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BRIEF COMMUNICATIONS

Theoretical Considerations on the Temperature and Pressure Dependence of the Kinetics of Reversible Thermal Decomposition Processes of Solids

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Whereas the temperature dependence of reaction rates of reversible solid-state decomposition processes of the type $A_{solid} \rightleftarrows B_{solid} + C_{gaseous}$ has been outlined in numerous theoretical as well as in experimental studies, its simultaneous dependence on the actual pressure of the gaseous product has not been taken into account sufficiently. Theoretical considerations elucidate, however, that specific and reproducible kinetic data, in particular umambiguous values for activation energies, can only be determined under vacuum conditions or in some cases by fulfilling the following precondition: $p_{exp}/p_{equ} = f(T) =$ constant, where p_{exp} is the actual pressure and p_{equ} the equilibrium pressure of the gaseous product. © 1985 Academic Press, Inc.

For a reversible thermal solid-state decomposition process of the type $A_{solid} \rightleftarrows B_{solid} + C_{gaseous}$ a reaction rate v can be determined by mathematical evalation of the equation

$$v = d\alpha/dt = k(T,p) \cdot f(\alpha),$$

where α is defined as the fraction of decomposition ($0 \leq \alpha \leq 1$), t as time, T as absolute temperature, k as the specific temperature- and pressure-dependent rate constant, and $f(\alpha)$ as an algorithm for the description of the actual macroscopic reaction mechanism (*1, 2*).

A conventional method for the quantitative determination of the respective kinetic

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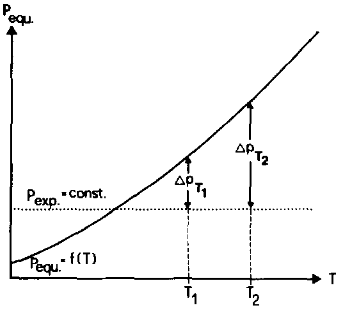

FIG. 1. Schematic representation of the nonlinear dependence of the equilibrium pressure p_{equ} on the reaction temperature T.

parameters, foremost of activation energies, is based on the mathematical evaluation of log k versus $1/T$ Arrhenius plots, which, in turn, are derived from a set of measurements of $\alpha = f(t)$ at different temperatures performed under isothermal conditions. For this procedure the actual pressure in the system is kept constant. The same situation is valid for quantitative measurements performed under nonisothermal conditions, i.e., $\alpha = f(T)$ with T/t = constant. The validity of $f(\alpha)$, i.e., the validity of one and the same macroscopic reaction mechanism within the temperature interval chosen for the quantitative measurements of α is verified by well-established procedures such as α versus $t/t_{0.5}$ plots (*3*).

As is schematically presented in Fig. 1 the equilibrium pressure p_{equ} of the gaseous product formed obeys a nonlinear temperature dependence for any reversible solid-state decomposition process. Therefore, under isobaric experimental conditions the ratio p_{exp}/p_{equ} (where $p_{exp} > 0$; const) obeys a nonlinear temperature dependence as well.

Accordingly, it can be visualized by a schematical $v/p/T$ diagram (Fig. 2) that any quantitative measurement of the temperature dependence of the reaction rate v under isobaric conditions, e.g., for $p_{exp} = p_1$ = constant or $p_{exp} = p_2$ = constant (where $0 < p_1 < p_2 < p_{equ}$), is simultaneously dependent on the actual ratios p_{exp}/p_{equ}, which, as has been shown in Fig. 1, obey a nonlinear temperature dependence.

Consequently, log v versus $1/T$ Arrhenius plots only show the ideally linear course (Fig. 3, curve 1), if the quantitative mea-

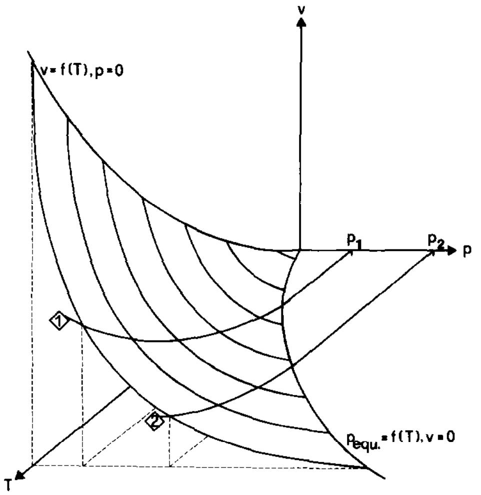

FIG. 2. Diagram representing the pressure and temperature dependence of the reaction rate v for a given reaction mechanism $f(\alpha)$. For curve 1 ($v = f(T, p_1)$) as well as for curve 2 ($v = f(T, p_2)$) the ratios p_{exp}/p_{equ} obey a nonlinear temperature dependence.

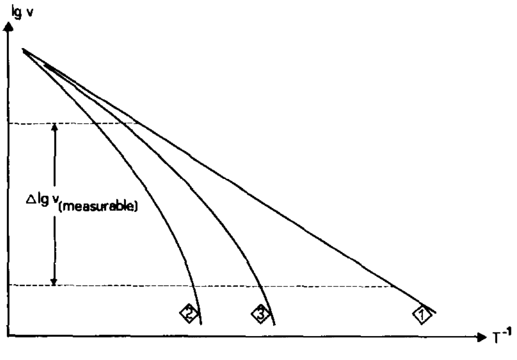

FIG. 3. Diagram showing the pressure dependence of log v versus $1/T$ Arrhenius plots. Curve 1, $v = f(T, p_{exp} = 0)$; curve 2, $v = f(T, p_{exp} = p_2 = \text{constant})$; curve 3, $v = f(T, p_{exp} = p_1 = \text{constant})$; $p_2 > p_1 > 0$. The mathematical determination of the corresponding activation energies E_a therefore yields: $E_a(p_2) > E_a(p_1) > E_a(p = 0)$.

surements of α or v, respectively, are performed under vacuum conditions or by maintaining the ratio $p_{\text{exp}}/p_{\text{equ}}$ constant (see, e.g., (*4, 5*)).

Any different experimental conditions, i.e., $p_{\text{exp}} > 0$, constant (see Fig. 2, curves for p_1 and p_2, respectively), lead to nonlinear curves in the Arrhenius plots (Fig. 3, curves 2 and 3, respectively).

Thus any mathematical evaluation of kinetic parameters, foremost of reaction specific activation energies, derived from experiments performed under isobaric conditions ($p_{\text{exp}} > 0$) yields approximate values. Whereas in many cases such kind of inadequacies are not significant, i.e., the temperature range, within which the respective reaction rates are determined, is relatively narrow and hence the deviations of the ideally linear course of the log v versus $1/T$ Arrhenius plots are negligible, major effects have been observed for the decomposition of calcite (*6*).

Apart from these aforementioned effects the role of merely sample-specific parameters such as the actual structures of the initial material, possible intermediates, and final products, which govern the (topotactic) structural reaction mechanism (*7, 8*) as well as the actual sample morphology (*9*), has to be taken into account for any reasonable determination of reaction specific and reproducible kinetic parameters.

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