PREFACE

The study of heterogeneous processes extends over reactions taking place in natural and artificial environments. In this way, the processes can be elucidated and predictions made for practical purposes. A quantitative description of the course of a process under given conditions can be made by obtaining all information about the reaction. Data collection makes it easier to achieve optimal conditions for technically important processes such as the extraction of energy via the combustion of fuels or of production yields as influenced by the design of chemical reactors. The quality of the product depends on the process mechanism such as in the burning of limestone or slaking of burnt lime. It is also necessary to restrict unwanted parallel and concomitant processes as encountered when burning gypsum to plaster of Paris.

The acquisition of such information usually begins with the examination of equilibrium states and ends with the establishment of the kinetics and the reaction mechanism. While looking at a reaction from these two points of view, one finds that they are closely related and reciprocally supported. A knowledge of the state of equilibrium is a necessary condition for finding the limits of the reaction path. On the other hand, the establishment of reaction kinetics enables us to arrive at the final state of equilibrium of the system.

The principles and the physical chemistry of heterogeneous processes can be investigated by means of thermal analysis (TA) techniques. The methods were originally developed by Le Chatelier[1] and Roberts-Austen[2] towards the end of the last century. Most textbooks, however, have treated TA as an analytical tool[3–11]. Thermal analysis has only recently reconquered its original position in physical chemistry[12], and is frequently used in the determination of phase equilibria, enthalpy of chemical reactions and phase transformations, specific heats, etc. Thermal analysis methods have been unfavorably reviewed probably because of ignorance and/or poor instrumentation. During the last five years, however, only three systems out of seven hundred phase equilibria investigated were examined by means of static equilibration techniques (Murphy's biannual reports)[13]. Thus TA, being a dynamic method, has also become a primary source of information concerning reaction kinetics; these techniques have certain advantages in comparison with the classical isothermal measurements.

Physical chemistry[14–16] has received little attention in existing books about TA[3–11]; the relevant material is spread out over a number of papers and reviews in a variety of journals[12]. This is particularly evident in the field of heterogeneous processes where TA appears to be one of the most important techniques for experimental studies. The wide variety of heterogeneous processes is determined by both the chemical character of the participating materials and the interfaces of phase boundaries. The process usually unfolds along the interfaces in which the latter may be developed between gaseous, liquid, and solid phases. The concept of heterogeneity in kinetics is thus broadened in comparison to thermodynamics. In a diffuse flame, the combustion of gases on the interface, gas–gas, can also be looked upon as a heterogeneous reaction. When examining the classification of heterogeneous processes and the shape, size, space arrangement and reciprocal movement of phases, one finds additional criteria. Electrode processes and corrosion show plane phase boundaries, whereas disperse powder systems possess curved phase boundaries. The processes can advance only in the phase boundary or in the bulk of one or more reacting phases. The start of a reaction may also be catalyzed by a solid surface such as the chamber wall. An unambiguous classification of heterogeneous processes is the following:

1) *Catalytic processes*, which take place at the fixed phase boundary between the absorbed molecules of the fluid phase. The shape, size, and specific activity of the solid surface remain unchanged.

2) *Non-catalytic processes*, where the phase boundary moves perpendicularly to itself, and/or changes its interfacial area with the propagation of the process.

Thermal analysis is applicable to both types of processes. It should be noted that an introduction to thermodynamics and reaction kinetics is desirable as a theoretical background to TA.

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