Chapter 1
Analysis of Rates of Geochemical Reactions

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1.1 Kinetics and Thermodynamics

Over the last several billion years, rocks formed at equilibrium within the mantle of the Earth have been exposed at the surface and have reacted to move towards a new equilibrium with the atmosphere and hydrosphere. At the same time that minerals, liquids, and gases react abiotically and progress toward chemical equilibrium at the Earth’s surface, biological processes harvest solar energy and use it to store electrons in reservoirs which are vastly out of equilibrium with the Earth’s other surface reservoirs. In addition to these processes, over the last several thousand years, humans have produced and disseminated non-equilibrated chemical phases into the Earth’s pedosphere, hydrosphere, and atmosphere. To safeguard these mineral and fluid reservoirs so that they may continue to nurture ecosystems, we must understand the rates of chemical reactions as driven by tectonic, climatic, and anthropogenic forcings.

Chemists approach the understanding of the natural world by defining parts of the world as systems of study. The mechanically separable parts of the system—the crystalline and amorphous solids, liquids and gases—are known as phases. All the phases that are not inside the system are defined as the environment surrounding the system. By definition, a system at equilibrium will be characterized by phases with uniform composition that exist at uniform temperature and pressure. To be precise, equilibrium is defined as that state where the chemical potential of every component in every phase is equal throughout the system.

To chemically understand a system, the chemical species within the system must be identified and characterized: the minimum number of species needed to define a system at equilibrium comprises the set of components of that system. Likewise, the thermodynamic state of any system is completely defined by specifying the values

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of a critical number of properties. For example, the Gibbs phase rule states that the number of properties that must be defined to completely describe a system (the degrees of freedom, F) is dependent upon the number of phases, P, and components, C:

\[ F = C - P + 2 \]  

(1.1)

So, for example, to completely define the one-component one-phase pure H₂O system, we must only define the temperature, \( T \), and pressure, \( P \), of the system (\( F = 2 \)). If one adds sufficient NaCl as a second component so as to supersaturate this water with respect to halite and then isolates the system, the second law of thermodynamics states that the properties of this isolated system will evolve until the equilibrium state is reached. Indeed, the degrees of freedom of the final two-component, two-phase (NaCl-saturated water and solid NaCl) system must also equal two: in effect, the state of this system is defined solely by the temperature and pressure. Thermodynamics completely defines the final state of the system: however, thermodynamics cannot define the rate at which the system evolves.

The field of irreversible thermodynamics treats systems that are removed from equilibrium by modeling how the entropy of the system changes with time as equilibrium is approached (Prigogine, 1967). Irreversible thermodynamics defines the change in entropy of the system, \( dS \), as the sum of the entropy supplied to the system by its surroundings, \( dS_e \), and the entropy produced inside the system, \( dS_i \). The second law of thermodynamics states \( dS \geq 0 \). For a reversible process, \( dS_i = 0 \), and for an irreversible process, this term is always positive, \( dS_i > 0 \). Furthermore, for a closed system at constant temperature and pressure, it can be shown that this term is related to the change in Gibbs free energy of the system, \( dG_{sys} \):

\[ T dS_i = -dG_{sys} \]  

(1.2)

Therefore, for spontaneous reactions in closed systems at constant \( T \) and \( P \), the entropy produced inside the system is related to the Gibbs free energy change of the system.

In the case of the system with one reaction, the differentiation of Eq. (1.2) over time and introduction of \( \xi \), the extent of reaction (see Eq. (1.9)), results in the expression

\[ T \frac{dS_i}{dt} = A \frac{d\xi}{dt} \]  

(1.3)

where the entropy production \( \frac{dS}{dt} \geq 0 \) and \( A = -\Delta G_{reaction} \), the chemical affinity of the reaction. The chemical affinity, introduced by T. DeDonder, is the driving force of the reaction. For a reaction that occurs spontaneously as written (e.g., reactants on the left and products on the right of the reaction), \( A > 0 \) and \( \Delta G_{reaction} < 0 \). At equilibrium, the chemical affinity \( (-\Delta G_{reaction}) \) is equal to 0. The negative driving force of reaction can be shown to be equal to a simple expression for any reaction defined by an equilibrium constant \( K_{eq} \) and a reaction activity quotient, \( Q \):

\[ \Delta G_{reaction} = -A = RT \ln \left( \frac{Q}{K_{eq}} \right) \]  

(1.4)