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Application of calorimetry to investigations of kinetics and energetics of oxidation of fuels. Experimental and calculational methods for initial rates

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Abstract

A calorimetric method for obtaining isothermal initial rates of reaction (applied to oxidation of bitumen) is reviewed and a new method for carrying out calculations with thermograms from electrical calibration and chemical reaction experiments is presented.

INTRODUCTION

It is common practice to determine the total heating value of a solid or liquid fuel by means of constant volume ("bomb") combustion calorimetry. This kind of calorimetry is well known and will not be discussed in this paper.

Recent investigations [1–5] have shown that a different kind of calorimetry is useful for investigating the rates of oxidation of bitumen (from "oil" or "tar" sands) that are important with respect to underground (in situ) combustion projects. In this paper we present a brief review of the experimental method (which can also be applied to other problems), followed by an account of a new method for obtaining the desired information from the experimental data.

REVIEW OF METHOD

The calorimeter [1] consists of a thin-walled metal tube that fits securely in a hole through the center of a cylindrical block of aluminum, which contains a heater for electrical calibration and a calibrated platinum resistance thermometer. The block of aluminum is enclosed in shields that minimize heat exchange with the surrounding furnace that is maintained at constant temperature. External equipment provides for a flow of oxidizing gas through the calorimeter at known flow rate and pressure, and also permits analysis of gaseous products that are swept out of the calorimeter. By suitable choice of mass of fuel in the central tube and mass of the block of aluminum, it is possible to make the temperature change resulting from oxidation of bitumen be in the range of 1–2 °C, which is large enough to permit meaningful measurement of temperature as a function of time and small enough to justify saying that the resulting rate of oxidation is an isothermal rate that applies at the average temperature of the experiment. In this way we have avoided the difficulties of trying to sort out the non-isothermal kinetics applicable to a system in which many reactions take place.

If heat transfer in the calorimeter (reaction tube and aluminum block with the thermometer and heater) were infinitely fast, our experimental results in the form of temperature as a function of time would lead directly to the desired initial rates of heat production, $(\mathrm{d}Q/\mathrm{d}t)_i$. For our real calorimeter with finite rates of heat transfer, it is necessary to carry out a more complicated calculation that makes use of appropriate electrical calibration.

CALCULATION METHODS

Our earlier analysis [1] of heat transfer led to

$$W = c(\mathrm{d}\,\Delta T/\mathrm{d}t) + \kappa\,\Delta T \tag{1}$$

in which W is the power delivered electrically to the calorimeter or produced by the chemical reaction under investigation, c is the total heat capacity, κ is the overall thermal conductance and ΔT is the temperature rise at time t. The solution of differential eqn. (1) for constant W is

$$\Delta T = \Delta T_\infty[1 - \exp(-\kappa t/c)] \tag{2}$$

in which ΔT_∞ is the temperature rise approached asymptotically when heating time becomes infinite. The first method [1–3] of applying eqn. (2) involved differentiation with respect to time and taking logarithms to obtain

$$\ln(\mathrm{d}\,\Delta T/\mathrm{d}t) = \ln[(\kappa/c)\,\Delta T_\infty] - (\kappa/c)t \tag{3}$$

From the record (thermogram) of temperature rise versus time, values of $\mathrm{d}\,\Delta T/\mathrm{d}t$ at various times were calculated graphically and then $\ln(\mathrm{d}\,\Delta T/\mathrm{d}t)$ was plotted against time, leading to a straight line with slope equal to $-\kappa/c$ and intercept equal to $\ln[(\kappa/c)\,\Delta T_\infty]$. Combining the slope and the intercept leads to a value for ΔT_∞. At long times when power input is just balanced by heat loss from the calorimeter, we have a constant $\Delta T = \Delta T_\infty$ and $\mathrm{d}\,\Delta T/\mathrm{d}T = 0$. Equation (1) therefore gives

$$W = \kappa\,\Delta T_\infty \tag{4}$$

from which κ was evaluated. With the value of κ known, c was evaluated from the slope of the line based on eqn. (3). All of these calculations were done with data from electrical calibration experiments that immediately preceded and followed chemical reaction experiments.

Tests [1] of the calculation method summarized above were satisfactory, but improvements of two kinds are possible. First, the procedure outlined above is time consuming, so that some computerized procedure is attractive. Second, it is desirable to replace unspecified fitting and extrapolation procedures by clearly (mathematically) specified procedures. Our new method of calculation is described as follows.

The basis for our method of calculation is the "maximum likelihood principle" [6], using values of ΔT_∞ and κ/c that will minimize some specified function. The specified function (F) used here is the sum of squares of differences between $\Delta T_j(\exp)$ values from electrical calibration experiments and $\Delta T_j(\text{calc})$ values obtained from eqn. (2). We express this F as

$$F = \sum_{j=1}^{n} f_j^2 = \sum_{j=1}^{n} \left[\Delta T_j(\exp) - \Delta T_j(\text{calc})\right]^2$$

$$= \sum_{j=1}^{n} \left[\Delta T_j(\exp) - \Delta T_\infty\left\{1 - \exp\left[-(\kappa/c)t_j\right]\right\}\right]^2 \tag{5}$$

where n is the number of data points taken from the thermogram resulting from an electrical calibration experiment.

Inspection of the electrical calibration thermogram leads to an initial estimate of ΔT_∞ that will be used later. First, however, we have used this initial ΔT_∞ to specify the distribution of data points taken from the continuous thermogram. For $\Delta t < 0.7\,\Delta T_\infty$, we use ΔT points at constant time intervals represented by Δt_1. For $\Delta T > 0.7\,\Delta T_\infty$, we use ΔT points at longer time intervals $\Delta t_2 = 2\ \Delta t_1$.

The necessary conditions for F to be a minimum are

$$\partial F/\partial(\Delta T_\infty) = 0 \qquad \text{and} \qquad \partial F/\partial(\kappa/c) = 0 \tag{6}$$

Direct application of eqns. (5) and (6) is awkward because of the non-linear relationship between ΔT and κ/c in eqn. (2), which requires that we have very good initial estimates of ΔT_∞ and κ/c or many iterations. To minimize the need for accurate initial estimates of ΔT_∞ and κ/c, we begin by expanding eqn. (5) into a first-order (linear) Taylor's series about ΔT_∞ and κ/c to obtain

$$F = \sum_{j=1}^{n} \left\{f_j^* + \left(\partial f_j/\partial\,\Delta T_\infty\right)^* \Delta(\Delta T_\infty) + \left[\partial f_j/\partial(\kappa/c)\right]^* \Delta(\kappa/c)\right\}^2 \tag{7}$$

For the first calculation based on eqn. (7), the superscript * indicates the initial estimates of ΔT_∞, κ/c and quantities derived from these initial estimates. For the second, third,... iterations, the superscript indicates the estimates of these quantities from the preceding iteration. Definitions of $\Delta(\Delta T_\infty)$, and $\Delta(\kappa/c)$ in eqn. (7) are

$$\Delta(\Delta T_\infty) = \Delta T_\infty - (\Delta T_\infty)^* \tag{8}$$

and

$$\Delta(\kappa/c) = \kappa/c - (\kappa/c)^* \tag{9}$$

Derivatives of f_j with respect to ΔT_∞ and (κ/c) are

$$\partial f_j/\partial(\Delta T_\infty) = \exp[-(\kappa/c)t_j] - 1 \tag{10}$$

and

$$\partial f_j/\partial(\kappa/c) = -\Delta T_\infty t_j \exp[-(\kappa/c)t_j] \tag{11}$$

Application of the conditions specified by eqns. (6) to eqn. (7) leads to two simultaneous equations that are linear in the unknowns ΔT_∞ and κ/c

$$\sum_{j=1}^{n} f_j^*(\partial f_j/\partial\,\Delta T_\infty)^* + \Delta(\Delta T_\infty)\sum_{j=1}^{n}(\partial f_j/\partial\,\Delta T_\infty)^{*2} + \Delta(\kappa/c)\sum_{j=1}^{n}[\partial f_j/\partial(\kappa/c)]^*(\partial f_j/\partial\,\Delta T_\infty)^* = 0 \tag{12}$$

$$\sum_{j=1}^{n} f_j^*[\partial f_j/\partial(\kappa/c)]^* + \Delta(\Delta T_\infty)\sum_{j=1}^{n}(\partial f_j/\partial\,\Delta T_\infty)^*[\partial f_j/\partial(\kappa/c)]^* + \Delta(\kappa/c)\sum_{j=1}^{n}[\partial f_j/\partial(\kappa/c)]^{*2} = 0 \tag{13}$$

The first step in our procedure is to look at the experimental recording of ΔT against time for an electrical calibration experiment and estimate the long-time value designated ΔT_∞^*. Then we use the experimental value of ΔT for some value of t in eqn. (2) with ΔT_∞^* to obtain the estimated $(\kappa/c)^*$.

Second, these initial estimates of ΔT_∞^* and $(\kappa/c)^*$ are used in eqn. (5) to obtain first estimates of f_j^* for each previously selected point on the experimental thermogram. Next, first estimates of the derivatives in eqns. (12) and (13) are evaluated with eqns. (10) and (11).

Third, the simultaneous eqns. (12) and (13) are solved for $\Delta(\Delta T_\infty)$ and $\Delta(\kappa/c)$. Using these values in eqns. (8) and (9) gives second estimates of ΔT_∞ and κ/c. These second (now the most recent) estimates are then used for another round of similar calculations leading to third estimates of ΔT_∞ and κ/c. The iterative procedure is continued until calculated values of $\Delta(\Delta T_\infty)$ and $\Delta(\kappa/c)$ are suitably small, thus making the first-order Taylor's series expansion (as in eqn. 7) an accurate approximation.

Equation (1) shows that the initial rate of power production in an oxidation (or other reaction) experiment is

$$W_{\mathrm{i}}^{\mathrm{ox}} = c(\mathrm{d}\,\Delta T/\mathrm{d}t)_{\mathrm{i}}^{\mathrm{ox}} \tag{14}$$

Using $(\Delta T,\ t)$ points from the oxidation thermogram, the constants in an equation of the form

$$\Delta T^{\mathrm{ox}} = A + Bt + Ct^2 + \cdots \tag{15}$$

are evaluated. Then $(\mathrm{d}\,\Delta T/\mathrm{d}t)_{\mathrm{i}}^{\mathrm{ox}} = A$ is used in eqn. (14) with the value of c from electrical calibration to obtain the desired initial rate of heat production as

$$W_{\mathrm{i}}^{\mathrm{ox}} = (\mathrm{d}Q/\mathrm{d}t)_{\mathrm{i}}^{\mathrm{ox}} = cA \qquad (16)$$

In relating the initial rate of heat production to a chemical rate of reaction it is convenient to work with the specific (per gram) initial rate represented by $w_{\mathrm{i}}^{\mathrm{ox}} = W_{\mathrm{i}}^{\mathrm{ox}}/m$, in which m is the mass of bitumen (or other reactive material) in the central reaction tube.

The value of κ from electrical calibration is not used for evaluation of the initial rate, but is used [1] for evaluation of the total heat of oxidation.

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