

Effect of sample mass on the kinetics of thermal decomposition of a solid.

Part 1. Isothermal mass-loss process of molten NH_4NO_3

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Abstract

The effect of sample mass on the kinetics of the isothermal mass-loss process of molten NH_4NO_3 was investigated by simultaneous TG–DSC. The conventional method of kinetic analysis derived for the thermal decomposition of a solid was adopted for calculating the kinetic parameters in order to evaluate the validity of the kinetic theory. The kinetic parameters obtained from these calculations were sample-mass dependent. A possible way of obtaining kinetic parameters that are independent of sample mass is discussed for the one-dimensional contracting model, i.e. the R_1 law.

INTRODUCTION

The overall kinetics of the thermal decomposition of solids is largely affected by various experimental factors [1]; this is due to the complexity of the kinetic process [2]. At the same time, the reliability of thermo-analytical (TA) curves as a possible source of kinetic data varies with the experimental conditions applied [3–5]. Both the physicochemical situation and the experimental condition are manifested as a change in the shape and position of the TA curves. The kinetic parameters calculated from these curves are not necessarily unique values; interdependence of the Arrhenius parameters, i.e. the kinetic compensation effect [6], can be observed within a series of Arrhenius parameters. This is one of the fundamental problems in the kinetic study of solid-state reactions, especially when the TA curves are used to obtain the rate data [7].

Sample mass is one such experimental variable. A change in the shape and position of the TA curves is observed when the sample mass changes [8–10]. The kinetic parameters calculated are sometimes sample-mass

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dependent [11–15]. The effects of self-cooling and the partial pressure of the evolved gas have been suggested as possible causes of this sample-mass dependence [12, 16]. It has been recommended that the kinetics should be studied under a moderate reaction rate, using a small sample mass to reduce these effects [5, 12]. The self-cooling effect can be reduced by using power compensation DSC [17]. Use of controlled transformation rate thermal analysis (CRTA) [16] and/or quasi-isothermal quasi-isobaric thermal analysis (QOTA) [18] seems to be useful in maintaining the self-generated reaction condition constant during the reaction. However, Flanagan et al. [11] and Guarini et al. [13] have proposed that the reciprocal of the apparent rate constant and the fractional reaction, respectively, be extrapolated to zero mass using the empirical linear relationships in connection with the sample mass. To be able to find a sample mass limit below which the kinetic parameters are sample-mass independent, is a necessary but not sufficient condition for believing that the invariant values have physicochemical meaning [19]. However, even when the sample mass was reduced down to 1.0 mg, a sample mass below which the kinetic parameters remained invariant could not be found in the studies of Gallagher and Johnson [12] and Ninan [13].

It is therefore desirable that the possible causes of the sample-mass dependence of the kinetic parameters be understood at a more fundamental level. The isothermal mass-loss process of molten NH_4NO_3 was chosen for the examination of the sample-mass dependence of the kinetic parameters, determined by the conventional method of kinetic calculation for the thermal decomposition of a solid. A possible way of obtaining kinetic parameters that fulfil the “independence of sample mass” criterion is discussed.

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 2.5, 5.0, 10.0, 12.5 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 power compensation DSC at various constant temperatures in the range 440–482 K were carried out using Rigaku Thermoflex TG-DSC(8085E1) instrument, in nitrogen flowing at a rate of 30 ml min^{-1} .

The isothermal mass-loss data were processed kinetically with a microcomputer. The linearity of the kinetic plots was assessed in terms of the correlation coefficient γ of the linear regression analyses to determine the kinetic obedience and the Arrhenius parameters.

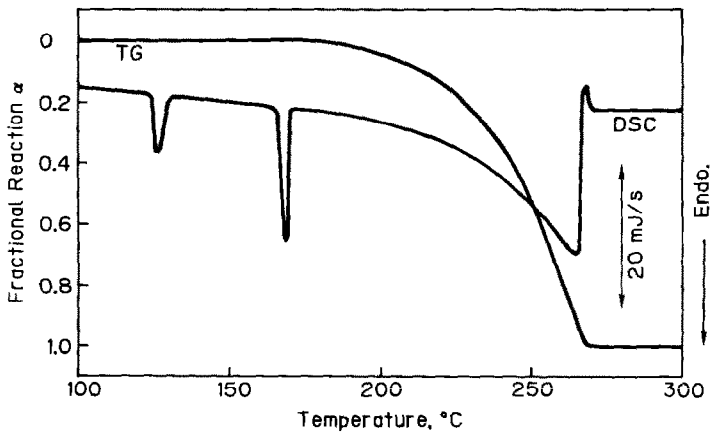


Fig. 1. Typical TG and DSC curves for the non-isothermal change of NH_4NO_3 at the heating rate of 5.0 K min^{-1} .

RESULTS AND DISCUSSION

Figure 1 shows typical TG and DSC curves for the thermal change of NH_4NO_3 recorded at a heating rate of 5.0 K min^{-1} . The endothermic peak at around 125°C corresponds to a crystallographic transformation. The mass loss follows the melting at around 165°C . This process seems to include evaporation [20] and/or decomposition



For safety, it must be remembered that the decomposition of NH_4NO_3 at reduced pressures or at much higher temperatures may lead to explosion.

Figure 2 shows the effect of sample mass on the plot of fractional reaction α versus time t for the mass-loss process of molten NH_4NO_3 at

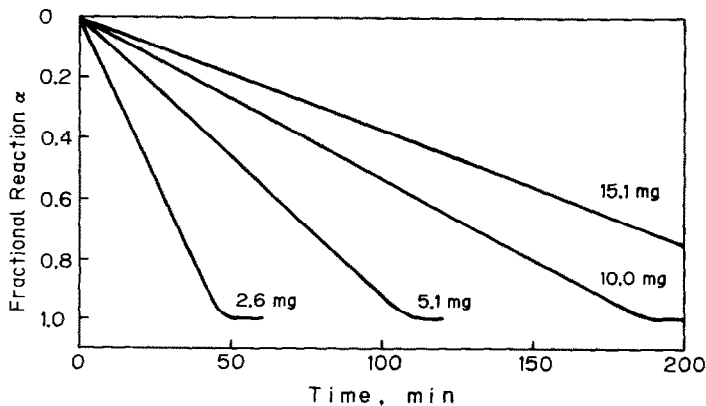


Fig. 2. Effect of sample mass on the plots of α against t for the isothermal mass-loss process of molten NH_4NO_3 at 460 K .

460 K. A linear relationship is observed between α and t , irrespective of the sample mass examined. This implies that the reaction proceeds at a constant rate and, thus, under a quasi-isothermal and quasi-isobaric condition. A longer time is required for the larger sample masses to complete the process. Kinetic obedience was determined by plotting various kinetic model functions $F(\alpha)$ versus t , according to

$$F(\alpha) = k_{\text{app}} t \quad (2)$$

where k_{app} is the apparent rate constant. The excellent kinetic obedience to the one-dimensional phase-boundary-controlled (R_1) law was confirmed within the range $0.03 < \alpha < 0.92$. It follows that the reaction proceeds according to the R_1 law by releasing the reactant and/or decomposition products, N_2O and H_2O , from the surface of the melt, as was expected. The temperature dependence of k_{app} was estimated using the Arrhenius equation

$$k_{\text{app}} = A_{\text{app}} \exp(-E_{\text{app}}/RT) \quad (3)$$

where A_{app} and E_{app} are the apparent pre-exponential factor and activation energy, respectively, R the gas constant and T the temperature. Table 1 lists the apparent Arrhenius parameters for the respective sample mass determined by plotting $\ln k_{\text{app}}$ against the reciprocal absolute temperature T^{-1} . With increasing sample mass, slight but detectable decrease was observed in both E_{app} and A_{app} .

The physico-geometrical model for the R_1 law is illustrated in Fig. 3. The value of α can be expressed as

$$\alpha = \frac{h_0 - h}{h_0} \quad (4)$$

where h_0 and h are the heights of reactant from the bottom at $t = 0$ and $t = t$, respectively. When the advancement of the reaction front obeys the

TABLE 1

The effect of sample mass on the apparent Arrhenius parameters, E_{app} and A_{app} , determined for the isothermal mass-loss process of molten NH_4NO_3

| Sample mass (mg) | Temp. range measured (K) | E_{app} (kJ mol ⁻¹) | lg A_{app} (s ⁻¹) | $-\gamma^a$ |
|------------------|--------------------------|--|--|-------------|
| 2.59 ± 0.03 | 441.9–476.6 | 88.6 ± 2.7 | 6.6 ± 0.3 | 0.9977 |
| 5.08 ± 0.02 | 445.3–481.5 | 85.2 ± 2.8 | 5.9 ± 0.3 | 0.9967 |
| 10.01 ± 0.02 | 449.0–478.0 | 85.1 ± 3.0 | 5.6 ± 0.4 | 0.9932 |
| 12.54 ± 0.02 | 442.8–482.5 | 84.6 ± 3.6 | 5.5 ± 0.4 | 0.9909 |
| 15.08 ± 0.01 | 441.8–483.6 | 83.8 ± 2.6 | 5.3 ± 0.3 | 0.9971 |

^a Correlation coefficient of the linear regression analysis of the $\ln k_{\text{app}}$ vs. T^{-1} plot.

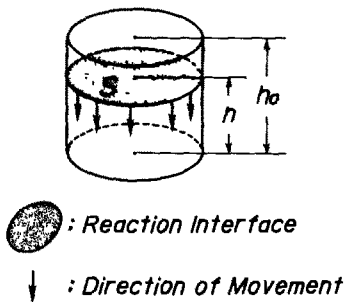


Fig. 3. Schematic representation of the one-dimensional phase-boundary-controlled, R_1 , model.

linear law, the value of h at t can be written as

$$h = h_0 - kt \tag{5}$$

with

$$k = \frac{d(h_0 - h)}{dt} \tag{6}$$

Combining eqns. (4) and (5), the R_1 law is obtained as

$$\alpha = \frac{k}{h_0} t \tag{7}$$

The term h_0 can be replaced by

$$h_0 = \frac{V_0}{S} = \frac{m}{S\rho} \tag{8}$$

where V_0 is the volume at $t = 0$, S the area of reaction interface, m the original sample mass, and ρ the volume density. Accordingly, the k_{app} used in the above kinetic calculation is expressed as

$$k_{app} = \frac{kS\rho}{m} \tag{9}$$

If we use k_{app} for the Arrhenius plot, the Arrhenius equation can be rewritten as

$$\ln\left(\frac{kS\rho}{m}\right) = \ln\left(\frac{AS\rho}{m}\right) - \frac{E_{app}}{RT} \tag{10}$$

with

$$\frac{AS\rho}{m} = A_{app}$$

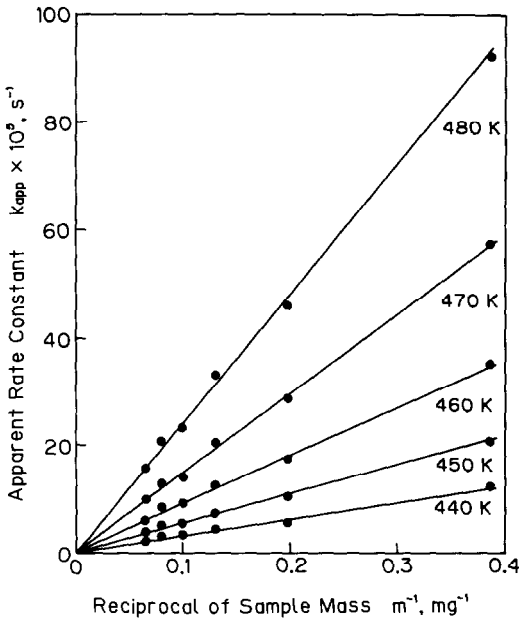


Fig. 4. Plots of the apparent rate constant k_{app} against the reciprocal of sample mass m^{-1} at various temperatures.

As can be seen from eqn. (10), E_{app} is not sample-mass dependent but A_{app} is. The gradual decrease in A_{app} in Table 1 can be explained by the above mathematical relationship, whereas the decrease in the E_{app} cannot.

According to eqn. (9), a linear interdependence is expected between k_{app} and m^{-1} . Figure 4 shows the k_{app} versus m^{-1} plots at various constant

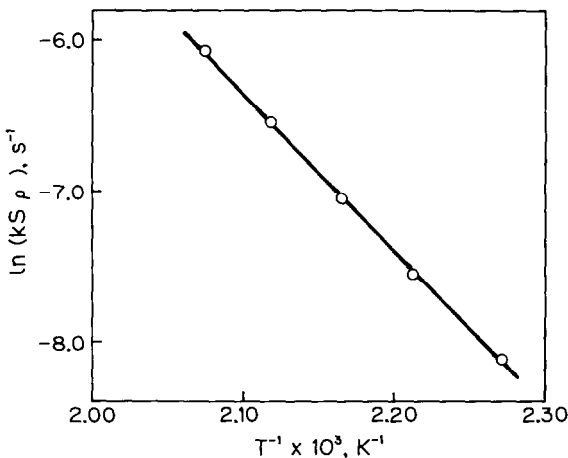


Fig. 5. A plot of the logarithm of apparent specific rate constant $\ln(kS\rho)$ against the reciprocal of temperature T^{-1} .

TABLE 2

The effect of sample mass on the apparent Arrhenius parameters, E_{app} and $AS\rho$, determined for the isothermal mass-loss process of molten NH_4NO_3

| Sample mass (mg) | E_{app} (kJ mol ⁻¹) | lg($AS\rho$) (s ⁻¹) | $-\gamma^a$ |
|------------------|-----------------------------------|-----------------------------------|-------------|
| 2.59 ± 0.03 | 86.6 ± 2.5 | 6.8 ± 0.3 | 0.9979 |
| 5.08 ± 0.02 | 85.2 ± 2.8 | 6.6 ± 0.3 | 0.9970 |
| 10.01 ± 0.02 | 85.5 ± 3.0 | 6.7 ± 0.3 | 0.9934 |
| 12.54 ± 0.02 | 85.0 ± 3.5 | 6.6 ± 0.3 | 0.9912 |
| 15.08 ± 0.01 | 85.9 ± 2.6 | 6.7 ± 0.3 | 0.9975 |

^a Correlation coefficient of the linear regression analysis of the $\ln(kS\rho)$ vs. T^{-1} plot.

temperatures. The slope of the plots, i.e. $kS\rho$, represents the apparent specific rate constant, independent of the sample mass. Sample-mass independent Arrhenius parameters can be obtained by plotting $\ln(kS\rho)$ against T^{-1} . Such an Arrhenius plot is shown in Fig. 5. The apparent values of E_{app} and $\lg(kS\rho)$ were 86.2 ± 2.0 kJ mol⁻¹ and 6.7 ± 0.2 s⁻¹, respectively, with $\gamma = -0.9992$.

The effect of sample mass on the apparent Arrhenius parameters was again estimated by plotting $\ln(kS\rho)$ against T^{-1} for the respective sample mass. Table 2 lists the apparent Arrhenius parameters, showing the unique values independent of sample mass. This implies that the unexpected change in E_{app} given in Table 1 is avoided by the sample-mass independent Arrhenius plot. However, the sample-mass dependence of E_{app} can be explained in relation to the so-called kinetic compensation effect, i.e. a linear interdependence among the values of E_{app} , $\ln A_{app}$ and the measured temperature interval ΔT [21], which is explained as a mathematical consequence of the exponential form of the temperature dependence of k_{app} [22–24]. Any variation in the respective terms should bring about such an undesired interdependence. When we use the sample-mass-dependent rate constant for the Arrhenius plot, the unexpected change in the E_{app} depending on the sample mass seems to arise from any change in $\ln A_{app}$.

In the case of the thermal decomposition of a solid, where the reaction proceeds by shrinking the reaction interface, the present relationship can be adopted for evaluating the effect of sample mass and particle size in the cases of the bulk and powdered samples, respectively [25]. The application of the present relationship to the actual thermal decomposition of solids will be discussed later [26].

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