

Diffusion in solids: a key process in heterogeneous kinetics

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Diffusion is a natural process which corresponds to species motion due to the existence of a concentration gradient of this species. The motion occurs in order to counteract this gradient and to balance the concentrations to lead towards equilibrium.

Diffusion of species in solids is an essential phenomenon in the field of solid state reactions (such as physical metallurgy, chemical transformations of solid or semi-conductors manufacturing...) since most of solid transformations require mass transport. For example the fabrication of doped structures to produce semi-conductors [1] involves atomic migrations in crystalline lattices.

In the case of chemical transformations of solid such a thermal decompositions or solid-gas reactions, there are two main hypotheses to consider first:

- such an heterogeneous reaction results from the combination of two successive processes: surface nucleation and growth;
- in the simplest case, the growth process is kinetically controlled by a single elementary step which can be adsorption, desorption, an interfacial reaction or a diffusion.

Diffusion steps account for the transport of point defects such as vacancies or interstitials from an interface to another and proceeds via identical jumps of these point defects from a position to another; in a periodical crystal, as all the jumps along the same direction are identical with the same activation energy, the resulting process may be regarded as an elementary step.

If the diffusion step can be the rate-determining step of the reaction and thus influences the rate law, another feature of the diffusion process has a significant importance. Indeed the nature of the diffusing point defects which diffuse through the product layer is fundamental since it determines if the growth process occurs with external or internal development; this impacts not only the rate law, but also both morphology and texture of the solid once the reaction has occurred.

Based on some general aspects of diffusion in solids including the mechanisms of point defects diffusion in crystallized solid, the influence of the nature of diffusing point defects on the growth direction can be explained. This approach has been applied to several solid-gas reactions such as copper oxidation [2] of zinc oxide sulfidation [3]. The establishment of kinetic laws for a rate-determining step of diffusion [4] and the confrontation of these laws with isothermal and isobaric thermogravimetric kinetic curves allow to determine the kinetic constants linked with the diffusion coefficient of the point defects.

[1] D. Shaw, Atomic diffusion in semiconductors, Plenum Press, London, 1973.

[2] M. Mansour, L. Favergeon, M. Pijolat, *Thermochimica Acta* 570 (2013) 41-50.

[3] L. Neveux, D. Chiche, D. Bazer-Bachi, L. Favergeon, M. Pijolat, *Chem. Eng. J.* 181-182 (2012) 508-515.

[4] L. Favergeon, M. Pijolat, M. Soustelle, accepted in *Thermochimica Acta*