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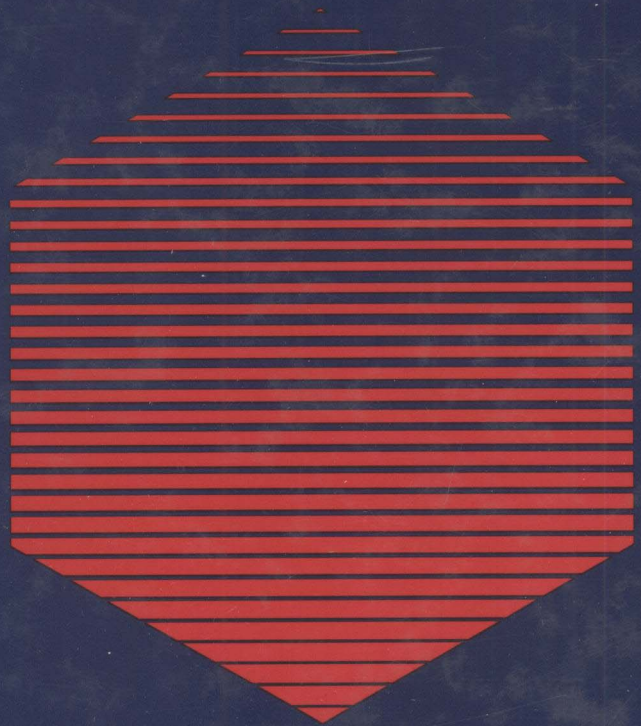
Parametric Sensitivity in Chemical Systems



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Parametric Sensitivity in Chemical Systems

The behavior of a chemical system is affected by many physicochemical parameters. The sensitivity of the system's behavior to changes in parameters is known as parametric sensitivity. When a system operates in a parametrically sensitive region, its performance becomes unreliable and changes sharply with small variations in parameters. Thus, it is of great value to those who design and operate chemical reactors and systems to be able to predict sensitivity behavior.

This book is the first to provide a thorough treatment of the concept of parametric sensitivity and the mathematical tool it generated, sensitivity analysis. The emphasis is on applications to real situations. The book begins with definitions of various sensitivity indices and describes the numerical techniques used for their evaluation. Extensively illustrated chapters discuss sensitivity analysis in a variety of chemical reactors – batch, tubular, continuous-flow, fixed-bed – and in combustion systems, air pollution processes, and metabolic processes. In addition, various plots and simple formulas are provided to readily evaluate the operational behavior of reactors. Chemical engineers, graduate students, researchers, chemists and other practitioners will welcome this valuable resource.

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To our parents

Preface

The behavior of physical and chemical systems depends on values of the parameters that characterize the system. The analysis of how a system responds to changes in the parameters is called *parametric sensitivity*. For the purposes of reliable design and control, this analysis is important in virtually all areas of science and engineering. While similar concepts and techniques can be applied in different types of systems, we focus on chemical systems where chemical reactions occur.

In many cases, when one or more parameters are varied slightly, while holding the remaining parameters fixed, the response of a chemical system also changes slightly. However, under other sets of parameter combinations, the chemical system may respond with an enormous change, even if one or more parameters are varied only slightly. In this case, we say that the system behaves in a *parametrically sensitive* manner. Clearly, it becomes difficult to control the chemical system when it operates in a parametrically sensitive region, and sometimes this leads to so-called *runaway* behavior that ends up with catastrophic results. This book is concerned with parametric sensitivity and parametrically sensitive behavior of chemical systems, analyzed with a unified conceptual and theoretical framework.

In Chapter 2, we define various sensitivity indices and illustrate numerical techniques that are commonly used for their evaluation. Then, in Chapters 3 to 4, sensitivity analysis is used to identify the parametrically sensitive regions in various types of reactors, such as batch, tubular, continuous-flow stirred tank, and fixed-bed, where either a single or complex reactions occur. In Chapter 7, we use explosions in hydrogen–oxygen mixtures as an example to show that the same analysis can be used to quantify critical ignition conditions in combustion systems. Chapters 8–10 comprise the second part of the book, where sensitivity analysis is employed as an effective mathematical tool to analyze various chemical systems. These include mechanistic studies and model reduction in chemical kinetics, air pollution, and metabolic processes.

This book should appeal to all who are interested in the behavior of chemical systems, including chemists and chemical, mechanical, aerospace, and environmental

engineers. Also, the applied mathematicians should find here a rich source of interesting mathematical problems. Finally, we hope that industrial practitioners will find the concepts and results described in this book to be useful for their work.

This book can be used either as a text for a senior graduate-level specialized course, or as a supplementary text for existing courses in reaction engineering, applied mathematics, design, and control. In this context, although we do not provide unsolved problems at the end of chapters, there are a relatively large number of examples illustrating the concepts and results. The book can also be used as a reference for industrial applications in reactor design, operation and control.

It is a pleasure to acknowledge here our debt of gratitude to Professor John H. Seinfeld of the California Institute of Technology. He encouraged our writing from the beginning, and looked over drafts of Chapters 2 and 9, providing valuable suggestions for improvements. In addition, Dr. Vassily Hatzimanikatis of du Pont Central Research Department kindly provided a keen evaluation of our draft of Chapter 10.

The last thought goes to our families. Our wives (Karen, Luisella, and Guixian) and children (Anita and Sophia; Melissa and Oreste; Xian and Dino) deeply support us and our work, even as they suffer some neglect during the course of writing projects such as this. We cherish their love and affection.

Arvind Varma
Massimo Morbidelli
Hua Wu

Contents

1

Introduction

1.1 The Concept of Sensitivity

The behavior of a chemical *system* is affected by many physicochemical *parameters*. Changing these parameters, we can alter the characteristics of the system to realize desired behavior or to avoid undesired behavior. In general, different parameters affect a system to different extents, and for the same parameter, its effect may depend on the range over which it is varied. By *parametric sensitivity*, we mean the sensitivity of the system behavior with respect to changes in parameters.

Let us illustrate the concept of sensitivity using some examples. Figure 1.1 shows the effect of changes in the initial temperature on the temperature evolution in a batch reactor for acetic anhydride hydrolysis, measured experimentally by Haldar and Rao (1992). There is a critical change in the temperature profile as the initial temperature increases from 319.0 to 319.5 K. In particular, an increase in the initial temperature by 0.5 K leads to a change in the temperature maximum by about 31 K. This experimental observation indicates that the system temperature becomes *sensitive to small variations* in the initial temperature in a specific region, called the *parametrically sensitive region.*

Figure 1.2 shows similar sensitivity phenomena in a tubular reactor obtained by numerical computations, given by Bilous and Amundson (1956) in their pioneering work on parametric sensitivity in the context of chemical reactors. In this example, the ambient temperature of a tubular reactor, where an exothermic reaction occurs, is changed. It is seen in Fig. 1.2a that when the ambient temperature increases by 2.5 K from 335 to 337.5 K, the temperature maximum (hot spot) along the reactor length changes by about 70 K. Moreover, such a variation also causes a sharp change in the corresponding concentration profile along the reactor, as shown in Fig. 1.2b. Thus, *when a system operates in the parametrically sensitive region, its performance becomes unreliable and changes sharply with small variations in parameters.*

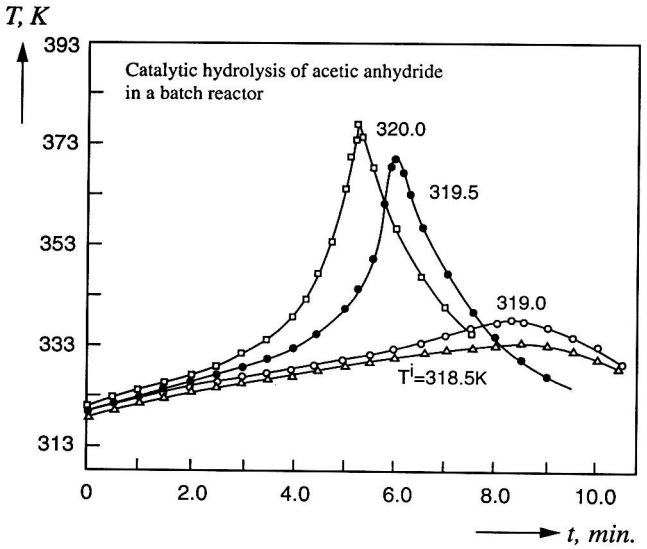
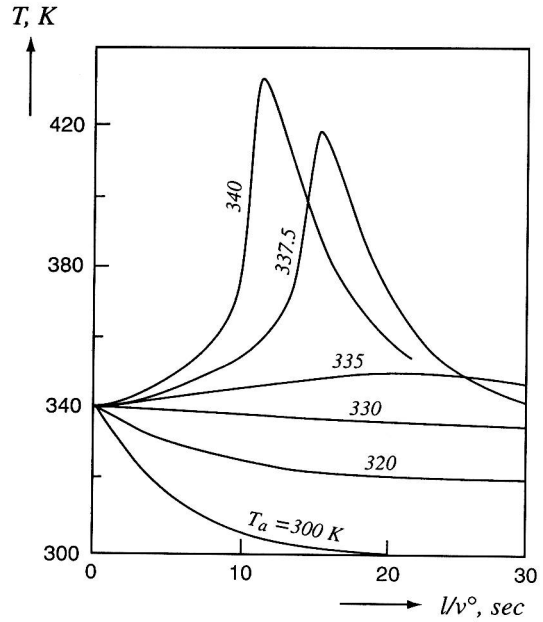


Figure 1.1. Catalytic hydrolysis of acetic anhydride in a batch reactor. Temperature profiles as a function of time for various values of the initial temperature, measured experimentally by Haldar and Rao (1992).

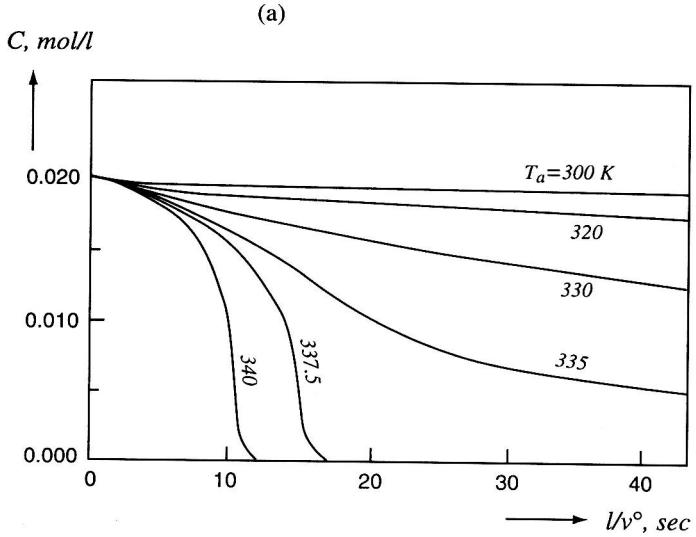
For a chemical system to operate in a reliable and safe manner, it is often required to identify the sensitive regions in the system *parameter space*. An example is shown in Fig. 1.3a, where for a fixed-bed catalytic reactor in which vinyl acetate synthesis occurs, the sensitive region in the cooling versus heat of reaction parameter plane was identified by Emig *et al.* (1980) through a large number of experiments. The symbols ○ and • denote low- and high-temperature operating conditions, respectively. These data clearly define a boundary (broken curve) separating the low-temperature from high-temperature operating conditions. In particular, let us consider two operating conditions in Fig. 1.3a near the boundary, indicated by points 1 and 2. The corresponding temperature profiles are shown in Fig. 1.3b. As may be seen, although the two conditions are close in terms of parameters, their temperature profiles are substantially different, indicating that the reactor is operating in the parametrically sensitive region.

Sensitive regions have also been investigated experimentally for other reacting systems, especially for combustion processes. An example is the sensitive region in the initial pressure-temperature plane for hydrogen oxidation in a closed vessel, identified by Lewis and von Elbe (1961), as shown in Fig. 1.4. In particular, the boundary representing the sensitive region divides the parameter plane into two parts. For a fixed initial pressure, as the initial temperature increases, the system undergoes a sharp transition near the boundary, from non-explosion on the left-hand side to explosion on the right-hand side.

It should be noted that although the sensitive region for each parameter can, in principle, be identified experimentally, only a few experimental studies on parametric



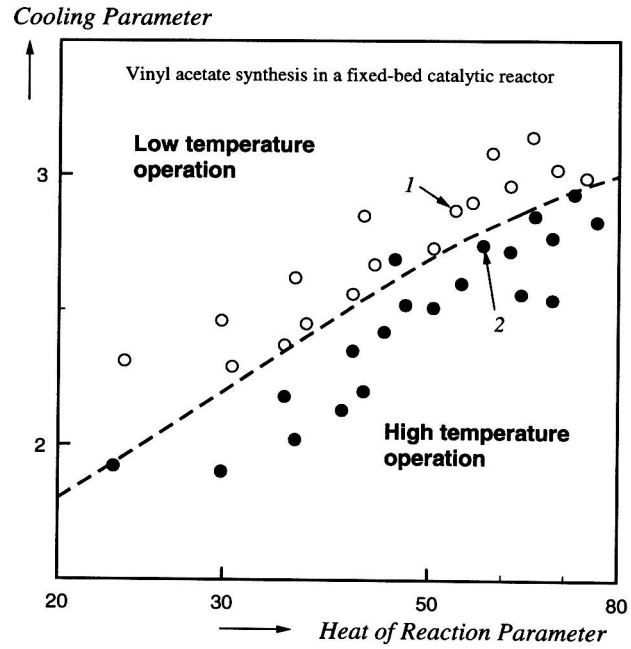
(a)



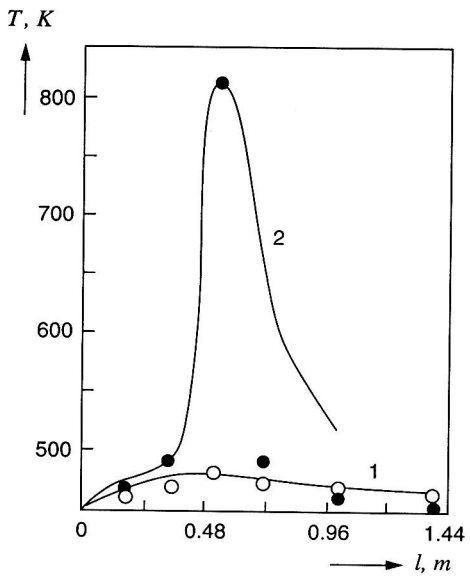
(b)

Figure 1.2. Numerical calculated (a) temperature and (b) concentration profiles along the length, l, of a tubular reactor; $v°$, represents the reaction mixture velocity. From Bilous and Amundson (1956).

sensitivity have been reported to date in the literature. This is because each system involves many physicochemical parameters, so that detailed experimental investigation becomes cumbersome. Thus, it is of great interest to predict theoretically the sensitivity behavior of a chemical system, through appropriate model simulations. The



(a)



(b)

Figure 1.3. Vinyl acetate synthesis in a fixed-bed catalytic reactor. (a) Sensitive operation region in the cooling versus heat of reaction parameter plane, measured experimentally by Emig *et al.* (1980), where ○ = low temperature operation and ● = high temperature operation. (b) Temperature profiles along the reactor length corresponding to the two operation conditions indicated by points *1* and *2* in (a).