TA Instruments

Thermal Analysis & Rheology

Thermal Analysis Application Brief
Kinetics of Drying by Thermogravimetric Analysis

Number TA-134

SUMMARY

Moisture content is an important property of many materials used in chemical reactions or processes since moisture levels that are too high or too low may adversely effect performance and reliability. In addition, drying usually increases production costs. Manufacturers must, therefore, ensure that materials are dried using the optimum conditions of time, temperature and atmosphere. Thermogravimetric analysis (TGA) which measures weight changes in a material as a function of temperature and time provides a convenient method for predicting optimum drying conditions. This is illustrated here for black powder (gun powder). However, the method used is perfectly general and may be used for many solid state decompositions.

INTRODUCTION

Thermal analysis techniques have been widely used to characterize energetic materials such as pyrotechnics, explosives, and solid propellants. For example, differential thermal analysis (DTA), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA) provide information about the thermal stability, heats of explosion and decomposition, ignition temperatures, and reaction kinetics of these materials (1,2).

Moisture content and rate of moisture loss on drying are two other important properties of many energetic materials including black powder. Thermogravimetric analysis (TGA), which can follow weight loss over a wide temperature range, or over a long period of time at a specific temperature, on small (10-100mg) samples, is a technique which rapidly provides data for understanding drying processes. The results yield not only quantitative information about the amount of moisture present, but also information about the rate of weight loss which can be used to determine kinetic parameters.

EXPERIMENTAL

In TGA, the sample is placed in a platinum pan located inside a programmable furnace. In the case of black powder, approximately 60mg of sample was used. Previous determinations under dynamic heating conditions indicated that the powder decomposes (explodes) above 200°C. Hence, the drying experiments were performed isothermally at temperatures below 185°C. The TGA furnace was preheated and equilibrated to the temperature of interest before the sample was introduced. A thermocouple located close to the sample ensured that the temperature during the experiment was within $\pm$ 0.1°C.

RESULTS

Figure 1 shows the weight loss (drying) profiles at several temperatures. The 181°C profile is chosen for further evaluation because it results in completely dried powder (-10.5% moisture) in a reasonable experimental time.

DRYING OF BLACK POWDER

Figure 1
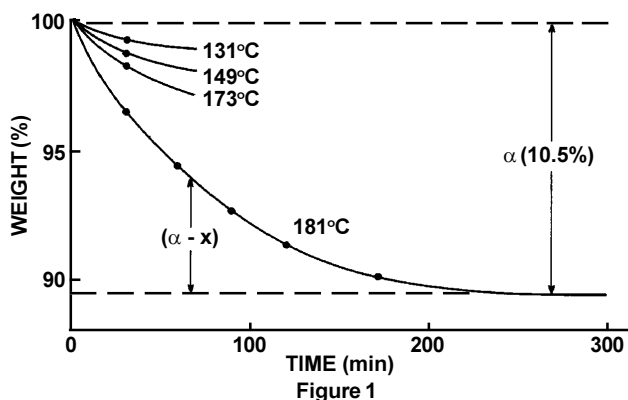
The first step in the treatment of the data for kinetic information is to recognize a reaction mechanism from the shape of the weight loss curve. Where a single mechanism predominates, as in the case of gas phase or solution reactions, it is often possible to describe the reaction by a general rate law:

$$\frac{dC}{dt} = k\,(1-C)^n$$

where: C = fractional conversion
         t = time (min)
         k = rate constant (min⁻¹)
         n = reaction order

where: C = fractional conversion
         t = time (min)
         k = rate constant (min^{-1})
         n = reaction order

Some relatively straightforward solid-to- (solid + gas) reactions include polymer drying, and polymer degradation. It would seem likely therefore that the drying of other materials, such as black powder, may also follow first order kinetics. This is quite simple to check using the experimental data.
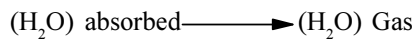
Example

Consider the reaction:

$$A \longrightarrow Products$$
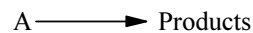
If first order kinetics are followed, then the rate of the reaction is proportional to the concentration of A:

$$Rate = k \bullet (conc.\ A)$$

In the case of drying the reaction is:

$$(H_2O)\ absorbed \longrightarrow (H_2O)\ Gas$$

Let α be the concentration of (H_2O) absorbed at t=o and $(\alpha - x)$ be the concentration of (H_2O) absorbed at any other time denoted by t.
The reaction rate for desorbtion is: $\dfrac{dx}{dt} = k\,(\alpha - x)$

On Integration, this equation becomes:

$$k = \frac{1}{t}\ln\left(\frac{\alpha}{\alpha - x}\right)$$

Using values of α, α-x, and t from the 181°C experimental curve shown in Figure 1, the rate constant, k, can be calculated at any point in the reaction. The actual data is shown in Table 1.

Table 1
Black Powder Drying
Experimental Data

t (min)	α-x (%wt)	k (min⁻¹)
30	7.20	0.0113
60	5.12	0.0113
90	3.50	0.0117
120	2.25	0.0125

Within experimental accuracy, this data is consistent with first order kinetics at least up to t = 60 min.

For more complex solid state reactions, the simple practice of guessing the reaction order is not applicable and a more general method must be used to find the reaction mechansim. Many solid state reactions take place in three stages, which may be described as follows:

1. Induction - formation of reaction sites or nuclei
2. Acceleration - reaction interface increasing
3. Deceleration - reaction interface decaying

It is expected that solid state reactions will follow a large variety of kinetic equations. In fact, the apparent occurance of simple "order" equations is mainly coincidential. Many authors have derived expressions which reflect the nature of various reaction types. These are summarized in the book by Keattch and Dollimore (3) and may be conveniently recognized from experimental data using the *Reduced Time Plot* method of Sharp et al (4). In this method, all forms of kinetic expression are written in the form:
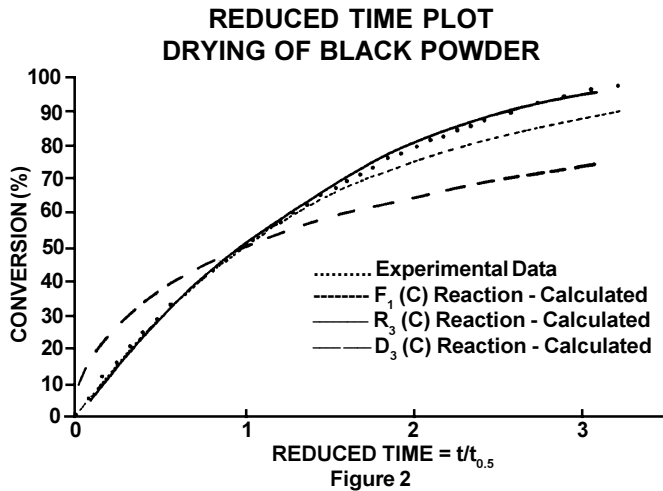
$$F\,(C) = A\,\frac{t}{t_{0.5}}$$

where: C   = fractional conversion
         $t_{0.5}$ = reaction's halflife
                      (time to 50% conversion)
         F (C)   = kinetic expression
         A   = a constant calculated from the actual
                      form of the kinetic expression.

Sharp treats nine kinetic equations in this way, calculating values of A and plotting graphs of C against $t/t_{0.5}$ for each, each graph having a characteristic shape. These nine reaction types and their corresponding A values are given in Table 2.

Table 2
Reaction Types

Reaction Type	A Value	Rate-controlling Process
D_1 (C)	0.2500	Diffusion, one dimensional
D_2 (C)	0.1534	Diffusion, two dimensional
D_3 (C)	0.0426	Diffusion, three dimensional (spherical symmetry)
D_4 (C)	0.0367	Diffusion, three dimensional (contracting sphere model)
R_2 (C)	0.2929	Moving phase boundary, two dimensional
R_3 (C)	0.2063	Moving phase boundary, three dimensional (contracting sphere model)
A_2 (C)	0.8326	Random Nucleation, two dimensional
A_3 (C)	0.8850	Random Nucleation, three dimensional
F_1 (C)	-0.6931	Random Nucleation, first order decay law

The experimental results at 181°C (Figure 1) can be reevaluated using Sharp's approach and plotted as shown in Figure 2. Three calculated curves from Sharp's paper are also shown in Figure 2. These are the theoretical curves for an F_1 (C) type reaction (first order decay), an R_3 (C) type reaction and a D_3 (C) diffusion controlled reaction.

**REDUCED TIME PLOT
DRYING OF BLACK POWDER**

.... Experimental Data
-------- F_1 (C) Reaction - Calculated
———— R_3 (C) Reaction - Calculated
— — D_3 (C) Reaction - Calculated

Figure 2

The theoretical F_1 (C) and R_3 (C) curves are both excellent fits to the experimental curve up to about $t/t_{0.5} = 1$ supporting the conclusions reached by substituting experimental data into the first order rate equation. Beyond $t_{0.5}$ the fit of the F_1 (C) curve becomes progressively poorer, but in the latter stages of the reaction the R_3 (C) curve becomes a good fit with the experimental curve.

The theoretical model on which the R_3 (C) curve is based assumes a reaction mechanism in which the rate determining step is the movement of a spherical reaction zone as it contracts towards the center of a solid particle (5). The mechanism for the loss of water from the black powder implied by this data is therefore easy to visualize. First, water is lost from the surface of the powder particles in a random manner, giving rise to the first order kinetics often found for many polymer drying processes. Approximately half the total moisture is lost in this way but, as the reaction proceeds, water from below the surface of the particles starts to vaporize. The rate of this reaction is now controlled by the speed with which the reaction zone moves into the powder particles, not by the rate with which the water diffuses to the surface of the particles. (This would follow D_3 (C) kinetics, the curve which does not fit the experimental data, as shown in Figure 2).

Having established the reaction mechanism, it is now possible to calculate the activation energy and Arrhenius frequency factor for the drying reaction using the equation:

$$\ln k = \ln Z - \frac{E}{RT}$$

where: k = rate constant (min⁻¹)
Z = Arrhenius frequency factor (min⁻¹)
T = temperature (K)
E = activation energy (J/mol)
R = gas constant (8.314 J/mol)

Using the data from the four isothermal weight loss curves in Figure 1, k values can be calculated according to first order kinetics* at=30 min and plotted as ln k against 1/T (Figure 3). This gives a reasonable straight line, the gradient of which is -E/R. The activation energy, E, measured from this line is 63.2 kJ/mol and, substitution of this value into the Arrhenius equation gives a value of 187000 min⁻¹ for the frequency factor, Z.

KINETICS OF DRYING BLACK POWDER

Figure 3
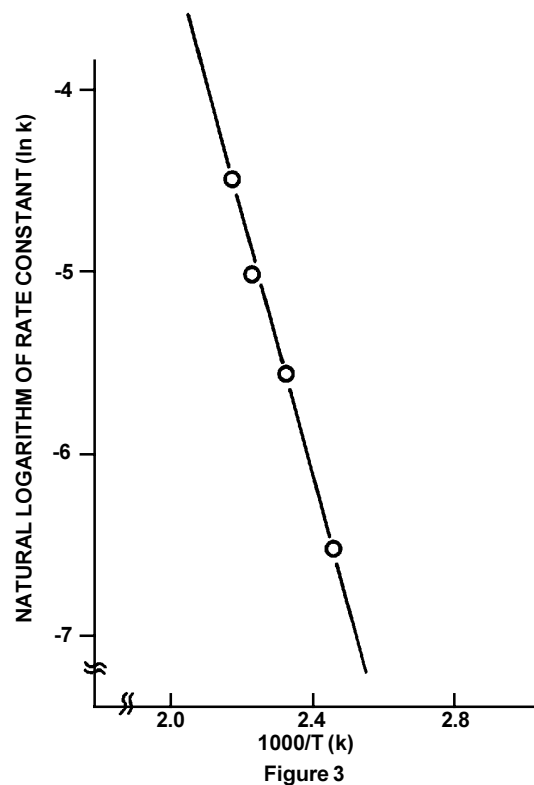
It is now possible to use all these kinetic values and experimental data at 181°C to calculate the approximate drying time at any temperature via the following equation:

$$t \text{ drying time} = \frac{4.5 \times 0.0113}{k_t}$$

where: t = drying time at the desired temperature (min)
k = calculated rate constant at the desired temperature (min⁻¹)

*It would also be possible to calculate k values using the R_3 (C) equation, but at this point in the reactions, the actual k value, would be very similar to the one used here.

Table 3 shows the drying times predicted by those calculations. Of course, this data needs to be tested experimentally, particularly since the reaction mechanism may change at high $t/t_{0.5}$ values.

Such figures could be used in this manufacturing process to help choose the optimum drying times bearing in mind the thermal stability of the material and balancing this against the cost of long drying periods.

Table 3
Predicted Black Powder Drying Time

Temperature (°C)	Drying Time at This Temperature (Hours)
100	202
110	118
120	71
130	44
140	28
150	18
160	12
170	8
180	5
190	4
200	3

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