New Aspects of the Decomposition Kinetics of Calcite, Part-I. Isothermal Decomposition

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Abstract
Under experimental conditions which tend to minimise the effects of heat and mass transfer, the kinetics of the decomposition of calcite according to CaCO3(s) CaO(s) + CO2(g) is split by the restriction of CO2 transport at the degree of conversion αt when the channels in the CaO(s) surrounding the reactant provide the only diffusion path. Because of the resulting convective cooling beyond αt, the phase boundary reaction proceeds initially with the reaction-only activation energy Ea(1) = 192.89 kJ mol−1 up to αt, after which the reaction proceeds with an apparent activation energy of Ea(2) = 210.33kJ mol−1. The diffusion-controlled reaction proceeds with the mean value of the activation energy Ea(D1) = 0.5 (Ea(1) + Ea(2)) = 201.65 kJ mol−1. The activation energies differ by the same amount, i.e. Ea(D1) − Ea(1) = Ea(2) − Ea(D1) = 8.72 kJ mol−1, equivalent to the degenerate deformation vibration v4 = δ(O-C-O) of calcite observed at 706 cm−1 (infrared) and 714 cm−1 (Raman), which for a transition state sensitive to the instantaneous transport of CO2, complements the cage effect exercised by the lattice, thus giving strong evidence supporting our mechanistic interpretation of the decomposition kinetics.