



J. DONALD RIMSTIDT

Geochemical Rate Models

An Introduction to Geochemical Kinetics

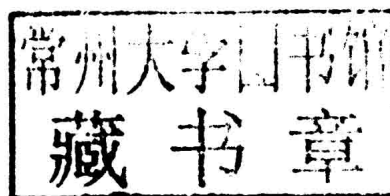
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An Introduction to Geochemical Kinetics

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Geochemical Rate Models

An Introduction to Geochemical Kinetics

Rate models (kinetic models) are used to predict rates of geochemical processes in the near-surface environment. Based on the author's 30 years of teaching and research experience, this combination of reference and textbook provides a systematic, comprehensive description of rate models, developed from fundamental kinetic theory and presented using consistent terminology and notation.

Major topics include rate equations, reactor theory, transition state theory, surface reactivity, advective and diffusive transport, aggregation kinetics, nucleation kinetics, and solid–solid transformation rates. The theoretical basis and mathematical derivation of each model is presented in detail and illustrated with worked examples from real-world applications to geochemical problems. The book is also supported by online resources: self-study problems put students' new learning into practice; and spreadsheets provide the full data used in figures and examples, enabling students to manipulate the data for themselves.

This is an ideal overview for advanced undergraduate and graduate students, providing a solid understanding of geochemical kinetics. It will also provide researchers and professional geochemists with a valuable reference for solving technical and scientific problems.

J. Donald Rimstidt is a Professor Emeritus of Geochemistry at Virginia Polytechnic Institute and State University (Virginia Tech). During his 30-year career there he has taught several graduate courses, including Aqueous Geochemistry, Environmental Geochemistry, Geochemical Kinetics, and Geochemical Thermodynamics. The effective pedagogic methods from those courses, for building quantitative skills and instructing modeling techniques, underlie this book. Professor Rimstidt is the author or co-author of more than 100 papers, including his seminal article, "The kinetics of silica-water reactions" (with Hu Barnes, 1980), which forms the basis of the quasi-thermodynamic presentation of transition-state theory presented in this book.

"Don Rimstidt brings 30 years of teaching experience at a world class geosciences department to the writing of this book. With its beautifully clear exposition of the theoretical and practical aspects of geochemical kinetics, and use of real-world examples, this book is essential reading for students and professionals with interests in geochemical rate models."

David J. Vaughan, *Research Professor, University of Manchester, and President of the Mineralogical Society of America*

For my students

Preface

This book is intended for use as a textbook for an upper-level undergraduate or a first-year graduate course and as a handy reference for professionals who need to refresh their memories about a particular rate model. It focuses on rate models that are well understood, widely used, and pertinent to geochemical processes. Its scope is limited to an amount of material that can be covered in a one-semester course and the depth of presentation is restricted to the principal aspects of each model. The reference list directs the reader to sources that contain the additional details needed to produce more sophisticated models.

As the scientific and technological enterprise grows larger, scientists cope with the onslaught of new knowledge by retreating to more narrowly defined sub-disciplines. Increasing specialization tends to make each sub-discipline less relevant to the overall scientific and technological enterprise. This tempts scientists to pursue questions of trivial importance relative to the larger picture. Furthermore, the terminology that grows up in these enclaves becomes abstruse and incomprehensible. Geochemistry is challenged to avoid this trap by aggressively integrating knowledge from cognate disciplines in order to remain vibrant and meaningful. This is my justification for choosing many of the topics in this book from scientific and technological areas that might not be considered as traditional geochemistry. Hopefully this intellectual cross-fertilization will improve geochemistry's vigor. My choice of topics was predicated on the question: What should everyone know about rates of geochemical processes? I hope that this book answers that question. If I have done my job properly, this book will provide an intellectual foundation for anyone, including scientists and technologists from cognate disciplines, who deal with geochemical processes. I have tried to meld these topics by using a standard notation and terminology that is consistent with that already used in geochemistry.

I believe that understandable and reliable models are the basis of scientific knowledge, so this book emphasizes the development of conceptual and quantitative models. In addition, effective models make predictions that have practical value so these models are a valuable contribution to society. The essence of the scientific method is to compare a model's predictions

with actual outcomes to test the validity of the underlying knowledge. Every scientist should understand and appreciate the importance of this model-building and -testing scenario.

This book does not delve into computer models of rate processes because there are already many good sources of information about this approach. Instead it focuses on fundamental and relatively simple models that are the foundations of the models incorporated into the various computer codes.

I have enjoyed the process of writing this book and learned a great deal from teaching this material to students. I hope that the readers will find it equally interesting and enlightening.

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Chapter 1

Geochemical models

Modern geochemistry studies the distribution and amounts of the chemical elements in minerals, ores, rocks, soils, waters, and the atmosphere, and the circulation of the elements in nature, on the basis of the properties of their atoms and ions.

(Goldschmidt, 1958)

The distribution and circulation of the chemical elements in and on the Earth is influenced by a myriad of chemical and physical factors, many of which have changed over geological time. Understanding the role of these factors in geological processes requires us to condense information about elemental abundances and distributions into models. This book is about geochemical models for situations where time plays a key role. Geoscientists have always appreciated the importance of time in fashioning the Earth. Many geological processes require time spans that are far too long for human observation, but we can use models to extrapolate rates based on short-term observations to predict geochemistry in deep time. Equally important are models that forecast the future behavior of geochemical systems because those models are needed for environmental management and resources recovery projects.

Some of the models described in this book were developed by geochemists but many others come from applied sciences and engineering. Because of this diverse provenance, the models in their original form used a confusing mix of units, terminology, and notation. This book attempts to remedy that problem by recasting the models using internally consistent notation, units, and terminology familiar to geochemists. Furthermore, whenever possible the models are developed from fundamental theory showing a sufficient number of intermediate steps to allow the reader to follow the derivations.

Thermodynamic models have been a mainstay of geochemistry since the early twentieth century. They are especially effective for deep earth conditions where local equilibrium conditions prevail. However, at and near the Earth's surface extensive amounts of mass transport and low temperatures keep many reactions from reaching equilibrium. Kinetics models are needed to properly describe these situations. This makes the models of kinetic and dynamic processes described in this book complementary to thermodynamic

models. The thermodynamic models describe the equilibrium endpoint for geochemical processes, and the kinetic and dynamic models predict how long it might take to reach that endpoint.

Kinetics and dynamics

Element redistribution in nature is the result of chemical reactions that are described by geochemical kinetics models and physical transport that is described by geochemical dynamics models. These geochemical kinetics and geochemical dynamics models are adapted from a diverse range of scientific and technological sources. Geochemical kinetics is grounded in well-established chemical kinetics theory (Laidler, 1987a, 1987b; Lasaga, 1998b) but that theory must be combined with practical methods to deal with the complexities of geological problems and technological applications. Valuable contributions to the field of geochemical kinetics and dynamics come from chemical engineering (Hill Jr., 1977; Levenspiel, 1972a), mineral processing (Burkin, 2001), civil and environmental engineering (Brezonik, 1994; Weber Jr. and DiGiano, 1996), soil science (Sparks, 1989), and even food processing (van Boekel, 2009). There are also several very useful books about mass transfer processes (Denny, 1993; Probstein, 1989; Vogel, 1994) that contain models that are readily adapted to deal with geochemical dynamics. Finally, there are many books that treat various aspects of geochemical kinetics (e.g. Berner, 1980; Lasaga, 1998b; Lerman, 1979; Stumm, 1990; Zhu and Anderson, 2002). Each of these sources has a particular scientific style that is reflected in different ways of making observations and constructing models. The challenge is to select relevant knowledge from these sources and to recast it in a way that makes it useful to geoscientists.

Model construction

Models organize our knowledge about the world. Doing science is the process of making observations, using those observations to develop a model, and then verifying the model's effectiveness by comparing its predictions with additional observations. The methods and scope of model-making vary from discipline to discipline, but the goal of creating reliable predictive tools is always the same. Developing a useful model requires a combination of creative thinking and disciplined use of modeling tools. There are many good discussions of modeling strategies (Aris, 1994; Bender, 1978; Bunge, 1997; Hall and Day, 1977; Hall *et al.*, 1977; Harte, 1988; Overton, 1977; Rescigno and Thakur, 1988; Shoemaker, 1977) but developing an effective model is in many ways a creative process. Good models are elegant and powerful. Elegance means that the model is expressed in the simplest, easiest to understand terms. Power means that the model explains the widest

possible range of behaviors of the system of interest. Finally, good models are beautiful. Perhaps some of this beauty comes from power and elegance, but some of the beauty arises when the model is congruent with our thought processes. The esthetics of scientific creation is a difficult concept to learn (Wechsler, 1988), but it is a necessary part of making a lasting contribution to science.

Models can be categorized in various ways. Predictive models forecast the future behavior of a system, whereas conceptual models are used to understand relationships between system parts and processes. Deterministic models are constructed from mathematical functions that unambiguously relate cause and effect so that a particular set of input parameters produces a clearly related set of predicted results. Probabilistic models use statistical data to estimate the chance that an event or condition will occur. Forward models predict the future behavior of a system, whereas inverse (or reverse) models are used to extract fundamental data or mathematical relationships from past observations.

Models can relate information in three formats. Visualization illustrates spatial, mathematical, or sequential relationships using diagrams, graphs, and images. Narration uses words to explain how processes occur and are related to each other. Mathematics uses computational operations to quantitatively relate processes and features to each other. Disciplined use of notation, reliable data sources, and homogeneous units (Bender, 1978) along with appropriate mathematical methods and effective error analysis are features of effective mathematical models. However, it would be impossible to understand most mathematical models without accompanying visualization and narration. Visualization plays an equally important role in the development of scientific ideas (Wainer, 2005). For example, flow charts showing subsystems as boxes connected by arrows are often used to show how mass and/or energy moves through a system (McClamroch, 1980). This method of model construction, which is reprised in the ideal chemical reactor models described in Chapter 4, is especially useful because it leads to quantitative relationships in a simple and natural way. Graphs that allow us to visualize mathematical relationships are critical to understanding how dependent variables are influenced by independent variables. Harris (1999) provides extensive and detailed descriptions of many kinds of graphical formats. Effective graphical illustrations are easy to understand without needing to consult descriptive text. Effective graphs and illustrations maximize the information to ink ratio (Tufte, 2001). All models are built upon a conceptual foundation. Although visualizations often nicely summarize the conceptual basis of a model, it is usually impossible to fully explain the model without the use of some text. Well-organized and clearly stated narrative descriptions of the conceptual basis of a model are a key part of model development.

Model reliability

No model is perfect (Oreskes *et al.*, 1994). Even the best models fail under some conditions. In addition, making mistakes is a natural part of the modeling process. Systematic methods should be used to find, analyze, and correct mistakes and to define the valid range of a model. Determining the cause of a model's failure and repairing the model is a key task in model building.

Models are used to understand how complex behaviors arise from the interaction of simple processes. Ideally models are built upon reliable principles such as the conservation of matter, energy, and charge or the principle of detailed balancing. Often less-reliable relationships such as empirical rate equations must also be used. All quantitative models require input data and relationships that come from measurements, which always contain some error. This error can propagate through a model in unexpected ways, especially if the model simulates nonlinear interactions. This challenges the modeler who must decide whether an unexpected result is a legitimate prediction or simply an artifact arising from an unfortunate combination of errors. Three classes of errors occur in models. Formal errors are incorrect assumptions and/or formulations. They include errors in the conceptual foundation of the model as well as errors in the input data. Structural errors are errors in mathematical manipulations such as programming errors or algebraic errors. They include software bugs. Computational errors are errors in numbers caused by incorrect rounding or by addition or multiplication errors. Because there are so many ways that a model might fail, models and their predictions must be verified and validated to delineate the bounds of their reliability.

Verification tests whether the model is internally consistent, incorporates the correct relationships in the correct ways, and uses correct data. It is a good idea to develop a set of standards and practices that can be used in geochemistry model-making to insure the validity of the resulting model. Table 1.1 is an example of a checklist that might be used. Models should use a consistent system of notation and units to avoid structural errors. Equations should be tested using dimensional analysis. The input data should be reviewed to insure its correctness and internal consistency. Verification should determine the expected precision of the model's predictions based on the propagation of errors through the model. Error analysis is probably the most undervalued part of model development. For simple models, error propagation can be done using simple algebraic methods described in Chapter 2. For complex models, simple error propagation is often not practical. In such cases sensitivity analysis is a good strategy. Sensitivity analysis uses various schemes to systematically vary, within the expected range of error, the values of important modeling parameters to see how those variations affect the model's predictions. The utility of

Table 1.1. *Checklist of recommended validation and verification procedures*

Verification Questions
Are the equations used dimensionally homogeneous?
Are the standard and reference states of the variables internally consistent?
Is the notation internally consistent and clearly stated in the documentation for the model?
Are the computational methods correct? Have numerical simulations been tested against analytical solutions?
Are the chemical reactions correctly balanced? Are all the important chemical reactions and chemical species accounted for?
Does error analysis demonstrate that the predicted values are accurate enough to be useful?
Has the range and domain of the model been documented and is the situation being modeled within the range and domain?
Are the model's outputs clearly related to the inputs? Does sensitivity analysis show that each input has a significant effect on the model output?
Are the spatial and conceptual relationships consistent and properly documented?
Validation Questions
Are the predictions geologically reasonable? Are they consistent with reasonable estimates?
Are the predictions consistent with other scientific observations and knowledge?
Are the quantitative predictions sufficiently close to the behavior of one or more natural analogs?

a particular model depends upon whether it predicts the behavior of the system of interest within a practical range of uncertainty. For example, a model of a process used to control the lead content of drinking water would be useless if uncertainty in the predicted lead content was larger than the regulatory level. Typically models are constructed using very conservative assumptions that are frequently chosen on an arbitrary basis. Error analysis, on the other hand, clearly demonstrates quantitatively which of the input data most strongly affects the uncertainty of the predicted behavior.

Validation determines whether the model correctly predicts observable outcomes with reasonable accuracy and precision. Showing that a model can predict an analytical solution might be a useful validation test. Validation should compare a model's predictions with geological analogs. Models are hypotheses; they can never be proven true (Nordstrom, 2012). However, a model with a record of consistently successful predictions is more useful

than an untested one. Finally, collecting new observations to test a model's predictions allows the model to be further refined. It is important to restate that the validating process does not prove that a model makes correct predictions; instead validation only decreases the probability of a model's failure.

Some technology models, usually related to resource recovery or waste disposal, involve predicting the behavior of the Earth after human intervention. Because there are frequently no precedents for such cases, models of the effects of human activities are sometimes validated using natural analogs, geological situations that are similar to the technological situation. In tests of technological models a clear definition of accuracy is needed. This definition is complicated because geochemical parameters almost always show a range of values, so comparison of a single model run with a single field observation has very little meaning. Instead, the input parameters for the model must be varied within the expected range to create a range of predictions that can be compared with the observed range of values. Then a statistical test can be used to estimate how often the model will fail.

Example 1.1. Estimation method for validation of a chemical weathering denudation rate model

Denudation is the lowering of the elevation of the Earth's surface by chemical weathering, erosion, and mass wasting. A model of chemical weathering would account for the rate of removal of material from soil and underlying rock by various dissolution processes. A first step toward validating such a model is to develop some independent estimates of the chemical denudation rate.

One estimate might be based on geological knowledge. We know that denudation rates must be smaller than uplift rates. Otherwise the continents would be reduced to the elevation of sea level. The maximum uplift rate is probably about 10% of the maximum ocean ridge spreading rate, which is ~ 10 cm/yr. That makes uplift rates smaller than 1 cm/yr. The uplift rate of the average crust is likely to be 100 to 1000 times smaller than the maximum rate. We might choose the geometric mean of these values and estimate that the overall crust uplift rate is 0.03 mm/yr or 3 mm/century. A terrain with such a low uplift rate is likely to be relatively flat so mass wasting and erosion might account for two-thirds of the denudation, which means that chemical weathering would account for about one-third. This gives an estimate of denudation by chemical weathering of ~ 1 mm/century.

Another way to estimate the chemical denudation rate is based on the realization that most of the soluble products of chemical weathering are carried away by infiltrating groundwater. If we consider 1 m² of land surface in a setting with about 100 cm of rainfall per year with 10% infiltration of the rainwater, ~ 100 L of water passes through each square meter annually. As that water infiltrates