Preface

The content of this book is a result of the courses given to the third-year students in École Nationale Supérieure des Mines de Saint-Étienne and the master's students in chemical engineering in Saint-Etienne and Grenoble.

We wish through this work to make the synthesis of two extremely different approaches of heterogenous kinetics and reactivity of solids.

The examination of literature shows that heterogenous kinetics has developed, thanks to the works of two groups of researchers, *a priori* not very dependant on one another: on the one hand, metallurgists, specialists in corrosion of metals and alloys by gases at high temperature, and on the other hand, chemists, specialists in thermal analysis and who are more focused on reactions of salt decompositions.

Those in the first group usually work on massive metals and were not often confronted with the variations of reaction rates with time, the laws encountered being rather simple; they thus were not much concerned with the effects of morphology on the kinetics; on the other hand, they helped deepen the understanding of reaction mechanisms quite a lot, their study being based on point defects of the solids, which helps with the understanding of influences of temperature and gas pressures.

Those in the second group most often work on powders and the essence of their concerns relates to the influence of morphologies on evolutions, integrating the superposition of the two processes of nucleation and growth; on the other hand this group is not so concerned with the reaction mechanisms in the strict sense of the term.

Each one of these two groups produced works more specialized on a particular type of reaction without connections between the approaches always being explicit. Among them we can mention the following:

For the first point of view, we can mention the books edited by P. Kofstad [KOF 66], P. Sarrazin, A. Galerie, and J. Fouletier [SAR 00], A.M. Huntz-Aubriot and B. Pieraggi [HUN 03], and David Young [YOU 08].

For the second point view, the most recent book is that by A.K. Galwey and M.E. Brouwn [GAL 99].

Perhaps, it is the merit of a true French School of heterogenous kinetics to have mixed these two populations, a school that was born and developed around the 40 annual "Heterogenous Days Kinetics" that have taken place since we initiated them in 1968 and that has seen the work of the teams from Cluny, Compiegne, Dijon, Grenoble, Limoges, Marseilles, Orsay, Rennes, Saclay, Saint-Etienne, and Toulouse

This work was generally carried out under the instigation of industrial companies (such as ECA, CEZUS, COGEMA, COMURHEX, FRAMATOME, IFP, IRSID, LAFARGE, PECHINEY the ALCAN, RHÔNE-POULENC then RHODIA, and USINOR) which, giving concrete problems, obliged the researchers to progress in the formulation of the concepts and in deepening the fundamental aspects. These works have shown that many industrial problems require very fundamental research when they touch fields of knowledge that are not developed enough compared with the needs and this is the case with heterogenous kinetics.

Heterogenous kinetics is not a completed science but the aim of this book is to put in perspective the concepts and methods common to a great number of types of transformations. We hope we have succeeded, thanks mainly to the introduction of two new properties: (1) reactivity – primarily a function of intensive variables (temperature, partial pressures, concentrations) and related to the chemical mechanism; and (2) space function, related to the morphology of the system at a given time. This introduction now makes it possible to realize that metallurgists were especially interested in the reactivity and chemists concentrated their efforts primarily on the space function.

This book is concerned with the modeling of transformation of solid gas systems under the action of temperature. It is divided into 19 chapters, which we have gathered, after an introduction describing the main experimental data (Chapter 1), into four parts.

The first part (Chapters 2 to 6) presents the basics that seem necessary to the comprehension of heterogenous kinetics and talks about point defects in solids

(Chapter 2), recalls thermodynamics, which is always very related to kinetics (Chapter 3), an introduction to the concept of elementary step reactions in solid state (Chapter 4), a study of diffusion (Chapter 5), and an approach to chemisorption, always present insofar as the solids are constantly placed in an external gas medium (Chapter 6).

The second part (Chapters 7 to 11) presents the modeling of the reactions of solids by the introduction of the general concepts with the installation of the mechanisms and their resolutions in a single process (Chapter 7), the study of the nucleation process of a new solid phase (Chapter 8), the growth of the nucleus (Chapter 9), and the superposition of the two processes of nucleation and growth (Chapter 10). This part finishes with Chapter 11 which makes it possible to connect the concepts introduced by modeling to the experimental data. This part is largely devoted to space function.

The third part (Chapters 12 to 16) is devoted to the application of the general concepts of modeling to a certain number of families of transformations such as the transformations of coalescence of grains (Chapter 12), decompositions of solids (Chapter 13), reactions between solids (Chapter 14), and reactions between gases and solids (Chapter 15). Finally, we approach the treatment of transformations involving solid solutions, a field still largely in the waste land (Chapter 16). Essentially, this part is concerned with the function reactivity.

Finally, the fourth part is made up of three chapters of exercises and problems with their solutions. Every chapter refers to the one of the preceding parts:

– Chapter 17: Modeling of Mechanisms (Chapters 1 to 7);

– Chapter 18: Kinetic Mechanisms and Laws (Chapters 8 to 11);

– Chapter 19: Mechanisms and Reactivity (Chapters 12 to 16).

The solution of an exercise requires the knowledge presented in the corresponding chapters and possibly discussed in the preceding ones.

Each exercise present four parts: the aim gives the list of concepts involved in the problem, the problem with the questions, the numerical data, and the solution.

We strongly advise the readers to try and think about the answers of questions with only the statement, without taking note of the data. This will enable them to define by themselves the data that will be necessary, a situation that researchers or engineers face in their daily practice.

Numerical calculations and the layouts of the curves were all carried out using a traditional spreadsheet provided with its usual mathematical and statistical functions. The corresponding Excel sheets for each problem can be downloaded from the following website: www.emse.fr/~soustelle.

In the appendices, we gather the main equations that can be developed from the modeling. To use these formulas, the reader can obtain the software "CIN3", which is available on request by sending an e-mail to the following address: favergeon@emse.fr

The bibliographical references at the end of the book do not claim to be exhaustive; they are there to illustrate the chronology of the appearance of the main concepts and can be used as a starting point for a targeted bibliography search.

As for any science based on experimentation, modeling in heterogenous kinetics requires assumptions, approximations and simplifications but these should not in any case be synonymous with a lack of rigor in the reasoning, calculations, and the control of the experiments. We hope to have been faithful to this policy.

Since this book obviously owes much to the whole French school, it could not have been possible without the fundamental contribution of all the people of my lab in Saint-Étienne and especially the team directed by Michele Pijolat. I want to acknowledge all the young researchers who developed original experimental methodologies and brought with them integrating concepts. I am greatly indebted to them and their boss for their help during numerous and fruitful discussions.

In addition, readers will notice active collaborations with Patrice Nortier for the writing of Chapter 8 about nucleation and Gerard Thomas for Chapter 14 about reactions between solids. The particular competence of each of them in the field concerned allied to their general knowledge of heterogenous kinetics enabled us to profit from contributions completely essential for the coherence of the whole of the work. We address to them our most sincere thanks.

Finally, I must not forget the hard work of Marie Prin-Lamaze who had the great task of translating the text from the French edition. I am greatly indebted to her for her help.

Michel Soustelle

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