ISOKINETIC PARAMETERS FOR IGNITION OF SOLIDS IN FIRE MODELS

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The study of the rates of chemical reactions and their relationship to temperature began in the 19th century with empirical measurements of the time required to reach a particular reaction endpoint at a constant temperature. By the mid-20th century the theory of reaction rates had advanced and instruments had been developed in which the temperature of the sample could be increased at a constant rate. These nonisothermal methods are now widely used to determine the kinetic parameters of thermal decomposition reactions of combustible solids for fire modeling because of their convenience. In this presentation, the mathematical relationship between measurements at constant temperature (isothermal) and constant heating rate (nonisothermal) is developed and it is shown that there is a point in the temperature history of a single-step reaction at which the isothermal and nonisothermal reaction rates are equal. This equal (iso) kinetic point occurs at a temperature, early in the heating history of nonisothermal experiments, at which the reaction rate begins to accelerate and ignition of the solid commences. The isokinetic temperature is the basis for a new method of nonisothermal kinetic analysis that provides a direct measurement of the Arrhenius frequency factor A and activation energy E_a for the elementary fuel generating reaction of solids without any assumptions about the relationship between these parameters (i.e., kinetic compensation) or the reaction mechanism.