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February 1986

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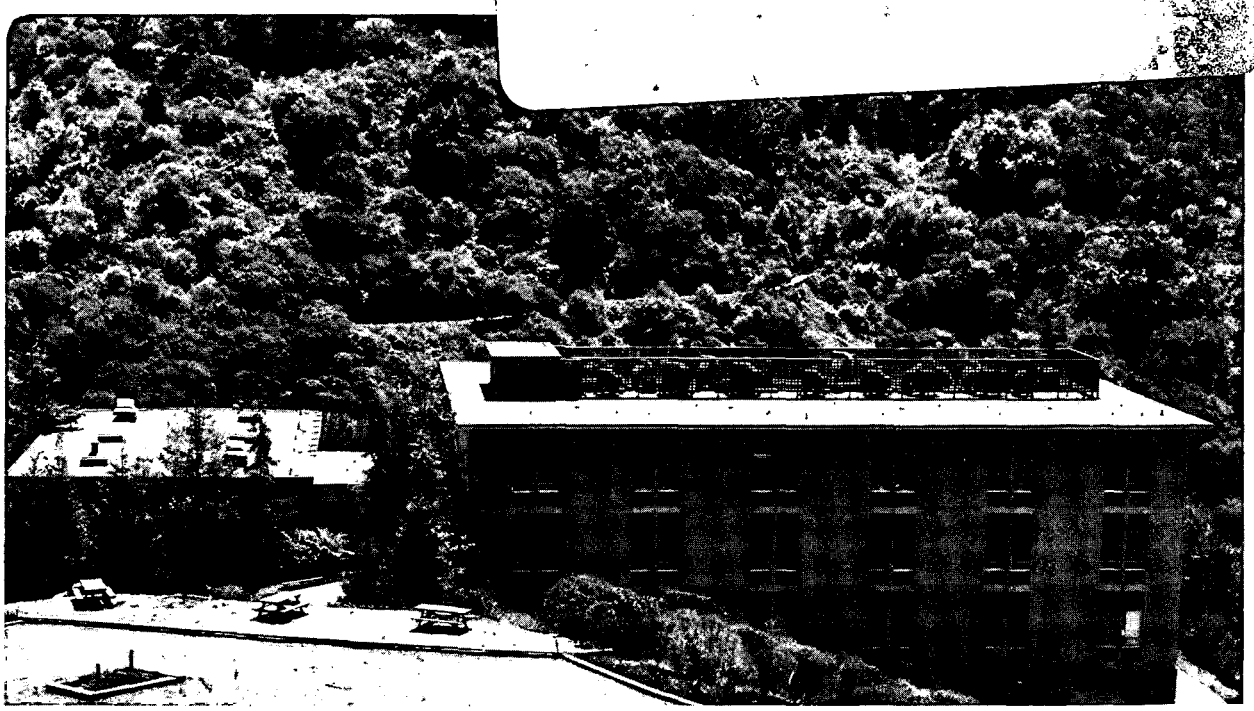

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GRAPHICAL ANALYSIS OF PROCESSES WITH MULTIPLE ACTIVATION ENERGIES

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ABSTRACT

The activation energies characterizing a kinetic process are derived from the slopes of the Arrhenius diagrams obtained by plotting rate constants *versus* reciprocal temperature. Those rate constants correspond to the shifts along the time axis needed to superpose the successive isotherms. A general method based on CHEBYSHEV interpolation is proposed for the optimization of the superposition of the experimental data points. This method is applied to determine the activation energies of the graphitization kinetics of the interlayer spacings of pitch coke and pyrocarbon samples.

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In kinetic investigations, a sample initially in a state 0 at a temperature Θ_0 is "instantly" brought to a temperature Θ_1, and the time evolution of a property P is followed at that temperature. This process is repeated at higher temperatures $\Theta_2 > \Theta_1$, ... In graphitization studies, i.e., investigations of the thermal transformations of an artificial carbon that is structurally disordered into graphite, the degree of evolution can be written as

$$\log \frac{k(\Theta_2)}{k(\Theta_1)} = \alpha \left[\frac{1}{\Theta_1} - \frac{1}{\Theta_2}\right] \tag{1}$$

where $k(\Theta_i)$ is the rate constant corresponding to the temperature Θ_i and α a constant independent of the property P. A rule first suggested by FISCHBACH [1] and then developed by PACAULT [2] states that two isotherms corresponding to temperatures Θ_1 and Θ_2 are "*affine*" with respect to time, i.e, they are superposable by a translation Δ along the time axis, with

$$\Delta = \log k(\Theta_2) - \log k(\Theta_1) \tag{2}$$

Consider two sets

$$(x_i^1, y_i^1), \quad i = 1, N_1 \quad \text{and} \quad (x_i^2, y_i^2), \quad i = 1, N_2 \tag{3}$$

of N_1 and N_2 experimental data points corresponding to isotherms taken at temperatures Θ_1 and Θ_2 respectively, as shown on Figure 1(a). If the ordinates y_i are decreasing in value, the verification of the rule stated above requires

$$\Delta y = y_1^2 - y_{N_1}^1 \neq 0 \tag{4}$$

Equation (4) implies that the two sets of points overlap if shifted along the x axis.

The question which then arises is how to estimate the shift which yields an *optimum* superposition of the two sets of points, since the data are generally shifted by hand and visually compared. However, graphical perception has been shown [3] to follow basic principles that have a non-negligible influence on the display of data, even though a visual fit is equivalent to a polynomial fit. For instance, the difference between the ordinates of two superposed curves is encoded by the vertical distances between the two curves. According to CLEVELAND and McGILL [4], it is difficult to evaluate vertical distances because visual comparisons tend to extract minimum distances which lie along perpendiculars to the curves. Curve differences can thus be poorly if not differently perceived. Examples can be found in the literature. FLANDROIS and TINGA [5] assess that the superposition of FISHBACH's isotherms [6] for which an activation energy of 260 kcal/mole has been derived is just "*as good*" when an energy of 160 kcal/mole is adopted. Also, the same authors estimate that the activation energy of 164 kcal/mole calculated by PACAULT and GASPAROUX [7] could very well be taken as 235 kcal/mole, with a superposition that is "*as good*". The necessity of having a method of eliminating the subjective perception of the superposition of curves is therefore evident. Such a method is described below. It consists of three steps.

1 - The first step is the *numerical* fit of the two sets of points with a functional form. Such an approximation is provided by a CHEBYSHEV series written as polynomials

$$P_1(x) = \sum_{i=o}^{m_1} a_i^1 x^i \quad \text{and} \quad P_2(x) = \sum_{i=o}^{m_2} a_i^2 x^i \tag{5}$$

where m_1 and m_2 are the degrees of the polynomials $P_1(x)$ and $P_2(x)$ respectively. In the example illustrated in Figure 1(a), $m_1 = m_2 = 3$. In most applications however, m_1 and m_2 range between 3 and 5. The choice of the CHEBYSHEV approximation is dictated by the fact that the polynomials are known to give a " *best*" fit within the interpolation interval. If the dependence of y *versus* x is theoretically known, $y = \Phi(x)$, then the function Φ is used to fit the experimental data points. However, if the data overlap interval

$$\Delta y \ll y_{N_1}^1 - y_1^1 \quad \textit{and/or} \quad \Delta y \ll y_{N_2}^2 - y_1^2 \tag{6}$$

i.e., Δy is small compared to the whole range of variation of the property P, then the fit for $P_1(x)$ and/or $P_2(x)$ must be restricted to the experimental data points lying in the Δy interval.

2 - The second step is the *generation* of two new sets of N points obtained as follows : a) The interval Δy is divided in $N-1$ intervals, (Figure 1(b)), leading to N values $\bar{y}_i$

$$[\,(\bar{y}_i = y_i^1 = y_i^2)\,, \quad i = 1,\ N\,] \tag{7}$$

with

$$\bar{y}_1 = y_1^2 \quad \text{and} \quad \bar{y}_N = y_{N_1}^1 \tag{8}$$

The choice of N is arbitrary even though it might depend on the magnitude of Δy and the shape of $P_1(x)$ and $P_2(x)$ in the interval Δy. A large value of

N ($10 < N < 100$) is always preferable. b) Using a root-finder algorithm, the zeros of the functions [$P_1(x) - \bar{y}_i$] and [$P_2(x) - \bar{y}_i$] are calculated for the N values of $\bar{y}_i$ to obtain the two sets of $\bar{x}_i$ values

$$\bar{x}_i^1, \quad i = 1, N \quad \text{and} \quad \bar{x}_i^2, \quad i = 1, N \tag{9}$$

3 - The last step involves a linear least-squares fit algorithm to minimize the quantities

$$\sum_{i=1}^{N} [\, \Delta \bar{x}_i \,]^2 = \sum_{i=1}^{N} [\, (\bar{x}_i^1 - \bar{x}_i^2) \,]^2 \tag{10}$$

in order to estimate the translation Δ. The process is repeated for each pair of successive isotherms and the master superposed curve is then given by

$$(x_k^i + \sum_{j=0}^{k-1} \Delta_j, \; y_k^i), \; k = 1, n, \; i = 1, N_i \; \text{ and } \; \Delta_o = 0 \tag{11}$$

where n is the number of isotherms in equation (11). The superposed curve resulting from the two sets of points of Figure 1(a) is shown on Figure 1(c). The method described above is applied to calculate the activation energies of the graphitization kinetics of two different artificial carbons : pitch coke and pyrocarbon, via changes in the interlayer spacing. The superposed master curves are drawn on Figures 2(a) and 2(b) for pitch cokes [8] and pyrocarbons [9] respectively.

A major point to be emphasized is that the algorithm used for the polynomial approximation weights each of the data points according to the experimental error. The calculated shifts Δ_i which then take into account all

errors are plotted *versus* the inverse of the heat treatment temperatures Θ_i in Figures 3(a) and 3(b).

Results indicate that the graphitization kinetics of the pyrocarbon is singly-activated with an energy equal to 241 ± 11 kcal/mole for $2300\,^{\circ}C < \Theta < 2600\,^{\circ}C$, while the graphitization kinetics of the pitch coke is multiply-activated with activation energies of 22 kcal/mole for $1250\,^{\circ}C < \Theta < 1500\,^{\circ}C$, 54 ± 1 kcal/mole for $1500\,^{\circ}C < \Theta < 2000\,^{\circ}C$ and 203 ± 24 kcal/mole for $2000\,^{\circ}C < \Theta < 2300\,^{\circ}C$.

The purpose of this paper is not to comment on the physical significance of the different activation energies observed. The value of 241 kcal/mole derived for the pyrocarbons is in good agreement with most of the kinetics studies found in the literature and related to such materials [2,10]. However, it is worth noting that the errors associated with the activation energies obtained for the pitch coke samples rule out the hypothesis that the graphitization of these samples is governed by a single activation energy.

In conclusion, a computational graphic method based on the CHEBYSHEV interpolation has been developed and used for the superposition of kinetics curves of interlayer spacings of pitch cokes and pyrocarbons. The results show that the kinetic process is singly-activated for pyrocarbons and multiply-activated for pitch cokes. The method can be applied to derive the activation energies governing any kinetic process and more generally to optimize the superposition of any kind of data.

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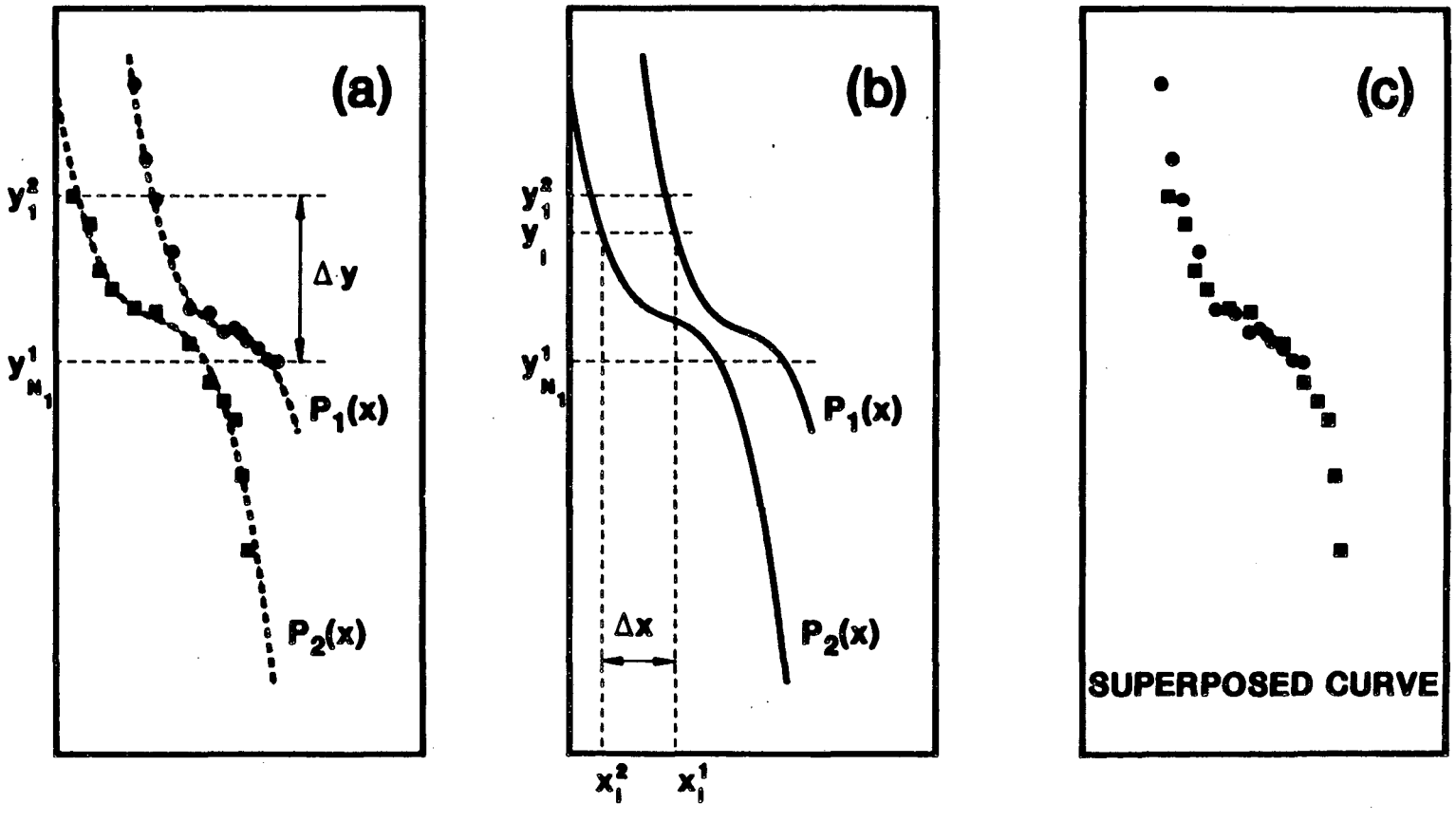

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Figure 1 : Steps illustrating the method of superposing data.

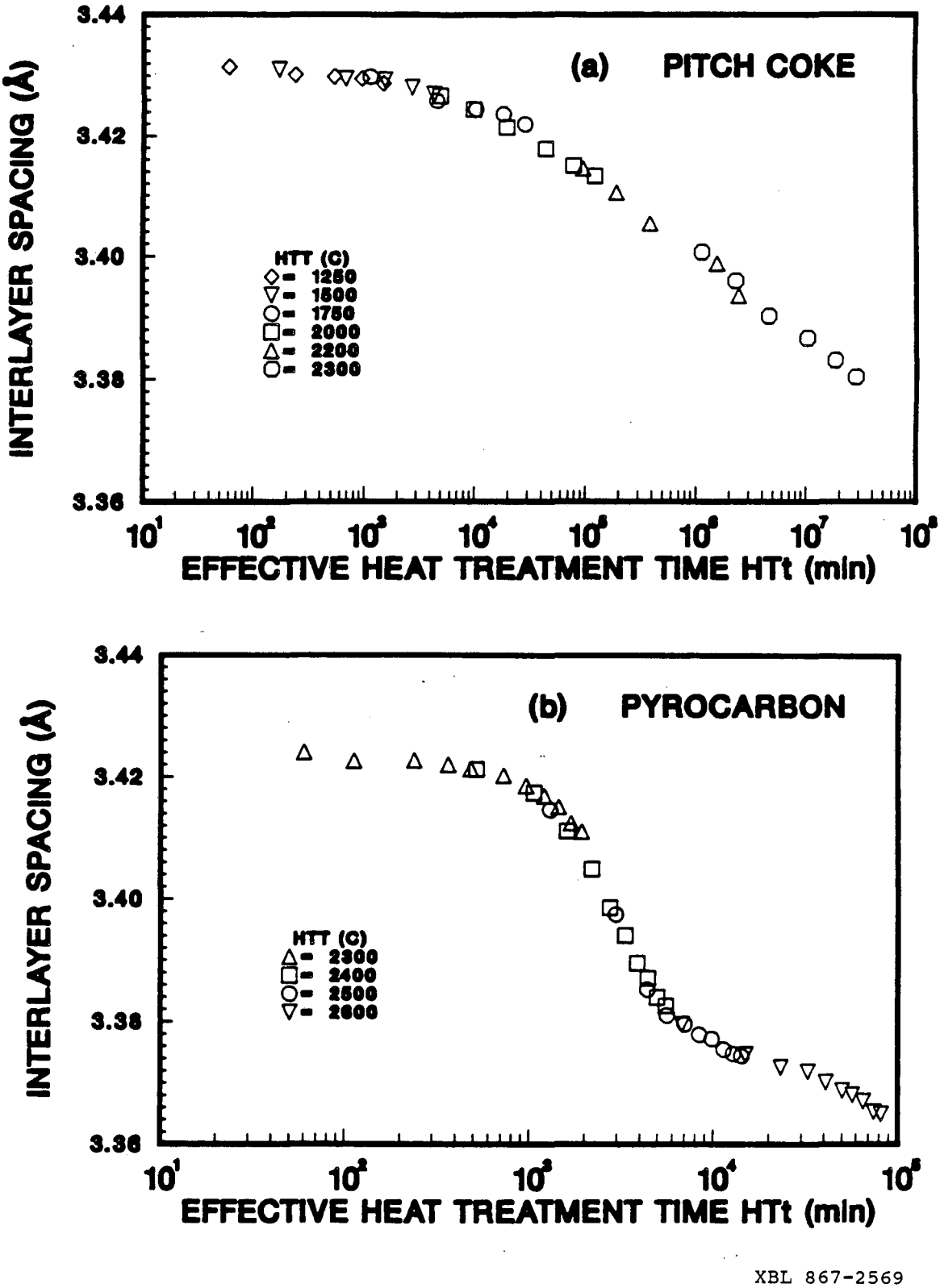

Figure 2 : Superposed master curves for pitch coke (a) and pyrocarbon (b).

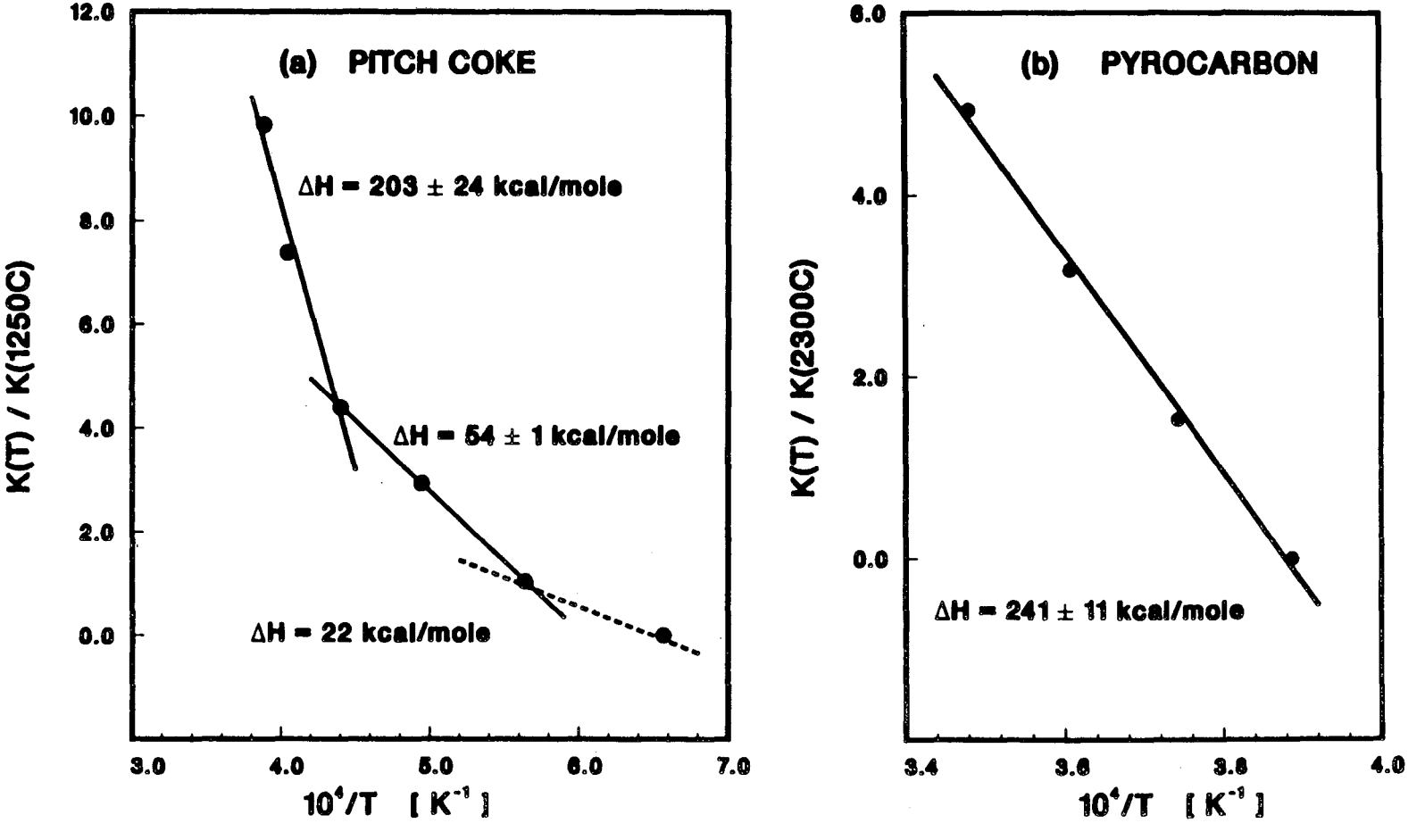

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Figure 3 : Arrhenius plots of the rate constants *versus* reciprocal temperature for pitch coke (a) and pyrocarbon (b).

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