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Note

REDUNDANCY OF ISOTHERMAL KINETIC DATA TO BACK UP NON-ISOTHERMAL KINETIC DATA

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Various mathematical methods have been proposed to analyse the non-isothermal kinetic data of heterogeneous transformation processes occurring in solid-state conditions. However, these methods are not always efficacious for determining unequivocally the exact kinetic model indicating the functional forms of $g(\alpha)$ and/or $f(\alpha)$ of the rate-controlling step. Criado et al. [1], in their thermogravimetric studies on the decomposition process of calcium carbonate, analysed the non-isothermal kinetic data utilizing the method of Coats and Redfern [2]. These analyses revealed that for the decomposition process of $CaCO_3$ under non-isothermal conditions, two rate-controlling mechanisms were equally probable: the interface chemical reaction controlled mechanism (R_3) and the Jander diffusion mechanism (D_3). With the Coats and Redfern method of analysis, it was practically impossible to distinguish between them. In order to obviate this difficulty, they concluded that the simultaneous analysis of both TG and DTG traces along with a single isothermal run makes it possible to establish the rate-controlling mechanism of a thermal decomposition reaction merely through a kinetic method, without any additional information.

Tang [3] has reiterated this point emphatically and claimed that isothermal data are, in fact, “indispensible” in such types of analysis despite their inherent problem of zero-time inaccuracy.

Bagchi and Sen [4], while reanalysing the non-isothermal kinetic data of Fong and Chen [5] for dehydroxylation of $Mg(OH)_2$, demonstrated the inadequacy of the Coats–Redfern method in identifying unambiguously the rate-controlling mechanism of the process. They have also demonstrated that with the help of the combined integral and differential method, suggested by them, it was possible to discern the most probable rate-controlling mechanism for the dehydroxylation process of $Mg(OH)_2$. In other words, this means that if the mathematical method of analysis of non-isothermal kinetic data is discerning enough to discriminate the probable rate-controlling mechanism, it is unnecessary to have the time-consuming isothermal runs to back up the non-isothermal kinetic data.

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It was further pointed out by Bagchi and Sen [6] that the calculated values of the Arrhenius doublets (i.e. E and A), especially for non-isothermal heterogeneous processes, have only limited validity and, therefore, cannot (and should not) be utilized for pin-pointing the rate-controlling mechanism solely on the basis of the values calculated. It has been amply demonstrated [6] that various process variables (e.g. heating rate, particle size, etc.) have a profound influence on the values of the derived Arrhenius parameters which are also influenced by the particular method of analysis employed. Any conclusion regarding the rate-controlling mechanism should, therefore, centre mainly on the physical phenomena occurring and also on the existence of the kinetic compensation effect.

Finally, the explicit advantages of non-isothermal experimentations over the traditional isothermal ones are summarized here.

(1) It is possible to determine the reaction onset temperature (T_0) very precisely by non-isothermal experiments, which is almost impossible for isothermal runs. The zero-time error is therefore absent for dynamic experimentations. For isothermal runs, the correction for zero-time error is usually done by extrapolation based on considerations which often tend to be purely arbitrary.

(2) A considerable portion of the specimen is likely to undergo some reaction during the initial heat-up period of an isothermal run particularly when the temperature of onset of reaction is considerably lower than the temperature of the isothermal experimentation. In these events, the values of the degree of reaction (α) will not be zero at $t = 0$ for an isothermal run. This is likely to bring in another correction for such errors under considerations which also tend to be arbitrary.

(3) For a dynamic run, a single specimen is sufficient to scan the whole experimental temperature range, whereas for every isothermal run, a fresh specimen is required. In the latter case, it would be almost impossible to ensure identical specimen characteristics for each isothermal run unless the specimen is chemically pure in nature, thus precluding the analysis of industrial samples.

Under these considerations, the authors strongly believe that it is of utmost importance to develop a suitable mathematical method of analysis of non-isothermal kinetic data which alone would be capable of unambiguously ascertaining the most probable rate-controlling mechanism of the process under study. In such cases, isothermal runs to back up the findings of non-isothermal kinetic data analysis is not considered necessary.

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