THE INFLUENCE OF HEAT TRANSFER ON REDUCED-TIME PLOTS

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Abstract

A theoretical approach has been used to show that, except for certain types of reaction mechanism, the ease with which it is possible to distinguish the form of the reaction mechanism by the reduced-time plot method depends particularly on the rate of transfer of heat into the sample. The original reduced-time plots [1] were calculated from model equations which assume that the sample is, from the outset, at a fixed temperature and remains under isothermal conditions throughout the reaction. The variations produced in the appearance of reduced-time plots when the sample is programmed to rise to a given fixed temperature through various temperature schedules have been investigated. It is shown that even relatively rapid temperature rises can produce distortion of the reduced-time plots for various reaction equations. If the reaction mechanism is known, however, fairly accurate values of the activation energy for the reaction can be determined, even when the furnace used has relatively poor heat-transfer characteristics.

Keywords: activation energy, heat transfer, kinetics, reaction mechanism, reduced-time plots

Introduction

The associated techniques of TG and DTG are often used to determine kinetic parameters, namely the pre-exponential factor and the activation energy of a given reaction. However, to determine these parameters it is necessary initially to be able to determine the kinetic mechanism of the reaction which is occurring. The classical method is to carry out an experiment under isothermal conditions (e.g. to follow the change in mass with respect to time at constant temperature). From the results, a reduced-time plot, of fraction reacted, \( x \), against \( t/t_{0.5} \), where \( t_{0.5} \) is the time taken to reach a fraction reacted of 0.5, can be drawn. This reduced-time plot can then be compared with a calculated set of reduced-time plots for many different reaction mechanisms in order to deter-
mine the most probable type of mechanism being followed by the reaction under study, as suggested by Sharp et al. [1].

Sometimes it is difficult to determine the specific equation from this technique, for some reduced time plots of experimental data do not follow precisely any of the curves given in reference [1]. These differences have been attributed to various causes, particularly that the reaction does not follow any of the model reactions under consideration, or that there is an ‘induction’ period prior to the main reaction. There is, however, an alternative explanation for many such deviations. The curves produced in reference [1] were generated from model equations, no account being taken of either the initial heating of the sample or the temperature variations which can occur within the sample during the reaction.

**Practical considerations**

In a practical experiment the sample has, in principle, to be heated up to the isothermal temperature infinitely quickly, which is, of course, impossible to achieve and difficult to approach. The time taken to reach the isothermal temperature is dependent on the furnace design and the size of the sample. If this time is relatively long, some degree of reaction will inevitably have taken place before the isothermal temperature is reached, thus distorting the shape of the resulting reduced-time plot. Once equilibrium has been established, and if no reaction has occurred in the sample, there will be a small but constant temperature difference between the measuring thermocouple and the sample, sufficient for some heat to flow to overcome heat losses. However, when an endothermic reaction is occurring within the sample, more heat must be supplied to sustain the reaction and so this temperature difference will increase, and the sample temperature will be lower than that of the measuring thermocouple. Furthermore the magnitude of this increase is dependent on the reaction rate, so that, as the rate of reaction varies, so does this temperature gradient. Thus the temperature of the sample will not be isothermal throughout the reaction. This temperature gradient will be dependent on the heat transfer characteristics of the space between the heat source and sample, as well as the conductivity of the sample. The space between the source of heat and sample will of necessity be a gaseous space, which is usually (except for helium) a poor conductor of heat.

For exothermic reactions, heat is given out from the sample as the reaction proceeds so that the temperature of the sample will be higher than that of the measuring thermocouple and will still vary with the reaction rate. It is also difficult to measure the actual sample temperature in a TG apparatus since the temperature measurement has, of necessity, to be located outside the sample. Theoretical calculations for endothermic reactions, using a heat-transfer model