

# Preface

I started to write this book in 2014 because I was seeing so many erroneous papers on applied chemical kinetics. Methods for practical problems that were developed 20–40 years ago were too often ignored. This might be expected, because the literature on applied chemical kinetics is so vast that no one would be expected to be aware of all of it. Also, much of this literature has one or more serious flaws, and people entering the field may or may not be able to distinguish between the good and bad. Furthermore, certain mistakes are so common that seeing a particular approach in multiple papers can lead one to the erroneous conclusion that the approach is valid.

To be sure, I have made mistakes. If I knew 35 years ago what I know now, I would have done some things differently in my early papers. Learning from our mistakes is a central part of both science and a person's life. So in one sense, I hope that others can learn from my mistakes rather than repeating them. A first example is that I did not understand initially that kinetics derived from a single constant heating rate are very unreliable, so my early kinetics for oil-shale char gasification have serious flaws. I learned that lesson in the mid-1980s while working on the kinetics of natural petroleum formation, and I subsequently contributed to ICTAC papers in 2000 and 2011 addressing the need for multiple thermal histories to derive valid kinetics. Numerous papers in the thermal analysis literature had claimed to be able to identify the reaction mechanism by the quality of fit to data from a single heating rate, and they were wrong. The ICTAC papers have contributed to improving the quality of kinetic determinations in the thermal analysis field. A second example is that I derived kinetic parameters for oil cracking by varying temperature at roughly constant reaction time. Because different reactivities are sampled at different conversions and reactivity tends to decrease with conversion, this procedure results in artificially low activation energies. It is a common mistake in kinetic determinations for complex materials.

Another career lesson is that each of us should seek out and recognize the understandings of other research communities. Coming from the fossil fuel community, I was steeped in 1st-order,  $n$ th-order, and distributed activation energy models. Then I ran into linear polymers and a few well-preserved algal kerogens

that had sigmoidal reaction profiles. We found a mathematical form that worked quite well, but it was a few years later that we realized the mathematical form had been in the solid-state reaction literature for decades—an extension of the Prout–Tompkins model common in the Russian literature, also known as the truncated Šesták–Berggren model. We also discovered that other people were using that form for linear synthetic polymers. Even 20 years later, some petroleum geochemists fail to realize the importance of using a sigmoidal reaction model for some source rocks. At the same time, some recent kinetic work related to oil shale processing disregards the greatly superior quantity and quality of oil generation kinetics from the petroleum geochemistry community. It seems that the energy barrier between different application areas is too high for such lessons to transfer to the other communities. That is unfortunate, because amongst all the mediocre papers in the literature, there are numerous gems that have a lot to offer.

I am often dismayed that many people try to write their own chemical kinetics fitting software for analyzing complex systems, given that several powerful and versatile commercial programs are readily available. Perhaps it is a matter of cost, but the cost to develop one's own software is also high, and the cost of publishing mediocre kinetic work is even higher. I have reviewed papers in which inappropriate models were used, and where better models were available in commercial software. On multiple occasions, the editor accepted the paper after the authors said that their home-grown software was not capable of doing the more appropriate analysis. While writing such software serves an excellent educational objective, software-limited research that does not measure up to standard commercial practice is substandard and should not be tolerated in peer reviewed literature. As such, this book emphasizes the virtues of the Kinetics2015 program and precursors. While not the best at all types of kinetic optimizations, it is very good at the subset it does address and far better than most programs written by students.

Often in this book I draw upon my own work for specific issues. Although I try to cite the best papers on any given topic, this book is not intended to be a complete collection of all relevant work, and there may be papers by others that are either as good as or better than mine. Sometimes those papers are referenced in the works cited in this book, and sometimes they may have missed my attention. I apologize in advance for any such omissions.

This book took a few turns during its writing. One possibility was more of user's manual for specific software developed by Robert Braun and myself, but its final form was strongly influenced by a course I taught during the spring of 2016 in the Department of Energy Resources Engineering at Stanford University. It was designed for graduate students, although advanced undergrads could also take it. Exercises are included at the end of each chapter to help probe student understanding of both concepts and implementation of concepts. These specific exercises do not require specific software, although the classes I teach do in order to achieve more complete training. Solutions to the exercises and additional problem sets are available at <http://extras.springer.com>. While useful as a textbook, this book is intended to help the experienced practitioner, also.

There are numerous people who helped me along my career that made this book possible, with most of them being coauthors on one or more publications. Jack Campbell helped bring me to LLNL and introduced me to nonisothermal kinetics. Art Lewis supported my work there in oil shale and petroleum geochemistry that led to most of the applications covered here. Robert Braun, both before and after his retirement from LLNL, supplied the computer expertise that converted many of my ideas into efficient computer codes. Paul Lerwick of EGL Resources, Howard Jonas of IDT, and Pierre Allix of Total brought me back into the fossil energy area after a substantial absence, which rejuvenated my interest in writing a book such as this. Total continued my involvement in this field via the Stanford-Total Enhanced Modeling of Source Rocks (STEMS) project, managed by Alex Lapene, Francois Gelin, Tony Kavscek, and Hamdi Tchelepi. Several reviewers gave helpful suggestions on the manuscript that improved it significantly: Ken Peters, Drew Pomerantz, Dan Jarvie, Justin Birdwell, Sergey Vyazovkin, and Andy Pepper, with Ken being the most thorough. However, their review does not imply that we agree on all things, and I take full responsibility for what I have written. And thanks, of course, to my wife, Mary, who endured my many long hours in front of the computer screen.

Livermore, USA

Alan K. Burnham

<http://www.springer.com/978-3-319-49633-7>

Global Chemical Kinetics of Fossil Fuels

How to Model Maturation and Pyrolysis

Burnham, A.K.

2017, XII, 315 p. 202 illus., 101 illus. in color. With  
online files/update., Hardcover

ISBN: 978-3-319-49633-7