

Kinetic Parameters from Temperature-Programmed Reactions: The Pyrolysis of Polytetrafluoroethylene

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Synopsis

Kinetic parameters from the Doyle thermograms have been calculated by the differential method. These results are compared with results calculated by an integral method. It is shown that in the case of a simple process having a single value for the activation energy and order of reaction, both methods lead to about the same results. For a more complex reaction, such as the volatilization of polytetrafluoroethylene, the integral method will lead to dubious results.

There are two general methods for obtaining the kinetic parameters when the temperature of the reaction is linearly programmed so that a single experiment may afford an evaluation of these parameters. The methods may be classed as differential and integral. During the past few years a number of kinetic papers have appeared in this field using thermogravimetric data. They have been based on the integral method,¹⁻³ each treatment apparently offering some special advantage. All papers have considered the serious precision limitation of the differential as proposed by Freeman and Carroll.⁴ It is the purpose of this article to examine some of the features of both methods that appear to have been overlooked. In so doing, the thermogravimetric data of one of these papers¹ will be used to calculate kinetic parameters differentially so as to point up those cases where the integral method is in serious error. The Doyle data were chosen because of the vast amount of kinetic work and interest in the pyrolysis of polytetrafluoroethylene. Also, in the Doyle paper we have the original experimental thermograms, these apparently having been done with great care. Because the kinetic parameters obtained present a picture different from what has been accepted, we have re-examined the work of other investigators on the pyrolysis of polytetrafluoroethylene.⁵⁻⁷

Regardless of the relative precision involved in the integral and differential method, there is a basic assumption in the integral method which in the case of reactions in the solid state is open to serious question; it is the assumption that a chemical change involves a single set of parameters. When the latter is the case it will be shown that both methods yield about

the same kinetic parameters. However it has been our experience that over the entire course of a solid-state reaction, seldom does a single set of kinetic parameters suffice. Close examination of the experimental data usually shows that the initial stages of a reaction indicate an abrupt change as compared to later values. Investigators are prone to dismiss the early part of a reaction; yet it is obvious that even in simple solid-state reactions the environment of the reactants changes markedly during the course of a reaction. Clearly, a solid-state reaction may have a spectrum of kinetic parameters which is inaccessible to the integral method. As the temperature is advanced in such cases, first one set and then another set of parameters may become predominant, the changing temperature tending to resolve overlapping reactions. Here we have one of the important aspects of the nonisothermal procedure; the differential method of analyzing experimental data offers the opportunity of taking advantage of this wealth of data.

A few investigators proposing integral methods have cited and confirmed our value of 22 kcal./mole for the activation energy for the dehydration of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$. However, it was found subsequently⁸ that for the

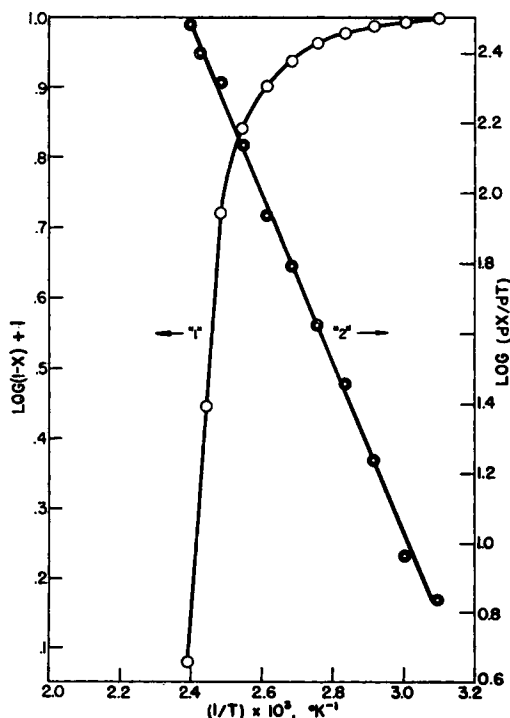


Fig. 1. Thermogravimetric data for octamethylcyclotetrasiloxane. Plot of (1) log of fraction of weight remaining (Curve "1"), and (2) log of rate loss of weight vs. the reciprocal of the absolute temperature. Vaporization in presence of N_2 . Add + 4 to log (dx/dt) .

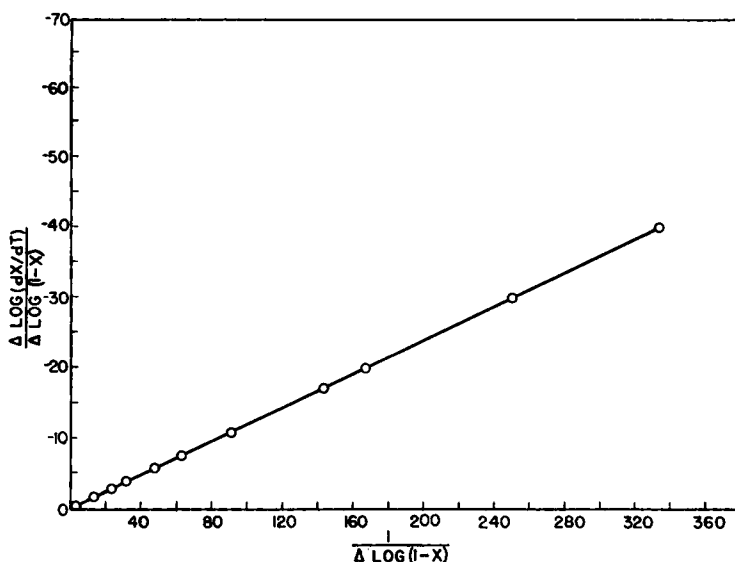


Fig. 2. Derived data for latent heat of vaporization of octamethylcyclotetrasiloxane. Plot of $\Delta \log(dx/dT)/\Delta \log(1 - X)$ vs. $1/\Delta \log(1 - x)$. $\Delta(1/T)$ kept constant at $5.0 \times 10^{-5} \text{K}^{-1}$. Data taken from Fig. 1. Data cover 90% of the total weight loss. Latent heat of vaporization equals 10.9_4 kcal./mole.

latter part of this reaction the activation energy dropped to 9 kcal./mole, an interesting value indeed.

Obviously the isothermal techniques in kinetics are intrinsically more precise than nonisothermal ones. Perhaps the desirable procedure would be to scan a reaction over the entire temperature spectrum and then to select for isothermal work those regions of greatest interest.

In the various forms of the integral method one should consider that there are mathematical approximations that are made in arriving at a practical equation. Then there is usually the tedious procedure of curve fitting, where some prior knowledge is invoked regarding the order of the reaction. No mathematical approximations are necessary in the differential method and order of the reaction is obtained directly in an analytical way.

In the differential method there is the question of precision in using the slopes taken from a thermogram. Doyle has claimed that they "are not only imprecise but also inherently inaccurate, being consistently greater than those indicated by comparable isothermal data." We do not agree entirely with this statement. Undoubtedly individual slopes are burdened with error, but the simple device of plotting slopes as a function of the temperature will help appreciably in smoothing out random errors. We have done just that with Doyle's data and have used a mechanical differentiator⁹ for determining slopes.

Frequently, slower heating rates will enhance the precision in determining slopes in a thermogram. The heating rate obviously should be adjusted

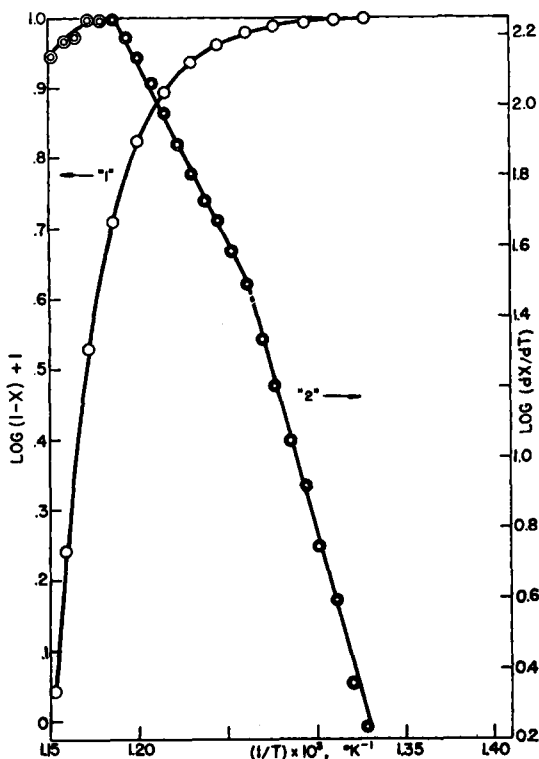


Fig. 3. Thermogravimetric data for volatilization of polytetrafluoroethylene. Plot of (1) log of fraction of weight remaining and (2) log of rate loss of weight vs. reciprocal of the absolute temperature. Volatilization in presence of N_2 . Add + 4 to $\log(dx/dt)$.

to the reaction being investigated and the precision desired. We note that for the pyrolysis of polytetrafluoroethylene (*in vacuo*) Anderson found the original Freeman-Carroll method reasonably precise. He used a heating rate one order of magnitude less than that used by Doyle.

Theory of Differential Method

Since in kinetic experiments fractional changes in weight are given in terms of the initial weight, the following equations will define and explain the procedure that is used subsequently.

We may assume that the differential equation is

$$-dw_t/dt = k(w_t)^n \quad (1)$$

where w_t is the weight of the sample being pyrolyzed at time t and n is the order of the reaction. If w_0 is the initial weight, then by defining the fractional loss at time t as $X = -w_t/w_0$,

$$dX/dt = k(1 - X)^n w_0^{n-1} \quad (2)$$

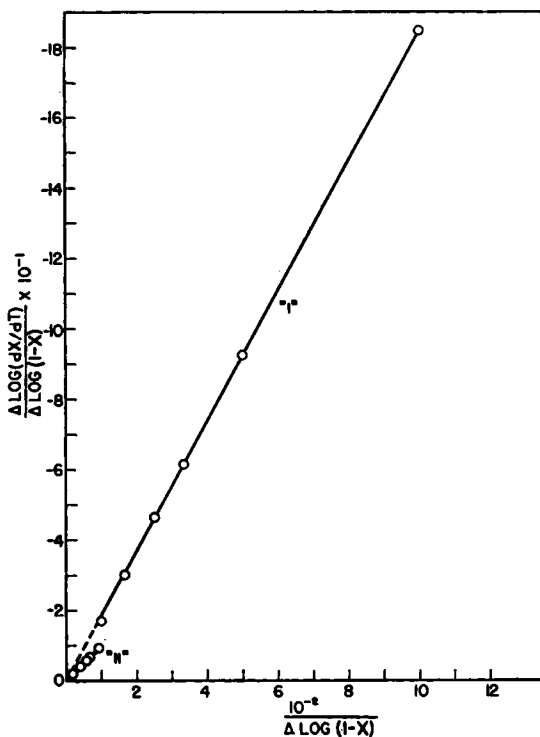


Fig. 4. Derived thermogravimetric data for volatilization of polytetrafluoroethylene; plot of $\Delta \log(dX/dT)/\Delta \log(1 - X)$ vs. $1/\Delta \log(1 - X)$; $\Delta(1/T)$ kept constant at $1.0 \times 10^{-5} \text{K.}^{-1}$: (I) 480–520°C., weight loss = 5%, activation energy = 84.5 kcal./mole; (II) 520–570°C., weight loss = 45%, activation energy = 45.7 kcal./mole.

Using the Arrhenius temperature dependence for the rate constant k , we have

$$dX/dt = Ae^{-\epsilon_a/RT}(1 - X)^n w_0^{n-1} \quad (3)$$

If a linear heating rate Φ is used, then

$$dX/dt = (A'/\Phi)e^{-\epsilon_a/RT}(1 - X)^n \quad (4)$$

Here we have incorporated w_0^{n-1} in the frequency factor A . To apply eq. (4) for the purpose of calculating the activation energy ϵ_a and n , we write eq. (4) as

$$\frac{\Delta \log(dX/dT)}{\Delta \log(1 - X)} = -\frac{\epsilon_a}{2.303R} \frac{\Delta(1/T)}{\Delta \log(1 - X)} + n \quad (5)$$

If the logarithm of the experiment slopes, $\log(dX/dT)$ is plotted against $1/T$, one may use the smoothed-out curve to obtain a set of values for constant increments in $1/T$. Keeping $\Delta(1/T)$ constant a subsequent plot of $\Delta \log(dX/dT)/\Delta \log(1 - X)$ versus $1/\Delta \log(1 - X)$ leads to a value of n as the intercept. The activation energy is obtained from the slope.

Vaporization of Octamethylcyclotetrasiloxane

The thermogravimetric experiment on the vaporization of the silicone fluid illustrates the case where the integral and differential methods should yield about the same results. Furthermore the order of this reaction is known to be zero as it is for any liquid evaporation process and the latent heat of vaporization has been determined by standard equilibrium measurements¹⁰ of the boiling point as a function of the pressure. The value found was 10.9 kcal./mole.

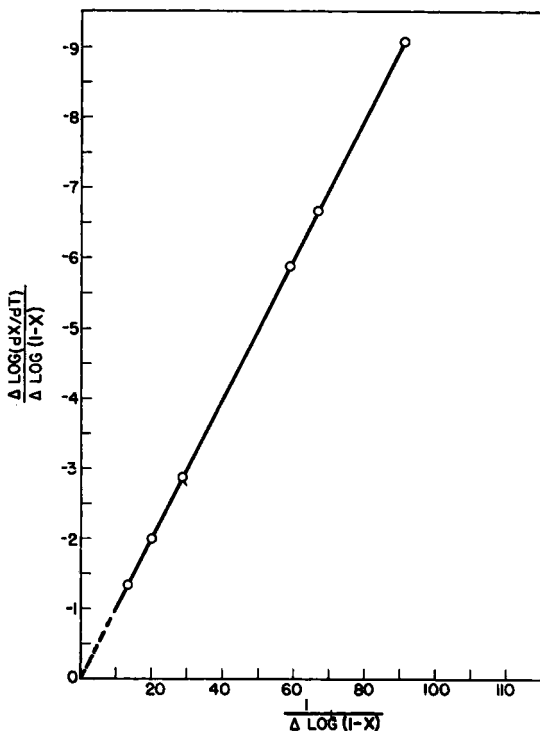


Fig. 5. Expanded scale for curve (II) of Fig. 4.

In Figure 1 we have a plot of both $\log(1 - X)$ and $\log(dX/dT)$ versus $1/T$ taken from one of the Doyle thermograms. It is immediately obvious that the linear relationship between $\log(dX/dT)$ and $1/T$ requires n to be zero. This is more clearly shown in Figure 2, where $\Delta \log(dX/dT)/\Delta \log(1 - X)$ is plotted against $1/\Delta \log(1 - X)$. In the latter figure, $\Delta(1/T)$ is fixed at $5.0 \times 10^{-5} \text{K.}^{-1}$ and about 90% of the vaporization process is covered. The slope yields a latent heat of 10.9₄ kcal./mole. Doyle assumed a value of $n = 0$ and reported a latent heat of 11.65 for the same data.

Pyrolysis of Polytetrafluoroethylene

The pyrolysis of this substance was carried out under dry N_2 .¹ The data taken from the thermogram has been plotted in Figure 3, and covers a temperature range from 480 to 595°C. This represents about 95% of the volatilization process. Slopes were taken at 5°C. intervals. The experimental rate data shows three regions. A break occurs in the $\log(dX/dT)$ curve (Fig. 3) at 520°C., after 5% of the volatilization has taken place. The region from 520 to 570°C. represents the next 45% of the reaction. It

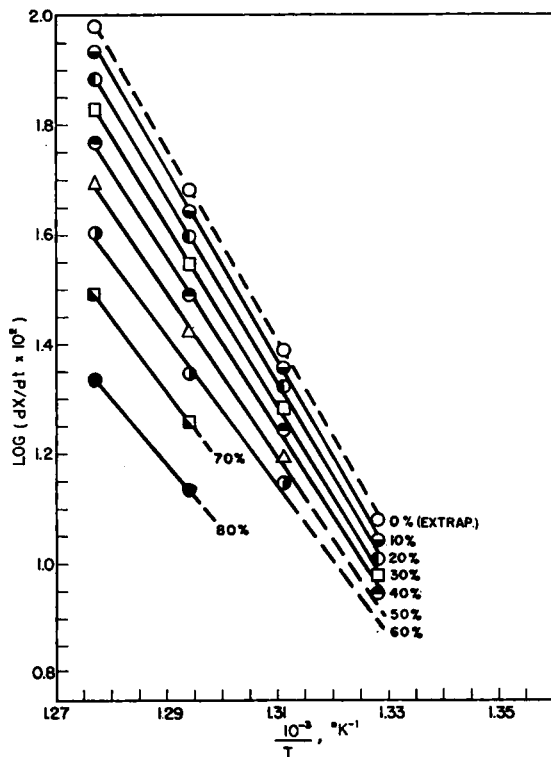


Fig. 6. Volatilization of polytetrafluoroethylene *in vacuo*. Plot of rate loss vs. reciprocal of the absolute temperature. Data taken from isothermal runs of Madorsky et al.² at various stages of volatilization.

has been often observed that, at the 50% point of volatilization, polytetrafluoroethylene undergoes a marked change in physical properties. Apparently the points toward the latter part of the reaction (570–595°C.) reflect this change. It can be seen that the activation energy for the latter part of the reaction is in the neighborhood of zero and represents the kinetic parameter for a reactant that is quite different from the initial material.

The data in Figure 3 for the first 50% of the reaction have been replotted in Figure 4 in accordance with eq. (5). One of the curves in Figure 4 is shown again in Figure 5 on a much expanded scale

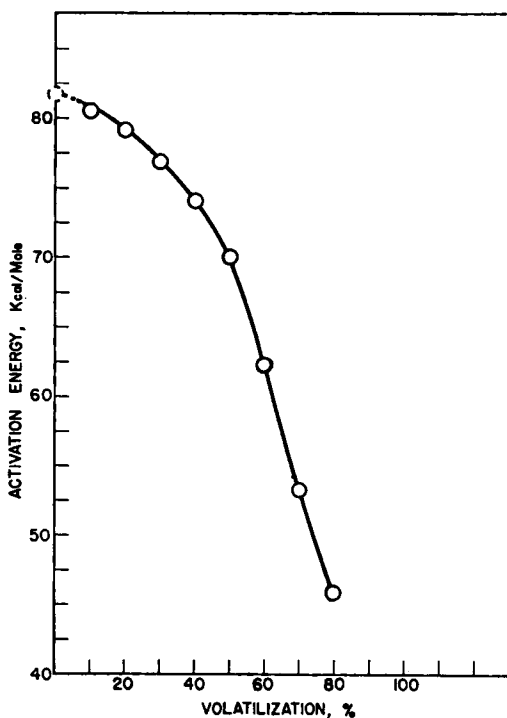


Fig. 7. Plot of activation energy for volatilization of polytetrafluoroethylene vs. per cent volatilization. Data taken from Fig. 6.

These graphs show that for the early stage of the reaction we have $\epsilon_a = 84.5$ kcal./mole. The next stage yields a value of $\epsilon_a = 45.7$ kcal./mole. In both cases the order is zero. Doyle reported a single value for the 520–610°C. range as being between 66 and 68 kcal./mole. He used a value of $n = 1$.

Discussion

It is interesting to note that Doyle found that isothermal tests for polytetrafluoroethylene in N_2 indicated zero-order reaction in the initial stages having an activation energy of 80 kcal./mole; further volatilization tended to increase the order towards one, and the activation energy decreased. In view of this behavior and the results shown above it will be seen that the integral method when applied to nonisothermal kinetics is inadequate to deal with complex reactions.

The fact that the differential method yielded a trend in the activation energy for polytetrafluoroethylene caused us to re-examine the isothermal data of Madorsky and co-workers.⁵ Their work was carried out *in vacuo*, where they found the volatilization to be first-order, although subsequently attention was called to the possibility of the reaction being zero-order at the lower temperatures.¹¹

In Figure 6 the log of the rate data (Mardorsky) has been plotted versus the reciprocal of the temperature at various stages of completion of the volatilization. The activation energy calculated from the graphs in Figure 6 is shown as a function of the per cent volatilization in Figure 7. Extrapolation to zero time yields $\epsilon_a = 81.7$ kcal./mole, regardless of the order that may be assumed for the reaction. Evidently there is a trend in the activation energy going towards zero as the volatilization goes to completion. The significance of the drop in activation energy is not clear at this time. However it appears that the effect is apparent in both the isothermal and nonisothermal procedures.

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Résumé

En utilisant la méthode différentielle, on a calculé les paramètres cinétiques à partir des thermogrammes de Doyle. Des résultats ont été comparés avec ceux calculés par une méthode intégrale. On montre que dans le cas d'un processus simple, possédant une valeur unique pour l'énergie d'activation et l'ordre de la réaction, les deux méthodes conduisent aux mêmes résultats. Pour une réaction plus complexe telle que la volatilisation du polytétrafluoroéthylène, la méthode intégrale donne des résultats douteux.

Zusammenfassung

Mittels der Differentialmethode wurden kinetische Parameter aus Doyle-Diagrammen berechnet. Die Ergebnisse werden mit den nach einer Integralmethode berechneten verglichen. Es wird gezeigt, dass im Falle eines einfachen Prozesses mit einem einzigen Wert der Aktivierungsenergie und der Reaktionsordnung beide Methode zu etwa den gleichen Ergebnissen führen. Bei einer mehr komplexen Reaktion wie der Volatilisierung von Polytetrafluoräthylen führt die Integralmethode zu zweifelhaften Ergebnissen.

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