

## Effect of sample mass on the kinetics of thermal decomposition of a solid. Part 3. Non-isothermal mass-loss process of molten $\text{NH}_4\text{NO}_3$

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### Abstract

The effect of sample mass on the kinetics of the non-isothermal mass-loss process of molten  $\text{NH}_4\text{NO}_3$  was investigated by TG–DTG. The apparent Arrhenius parameters were shown to decrease with increasing sample mass. Using the conventional method of kinetic calculation, it was shown that the sample-mass-dependent variation in the apparent pre-exponential factor results from the use of fractional reaction in the kinetic expression. The value of the apparent activation energy varies consequently to compensate the sample-mass-dependent change in the apparent pre-exponential factor on the regime of the mutual dependence of the Arrhenius parameters; this is known as the kinetic compensation effect. The specific Arrhenius parameters that are independent of sample mass were obtained by using the specific pre-exponential factor that is independent of sample mass, instead of the apparent pre-exponential factor.

### INTRODUCTION

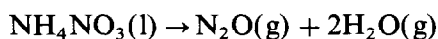
It has been reported that the kinetic parameters obtained from thermoanalytical (TA) measurements of solid-state decompositions change depending on the sample mass examined [1–5]. The change in the gradients of temperature and partial pressure of the evolved gas in the sample matrix, caused by the change in the sample mass, possibly results in sample-mass-dependent kinetic parameters [2, 4, 5]. Recently, we have reported that even for the isothermal decomposition of molten  $\text{NH}_4\text{NO}_3$ , in which the gradients of temperature and pressure are negligible, the apparent Arrhenius parameters are affected by sample mass [6]. This is due to the sample-mass-dependent rate constant which results from the use of the fractional reaction  $\alpha$  in the kinetic expression [7]. By using the specific rate constant instead of the apparent rate constant, Arrhenius parameters that are independent of

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sample mass were obtained. A similar relationship was observed for the isothermal dehydration of crushed crystals of  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  [8]. It seems important to clarify such a causation of sample-mass dependence of the Arrhenius parameters inherent in the conventional kinetic expression of solid-state decomposition, as well as to discuss the problem in relation to the effect of self-generated reaction conditions which are not necessarily controlled in conventional TA techniques [9, 10].

In the present study, the effect of sample mass on the kinetics of the non-isothermal decomposition was investigated to understand extensively the relationship of sample-mass dependence inherent in the kinetic expression. The thermal decomposition of molten  $\text{NH}_4\text{NO}_3$  was selected as a suitable system. The decomposition [6, 11], which follows the melting at around  $165^\circ\text{C}$ , is expressed as



Under isothermal conditions [6], the kinetics is obeyed by the one-dimensional phase-boundary-controlled  $R_1$  law, and the specific activation energy, which is independent of the sample mass, is  $86.2 \pm 2.0 \text{ kJ mol}^{-1}$ .

## EXPERIMENTAL

Reagent grade ammonium nitrate (Katayama Chem. Co.) was ground with a vibrating ball mill for two hours. A fraction of  $-280 + 300$  mesh was sieved and stored for two weeks for TA measurements. The sample was identified by TG and IR spectroscopy.

The nominal sizes were 5.0, 6.0, 7.5, 10.0 and 15.0 mg, packed by light tapping into a cylindrical platinum crucible 5 mm in diameter and 2.5 mm in height. Simultaneous measurements of TG and DTG at various heating rates in the range  $0.5\text{--}10.0 \text{ K min}^{-1}$  were carried out using a Shimadzu TGA-50 instrument, with nitrogen flowing at a rate of  $30 \text{ ml min}^{-1}$ .

## RESULTS AND DISCUSSION

Typical plots of  $\alpha$  against  $T$  for the mass-loss process of various sample sizes at a heating rate of  $1.0 \text{ K min}^{-1}$  are shown in Fig. 1. With increasing sample mass, the kinetic curves shift toward the higher temperature region.

Kinetic analyses of the mass-loss process were carried out by assuming the equation

$$\frac{d\alpha}{dt} = A_{\text{app}} \exp\left(-\frac{E_{\text{app}}}{RT}\right) f(\alpha) \quad (1)$$

where  $A_{\text{app}}$  and  $E_{\text{app}}$  are the apparent Arrhenius parameters, and  $f(\alpha)$  is the kinetic model function obtained on the basis of physico-geometric assumption of the movement of the reaction interface [12]. Application of eqn. (1)

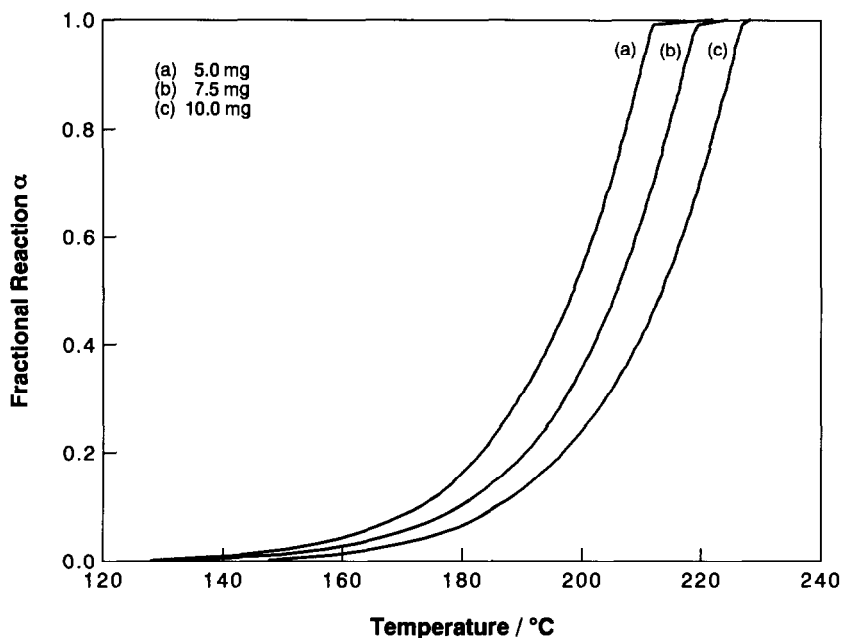


Fig. 1. The effect of sample mass on the plot of  $\alpha$  against  $T$  for the non-isothermal mass-loss process of molten  $\text{NH}_4\text{NO}_3$  at a heating rate of  $1.0 \text{ K min}^{-1}$ .

to one of the isoconversional methods, e.g. the extended Friedman method [13, 14], requires a set of kinetic curves at different heating rates. Figure 2 shows the heating-rate dependence of the differential kinetic curves for the mass-loss process with a sample mass of 10.0 mg. According to eqn. (1) the value of  $E_{\text{app}}$  can be calculated, at various  $\alpha$ , by plotting  $\ln(d\alpha/dt)$  against  $1/T$ . Typical plots at given  $\alpha$  values from 0.1 to 0.9 in steps of 0.1 are shown in Fig. 3. The plots of  $\ln(d\alpha/dt)$  versus  $1/T$  show fairly good linearity with the correlation coefficient of the linear regression analysis being better than  $\gamma \approx -0.995$ . A constant value of  $E_{\text{app}}$  during the  $\alpha$  range of the analysis is a prerequisite of the application of eqn. (1). Figure 4 represents the  $\alpha$  dependence of the values of  $E_{\text{app}}$  for the mass-loss process with a sample mass of 10.0 mg. The prerequisite of the extended Friedman method described above is satisfied by the approximately constant value of  $E_{\text{app}}$  within the  $\alpha$  range of 0.3–0.9. The change in  $E_{\text{app}}$  during the early stage of the reaction is probably due to the influence of the melting process. Similar behaviours were observed for the mass-loss process with the different sample masses examined. Table 1 shows the mean values of  $E_{\text{app}}$  over the  $\alpha$  range 0.3–0.9 for the respective sample masses. A slight but detectable decrease in the  $E_{\text{app}}$  value is observed with increasing sample mass, as is the case with an isothermal mass-loss process [6].

Further kinetic analyses were made by introducing the generalized time  $\theta$  [15–17]

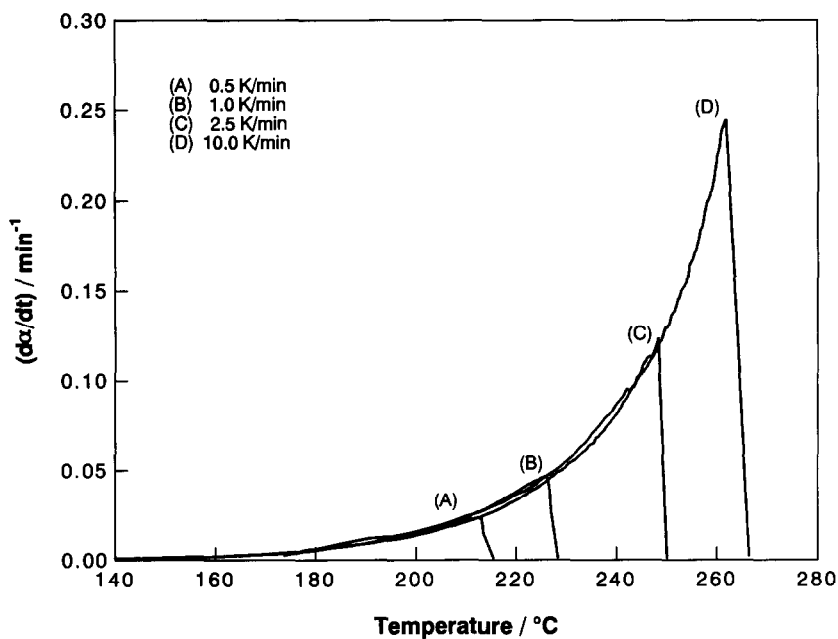


Fig. 2. The effect of heating rate on the plot of  $d\alpha/dt$  against  $T$  for the non-isothermal mass-loss process of molten  $\text{NH}_4\text{NO}_3$  with a sample size of 10.0 mg.

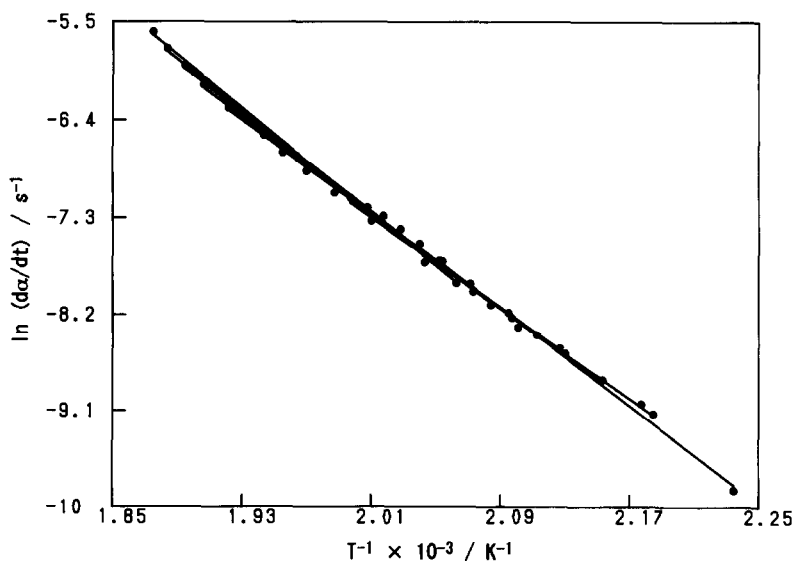


Fig. 3. Typical plots of  $\ln(d\alpha/dt)$  against  $1/T$  at different constant  $\alpha$  values of 0.1–0.9 in steps of 0.1 for the non-isothermal mass-loss process of molten  $\text{NH}_4\text{NO}_3$  with a sample size of 10.0 mg.

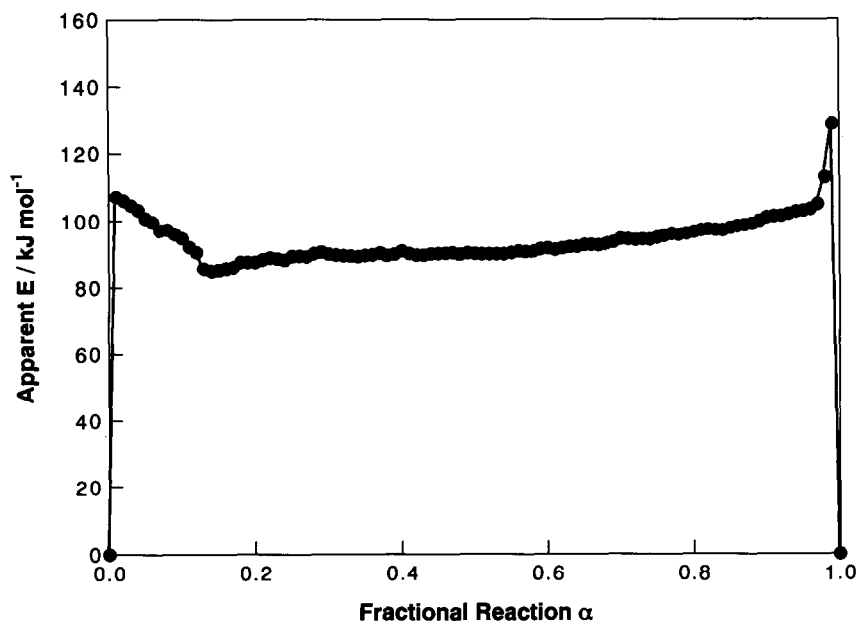


Fig. 4. The  $\alpha$  dependence of the apparent activation energy for the non-isothermal mass-loss process of molten  $\text{NH}_4\text{NO}_3$  with a sample size of 10.0 mg.

$$\theta = \int_0^t \exp\left(-\frac{E_{\text{app}}}{RT}\right) \quad (2)$$

First differentiation gives

$$\frac{d\theta}{dt} = \exp\left(-\frac{E_{\text{app}}}{RT}\right) \quad (3)$$

Combining eqn. (1) with eqn. (3)

$$\frac{d\alpha}{d\theta} = A_{\text{app}} f(\alpha) \quad (4)$$

TABLE 1

The effect of sample mass on the apparent Arrhenius parameters obtained for the non-isothermal mass-loss process of molten  $\text{NH}_4\text{NO}_3$

Sample mass/mg	$E_{\text{app}}/\text{kJ mol}^{-1}$	$A_{\text{app}} \times 10^6/\text{s}^{-1}$	$\log(A_{\text{app}}/\text{s}^{-1})$
5.0	$97.9 \pm 0.5$	$29.6 \pm 0.3$	$7.47 \pm 0.01$
6.0	$95.8 \pm 0.5$	$18.1 \pm 0.7$	$7.25 \pm 0.02$
7.5	$94.9 \pm 0.7$	$10.4 \pm 0.2$	$7.02 \pm 0.01$
10.0	$92.7 \pm 0.4$	$3.9 \pm 0.1$	$6.59 \pm 0.01$
15.0	$90.8 \pm 0.7$	$2.4 \pm 0.1$	$6.38 \pm 0.01$

Equations (1) and (4) give

$$\frac{d\alpha}{dt} = \frac{d\alpha}{d\theta} \exp\left(-\frac{E_{\text{app}}}{RT}\right) \quad \text{with} \quad \frac{d\alpha}{dt} = \frac{d\alpha}{d\theta} \frac{d\theta}{dt} \quad (5)$$

Equation (5) shows that  $d\alpha/dt$  is proportional to  $\exp(-E/RT)$  at a given  $\alpha$ , having a slope of  $d\alpha/d\theta$ . Thus the kinetics can be characterized by dividing the rate process into the enthalpy- and entropy-dependent terms, expressed by  $d\theta/dt$  and  $d\alpha/d\theta$ , respectively [18, 19]. Using the values of  $E_{\text{app}}$  listed in Table 1, the entropy-dependent term was determined at various  $\alpha$  values. Figure 5 represents the  $\alpha$  dependence of the  $d\alpha/d\theta$  values at different sample masses. The nearly constant values of  $d\alpha/d\theta$  at different  $\alpha$  values for the respective sample masses support obedience of the one-dimensional phase-boundary-controlled  $R_1$  law,  $f(\alpha) = 1$ , in accordance with the kinetic obedience under isothermal conditions. Then the value of  $d\alpha/d\theta$  corresponds directly to the value of  $A_{\text{app}}$ , according to eqn. (4). It is also noted that the value of  $A_{\text{app}}$  averaged over the course of the reaction decreases with increasing sample mass. The mean values of  $A_{\text{app}}$  and their logarithms are also listed in Table 1. We see that the sample-mass-dependent variation of the apparent Arrhenius parameters is substantiated by the experimental evidence.

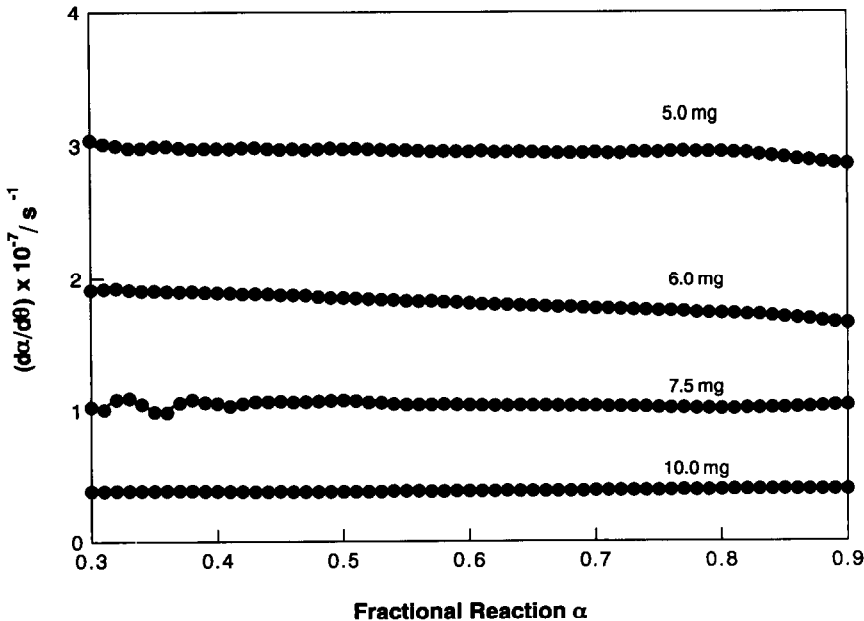


Fig. 5. The  $\alpha$  dependence of the value of  $d\alpha/d\theta$  for the non-isothermal mass-loss process of molten  $\text{NH}_4\text{NO}_3$  with various sample sizes.

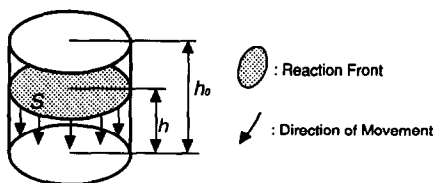


Fig. 6. Schematic representation of the geometry of the mass-loss process for the  $R_1$  model.

Figure 6 illustrates the geometric feature of surface movement for the mass-loss process of the molten  $\text{NH}_4\text{NO}_3$ . Geometric consideration gives

$$\alpha = \frac{h_0 - h}{h_0} \quad (6)$$

where  $h_0$  and  $h$  are the heights of the reaction front from the bottom at  $t = 0$  and  $t = t$ , respectively [6]. When the advancement of the reaction front obeys the linear law under isothermal conditions, the rate expression under a linearly increasing temperature is written

$$\frac{d(h_0 - h)}{dt} = A_s \exp\left(-\frac{E_s}{RT}\right) \quad (7)$$

where  $E_s$  and  $A_s$  are the specific Arrhenius parameters for the advancement of the reaction front. If we introduce the generalized time and fractional reaction for the specific Arrhenius parameters, eqns. (3), (6) and (7) give

$$\frac{d\alpha}{d\theta} = \frac{A_s}{h_0} \quad (8)$$

The term  $h_0$  can be replaced by

$$h_0 = \frac{V_0}{S} = \frac{m}{S\rho} \quad (9)$$

where  $V_0$  is the volume at  $t = 0$ ,  $S$  the area of reaction front,  $m$  the original sample mass and  $\rho$  the volume density [6]. Accordingly, the  $A_{\text{app}}$  used in the above kinetic calculation for the overall process is expressed as

$$A_{\text{app}} = \frac{A_s S \rho}{m} \quad (10)$$

It is thus expected that the values of  $A_{\text{app}}$  obtained at different sample masses are proportional to the reciprocal of the sample mass examined, as is the case of the apparent rate constant under isothermal conditions [6, 8]. The dependence of the  $A_{\text{app}}$  value on the reciprocal sample mass  $1/m$  for the present mass-loss process is shown in Fig. 7. The plot is fairly linear, although the regression line does not pass through the origin of the coordinate axes. Deviation from the origin seems to be due to the influence of a melting process in the sample at the beginning of the mass-loss process.

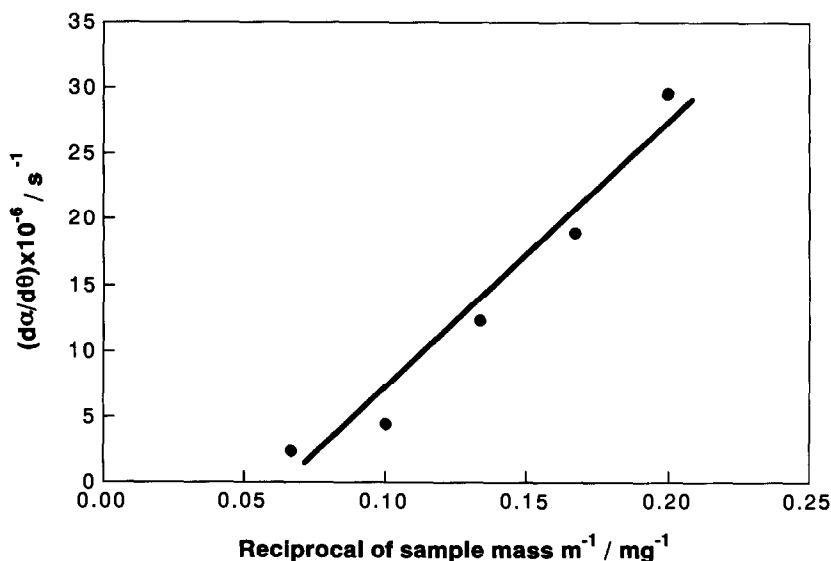


Fig. 7. A plot of  $d\alpha/d\theta$  against  $1/m$  for the non-isothermal mass-loss process of molten  $\text{NH}_4\text{NO}_3$ .

The slope of the plot,  $A_s S \rho = 2.07 \times 10^8$ , corresponds to the specific pre-exponential factor that is independent of the sample mass examined.

Employing the relationship of eqn. (10), the following kinetic expression is obtained

$$\frac{d\alpha}{dt} m = A_s S \rho \exp\left(-\frac{E_s}{RT}\right) \quad (11)$$

Assuming that the kinetic obedience is constant, irrespective of the sample mass examined, eqn. (11) is considered as the normalized kinetic equation, from which sample-mass-independent Arrhenius parameters are derived. By plotting  $\ln[(d\alpha/dt)m]$  against  $1/T$ , the values of  $E_s$  at different  $\alpha$  values can be determined from the slope. Typical plots at given  $\alpha$  values from 0.1 to 0.9 in steps of 0.1 are shown in Fig. 8. Using the mean value of  $E_s$ , the values of  $A_s S \rho$  at given  $\alpha$  values can also be calculated according to eqns. (3)–(5). Figure 9 shows the values of  $E_s$  and  $A_s S \rho$  within the range of  $0.3 \leq \alpha \leq 0.9$ , in which nearly constant values of  $E_s$  and  $A_s S \rho$  are obtained, irrespective of  $\alpha$ . The mean values are  $E_s = 97.1 \pm 0.6 \text{ kJ mol}^{-1}$  and  $A_s S \rho = 1.21 \times 10^8 \pm 1.32 \times 10^6 \text{ s}^{-1}$ . The value of  $A_s S \rho$  corresponds fairly well to that calculated from eqn. (10) (see Fig. 7). It follows that the specific value of the activation energy is derived by using the specific pre-exponential factor,  $A_s S \rho$ , which is independent of sample mass, instead of the conventional  $A_{\text{app}}$ .

Although there is experimental evidence of the sample-mass-dependent  $E_{\text{app}}$ , no reasonable explanation for it seems to have been made in terms of a mathematical formalism of kinetic analysis. A probable interpretation is



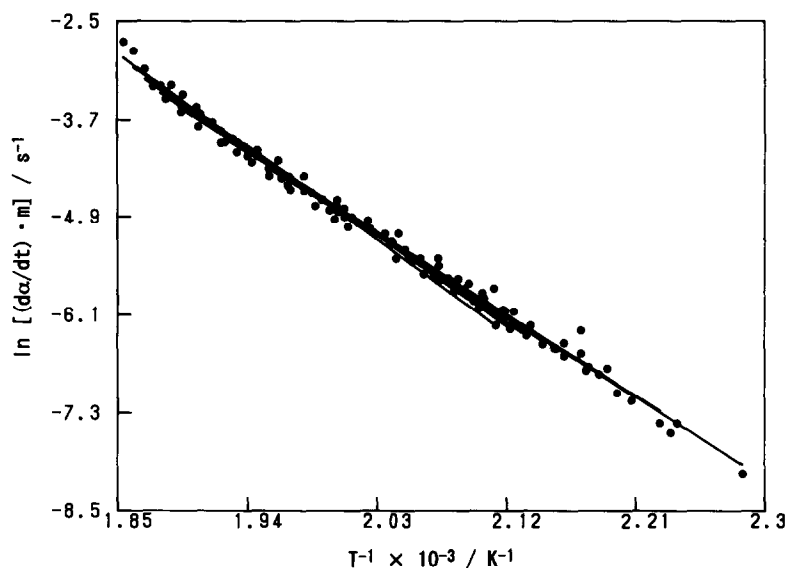


Fig. 8. Typical plots of  $\ln[(d\alpha/dt)m]$  against  $1/T$  at different constant  $\alpha$  values of 0.1–0.9 in steps of 0.1 for the non-isothermal mass-loss process of molten  $\text{NH}_4\text{NO}_3$ .

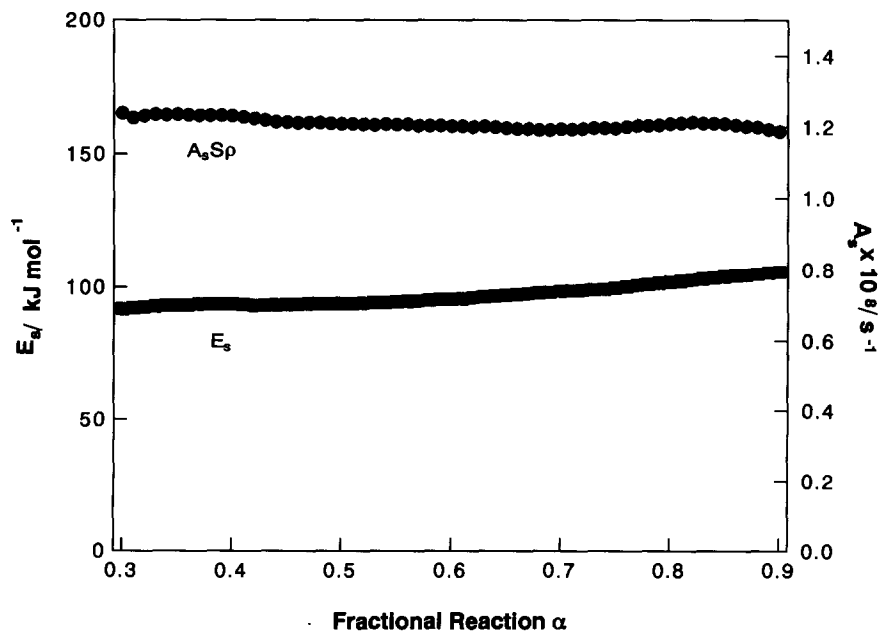


Fig. 9. The  $\alpha$  dependence of the values of  $E_s$  and  $A_s S \rho$  for the non-isothermal mass-loss process of molten  $\text{NH}_4\text{NO}_3$ .

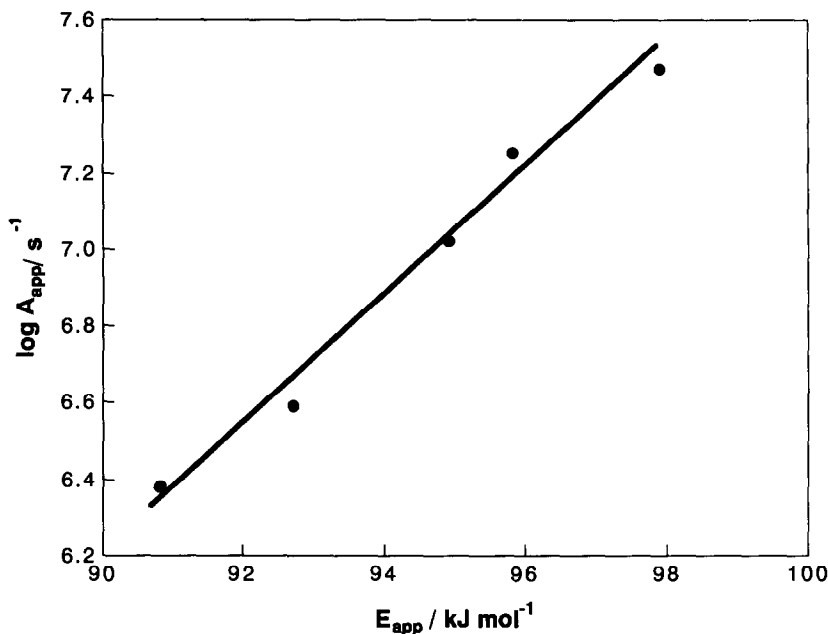


Fig. 10. The mutual dependence of the apparent Arrhenius parameters obtained for the different sample sizes.

concerned with the kinetic compensation effect (KCE), i.e. a linear interdependence among the values of  $E_{app}$ ,  $\ln A_{app}$  and the measured temperature interval  $\Delta T$  [20]. Any variation in the respective terms should bring about such an undesired interdependence, as a mathematical consequence of the exponential form of the Arrhenius equation [21, 22]. The mutual dependence between  $E_{app}$  and  $\log A_{app}$  caused by changing the sample mass is shown in Fig. 10. As the sample-mass dependence of  $A_{app}$  for the present system is evident from eqn. (10), the mutual dependence of the Arrhenius parameters is likely to be responsible for the change in  $E_{app}$  with the sample mass.

The present results indicate that, if the sample matrix behaves as a single body, the apparent pre-exponential factor depends on the sample mass, which results from the use of the fractional reaction  $\alpha$  in the kinetic expression. The  $E_{app}$  value changes to compensate the sample-mass-dependent variation in the  $A_{app}$  value, but the undesirable change in  $E_{app}$  can be avoided as stated above. When the kinetics is interpreted on a single particle basis in the sample assemblage, as is the case for the usual solid-state decomposition, a similar relationship would be observed due to an effect of particle size. It should be recognized that, provided the apparent Arrhenius parameters are concerned, these parameters vary with both sample mass and particle size, and that such a variation may also be affected by any gradients in temperature and/or pressure in the sample matrix.

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