

Why reaction rate does not always obey Arrhenius law during gas-solid reactions?

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Gas-solid reactions are extensively studied by thermal analysis. To describe the kinetics of these reactions, the reaction rate $d\alpha/dt$ (i.e. the derivative of the extent of conversion vs. time) is almost exclusively expressed by the product of a temperature function $k(T)$ by a mathematical function $f(\alpha)$ depending on the kinetic model.

In general, the temperature function $k(T)$ is supposed to follow Arrhenius law with a pre-exponential term and the apparent activation energy E_{app} according to :

$$k(T) = Ae^{-\frac{E_{app}}{RT}} \quad (1)$$

Non-Arrhenius behavior has been observed in many cases such as for example CaO hydroxylation [1] and carbonation [2]. Simon [3] suggested that other $k(T)$ functions than Arrhenius equation may be equally used. Moreover, the use of the Arrhenius equation in model-free methods when such equation is not relevant will necessarily induce E_{app} variation with the extent of conversion. Galwey [4] has recently stated that such variations are inconsistent with the Arrhenius activation model and he wonders how and why this variation.

To precise the origin of such a complexity, it is necessary to come back to the mechanism of growth of the solid product phase which can be decomposed into a series of elementary steps: adsorption/desorption, external interface reaction, internal interface reaction, diffusion of species transferring from an interface to the other.

Several reasons may be invoked to explain the non-Arrhenius behavior of $k(T)$ function (in case of single reaction):

- when the reaction conditions are far from equilibrium, and if a rate-determining step i governs the kinetics, the rate equation involves concentration terms which can be expressed by means of the equilibrium constants K_j (i and j are elementary steps of the growth mechanism, $i \neq j$). Due to adsorption and/or desorption steps, it comes out that the rate may depend of temperature through terms deriving from Langmuir isotherm equation, and thus that it will not follow Arrhenius equation,
- when the reaction conditions are near the equilibrium, the rate will never follow Arrhenius equation since the rate of the opposite reaction of the elementary rate-determining step cannot be neglected compared to that of the direct one.

This is why we generally propose to write the rate equation using a function which accounts for possible complexity of the rate with thermodynamic variables [5]. Examples of rate equations where the temperature term is complex will be presented to illustrate these theoretical considerations.

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