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REANALYSIS OF THE DATA**

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# KINETICS OF SURFACE AREA CHANGES IN GLASS-LIKE CARBON : REANALYSIS OF THE DATA

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## ABSTRACT

Previous small angle scattering measurements of the kinetics of changes of the surface area of pores in an annealed glass-like carbon have been reanalyzed in terms of the LIFSCHITZ, SLYOZOV and WAGNER coarsening theory in which the surface area is used to obtain an average spherical pore size. When the data are corrected for the transient heat-up time to reach the annealing temperature, the reanalysis leads to an activation energy of  $75 \pm 7.2$  kcal/mole, in agreement with recent results ( $75 \pm 3.6$  kcal/mole) obtained using direct measurements of changes in pore size as determined by the pore radius of gyration. The best value for the activation energy for vacancy migration in carbon is therefore estimated at  $75 \pm 3.2$  kcal/mole.

## I - INTRODUCTION

In studying the kinetics of growth of the pores in a glass-like carbon material, GC, LACHTER et al [1] derived an average activation energy of  $75 \pm 3.6$  kcal/mole using small angle scattering measurements of the radius of gyration  $R_g$ . However, this activation energy is quite different from that obtained by BOSE and BRAGG [2],  $64 \pm 10$  kcal/mole, derived from the kinetics of decreases in surface area of the pores in glass-like carbon samples similar to those investigated by the aforementioned authors. The purpose of the present paper is to apply the pore coarsening analysis to BOSE and BRAGG's surface area data [2] assuming the pores are spherical as a close approximation. In this re-examination of the data it is necessary to correct for the total time of isothermal heat treatments since BOSE and BRAGG's data were not corrected for the transient time required to heat the sample to the desired heat treatment temperature, HTT. The annealing times, HTt, were measured from the point after HTT was reached and hence BOSE and BRAGG's HTts were underestimated.

## II - PORE COARSENING THEORY

LACHTER et al [1] showed that the LIFSHITZ, SLYOZOV and WAGNER theory [3,4] of bulk diffusion with controlled second stage growth of precipitates can be successfully applied to describe the pore growth kinetics in an annealed glass-like carbon material. If  $R_g$  is the radius of gyration of the pores at time  $t$  and  $R_{g_0}$  the radius of gyration extrapolated to time  $t_0 = 0$  at a given

temperature  $T$ , then the changes in pore size can be written in the form :

$$T \left[ (R_g)^3 - (R_{g_0})^3 \right] = \frac{8\gamma DC_0 \phi (t - t_0)}{9\nu kR} = K D (t - t_0) \quad (1)$$

where  $\gamma$  is the interfacial energy between matrix and solute species (in this instance vacancies),  $D$  their diffusion coefficient,  $C_0$  their equilibrium solubility,  $\phi$  their molar volume,  $\nu$  their stoichiometric factor or weight fraction,  $k$  a pore shape factor and  $R$  is the gas constant. In this equation,  $D = D_0 \exp(-\Delta H/RT)$ , where  $\Delta H$  is the activation energy characterizing the pore coarsening process. LACHTER et al [5] showed that the shape of the pores in GC samples can be modelled as ellipsoids of revolution that are randomly oriented in the matrix material with axial ratios ranging between 0.94 and 1.16. The pores can then be assumed as roughly spherical in shape and the surface area can be related to the radius of gyration through the relation  $S_v = \frac{3}{k' R_g}$  where  $k'$  is a pore shape factor of the order of unity, not necessarily equal to  $k$  above.

Thus Eq. (1) can be rewritten :

$$T \left[ \left( \frac{3}{S_v} \right)^3 - \left( \frac{3}{S_{v_0}} \right)^3 \right] = \bar{K} D (t - t_0) \quad (2)$$

or equivalently

$$T \left[ \left( \frac{3}{S_v} \right)^3 - \left( \frac{3}{S_{v_0}} \right)^3 \right] / \bar{K} (t - t_0) = D_0 \exp(-\Delta H/RT) \quad (3)$$

where  $\bar{K} = k' K$ .

For notation clarity  $T$  is the heat treatment temperature HTT and  $t$  is the heat treatment time HTt in all the above equations. According to Eq. (2), isothermal curves of  $\left(\frac{3}{S_v}\right)^3$  plotted versus  $t$  will have a slope  $\bar{K}\frac{D}{T}$ . According to Eq. (3), a graph of the logarithm of the slope thus derived times the corresponding  $T$ , plotted versus the inverse temperature  $\frac{1}{T}$ , will have then a slope  $-\Delta H/R$ .

### III - EXPERIMENTAL DETAILS AND RESULTS

The samples were glass-like carbon materials annealed at temperatures HTT ranging between 2000 °C and 2700 °C for times HTt varying between 0 and 24 hours. The results analyzed in the present paper are those of BOSE and BRAGG [2]. They are plotted on Fig. 1 as surface area versus heat treatment time. A point to be noted is the large scattering of the data corresponding to HTT = 2200 °C. To test for accordance with Eq. (2), the variations of the cube of  $\frac{3}{S_v}$  as a function of HTt are shown in Fig. 2 for each HTT after correcting the HTt for the transient heat-up time according to FISCHBACH [6]. It can be seen that the expected linearity is obtained. The logarithm of  $T \left[ \left(\frac{3}{S_v}\right)^3 - \left(\frac{3}{S_{v_0}}\right)^3 \right] / (t - t_0)$  is plotted on Fig. 3 as a function of the inverse HTT. An activation energy of  $75 \pm 9$  kcal/mole is calculated from the slope of this Arrhenius plot.



FISCHBACH's superimposition method [7] provides another means of determining the activation energy characterizing the kinetics of changes in pore size. This method consists of superimposing all the isotherms in a single curve, often labelled as master curve or superimposed master curve, by translation along the  $\ln t$  axis. The different shifts required to achieve such a superimposition are proportional to the rate constants  $\kappa(T)$  in a thermally activated process when these rate constants depend on temperature through a Boltzmann factor,  $\kappa(T) = \kappa_0 \exp(-\Delta H/RT)$ .

Non-kinetic changes in the microstructure occur when any non-cubic material is annealed, and result from mismatch in the thermal expansion coefficients in different crystallographic directions. The effect is especially large in carbon materials, and for example, is responsible for an irreversible decrease of the bulk density of GC from about  $1.5 \text{ gr/cm}^3$  to  $1.3 \text{ gr/cm}^3$  when material initially processed at  $1000^\circ\text{C}$  is heated very rapidly to  $2700^\circ\text{C}$  [8]. Thus in employing the superimposition analysis, prior to translating the data along the  $\ln \text{HTt}$  axis, it is necessary to correct for the non-kinetic changes in  $S_v$  that occur when the HTT is rapidly increased to a higher value. To achieve this, the data of Fig. 2 are shifted along the  $S_v$  axis in such a way that the extrapolated surface area value to  $\text{HTt} = 0$  for any given HTT coincides with the surface area value corresponding to the as-received material processed at  $1000^\circ\text{C}$ ,  $1134 \text{ m}^2/\text{cm}^3$ . The results is illustrated in Fig. 4. The data corresponding to  $\text{HTT} = 2200^\circ\text{C}$  have been disregarded because of the large scattering associated with the surface area measurements at this HTT.

The master curve displayed in Fig. 5 was obtained by superimposing the data corrected for non-kinetic changes plotted as  $S_v$  versus  $\ln HTt$ . First, the data corresponding to  $HTT = 2300^\circ C$  are translated along the  $\ln HTt$  axis in such a way that they coincide optimally with the data corresponding to  $HTT = 2000^\circ C$  taken as reference [9]. This gives a  $\ln HTt$  translation proportional to  $\kappa(2300)$ . Next, the data for  $HTT = 2500^\circ C$  are translated along the  $\ln HTt$  axis until they overlap smoothly with the two previous curves, and this gives a  $\ln HTt$  change proportional to  $\kappa(2500)$ , and so on. The resulting superimposed master curve shown in Fig. 5 represents the time evolution of the surface area changes if all the annealing was conducted at  $2000^\circ C$ . Figure 6 is a graph of the  $\ln HTt$  shifts derived as described plotted versus inverse  $HTT$ . The activation energy derived from this Arrhenius plot is  $75 \pm 12$  kcal/mole.

#### IV - DISCUSSION

In this reanalysis of BOSE and BRAGG's data [2], there is seen to be an excellent agreement between the activation energies derived using either the pore coarsening analysis via  $S_v$  ( $75 \pm 9$  kcal/mole) or the superimposition analysis employing  $S_v$  ( $75 \pm 12$  kcal/mole). These values are also in excellent accord with those previously derived by LACHTER et al [1] from a pore coarsening analysis via  $R_g$  ( $76 \pm 4$  kcal/mole) and a superimposition analysis employing  $R_g$  ( $74 \pm 9$  kcal/mole). However, all the above values are quite different from that previously derived by BOSE and BRAGG,  $64 \pm 10$  kcal/mole [2].

The disagreement stems from an underestimation of the actual values of the heat treatment times  $HTt$  on the one hand, and to use of the large scattering of the surface area measurements corresponding to  $HTT = 2200^\circ C$  by BOSE and BRAGG in their analysis on the other hand. The correction for the transient heat-up time is much larger at high  $HTTs$  than at lower  $HTTs$ , and increases from 20 minutes at  $2000^\circ C$  to 40 minutes at  $2700^\circ C$ . This correction in  $(t - t_0)$  will give a higher slope in both graphs of Figs. 2 and 3, leading to a higher activation energy. The increase in  $\Delta H$  due to the time error alone is however small, from 64 kcal/mole to about 68 kcal/mole and does not fully explain the much higher value of  $\Delta H$ , 75 kcal/mole. However, if one disregards BOSE and BRAGG's data corresponding to  $HTT = 2200^\circ C$ , then an activation energy of 71 kcal/mole is derived and the correction for the transient time leads to  $\Delta H$  of about 75 kcal/mole. The activation energies obtained by the different methods are given in Table 1, along with those found by LACHTER et al [1].

It is important to note the very good agreement obtained when surface area measurements are employed to represent pore sizes with the functional form of Eq. (2) which was derived for a pore coarsening. Here, as in the case of the  $R_g$  kinetics, the superimposition method alone would suffice to derive the activation energy which characterizes the pore coarsening process, even though this method does not require knowledge of a functional form, i.e., it is only necessary that the physical process be thermally activated. The excellent accord between the activation energies calculated using either Eq. (2) or the superimposition method then validates the general functional form of Eq. (1), but probably not all the

basic assumptions, as in the case of the analysis employing the radius of gyration. This question is addressed in detail by LACHTER et al [5].

## V - CONCLUSION

A reanalysis of the data for the kinetics of decreases in the pore surface area was made for the heat treated glass-like carbon studied by BOSE and BRAGG [2]. When appropriate corrections were performed to obtain the effective time of heat treatment and when the appropriate functional form for pore coarsening was employed in the kinetic analysis, excellent agreement was found between the revised value of the activation energy,  $75 \pm 7.2$  kcal/mole, and those obtained by LACHTER et al [1],  $74 \pm 9$  kcal/mole and  $76 \pm 4$  kcal/mole, by two different analyses on a similar glass-like carbon. An overall value for the activation energy for vacancy migration in carbon is therefore estimated at  $75 \pm 3.2$  kcal/mole.

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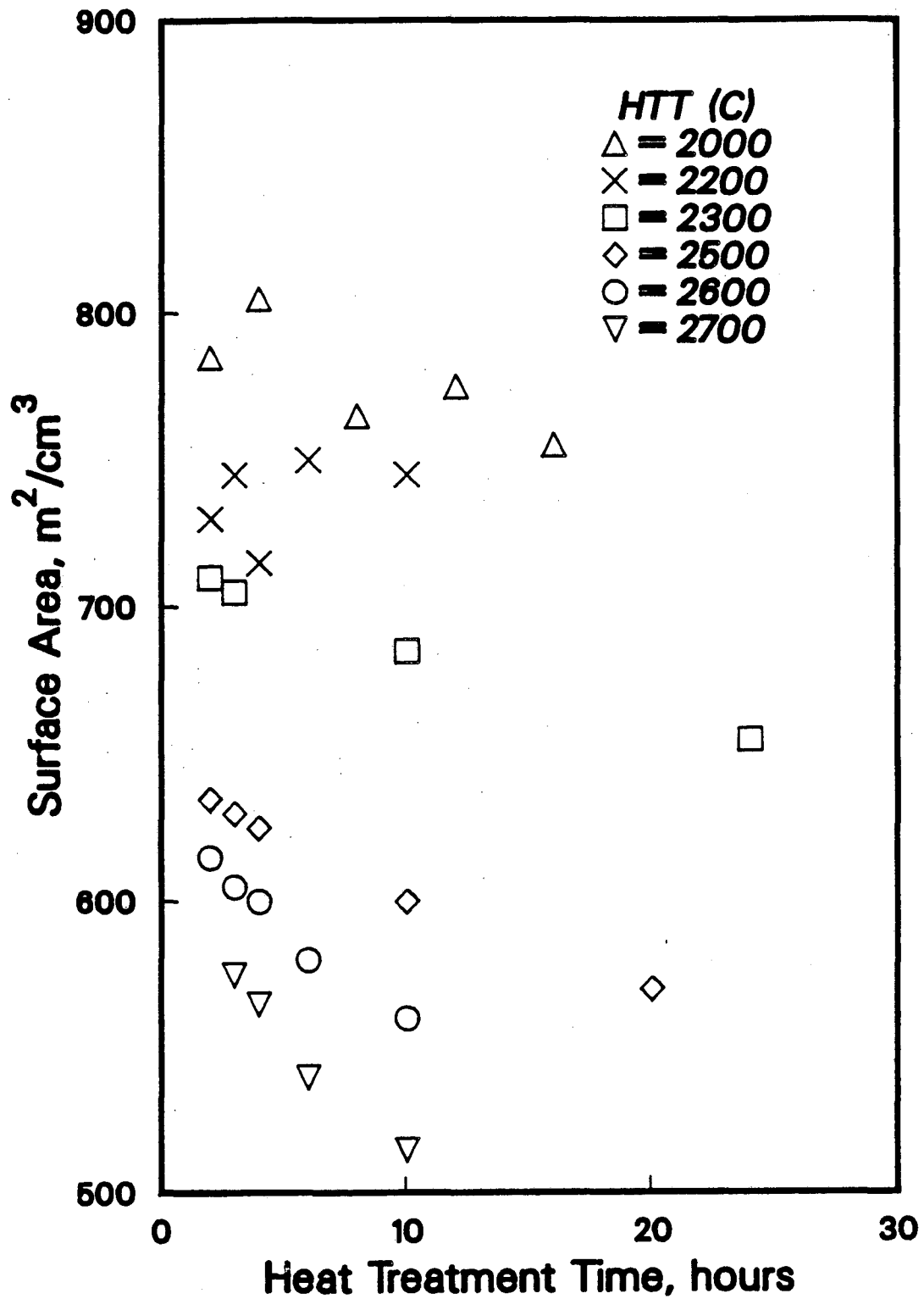
**TABLE 1**

Method	$\Delta H$ (kcal/mole)	$\overline{\Delta H}$ (kcal/mole)	Vacancy Migration Energy in GC (kcal/mole)
$R_g$ Pore Coarsening <sup>1</sup>	$76 \pm 4$	$75 \pm 3.6$	$75 \pm 3.2$
$R_g$ Superimposition <sup>1</sup>	$74 \pm 9$		
$S_v$ Pore Coarsening <sup>2</sup>	$75 \pm 9$	$75 \pm 7.2$	
$S_v$ Superimposition <sup>2</sup>	$75 \pm 12$		

<sup>1</sup> : Reference [1]

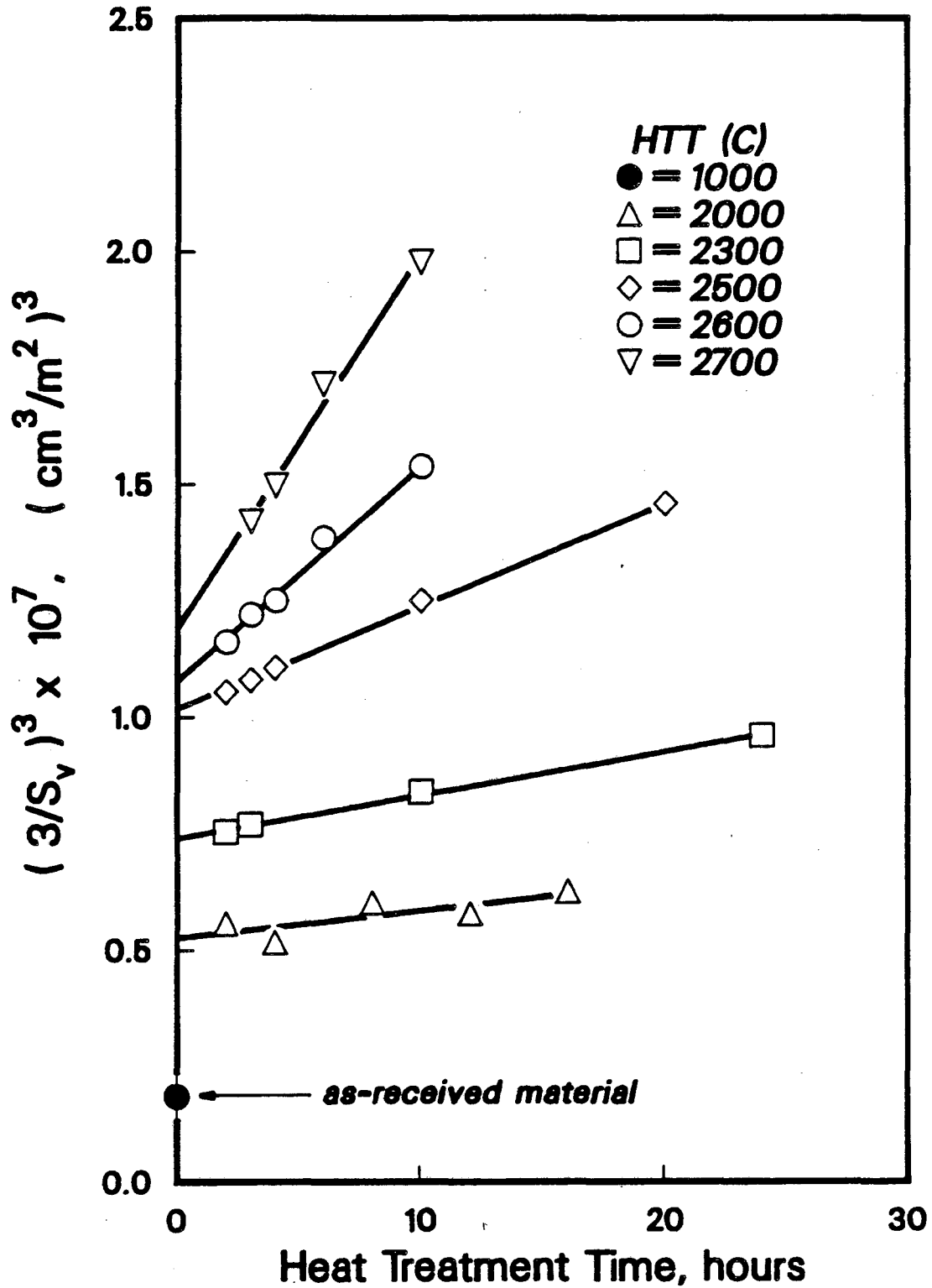
<sup>2</sup> : Present work

Table 1: Activation energies derived from the pore radius of gyration and surface area kinetics. The  $\Delta H$  values given in column 3 represent the average activation energy derived from analyses (pore coarsening and superimposition) employing  $R_g$  and  $S_v$ . The activation energy given in column 4 represents the average value of the activation energies listed in column 3.



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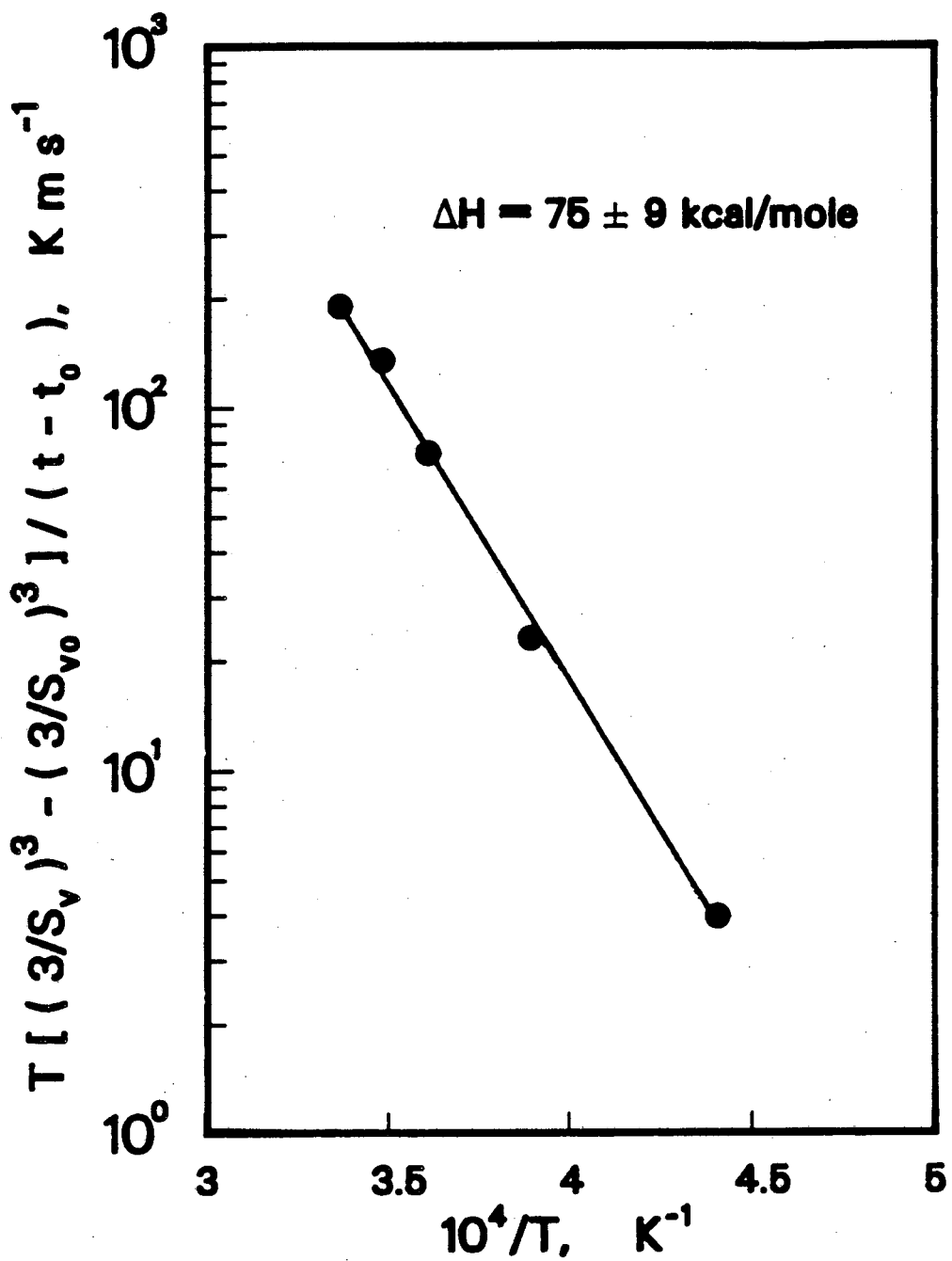
Figure 1: BOSE and BRAGG's surface area measurements taken from reference [2].



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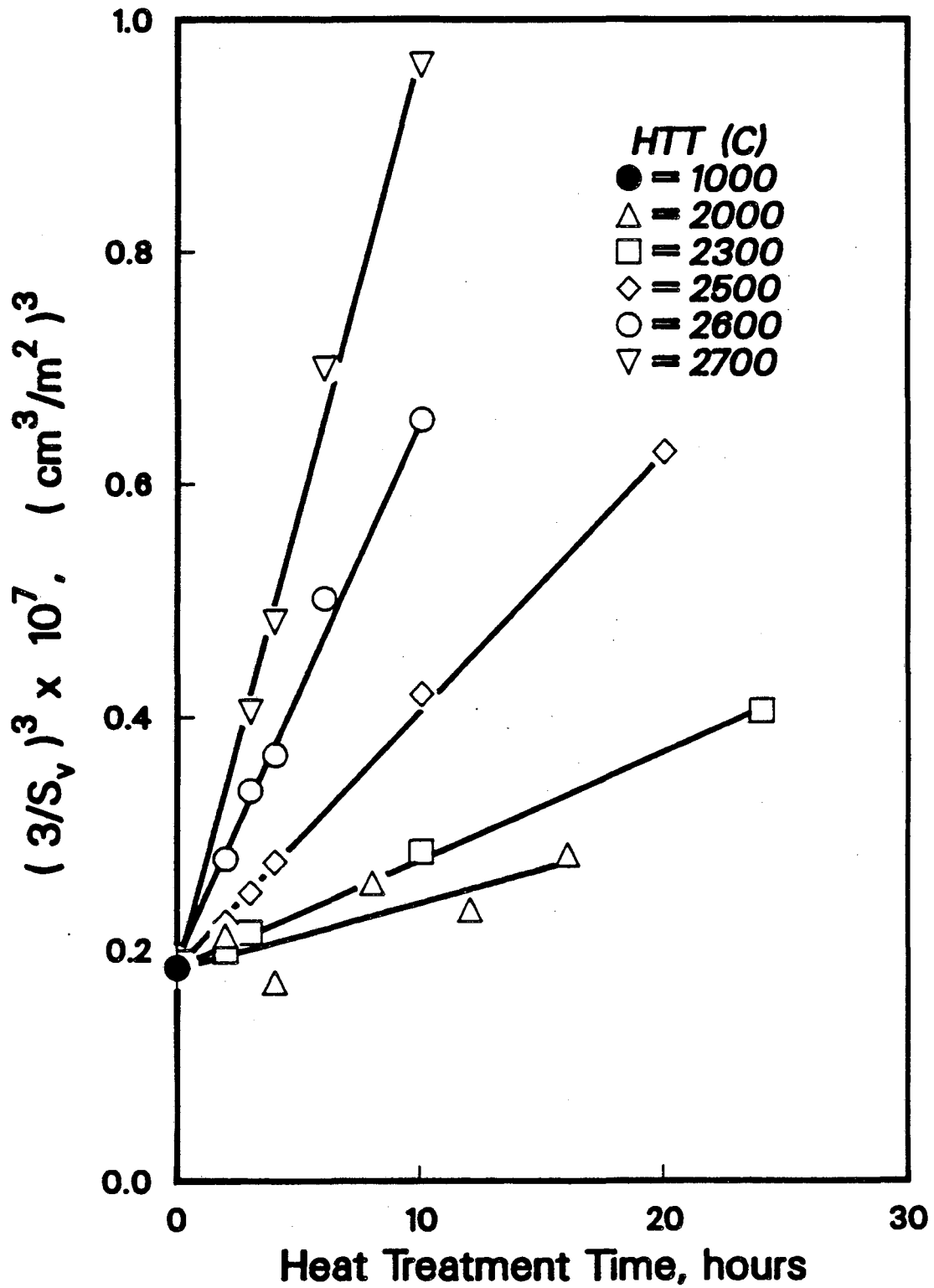
Figure 2: Variations of the cube of  $3/S_v$  as a function of the heat treatment times, HTt, for BOSE and BRAGG's data [2] corrected for the transient heat-up time.





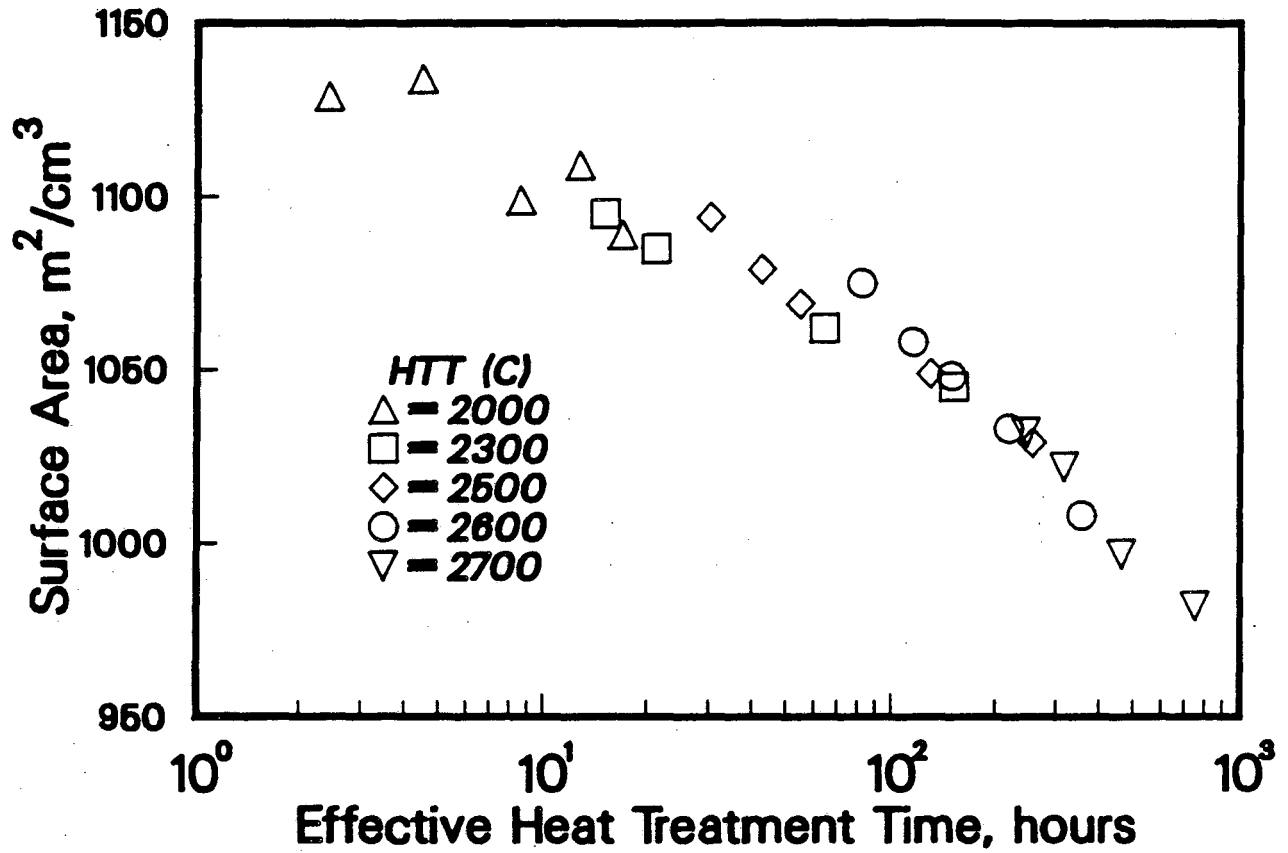
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Figure 3: Variations of  $T[(3/S_v)^3 - (3/S_{v_0})^3]/(t - t_0)$  versus the inverse of the heat treatment temperature.



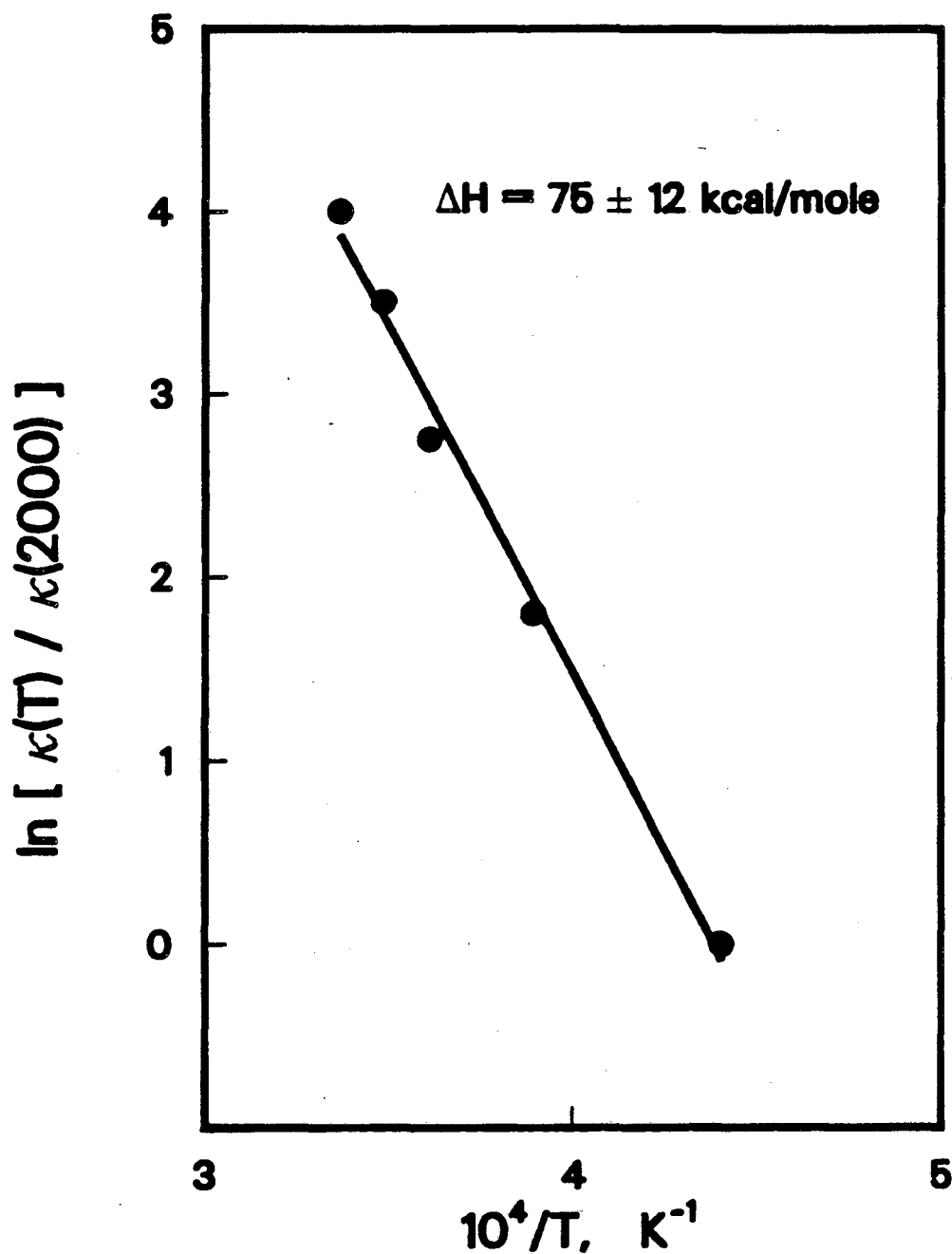
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Figure 4:  $S_v$  corrected for non-kinetic changes. The data are shifted along the  $S_v$  axis in such a way that all the extrapolated values to  $HTt = 0$  coincide with the as-received material value,  $1134 \text{ cm}^2/\text{m}^3$ .



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Figure 5: Superimposed master curve for  $S_v$ . This curve is obtained by first translating along the  $\ln$  HTt axis the data corresponding to  $HTT = 2300^\circ C$  until they coincide with the data corresponding to  $HTT = 2000^\circ C$ . The process is repeated sequentially for  $HTT = 2500^\circ C$  and  $HTT = 2700^\circ C$ .



XBL 879-3801

Figure 6: Arrhenius plot derived from the shifts needed to obtain Fig. 5. These shifts are the dimensionless ratio  $k(T)/k(2000)$ , where  $k(T)$  is the rate constant corresponding to a given heat treatment temperature and  $k(2000)$ , the rate constant for  $\text{HTT} = 2000^\circ\text{C}$  taken as reference.

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