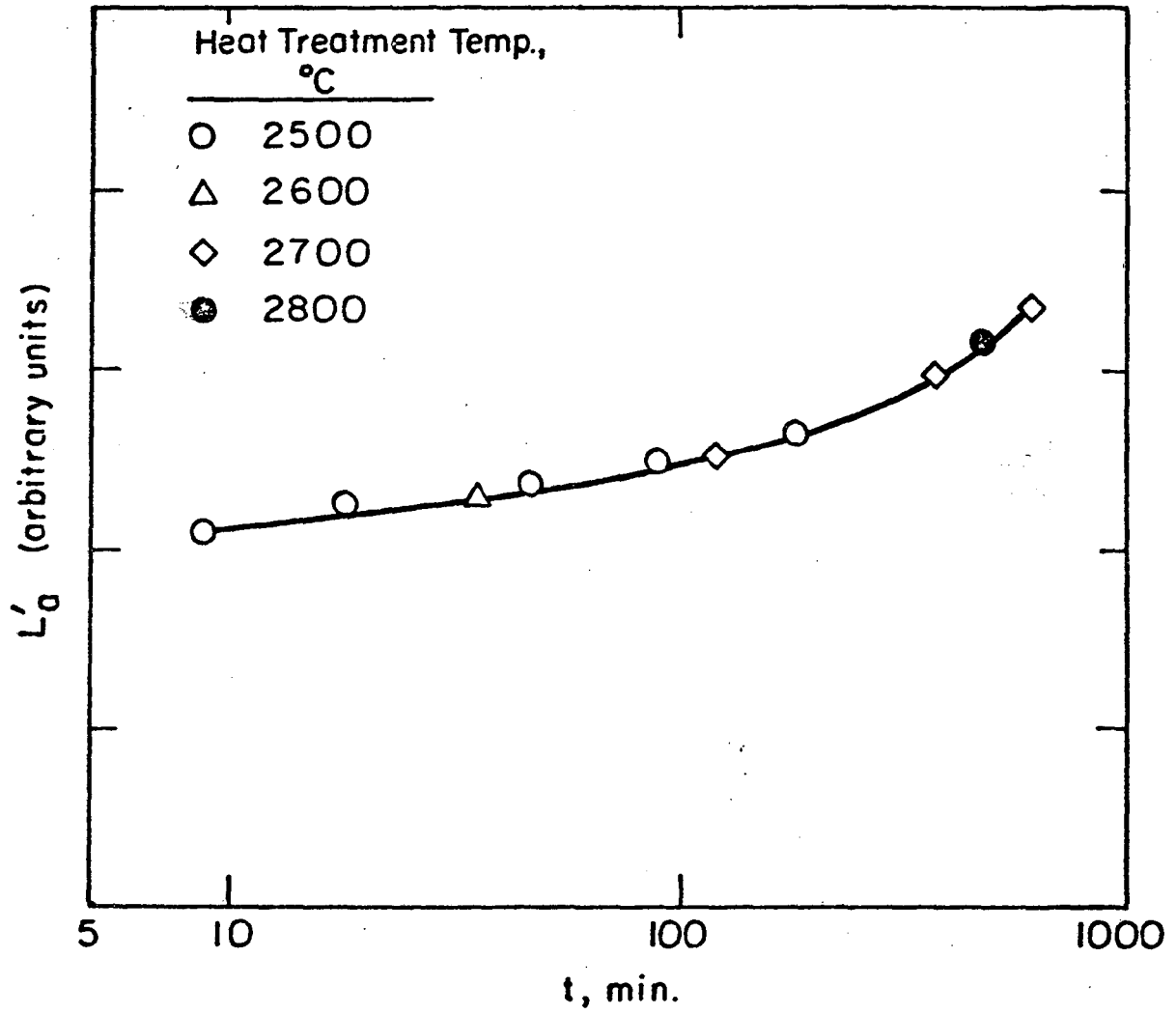
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Fig. 3



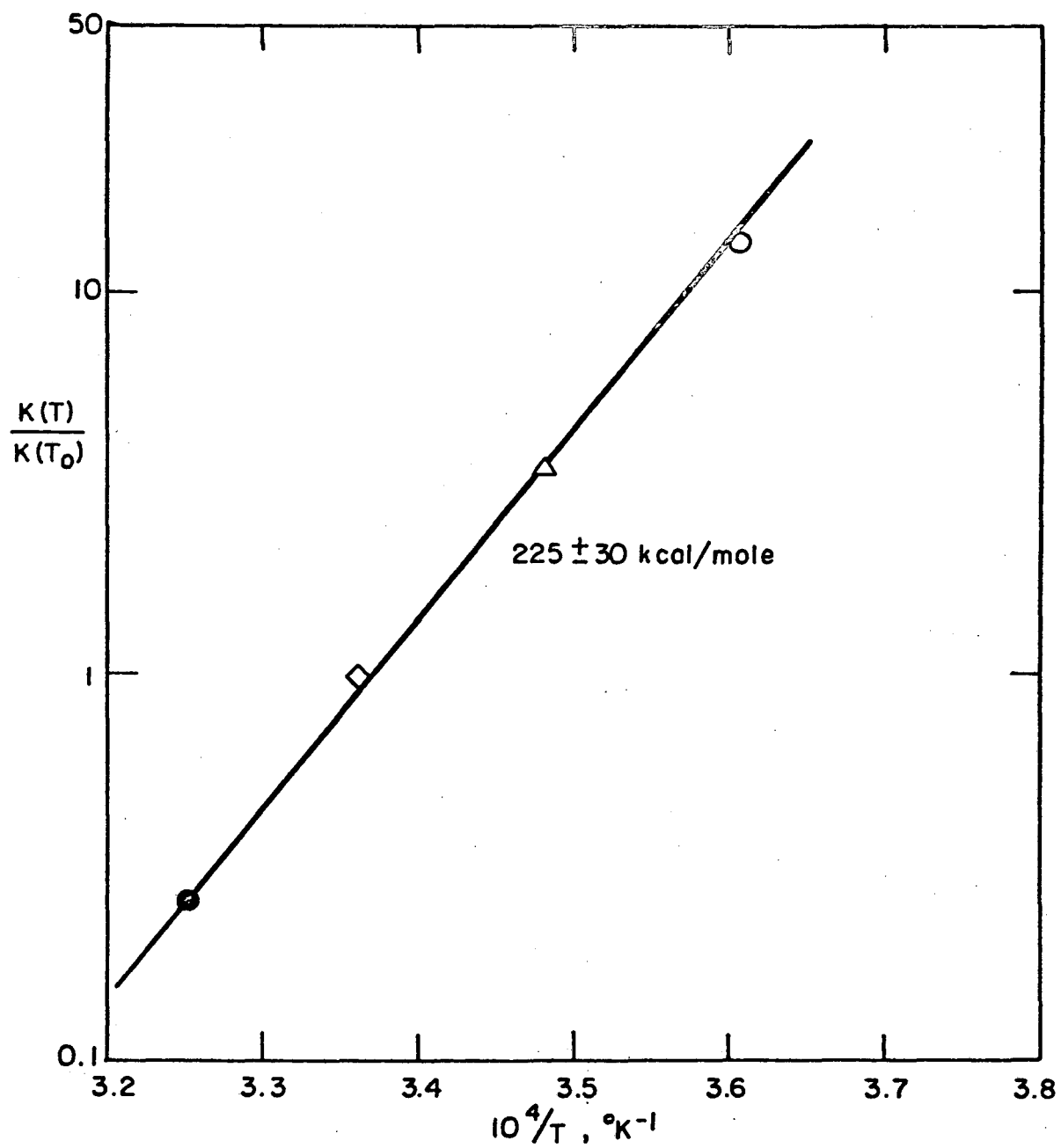
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Fig. 4



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Fig. 5



XBL 765-6906

Fig. 6

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