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TITLE Determining Desorption Pre-Exponential Factors from Temperature-Programmed Desorption Spectra when the Surface is Nonuniform

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DETERMINING DESORPTION PRE-EXPONENTIAL FACTORS FROM TEMPERATURE-PROGRAMMED
DESORPTION SPECTRA WHEN THE SURFACE IS NONUNIFORM

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ABSTRACT

To find desorption pre-exponential factors from temperature-programmed desorption (TPD) spectra, we develop procedures using both the TPD spectra and their derivatives. First, an approximate method is derived using peak temperatures. This method is formally identical with one used for determining pre-exponential factors and desorption activation energies when desorptions are energetically uniform. The method can be used when the pre-exponential factor is constant. We next develop an iterative process that also uses peak temperatures, and again is usable when the pre-exponential factor is constant. This iterative approach should give more exact values of pre-exponential factors than the approximate approach. Using the first derivatives of TPD spectra over the entire range of temperatures leads to a second iterative process. This last procedure allows determination of energy-dependent pre-exponential factors.

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INTRODUCTION

This paper presents new approaches to the problem of determining desorption pre-exponential factors from temperature-programmed desorption (TPD) spectra when the desorption energy varies during the experiment. In TPD, the adsorbate desorbs from a surface heated through a time-dependent temperature schedule (Falconer and Schwarz, 1983). For energetically uniform desorption with a desorption activation energy E , the desorption rate follows the relationship

$$\frac{r_{\text{SURF}}}{\beta} = \frac{d\theta(E,T)}{dT} = \frac{A(E)}{\beta} [\theta(E,T)]^n e^{-E/RT} \quad (1)$$

(The symbols are defined at the end of this paper.) For a nonuniform surface the analogous equation is

$$\frac{r_{\text{SURF}}}{\beta} = \frac{d\theta}{dT} = \frac{1}{\beta} \int_{E_{\text{min}}}^{E_{\text{max}}} A(E) [\theta(E,T)]^n e^{-E/RT} \eta(E) dE \quad (2)$$

a Fredholm integral equation of the first kind. Earlier work (Bischke et al., 1991) showed that if the pre-exponential factor $A(E)$ is known, the site-energy distribution (SED) for the given sample, $\eta(E)$, can be calculated by inversion of Eq. (2). Not knowing $A(E)$, however, prevents determination of a unique $\eta(E)$.

Techniques exist for determining $A(E)$ when the desorption energy is nonuniform. Seebauer et al. (1988) recommend the use of the Clausius-Clapeyron equation at different equilibrium surface coverages to obtain heats of adsorption at the various coverages, followed by evaluation of the pre-exponential factors from the equality of adsorption and desorption rates. Knowledge of the sticking coefficient is required in their method. Falconer and Madix (1975) and Feulner and Menzel (1985) use different approaches for acquiring TPD measurements at varying surface coverages. Their methods can obtain both the variation of desorption energy with coverage and the pre-exponential factors at those coverages.

The equilibrium measurements reviewed by Seebauer and coworkers are tedious and frequently subject to uncertainties, particularly in the sticking coefficient. Carrying out TPD measurements at varying initial

coverages can be difficult. Satisfactory solution of the problem of determining $A(E)$ solely from TPD spectra remains a desirable goal.

This paper develops techniques for solving this problem that can also find a dependence of the pre-exponential factor on the desorption activation energy if such dependence exists. The work of Seebauer et al. showed that pre-exponential factors often vary with surface coverage. In their analysis of desorption energies and pre-exponential factors from 48 single-crystal-face systems, only about half of them exhibited essentially constant pre-exponential factors. Variations by factors up to 10^{10} were observed in the remaining systems.

The following derivations assume first-order desorption, i.e., $n = 1$, and Eqs. (1) and (2) become

$$\frac{d\theta(E,T)}{dT} = -\frac{A(E)}{\beta} \theta(E,T) e^{-E/RT} \quad \text{or simply} \quad \frac{d\theta}{dT} = -\frac{A}{\beta} \theta e^{-E/RT}, \quad (3)$$

and

$$\frac{d\theta_{\text{tot}}}{dT} = -\frac{1}{\beta} \int_{E_{\text{min}}}^{E_{\text{max}}} A(E) \theta(E,T) e^{-E/RT} \eta(E) dE. \quad (4)$$

For other orders, the developments of the methods follow the same paths as those described here.

AN APPROXIMATE APPROACH FOR DETERMINING THE PRE-EXPONENTIAL FACTOR

In the analysis of TPD spectra, there are well-established methods for determination of the desorption pre-exponential factor if energetically uniform desorption is assumed. It is assumed that energetically uniform desorption would result in a constant pre-exponential factor A_0 . Equation (3) may be applied to the entire spectrum or to several spectra in their entirety. Numerical optimization methods obtain values of A_0 and E that provide the best fit of the calculated spectra to the those experimentally obtained. Peak-shape analysis has also been suggested as a method for obtaining E and A_0 when the desorption energy is constant (e.g., Chen et al., 1978).

Another approach uses the peak temperatures (T_p 's) in several desorption spectra, i.e., the temperature at which the second

differentials $d^2\theta/dT^2$ equal zero and the desorption rates exhibit maxima. Differentiating Eq. (3), setting it equal to zero, then carrying out some manipulation yields

$$(A_c/\beta)\exp(-E/RT_p) = E/RT_p^2 \quad (5)$$

If two or more TPD spectra at different heating rates are available, these would then have different T_p 's. A system of nonlinear implicit equations results with unknowns E and A_c , one Eq. (5) for each spectrum. Standard numerical techniques can solve this system for the unknowns A_c and E . A graph also may yield the solution, though this is not as precise. A simple plot of $\ln(\beta/T_p^2)$ vs. $1/T_p$ should give a straight line, and the slope and intercept determine the values of E and A_c . This graphical approach to obtaining E and A_c has long been known (e.g., Redhead, 1962).

This concept can be applied to TPD from a nonuniform surface with a continuous SED. Equation (2) gives the desorption rate from such a nonuniform surface; the derivative of this rate with respect to (w.r.t.) temperature is

$$\frac{dr}{\beta dT^2} = \frac{d^2\theta}{dT^2} = \frac{1}{\beta} \int_{E_{\min}}^{E_{\max}} A(E) \left[\frac{d\theta(E,T)}{dT} \cdot e^{-E/RT} + \frac{E}{RT^2} \cdot \theta(E,T) e^{-E/RT} \right] \eta(E) dE \quad (6)$$

Substituting the left-hand side (LHS) of Eq. (3) for $\frac{A(E)}{\beta} \left[\theta(E,T) e^{-E/RT} \right]$ in Eq. (6) gives

$$\frac{d^2\theta}{dT^2} = \int_{E_{\min}}^{E_{\max}} \left[-\frac{A(E)}{\beta} e^{-E/RT} + \frac{E}{RT^2} \right] \left[\frac{d\theta(E,T)}{dT} \right] \eta(E) dE \quad (7)$$

At the peak temperature, $T = T_p$ and the second derivative equals zero. Setting Eq. (7) equal to zero at T_p gives

$$\int_{E_{\min}}^{E_{\max}} \left[-\frac{A(E)}{\beta} e^{-E/RT_p} + \frac{E}{RT_p^2} \right] \left[\frac{d\theta(E,T_p)}{dT} \right] \eta(E) dE = 0 \quad (8)$$

Equation (8) leads to an approximate approach for extracting a pre-exponential factor. The sites whose desorption energies are significantly lower than some average energy have mostly emptied when the peak temperature is reached. Their desorption rates, $d\theta(E, T_p)/dT$, are negligible at the peak temperature. Analogously, sites whose desorption energies are significantly higher than this average energy have not begun to empty yet. As a result, their desorption rates at the peak temperature, $d\theta(E, T_p)/dT$, are also negligible. Only over a narrow desorption-energy range, δE , is any contribution made to the integral in Eq. (8) at the peak temperature. If a delta function approximates this narrow range, then the portion of the LHS of Eq. (8) that is within the first set of brackets must equal zero at the peak temperature. This is true because neither $d\theta(E, T_p)/dT$ nor $\eta(E)\delta E$ is zero at this point. If the sum of the terms within the first set of brackets equals zero, a minor manipulation results in Eq. (5).

This says that Eq. (5) is approximately valid for heterogeneous surfaces, with E being the postulated average energy of desorption at the peak temperature. This in turn means that an approach identical with that for obtaining the pre-exponential factor for TPD from uniform surfaces is employable for obtaining an approximate value of the pre-exponential factor for TPD from heterogeneous surfaces. This is valid for pre-exponential factors that are independent of the sorption activation energy. If the pre-exponential factor depends on the activation energy, then the pre-exponential factor obtained in this fashion would be the value for the average energy postulated above.

AN ITERATIVE APPROACH FOR DETERMINING INVARIANT PRE-EXPONENTIAL FACTORS

As mentioned, the approximate approach presented above appears usable when the pre-exponential factor is invariant in the vicinity of a particular peak in a TPD spectrum. The approximate approach also is convenient as the first step in an iterative process for obtaining a more precise invariant pre-exponential factor.

In this iterative process, the approach detailed in the previous section obtains the first approximation to the pre-exponential factor. The algorithm then substitutes the first approximation $\{A_p^{(1)}\}$ into Eq. (5) and

solves Eq. (4) for $\eta(E)$. Equation (4) is a first-kind Fredholm integral equation; the regularization technique solves this equation for $\eta(E)$. The optimal value of the regularization smoothing parameter is the one that makes the maximum number of peaks in $\eta(E)$ equal to the number of peaks in the TPD spectrum. Previous work (Bischke et al., 1991) reported this approach for solving Eq. (4) to obtain $\eta(E)$; it gives excellent resolution of peaks in an SED.

The $\eta(E)$ obtained from Eq. (4) using $A_c^{(1)}$ is called $\eta^{(1)}(E)$. The algorithm substitutes the distribution function $\eta^{(1)}(E)$ into Eq. (6) and solves this equation for a new A_c , $A_c^{(2)}$. As many values of $A_c^{(2)}$ can be obtained as there are peaks in the spectra. The various values probably will not differ by a large amount.

The average of these values of $A_c^{(2)}$ is then substituted into Eq. (4) and this equation solved as before to obtain an improved $\eta(E)$, $\eta^{(2)}(E)$. The algorithm repeats the process until there are no more changes in A_c . The final A_c so obtained is judged to be the best obtainable, and the associated site-energy distribution function also the best obtainable. Figure 1 presents schematically the algorithm for this iterative approach.

An alternative approach to averaging the values of $A_c^{(2)}$ would be to substitute all the values into a sum of the Eqs. (4). Summing the Eqs. (4) over the K spectra from $k=1$ to $k=K$ yields

$$\sum_{k=1}^K \frac{d\theta_{gr(k)}}{dT}(T) = \int_{E_{\min}}^{E_{\max}} \left[\sum_{k=1}^K \frac{A_k}{\beta_k} \right] \theta(E, T) e^{-E/RT} \eta(E) dE \quad (9)$$

and this first-kind Fredholm equation may be solved for $\eta(E)$.

OBTAINING ENERGY-DEPENDENT PRE-EXPONENTIAL FACTORS

The second derivative of the gross surface coverage w.r.t. temperature is itself a function of temperature, here called $r(T)$. From Eq. (6),

$$\frac{d^2\theta}{dT^2}(T) = \int_{E_{\min}}^{E_{\max}} \left[\frac{A(E)}{\beta} e^{-E/RT} + \frac{-E}{RT^2} \right] \left[\frac{d\theta(E, T)}{dT} \right] \eta(E) dE = r(T) \quad (10)$$

If the SED $\eta(E)$ is known, Eq. (10) may be converted into a first-kind Fredholm integral equation with the energy-dependent pre-exponential factor as the unknown distribution. Some minor manipulation of Eq. (10) yields

$$\gamma(T) = \int_{E_{\min}}^{E_{\max}} \left[\frac{E}{RT^2} \right] \left[\frac{d\theta(E,T)}{dT} \right] \eta(E) dE = \int_{E_{\min}}^{E_{\max}} \left[\frac{e^{-E/RT}}{\beta} \right] \left[\frac{d\theta(E,T)}{dT} \right] [\eta(E)] A(E) dE \quad (11)$$

The LHS of Eq. (11) depends on T only, the kernel of the RHS integral is a known function of both E and T , and the unknown distribution $A(E)$ depends on E only, as in all first-kind Fredholm equations.

Equations (4) and (11) can be incorporated into an iterative scheme to calculate both the SED and an energy-dependent pre-exponential factor. The first step is to obtain starting values of A and E at the peaks of the spectra. This step follows the procedure described in the previous section for obtaining invariant pre-exponential factors. This time, though, the values of A obtained are only the initial values of A for these peaks. Simple power series dependences of A on E achieve functional dependence of A on E using A 's and E 's obtained from the peaks of the spectra. If there is but one peak per spectrum, A will be a constant; if two peaks, the dependence of A on E will be linear (assuming different values of A for the two peaks). For three peaks, a quadratic dependence will result, and so forth.

Once the initial approximation $A^{(1)}(E)$ is obtained, the algorithm substitutes it into Eq. (4) and solves the equation for $\eta^{(1)}(E)$. The SED $\eta^{(1)}(E)$ is then substituted into Eq. (11) and this equation solved for $A^{(2)}(E)$. The function $A^{(2)}(E)$ is substituted into Eq. (4) to obtain $\eta^{(2)}(E)$ and the cycle then continued until convergence occurs. The results are the best obtainable values of $A(E)$ and $\eta(E)$. Figure 2 shows the process schematically.

When several different spectra are used, Eq. (11) can be summed in the same manner as Eq. (4) was summed to give Eq. (9).

DISCUSSION

The preceding paragraphs have presented the mathematical bases for acquiring desorption pre-exponential factors from TPD spectra. What remains is to carry out numerical experiments to test the techniques.

Equation (5) is rigorously true only when the desorption energy is constant throughout the TPD experiments. But the desorption energy cannot be constant throughout a series of TPD experiments unless the surface is homogeneous and the adsorbates do not interact. In combination, these constraints are rarely, if ever, satisfied. However, the analysis presented earlier shows that Eq. (5) is approximately valid for systems with nonuniform desorption energies. Thus, if the pre-exponential factor is constant, applying Eq. (5) to a series of TPD experiments probably gives values of the pre-exponential factor very close to the true value. The apparent success of applying Eq. (5) to TPD spectra which almost certainly were obtained from systems whose desorption energy was not constant is now understandable. For example, Britten (1981) obtained TPD spectra at different heating rates for the desorption of carbon monoxide from graphite. His spectra were much too broad for single-energy desorption, but Fig. 3 shows his plot of $\ln(T_p^2/\beta)$ vs. $1/T_p$ gives a good straight line. The slope and intercept in turn give reasonable values of both pre-exponential factor and average desorption energy for his system ($8 \times 10^{14} \text{ s}^{-1}$ and 376 kJ/mol, respectively). The heating rate in this case was varied over a factor of 10, which is sufficient for this type of experiment (Falconer and Schwarz, 1983).

NOMENCLATURE

- A Pre-exponential factor, s^{-1} for a first-order desorption.
- A_0 Pre-exponential factor when it is a constant, either in the case of energetically uniform adsorption or when it is independent of desorption energy, s^{-1} for a first-order desorption.
- $A(E)$ Pre-exponential factor at a particular desorption activation energy (E), s^{-1} for a first-order desorption.
- E Desorption activation energy, J/mol.
- E_{max} Maximum desorption activation energy in site-energy distribution, J/mol.

E_{\min}	Minimum desorption activation energy in site-energy distribution, J/mol.
LHS	Left-hand side.
r_{sorb}	Rate of sorption, fractional coverage/s.
R	Gas constant, J/(mol)(K).
RHS	Right-hand side.
SED	Site-energy distribution.
T	Temperature, K.
T_p	Peak temperature in desorption spectrum, K.
TPD	Temperature-programmed desorption.
β	Heating rate, K/s.
γ_1	Derivative of the desorption rate w.r.t. temperature at a particular temperature (T_1), K^{-2} .
η	Site-energy distribution function, for which $\eta(E)dE$ is the fraction of sites with desorption activation energies between E and $E + dE$.
θ or $\theta(E,T)$	Fractional coverage of sites with a single desorption activation energy (E) at a particular temperature (T).
θ_{gr} or $\theta_{\text{gr}}(T)$	Gross fractional coverage of sorption sites at a particular temperature (T).

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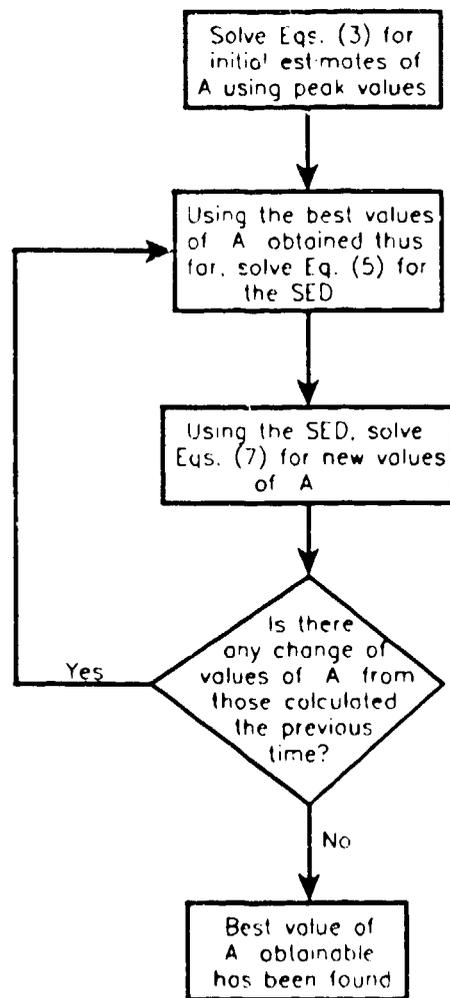


Figure 1. Algorithm for constant pre-exponential factor iterative method.

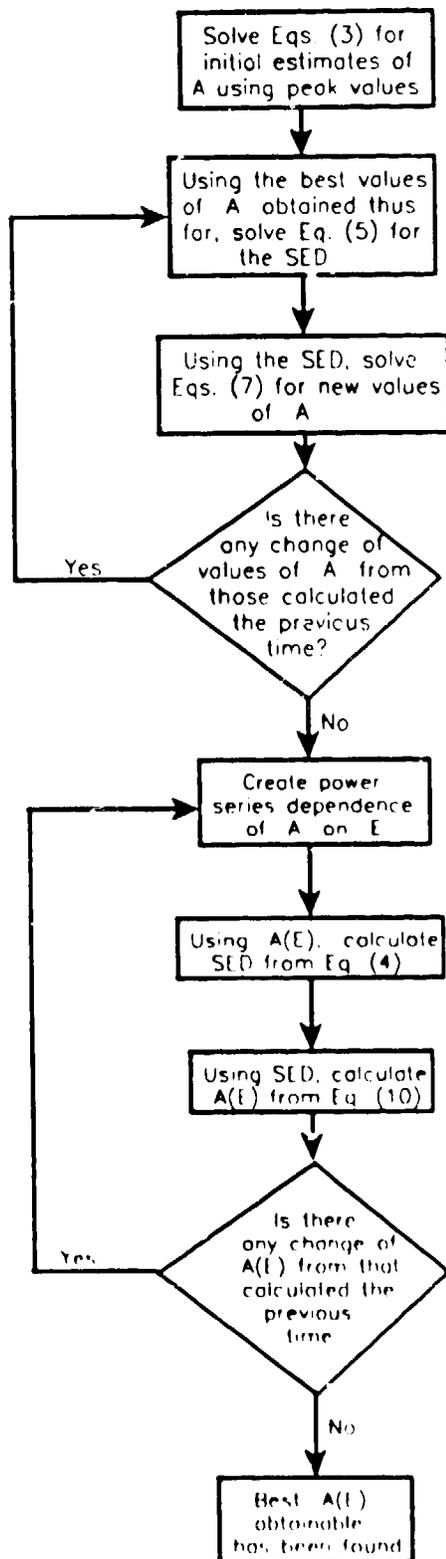


Figure 2. Algorithm for variable pre-exponential factor iterative method.

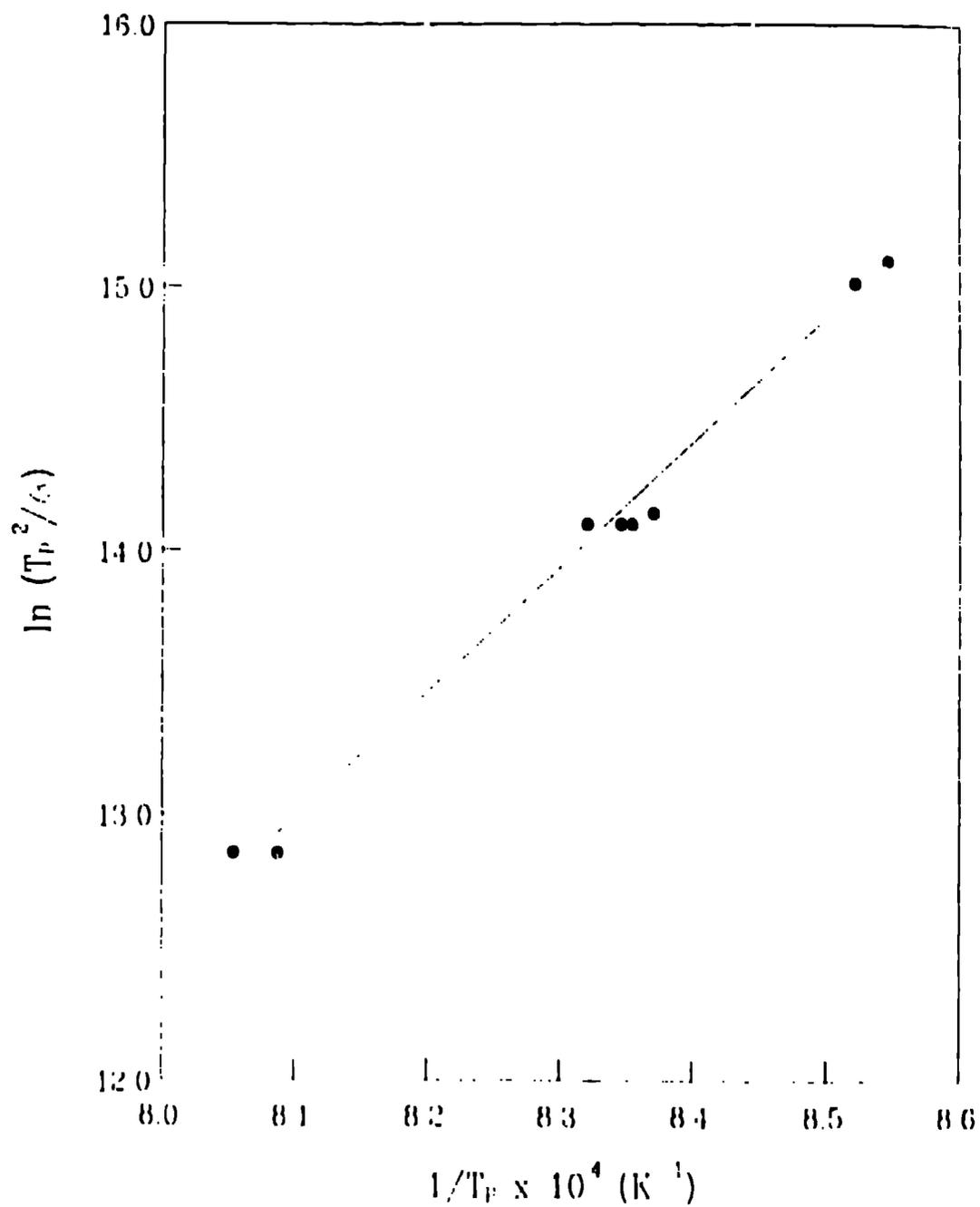


Figure 3. Plot of Eq. (5). Slope is E/R , Intercept is $-\ln (A_p/E)$. [Data of Britten (1981) for desorption of reaction created CO from graphite.]