Chapter 10  Application of Thermodynamic Calculations to Geochemical Processes Involving Organic Acids

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Summary

This chapter summarizes some of the insights gained about the behavior of organic acids in geochemical processes through thermodynamic calculations. Such calculations are possible because of the combination of numerous experimental studies on aqueous organic acids and theoretical equations of state, which allow accurate extrapolations of the measurements as well as predictions of thermodynamic properties of aqueous organic acids for which data have not been measured. Estimates of thermodynamic data for aqueous organic acids allow quantitative tests of several hypotheses concerning the role of organic acids in geochemical processes. For example, thermodynamic calculations described in this chapter indicate that decarboxylation of organic acids is unlikely to proceed to any significant extent under sedimentary basin conditions. At the partial pressures of CO₂ and CH₄ associated with oil-field brines, equilibrium constants for the decarboxylation of acetic acid require the acid concentrations to be many orders of magnitude lower than reported values.

Although the concentrations of acetic acid in oil-field brines cannot be in equilibrium with both CO₂ and CH₄, they may be in redox equilibrium with CO₂ as demonstrated by additional calculations described in this chapter. This means that there is an enormous kinetic barrier blocking reactions between acetic acid and CH₄ under sedimentary basin conditions. Therefore, acetic acid is preserved in a metastable state in oil-field brines, and appears to be in metastable equilibrium with CO₂.

In addition, thermodynamic evaluation of acetic acid and propanoic concentrations in many brines indicates that these acids are in homogeneous metastable equilibrium. As a consequence, the ratio of the concentrations of acetic and propanoic acids in basinal brines can be used as a tracer of the oxidation state of sedimentary basins. Additional thermodynamic calculations described in this chapter allow tests of the plausibility of the hypothesis

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that the complex mixture of liquid hydrocarbons found in petroleum may buffer the oxidation state recorded by the acid ratios. It is found that this is a plausible argument not only for sedimentary basins but for hydrous pyrolysis experiments as well.

Thermodynamic calculations can only demonstrate whether compounds are in equilibrium with one another (stable or metastable) and reveal nothing about the reaction mechanisms through which such equilibrium states are reached and maintained. In the case of metastable equilibrium among petroleum hydrocarbons, organic acids, and CO$_2$ in sedimentary basins, thermophilic microorganisms may catalyze otherwise sluggish reactions so that the geologically observable metastable state is reached. If so, then many of the reactions shown to be in metastable equilibrium may represent overall metabolic processes, and the application of thermodynamic calculations enters the area of geochemical bioenergetics. Some preliminary examples for dehydrogenation, hydrogenation, sulfate reduction, and methanogenesis reactions involving organic acids are discussed in this context at the end of this chapter. It appears that chemical reactions, which supply energy to microorganisms at low temperatures, provide considerably more energy at the elevated temperatures encountered in sedimentary basins.

1 Introduction

Organic acids have been invoked to account for the differences between measured alkalinites for oil-field brines and those calculated based on carbonate equilibria (Willey et al. 1975), as a source and transport mechanism for natural gas through decarboxylation reactions (Carothers and Kharaka 1978), in the transport of metals through metal-organic complexes (Giordano and Barnes 1981), in the development of secondary porosity (Surdam et al. 1984), as pH buffers that could potentially control mineral-fluid reactions (Lundegard and Land 1989), and as tracers of metastable equilibrium states among organic compounds in natural systems (Shock 1988, 1989, 1990a). These acids have also been used as indicators of oil migration (Jaffe et al. 1988a,b) and in petroleum prospecting techniques (Zinger and Kravchik 1970). The relatively high concentrations of organic acids in some natural fluids (up to ~10000 ppm in oil-field brines; MacGowan and Surdam 1990) suggest that these compounds may be major aqueous species in biogeochemical cycles of carbon, hydrogen, oxygen, and nitrogen between detrital organic matter, petroleum, minerals, natural aqueous solutions, and the atmosphere. The consumption and production of aqueous organic acids by microorganisms in soil, groundwater, and petroleum reservoir environments indicate that these compounds are involved in subsurface metabolic processes. Understanding the wide variety of processes that may involve organic acids, including the energetics of biologically mediated reactions, requires