

Universal kinetic approach to the thermal decomposition of solids under different partial pressures of evolved gas

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The effect of the partial pressure of evolved gas ($p(\text{gas})$) on the kinetics of reversible reactions in solid–gas systems has long been studied for gaining more rigorous kinetic descriptions of many important reactions. For the formal kinetic analysis of the process, an accommodation function $a(p(\text{gas}), P_{\text{eq}}(T))$ can be introduced in the fundamental kinetic equation [1].

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) f(\alpha) a(p(\text{gas}), P_{\text{eq}}(T)) \quad (1)$$

An accommodation function such as $a(p(\text{gas}), P_{\text{eq}}(T)) = [1 - (p(\text{gas})/P_{\text{eq}}(T))^n]$ has been used for the formal kinetic analysis [2,3]. However, for some reactions that exhibit significant temperature shift by the effect of $p(\text{gas})$, the conventional accommodation function for $p(\text{gas})$ is not necessary applicable. In addition, the reactions in solid–gas systems are characterized by specific physico-geometric constraints and the consecutive processes comprising the induction period (IP), surface reaction (SR), and phase-boundary-controlled reaction (PBR) [4,5]. Therefore, the effect of $p(\text{gas})$ should be considered separately for each kinetic process.

This study aimed at solving the problem of the influence of $p(\text{gas})$ on each kinetic process of the reactions in solid–gas systems. On the basis of classical theories of the surface nucleation and interface reactions, many possible functional forms of $a(p(\text{gas}), P_{\text{eq}}(T))$ were derived by assuming the component elementary steps in each reaction process and different rate limiting steps. Finally, we obtained a simple analytical form of $a(p(\text{gas}), P_{\text{eq}}(T))$:

$$a(p(\text{gas}), P_{\text{eq}}(T)) = \frac{1}{p(\text{gas})^m} \left[1 - \left(\frac{p(\text{gas})}{P_{\text{eq}}(T)} \right)^n \right] \quad (2)$$

Eq.(2) can be directly introduced into the differential kinetic equation of Eq.(1) and applicable to the kinetic analyses of IP, the isoconversional kinetic analysis for the main reaction process, and the Arrhenius plots for SR and PBR. The variable exponents (m, n) in $a(p(\text{gas}), P_{\text{eq}}(T))$ and the kinetic parameters, E_a , A , and $f(\alpha)$ are optimized simultaneously from the kinetic data recorded under different temperature profiles and different $p(\text{gas})$ through a universal kinetic plot using linear and/or nonlinear least squares analyses. In this presentation, the theoretical basis of Eq.(2) is discussed, and the practical applicability is demonstrated as exemplified by the thermal decompositions of $\text{Ca}(\text{OH})_2$ and $\text{Cu}(\text{OH})_2$ and thermal dehydration of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$.

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