

NON-ISOTHERMAL KINETICS OF DIFFUSION AND ITS APPLICATION TO THERMAL ANALYSIS

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Non-isothermal kinetics of diffusion are derived, extending the fundamental equation of diffusion to non-isothermal conditions, and the equation is solved for a few typical cases. From these theoretical considerations, two methods of analyzing thermo-analytical data of diffusion are proposed. One of the methods is applied to EGA curves of the volatilization of toluene from epoxy resin cured with ethylenediamine. The diffusion constants obtained as a function of temperature for two plate-specimens of different thicknesses at various heating rates are in good agreement with each other. The temperature dependence of the diffusion constant observed for a powdered sample is also in good agreement with those observed for the two plate-specimens.

To date, the majority of kinetic researches have been made isothermally. However, the kinetics need to be extended to non-isothermal conditions, since there are many practical processes which proceed non-isothermally, and moreover thermal analyses are widely applied to kinetic investigations. While the isothermal investigation of kinetics is easy and desirable and the analysis of the thermo-analytical data is somewhat complicated, the isothermal method cannot be utilized when the thermal response time of the observed system is large compared with the rate of the process.

Although many methods have been proposed to analyse thermoanalytical data kinetically, most of them are based on the simple homogeneous chemical reaction and hence their applicability is limited. The author earlier [1, 2] set forth methods of kinetic analysis of thermoanalytical data in which kinetic equations of homogeneous chemical reactions of the general type are extended to the non-isothermal case. Flynn [3] recently pointed out the necessity of non-isothermal kinetics and discussed non-isothermal kinetics of homogeneous chemical reactions. The non-isothermal kinetics of homogeneous chemical reactions have been reported for fairly complicated polymer reactions [1, 2] and the nucleation-and-growth process [4], and have been applied to the thermal decomposition of polymers [1, 5–7], the volatilization of hydrogen chloride combined with amino groups in epoxy resins [8], and the crystallization of polymers [4, 9, 10]. However, many other types of process remain for which the kinetics have not yet extended to the non-isothermal case, and this needs to be done. In the present paper the equations of

diffusion are extended to non-isothermal conditions and applied to analyse thermoanalytical data of vaporization of toluene from an epoxy resin cured with ethylenediamine.

Theory of non-isothermal kinetics of diffusion

When there is no formation and no consumption of the diffusing substance, the fundamental equation of diffusion is as follows:

$$D\nabla^2\xi = \frac{\partial\xi}{\partial t} \quad (1)$$

where D , ξ , t and ∇^2 are the diffusion constant, the concentration of the diffusing substance, the time and a Laplacian, respectively. Generally, the diffusion constant is a function of temperature, T , i.e.:

$$D = D_0h(T) \quad (2)$$

where D_0 is a constant. When Eq. (1) is extended to non-isothermal conditions, we obtain:

$$D_0\nabla^2\xi = \frac{\partial\xi}{\partial\theta} \quad (3)$$

where:

$$\theta = \int_0^t h(T) dt \quad (4)$$

In the previous papers [1, 2], θ is called the reduced time, and is applied to the rate constant of chemical reactions of the Arrhenius type. It is now generalized for the rate constant to have any temperature-dependence. When the temperature-dependence of the diffusion constant is of the Arrhenius type:

$$\theta = \int_0^t \exp\left(-\frac{\Delta E}{RT}\right) dt \quad (5)$$

where ΔE and R are the activation energy and the gas constant, respectively, and for the case when the substance is heated at a constant rate, α , from low temperature where little reaction occurs:

$$\theta = \frac{\Delta E}{\alpha R} p\left(\frac{\Delta E}{RT}\right) \quad (6)$$

where p is the p -function proposed by Doyle [11], its value having been published by Akahira [12] and Doyle [11].

Now, Eq. (3) is the fundamental equation for non-isothermal diffusion, and the reduced time is used instead of the actual time. We can easily find the solution

of Eq. (3) [13, 14]. A few typical solutions follow which are useful for the analysis of thermoanalytical data of diffusion.

1 - *Diffusion in a sphere*. When the concentration is uniform, ξ_0 initially ($\theta = 0$), and the concentration is kept zero outside the sphere, we have:

$$\xi = \frac{2a\xi_0}{\pi r} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \sin \frac{n\pi r}{a} \exp(-D_0 n^2 \pi^2 \theta / a^2) \quad (7)$$

where a and r are the radius of the sphere and the distance from the center of the sphere, respectively. For the average concentration, $\bar{\xi}$, the following equation is derived:

$$\bar{\xi} = \frac{6\xi_0}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-D_0 n^2 \pi^2 \theta / a^2) \quad (8)$$

Let us define the conversion, C , as the ratio of the amount of volatilized substance to the initial amount as follows:

$$C = 1 - \bar{\xi} / \xi_0 \quad (9)$$

The conversion and the rate of conversion are:

$$C = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 \pi^2 \Theta) \quad (10)$$

$$\frac{dC}{d\Theta} = 6 \sum_{n=1}^{\infty} \exp(-n^2 \pi^2 \Theta) \quad (11)$$

where Θ is $D_0 \theta / a^2$, and is a dimensionless quantity corresponding to the time.

2 - *Diffusion in an infinite cylinder*. When the concentration is uniform, ξ_0 initially ($\theta = 0$), and the concentration is kept zero outside the cylinder, we have:

$$\xi = \frac{2\xi_0}{a} \sum_{n=1}^{\infty} \frac{aJ_0(\beta_n r/a)}{\beta_n J_1(\beta_n)} \exp(-D_0 \beta_n^2 \theta / a^2) \quad (12)$$

where r , a and J are the distance from the axis, the radius of the cylinder and the Bessel function, respectively, and β_n 's are the roots of the Bessel function of the zeroth order, J_0 ; i.e.:

$$J_0(\beta_n) = 0 \quad (13)$$

and for the average concentration, $\bar{\xi}$:

$$\bar{\xi} = 4\xi_0 \sum_{n=1}^{\infty} \frac{1}{\beta_n^2} \exp(-D_0 \beta_n^2 \theta / a^2) \quad (14)$$

The conversion and the rate of conversion are also derived as follows:

$$C = 1 - 4 \sum_{n=1}^{\infty} \frac{1}{\beta_n^2} \exp(-\beta_n^2 \Theta) \quad (15)$$

$$\frac{dC}{d\Theta} = 4 \sum_{n=1}^{\infty} \exp(-\beta_n^2 \Theta) \quad (16)$$

3 - *Diffusion in an infinite plate.* When the concentration is uniform, ξ_0 initially ($\theta = 0$), and the concentration is kept zero outside the plate, we have:

$$\xi = 8\xi_0 \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2 \pi^2} \sin \frac{(2n+1)\pi x}{a} \exp\{-D_0(2n+1)^2 \pi^2 \theta / a^2\} \quad (17)$$

where a and x are the thickness of the plate and the distance from the surface, and for the average concentration, $\bar{\xi}$:

$$\bar{\xi} = 8\xi_0 \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2 \pi^2} \exp\{-D_0(2n+1)^2 \pi^2 \theta / a^2\} \quad (18)$$

The conversion and the rate of conversion are derived as follows:

$$C = 1 - 8 \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2 \pi^2} \exp\{-(2n+1)^2 \pi^2 \Theta\} \quad (19)$$

$$\frac{dC}{d\Theta} = 8 \sum_{n=0}^{\infty} \exp\{-(2n+1)^2 \pi^2 \Theta\} \quad (20)$$

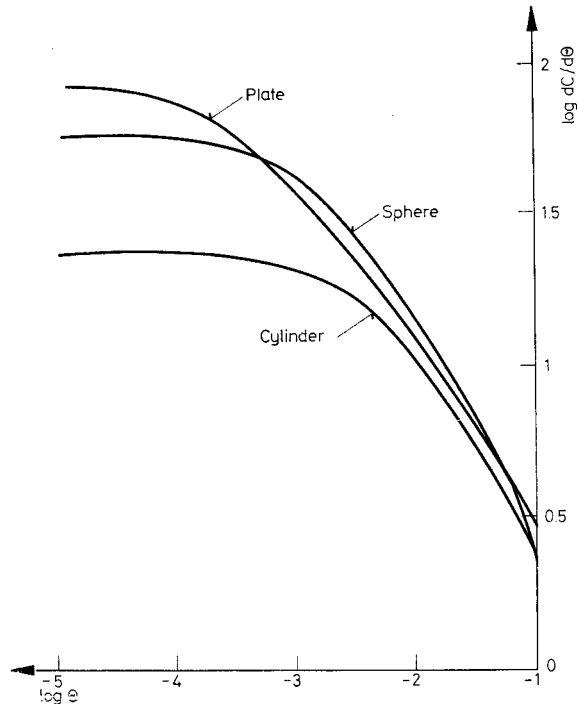


Fig. 1. The theoretical relation between $dC/d\Theta$ and Θ

The relationships of $dC/d\theta$ versus θ , C versus θ and $dC/d\theta$ versus C are shown in Figs 1, 2 and 3 for these three cases. The concentration of the diffusing substance is usually constant within the sample initially and zero outside the sample in the thermal analysis. These relationships are applicable to thermal analysis.

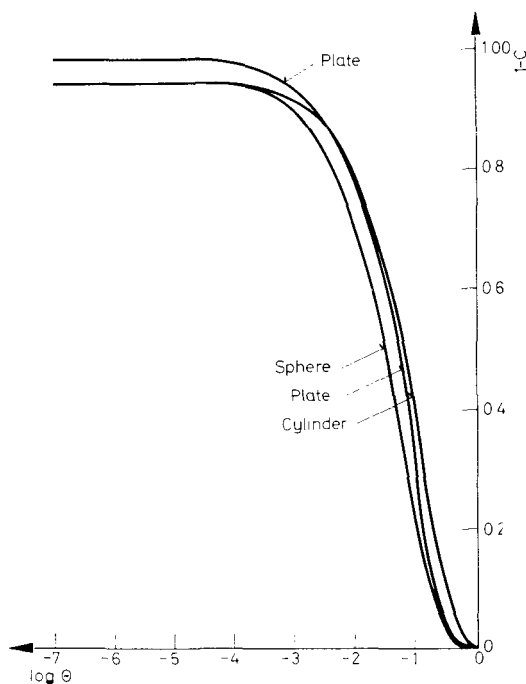


Fig. 2. The theoretical relation between C and θ

Methods of kinetic analysis of thermoanalytical data

A method applicable to the case of the diffusion constant of general temperature-dependence of Eq. (2) will first be discussed. We can obtain $dC/d\theta$ by using both the observed value of C and the relation between $dC/d\theta$ and C in Fig. 3. The difference between the logarithm of $dC/d\theta$ thus obtained and that of dC/dt observed at the same conversion is equal to the logarithm of D/a^2 , since

$$\begin{aligned} \frac{dC}{d\theta} &= \frac{dC}{dt} \frac{dt}{d\theta} \\ &= \frac{a^2}{D} \frac{dC}{dt} \end{aligned} \quad (21)$$

When we estimate D/a^2 along the conversion, we have D/a^2 as a function of temperature. If the process is really diffusion, the temperature-dependence of D/a^2 thus obtained at different heating rates are superposed on each other. If the superposition cannot be made, the process is not diffusion. This method is the same

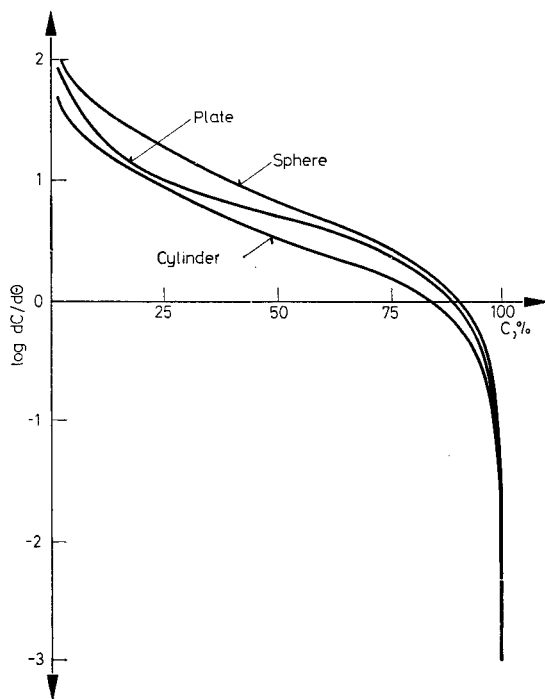


Fig. 3. The theoretical relation between $dC/d\theta$ and C

as the second method of the previous paper [2], in which the Arrhenius plot is made for the rate constant of chemical reaction obtained by the similar procedure; examples of the results of this procedure have been shown earlier [5, 6, 8]. The diffusion constant can be estimated when the radius or the thickness is known, and the plots of the diffusion constants versus the temperature for different radii or thicknesses can be superposed on each other again; this superposition is also applied to check whether the process is really diffusion or not.

Second, another method applicable to the case where the temperature-dependence of the diffusion constant is of the Arrhenius type will be discussed. In this case, the Ozawa plot [1, 2, 7] can be applied, i.e., the activation energy can be estimated by using the linear relation of the logarithm of the heating rate to the reciprocal absolute temperature for a given conversion, since the conversion is a single-valued function of the reduced time as is seen in Eqs. (10), (15) and (19).

The same plot can also be applied to the peaks of derivative thermoanalytical curves of different heating rates. As seen above:

$$C = \phi(\theta) \quad (22)$$

and

$$\frac{d^2C}{dt^2} = \frac{d^2\phi(\theta)}{d\theta^2} \exp\left(-\frac{2\Delta E}{RT}\right) + \frac{\alpha\Delta E}{RT^2} \frac{d\phi(\theta)}{d\theta} \exp\left(-\frac{\Delta E}{RT}\right) \quad (23)$$

At the peak, $d^2C/dt^2 = 0$. Thus, since $p(y)$ can be approximated to $\exp(-y)/y^2$ [11]:

$$\frac{d\phi(\theta_m)}{d\theta_m} + \frac{d^2\phi(\theta_m)}{d\theta_m^2} \theta_m = 0 \quad (24)$$

where the subscript m denotes the peak. Eq. (24) implies the following facts:

(i) At the peak the reduced time becomes nearly constant, regardless of the heating rate.

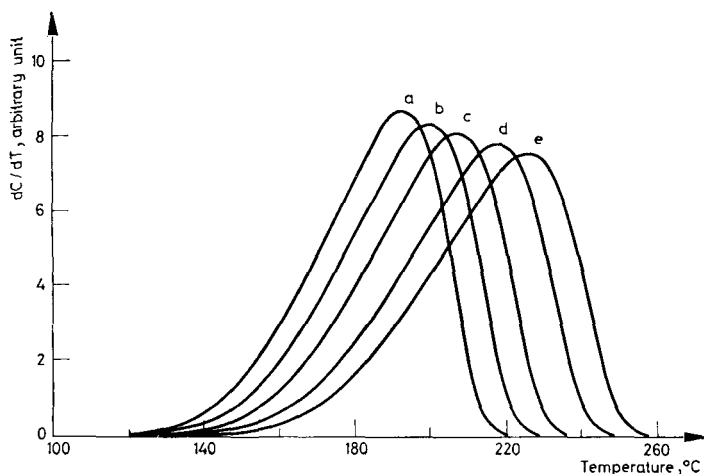


Fig. 4. Theoretical derivative curves calculated for diffusion in a sphere with $D_0/a^2 = 10^{19}$ and $\Delta E = 40$ kcal/mole; a: $0.25^\circ/\text{min}$, b: $0.5^\circ/\text{min}$, c: $1^\circ/\text{min}$, d: $2.5^\circ/\text{min}$, e: $5^\circ/\text{min}$

(ii) Then, the conversion is also the same.

(iii) The Ozawa and Kissinger plots [2, 15] are both applicable to the peak.

Thus, for any given conversion including that at the peak of the derivative curve, using Doyle's approximation [11]:

$$\log \alpha + 0.4567 \frac{\Delta E}{RT} = \text{constant} \quad (25)$$

By using the activation energy thus obtained, the observed experimental relations of the conversion and the rate of conversion, dC/dt , with the temperature can be converted to the relations of the conversion and the reduced rate of conversion, $dC/d\theta$, with the reduced time, θ . If the temperature-dependence of the diffusion

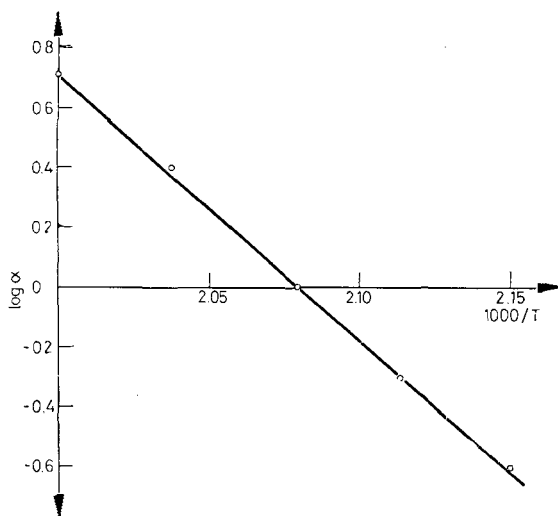


Fig. 5. Typical plot of the logarithm of the heating rate versus the reciprocal absolute peak temperature for the derivative curves shown in Fig. 4

constant is truly of the Arrhenius type in the temperature range observed, the reduced relations obtained at different heating rates are superposed on each other, and the experimental master curves are obtained. If the superposition cannot be made, the situation is one of the following alternatives: either the process is not diffusion, or the temperature-dependence is not of the Arrhenius type. For the latter alternative, we can apply the first method mentioned above.

Next, by comparison of the experimental master curves and the corresponding theoretical curves shown in Figs 1, 2 and 3, D_0/a^2 can be estimated. When a is known, D_0 too is evaluated, and the D_0 values evaluated for different a 's should be equal to each other if the process is really diffusion.

Since Eq. (24) is an approximated equation, the accuracy of the Ozawa plot based on Eq. (25) should be examined; the theoretical derivative curves of dC/dT versus T are obtained with an electronic digital computer by using Eqs (11), (16), (20) and a highly approximated equation for $p(y)$, as seen in Fig. 4, and the peak temperatures are obtained to an accuracy of 2.5° for heating rates of 0.25, 0.5, 1, 2.5 and $5^\circ/\text{min}$. The logarithm of the heating rate is plotted against the reciprocal absolute peak temperature using the calculated peak temperature in Fig. 5. It is clearly seen that a straight line is obtained, from the slope of which the activation energy is estimated to be 40.6 kcal/mole, compared with the theoretical value of 40 kcal/mole. The result is satisfactorily good.

Experimental

The material used is epoxy resin epon 827 (Shell Chemical Co.) cured with ethylenediamine of E. P. grade purchased from Wako Pure Chemical Industries, Ltd. Epoxy resin and ethylenediamine are mixed so that the number of amino groups of the amine is equal to the number of epoxide groups, and they are left for curing for more than 24 hr at room temperature. The undercured resin is post-cured at about 140° for more than 24 hr. The powdered sample is obtained by filing the resin. The samples are left in a desiccator for several days before the measurement.

Evolved gas analysis (EGA) is made with an apparatus described elsewhere [5, 6]. Briefly, the sample is heated at a constant rate in a sample container put beneath the ionization chamber of a time-of-flight mass-spectrometer of the Bendix type. The pressure is less than 10^{-5} torr. The volatilized products are analyzed immediately.

Results and discussion

A mass-spectrum observed on the powdered sample is reproduced in Fig. 6. The ions of mass number, M/e 92, 91, 65 and 39 are observed, these being a parent ion and fragment ions of toluene [16]. The ions of M/e 60 and 30 due to ethylenediamine are also found in the same temperature range, while the ions due to water are found in a somewhat lower temperature range. The volatilization of hydrogen chloride occurs in a higher temperature range; its kinetics have already been analyzed and reported elsewhere [7].

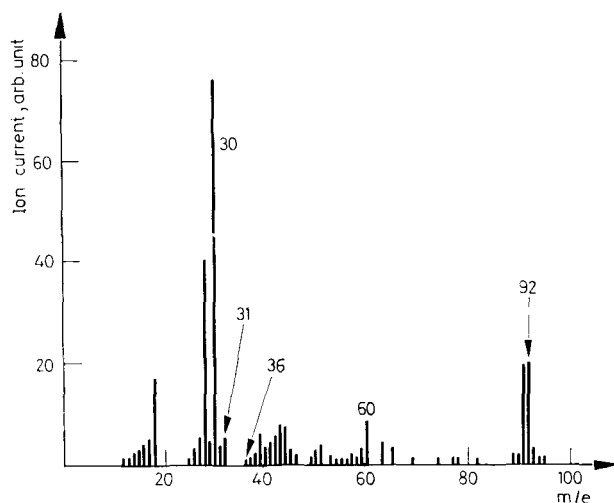


Fig. 6. Mass-spectrum observed for the powdered sample at 70° at a heating rate of 1°C/min with an ionization voltage of 70 eV

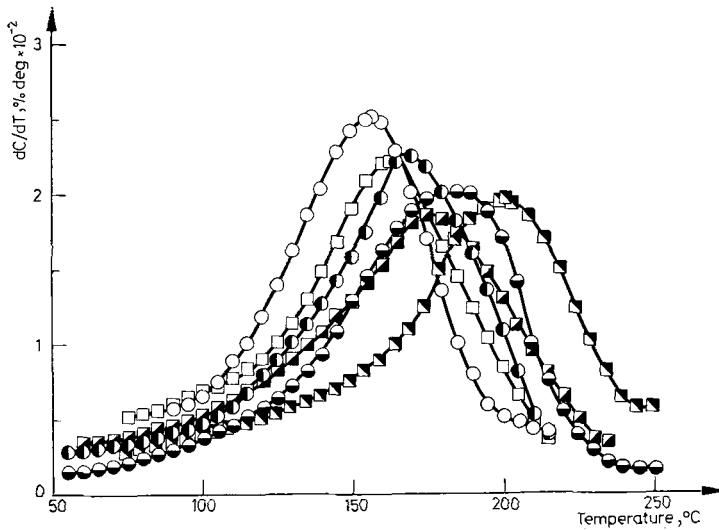


Fig. 7. MTA curves of *M/e* 91 obtained at various heating rates for two plate specimens of 0.33 mm and 0.69 mm thickness, respectively; \circ . . . 0.33 mm thickness and $2^\circ/\text{min}$, \bullet . . . 0.33 mm thickness and $4^\circ/\text{min}$, \circ . . . 0.33 mm thickness and $8^\circ/\text{min}$, \square . . . 0.69 mm thickness and $1^\circ/\text{min}$, \blacksquare . . . 0.69 mm thickness and $2^\circ/\text{min}$, \blacktriangle . . . 0.69 mm thickness and $3^\circ/\text{min}$

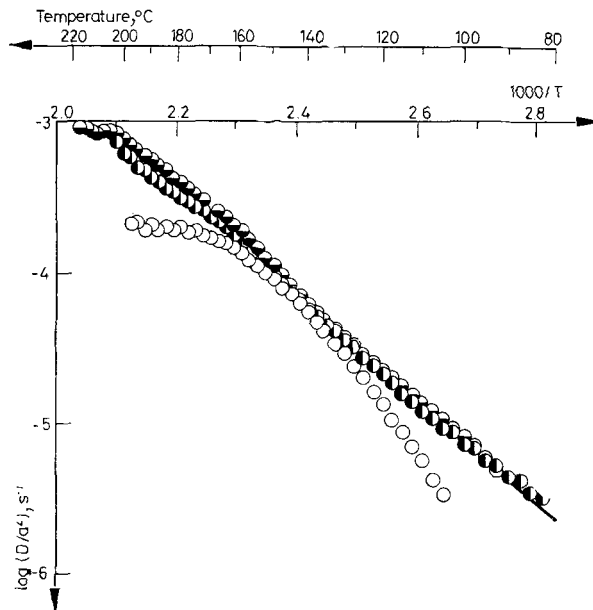


Fig. 8. Plot of the logarithm of D/a^2 versus the reciprocal absolute temperature for the specimen of 0.33 mm thickness. The symbols are the same as in Fig. 7, and the dimensions of D are mm^2/sec

In this paper, the ion of M/e 91 observed on plates of the resin are analyzed in order to elucidate the applicability of the method proposed here to the actual process. The EGA curves, which are plots of the ion currents versus the temperature, for M/e 91 on two plate-specimens of different thicknesses are shown in Fig. 7. It can be seen that the volatilization occurs in a higher temperature range, the higher the heating rate and the thicker the specimen. The tendency is in accordance with the theory. Decomposition begins to occur in the higher temperature range, where the measurement is discontinued.

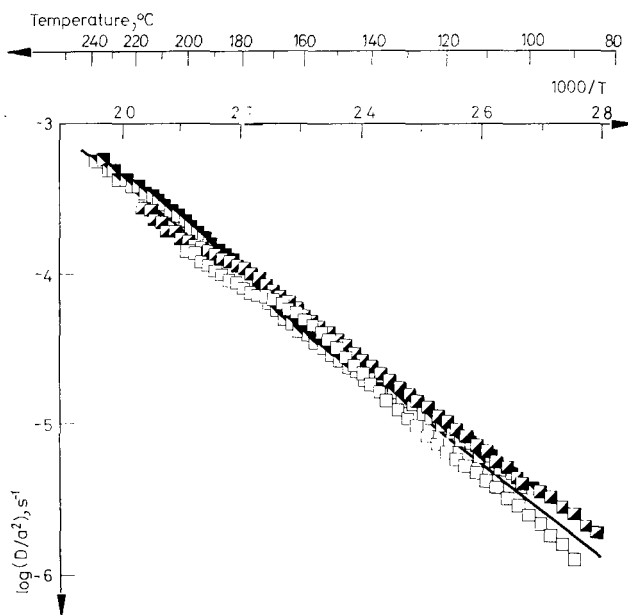


Fig. 9. Plot of the logarithm of D/a^2 versus the reciprocal absolute temperature for the specimen of 0.69 mm thickness. The symbols and dimensions are the same as in Figs 7 and 8

The first method mentioned above is examined. The conversion is calculated by Simpson's method over the range of the measurement. The logarithm of D/a^2 is obtained in the range of conversion from 5% to 95% as a function of temperature, and is plotted against the reciprocal absolute temperature in Figs 8 and 9. In the other ranges the estimation of D/a^2 is difficult, as is seen in Fig. 3. The values of D/a^2 obtained for various heating rates are on the same line, though the plots are somewhat scattered; this implies that the volatilization of toluene from the epoxy resin really is diffusion. The diffusion constant, D , is calculated from the values of D/a^2 , and plotted in Fig. 10. The fact that the diffusion constants obtained for different thicknesses at various heating rates are in good agreement with each

other is also evidence that the process is really diffusion and that free toluene is present in the resin as residual solvent.

A similar plot of D/a^2 versus the reciprocal absolute temperature for the powdered sample is given in Fig. 11, making use of Eq. (11). The values obtained at

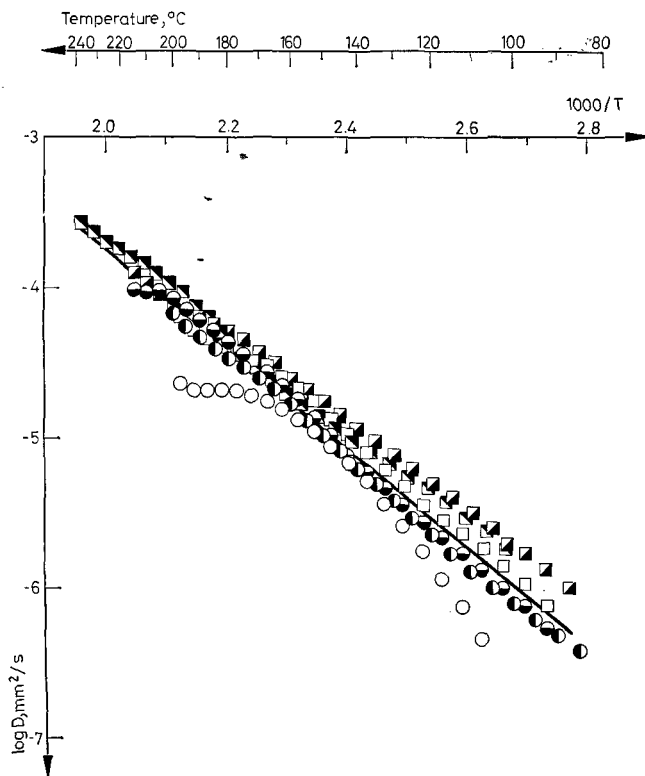


Fig. 10. Plot of the diffusion constant versus the reciprocal absolute temperature for toluene in ethylenediamine-cured epoxy resin. The symbols and dimensions are the same as in Figs 7 and 8

the different heating rates are also on the same line, but deviations are observed for the range of conversion larger than 85%; these deviations seem to be due to the distribution of the radius values of the powder. Superposition of Fig. 11 on Fig. 10 can be done, and from the longitudinal shift the average radius is estimated to be about $30 \mu\text{m}$.

It is apparent from the results of kinetic analysis that the first method proposed in this paper is applicable to thermoanalytical data of diffusion in order to characterize the process. However, the second method cannot be applied to the EGA

curves, since the temperature-dependence of the diffusion constant is not of the Arrhenius type, as is seen in Fig. 10. EGA curves of vaporization of water and ethylenediamine from the resin are also analyzed, and similar results are obtained.

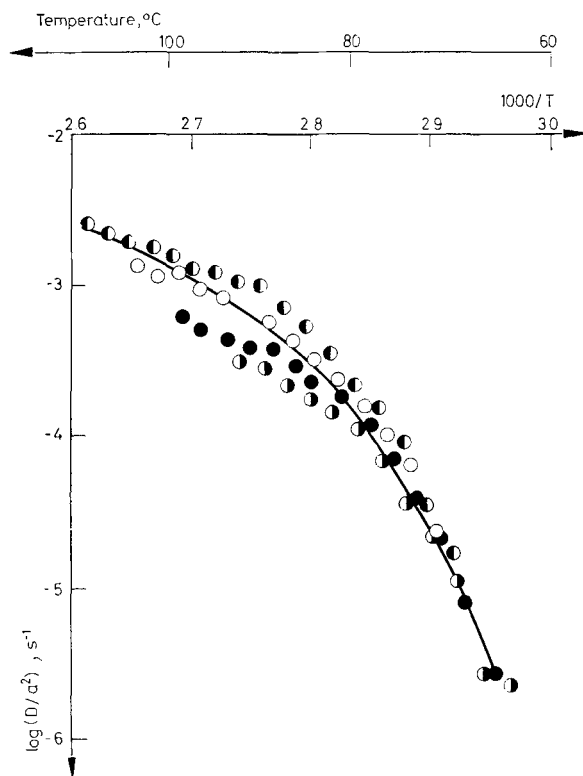


Fig. 11. Plot of the logarithm of D/a^2 versus the reciprocal absolute temperature for toluene in the powdered sample of ethylenediamine-cured epoxy resin. The dimensions are the same as in Fig. 8

As pointed out previously [2], most methods of kinetic analysis of thermo-analytical data involve the dangerous tendency to study processes of great variety within the limited framework of the particular specialized formulae, and to lead to false results; the examination of the validity of the applied method by these superpositions is a necessary procedure even in the kinetic analysis of diffusion.

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RÉSUMÉ — On étudie la cinétique de diffusion en régime non isotherme, en étendant l'équation fondamentale de la diffusion aux cas non isothermes et l'on donne la solution de l'équation pour quelques cas typiques. A partir de ces considérations théoriques, on propose deux méthodes pour analyser les données thermoanalytiques de la diffusion. On applique l'une d'elles aux courbes AGE de stabilisation du toluène à partir des résines époxy traitées à l'éthylène diamine. Les constantes de diffusion obtenues en fonction de la température pour plusieurs vitesses d'échauffement sur deux échantillons en forme de plaquette sont en bon accord, de même que pour des échantillons pulvérulents.

ZUSAMMENFASSUNG — Die nicht-isotherme Kinetik der Diffusion wird abgeleitet, indem die Grundgleichung der Diffusion auf nicht-isotherme Fälle erweitert und für einige typische Fälle gelöst wird. Von diesen theoretischen Erwägungen ausgehend werden zwei Methoden zur Analyse thermoanalytischer Diffusionsangaben vorgeschlagen. Eine der Methoden wird für die EGA-Kurven der Verflüchtigung von Toluol aus mit Ethyländiamin behandeltem Epoxyharz angewandt. Die an zwei Platten-Arten verschiedener Dicke bei verschiedenen Aufheizgeschwindigkeiten als Funktion der Temperatur erhaltenen Diffusionskonstanten stimmen gut überein. Die an einer pulverförmigen Probe beobachtete Temperaturabhängigkeit der Diffusionskonstante ist ebenfalls in guter Übereinstimmung mit der an den zwei Plattenkörpern erhaltenen.

Резюме — Распространение основного уравнения диффузии на неизотермические условия позволяет вывести неизотермическую кинетику диффузии. На основании этих теоретических соображений предлагается два метода обработки термоаналитических данных диффузии. Один из методов использован для кривых испарения толуола из эпокси смолы. Константы диффузии, полученные как функция температуры для двух пластинчатых образцов разной толщины при различных скоростях нагревания, хорошо совпадают друг с другом. Температурная зависимость константы диффузии, в случае порошкообразного образца также хорошо согласуется с наблюдаемой для двух пластинчатых образцов.