

THE THERMODYNAMICS OF SOIL SOLUTIONS

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To
J. WILLARD GIBBS
who saw that it must be so
KENNETH L. BABCOCK
who made it work
and
DOUGLAS, DINA, FRANK, AND JENNIFER
who always took my word for it

PREFACE

Chemical thermodynamics is the theoretical structure on which the description of macroscopic assemblies of matter at equilibrium is based. This branch of physical chemistry was created 105 years ago by Josiah Willard Gibbs and was completed by the 1930s in the works of G. N. Lewis and E. A. Guggenheim. The fundamental principles of the discipline thus have long been established, and its scope as one of the five great subdivisions of physical science includes all of the chemical phenomena that material systems can exhibit in stable states. It was in the spirit of these attributes that Lewis and Randall¹ framed their well-known aphorism: "The fascination of a growing science lies in the work of the pioneers at the very borderland of the unknown, but to reach this frontier one must pass over well travelled roads; of these one of the safest and surest is the broad highway of thermodynamics."

Given the firm status of chemical thermodynamics, its application to describe chemical phenomena in soils would seem to be a straightforward exercise, but experience has proven different. An obvious reason for the difficulty that has been encountered is the preponderant complexity of soils. These multicomponent chemical systems comprise solid, liquid, and gaseous compounds that are continually modified by the actions of biological, hydrological, and geological agents. In particular, the labile aqueous phase in soil, the soil solution, is a dynamic, open, natural water system whose composition reflects especially the many reactions that can proceed simultaneously between an aqueous solution and a mixture of mineral and organic solids that itself varies both temporally and spatially. The net result of these reactions may be conceived as a dense web of chemical interrelations mediated by variable fluxes of matter and energy from the atmosphere and biosphere. It is to this very complicated milieu that chemical thermodynamics must be applied.

This book is intended primarily as an introduction to the use of chemical thermodynamics for describing reactions in the soil solution. Therefore no account is given of phenomena in the gaseous and solid portions of soil unless they impinge directly on the properties of the liquid phase. This restriction is conducive to a clarity in presentation and relevant to the interests of most soil chemists. Although the discussion in this book is self-contained, it does require

¹G. N. Lewis and M. Randall, *Thermodynamics and the Free Energy of Chemical Substances*, McGraw-Hill, New York, 1923. Used with the permission of the McGraw Hill Book Company.

exposure to thermodynamics as taught in courses on physical chemistry that employ differential and integral calculus. Since most of the examples discussed relate to soil chemistry, a background or interest in that discipline will be of direct help in understanding the applications presented.

The first two chapters of this book review the fundamental concepts of chemical thermodynamics. Care is taken to show how these concepts relate to soils and the soil solution. Much attention is given to the definitions of the Standard State and the Reference State and to the Standard State chemical potential of a substance, for these topics are seldom discussed carefully in the literature of soil chemistry. The third, fourth, and fifth chapters take up the application of chemical thermodynamics to solubility, electrochemical (including redox), and ion-exchange phenomena as they occur in soils; they contain the bulk of thermodynamics that is of concern to soil chemists. The sixth chapter digresses to consider the molecular theory of cation exchange. This topic has been included because of the widespread use of model approaches, such as diffuse double layer theory, to interpret soil exchange phenomena. A discussion of these approaches from first principles should clarify their subordinate relation to the thermodynamic theory of ion exchange and the more tenuous position they occupy as descriptions of chemical behavior. The seventh chapter presents the thermodynamic theory of water in soil from the perspective taken in soil physics (i.e., that the soil is a three-component, single-phase system). This chapter will introduce soil physicists to a thermodynamic formulation of the problem of soil water while, at the same time, bringing to soil chemists a view of soil as other than a multicomponent, heterogeneous system.

Throughout this book there is much reference also to the *limitations* of chemical thermodynamics in treating natural soil solutions. These limitations refer especially to the influence of kinetics on stability, to the accuracy of thermodynamic data, and to the impossibility of deducing underlying mechanisms. The problem of mechanisms *vis-à-vis* thermodynamics cannot be expressed better than in the recent words of M. L. McGlashan:² "... what can we learn from thermodynamic equations about the microscopic or molecular explanation of macroscopic changes? Nothing whatever. What is a 'thermodynamic theory'? (The phrase is used in the titles of many papers published in reputable chemical journals.) There is no such thing. What then is the use of thermodynamic equations to the chemist? They are indeed useful, but only by virtue of their use for the calculation of some desired quantity which has not been measured, or which is difficult to measure, from others which have been measured, or which are easier to measure." These points cannot be stated often enough.

I have been helped in the development of this book by the constant encouragement and guidance of Dr Kenneth L. Babcock, who rightly may be considered the progenitor of chemical thermodynamics as applied to the soil solution.

²M. L. McGlashan, The scope of chemical thermodynamics, *Chemical Thermodynamics, Spec. Periodical Rpt.* 1:1-30 (1973). Used with the permission of the author and the Chemical Society, London.

To whatever extent soil physical chemists have been able to look more keenly at soil solution phenomena in the past 20 years, they must acknowledge their privileged vantage point on the firm pedestal of his seminal papers.

Perhaps more often than they realize, I have benefited greatly from comments made in seminars and informal discussions by my colleagues, Dr William A. Jury, Dr Shas V. Mattigod, and Dr Albert L. Page. The lecture notes for my course on soil physical chemistry that were provided by Nancy Ball and Carlos Ramos also were of great value in organizing my thoughts, as were the suggestions from the students who read and used this book in draft form: Sabine Goldberg, Cliff Johnston, José Moraes, John Ojala, Marcos Pavan, Tom Quinn, Jeff Stark, Scott Strathouse, and Mohammad Yousaf. Chapter 5 was reviewed in draft by Dr Adel M. Elprince, who suggested the derivation of Eq. 5.52. Chapter 7 was reviewed by Dr William A. Jury, who exorcised a number of unclear passages and errors in the text and guided me as to the current thinking of soil physicists. The entire manuscript was read by Dr Hinrich L. Bohn and Dr James A. Kittrick, to whom I am most deeply grateful for their many suggestions and corrections. Finally, I must thank Ms Mary Campbell-Sposito for her assistance in preparing the indexes, Mr Karolyi Fogassy for his skill in drawing the figures, and Mrs Sharon Conditt for her patience in making a clear typescript from a great pile of handwritten, yellow sheets. None of these people, of course, is responsible for the errors or obscurities that may remain in this book; each only deserves gratitude for keeping the flaws to a relative minimum.

Riverside, California
March 1980

G. S.

*If you have built castles in the air,
your work need not be lost; that
is where they should be. Now put
the foundations under them.*

DAVID HENRY THOREAU

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THE THERMODYNAMICS OF SOIL SOLUTIONS

THE CHEMICAL THERMODYNAMICS OF SOIL SOLUTIONS

I. Variables of State and Thermodynamic Potentials

1.1. SOILS AS THERMODYNAMIC SYSTEMS

From the point of view of thermodynamics, a soil is an assembly of solid, liquid, and gaseous matter, as well as a repository of electromagnetic and gravitational fields. These characteristics, together with a surface that encloses the macroscopic region of space filled by the soil, define the *thermodynamic soil system*. Thus a thermodynamic soil system contains both matter and physical fields and is bounded by a surface of arbitrary shape. This bounding surface is called the *thermodynamic wall* surrounding the soil system.

A thermodynamic soil system is studied through information about its properties which, in turn, are concepts that can be associated with numerical magnitudes obtained from experiment. The properties of a thermodynamic soil system by definition refer to a macroscopic region of space and do not depend for their measurement or interpretation on the previous history of the system. It is important to understand that the thermodynamic properties constitute only a part of all the properties of a soil. Those soil properties that describe phenomena at the molecular scale or those that relate directly to the effect of time are not included, for example. Therefore the concentration of protons and the electric potential at a point of few nanometers away from the surface of a soil colloid suspended in water are not properties of a thermodynamic soil system, nor are the length of time the soil has weathered and the number of occasions that water has percolated through it. Thermodynamics has nothing to say about these properties, although they could be studied in other disciplines of physical chemistry.¹

The properties of a thermodynamic soil system, hereafter to be called simply a soil, may be divided into those that are fundamental and those that are derived. This division is to some extent arbitrary. However, the fundamental properties of a soil always have the distinguishing feature that together they make up the smallest set of properties that provide a complete thermodynamic description but yet can be varied independently (i.e., varied without any change in the values of other fundamental properties). The fundamental properties of

a soil are chosen on the basis of experience, as will be discussed in Section 1.3. A set of numerical values of the fundamental properties is called the *state* of the soil to which they refer. For this reason, fundamental properties also are termed *independent variables of state*.

The properties of a soil, whether fundamental or not, whose numerical values depend on the quantity of matter in the soil (e.g., volume and entropy) are called *extensive*; the properties whose values are not dependent on the quantity of matter in the soil (e.g., pressure, bulk density, and temperature) are called *intensive*. The intensive properties of a soil are mathematical field variables (i.e., their values are associated with points in space that are located in the soil). Since a thermodynamic property always refers to a macroscopic region of space, it is understood that the value of an intensive property at some point in a soil applies to a macroscopically small neighborhood of that point that encloses many solid grains and interstices. If the values of its intensive properties are the same everywhere in a soil, the soil is said to be *homogeneous*. If any one of its intensive properties varies (on the macroscopic scale) from point to point, the soil is said to be *heterogeneous*.

Natural soils are invariably heterogeneous because their intensive properties vary spatially on a macroscopic scale, both from the effects of pedochemical processes and from the direct effect of the gravitational field of the earth. Thermodynamic soil systems, on the other hand, often may be treated as if they were homogeneous in respect to the analysis of experimental data. For example, a small sample of soil being studied in a pressure membrane apparatus may be regarded as homogeneous if gravitational effects are ignored and if the solid and fluid portions of the soil are not differentiated chemically. This point of view, which is conventional in soil physics, will be discussed in detail in Chapter 7.

Every soil consists of *components*, which are defined to be material substances of fixed chemical composition whose amounts can be varied independently in the soil. For example, a synthetic soil consisting of liquid water, NaCl, CaCl₂, Na-montmorillonite, and Ca-montmorillonite contains four components. These are water plus any three of the four solid substances mentioned. There are not five components in this case because it is not possible to vary the amounts of the two chloride salts and the two forms of montmorillonite in the soil independently; a cation exchange reaction links these four compounds.

The composition of a soil is specified in terms of its components. A homogeneous portion of a soil that has a variable composition is called a *solution*. Thus the gaseous, liquid, and solid portions of a soil each may be solutions. The interstices in the soil may contain *air*, a gaseous solution composed principally of nitrogen, oxygen, carbon dioxide, and water vapor, as well as the *soil solution*, an aqueous solution composed of liquid water and dissolved solids. The solid portion of a soil also may be a solution if its composition is mixed. Thus the montmorillonite exchanger containing both Na- and Ca-clay, mentioned above, is a solution. Solutions are special cases of *phases*, which are conditions of pure substances, or mixtures of pure substances, wherein the intensive properties do

not vary with position. For example, consider again the interstices of a sample of soil. If water is the only compound in the interstices and the effects of gravity are neglected, the interstices contain a homogeneous portion of the soil. That homogeneous portion can exist in three phases—gaseous, liquid, or solid. On the other hand, suppose that liquid water and dissolved NaCl were in the interstices. Again neglecting gravitational effects, the interstices now contain a homogeneous system that is in the liquid phase and that is a solution because its composition can be varied. If undissolved air, liquid water, and dissolved NaCl were in the interstices of a soil, the interstices would comprise a heterogeneous system consisting of two solutions: air and an aqueous solution. Both of these solutions, of course, are phases.

The thermodynamic wall surrounding a soil is a very important part of the system. If the wall permits the free transfer of both matter and thermal energy either in or out, the soil is called an *open system* and the wall is said to be *diathermal* and *permeable*. If only certain types of matter may be transferred through the wall, it is said to be *semipermeable*. If the wall permits only the transfer of thermal energy, it is said to be *diathermal* and the soil is called a *closed system*. Finally, if the wall does not permit the transfer of either matter or thermal energy, it is said to be *insulating* and the soil is called an *adiabatic system*. Note that mechanical energy or the energy associated with gravitational and electromagnetic fields may be transferred through any of the walls that have been discussed. Thermodynamic walls are differentiated only by their behavior toward the transfer of matter and thermal energy.

The intensive properties of a soil, excepting those that are simply ratios of extensive properties (e.g., the bulk density), are not strictly characteristics of the soil alone; they are determined by the thermodynamic wall and by the properties of suitable reservoirs that are separated by the wall from the system under study. (A *reservoir* is a large thermodynamic system whose intensive properties do not change in value when the transfer of matter or thermal energy into it or out of it takes place.) Consider, for example, the temperature of a soil. This intensive property is determined by the temperature of a thermal reservoir that is in contact with the soil through a diathermal wall. Under the condition that no net thermal energy transfer occurs through the wall between the reservoir and the soil, the temperature of the soil is said to be equal to the temperature of the reservoir. Similarly, the pressure on a soil is determined by a movable, diathermal wall that connects the soil to a volume reservoir (e.g., a very large cylinder of chemically inert gas). Under the condition that no net mechanical energy transfer occurs through the motion of the wall between the reservoir and the soil, the pressure on the soil is said to be equal to that of the substance in the reservoir. This basic characteristic of certain intensive properties is very important to remember when analyzing thermodynamic processes in soils. For example, needless confusion is introduced by forgetting that no internal thermodynamic pressures exist in a soil containing air and water. Only the thermodynamic pressure exists that is exerted externally on the soil.

1.2. THERMODYNAMIC PROCESSES IN SOILS

A thermodynamic process takes place in a soil when its thermodynamic properties are changed in some fashion. Thus a thermodynamic process will result in a change in the state of a soil. If, during a thermodynamic process, a soil passes exclusively through states of equilibrium, that process is said to be *reversible*. The concept of equilibrium will be developed in Section 2.1. It suffices to recall here that equilibrium states are characterized by a relative maximum in the value of the total entropy of a system and its surroundings, including the reservoirs that control its properties.

Reversible processes are limiting cases of *natural processes*, which are defined as the thermodynamic processes that bring a system into a state of equilibrium. In practice, it is almost always possible to arrange a natural process to be arbitrarily close in behavior to a reversible process. Consider, for example, a very wet soil slurry that is in equilibrium with a thermal reservoir at some temperature and around which is a thermodynamic wall permeable only to water vapor. A water vapor reservoir contacting the soil through the wall is maintained by a salt solution at some vapor pressure $p = p_{\text{eq}} + \epsilon$, where p_{eq} is the equilibrium vapor pressure of water in the soil and $\epsilon < 0$. Under this condition, the natural process of evaporation of the soil water into the reservoir will take place. In the limit that $\epsilon \uparrow 0$ (" ϵ goes to 0 through negative values"), the evaporation becomes a reversible process. This limit is approached as closely as one wishes by a suitable experimental adjustment of the vapor pressure in the water reservoir.

There are several important special cases of thermodynamic processes in soils. If a process results only in an infinitesimal change in one or more properties, it is an *infinitesimal process*. Soil initially in an equilibrium state can undergo only reversible infinitesimal processes, by definition. A thermodynamic process that occurs in a soil surrounded by an insulating wall is an *adiabatic process*. This kind of process takes place, for example, when the heat evolved in a cation exchange reaction occurring in a clay suspension is measured in a calorimeter. It is important to note that adiabatic processes always involve a change in the temperature of a soil, since no thermal reservoir is permitted to exchange energy with the soil and control its temperature. If such a reservoir is present and the temperature is controlled during a process, the process is *isothermal*. If a volume reservoir is present and the pressure applied to a soil is controlled during a process, the process is *isobaric*. If, instead, the volume of the soil is controlled by the reservoir (by an increase or decrease in the applied pressure), the process is *isochoric*.

Consider once again the system consisting of liquid water, NaCl, CaCl₂, Na-montmorillonite, and Ca-montmorillonite. A movable, diathermal wall permeable to water and the two chloride salts (a wall known as a dialysis membrane) surrounds the system. As a combined thermal, volume, and matter res-

ervoir, one may employ a mixed aqueous solution of NaCl and CaCl_2 contained in a water bath apparatus equipped with flow-through capability. The montmorillonite exchanger in the dialysis membrane is immersed in the water bath containing the mixed chloride salt solution. The amounts of NaCl and CaCl_2 in the reservoir are such that no net flow of these salts occurs across the membrane (i.e., the exchanger is in a state of equilibrium with respect to these two components). Similarly, it is arranged that there is no net thermal energy transfer across the membrane and, therefore, thermal equilibrium exists, with the temperature of the system equal to that of the reservoir. Finally, the volume of the dialysis membrane has adjusted itself until no more movement of the membrane occurs and mechanical equilibrium is achieved. Assuming that the montmorillonite structure itself does not dissolve at a significant rate, it may be concluded that the exchanger is in a state of thermodynamic equilibrium with the reservoir that controls its properties.

Now suppose that a small increase in the amount of CaCl_2 and a small decrease in the amount of NaCl in the reservoir occur through an appropriate change in the composition of the solution flowing through the water bath apparatus. If these changes are quite small, the exchanger and the aqueous solution bathing it will undergo an approximately reversible process that will result in a shift in the amounts of NaCl , CaCl_2 , Na-clay, and Ca-clay. This shift is an isothermal cation exchange process. The process is not generally isobaric or isochoric. If, instead of altering the amounts of chloride salts in the reservoir, the temperature of the reservoir were increased by a small fraction of a degree, a nonisothermal cation exchange process would be produced in the system. This process could be arranged so as to bring the exchanger to the same final composition as did the first-mentioned adjustment of the amounts of NaCl and CaCl_2 . These brief remarks and the description of the cation exchange process through dialysis equilibrium are perhaps familiar already. The intent here has been to stress the fundamental thermodynamic aspects of a simple laboratory exchange experiment. The soil process of interest involves changes in the macroscopic properties of the soil produced by adjustments in the reservoirs contacting the soil and controlling its state.

1.3. VARIABLES OF STATE FOR THERMODYNAMIC SOIL SYSTEMS

The set of properties from which the independent variables of state for a soil may be chosen is determined by experience. This experience relates not only to experimentation with the chemical properties of soils and the subsequent development of conceptual models to interpret soil chemical phenomena but also to experience with thermodynamics itself. The following list of soil properties² will prove adequate for the thermodynamic description of soil solution phenomena in the absence of externally applied fields. A generalization to include gravitational fields will be given in Section 7.6.

Temperature Temperature is the criterion for equilibrium with respect to thermal energy transfer. It is measured on the Kelvin scale in units of kelvins (K) and is, of course, an intensive property of a soil.

Entropy Entropy is the principal criterion for thermodynamic equilibrium. It is an extensive property of a soil measured in units of joules per kelvin (J K^{-1}).

Pressure Pressure is the criterion for mechanical equilibrium and refers always to the force per unit area exerted by a volume reservoir on the thermodynamic wall enclosing a soil. Pressure is an intensive property measured in units of newtons per square meter (N m^{-2}) or in the practical equivalent units of atmospheres ($1 \text{ atm} = 1.01325 \times 10^5 \text{ N m}^{-2}$) or millimeters of mercury ($1 \text{ mm Hg} = 1.33322 \times 10^2 \text{ N m}^{-2}$). The unit N m^{-2} is called the pascal (Pa). A pressure of 10^5 Pa is called a bar, a unit that is a common alternative to the atmosphere.

Volume Volume is the extensive variable that describes the spatial extent of a soil and, therefore, is a means of assessing mechanical energy transfer to or from a soil. It is measured in units of cubic meters (m^3), or in the practical units of liter ($1 \text{ liter} = 10^{-3} \text{ m}^3$) or cubic centimeters ($1 \text{ cm}^3 = 10^{-6} \text{ m}^3$).

Chemical Potential The chemical potential is the intensive property that is the criterion for equilibrium with respect to the transfer of matter. Each component in a soil has a chemical potential that determines the relative propensity of the component to be transferred from one phase to another or to be transformed into an entirely different chemical compound in the soil. Just as thermal energy is transferred from regions of high temperature to regions of low temperature, so matter is transferred from phases or substances of high chemical potential to phases or substances of low chemical potential. Chemical potential is measured in units of joules per kilogram (J kg^{-1}) or joules per mole (J mol^{-1}).

Mass Mass is the extensive composition variable for a component of a soil. The quantity of each component is measured by its mass in units of kilograms (kg). Often the mass of a component may be replaced by a secondary variable, the mole number, n , that is simply proportional to the mass for a substance of known, fixed composition. In soils the components do not always have known or fixed compositions, however, and the use of mole numbers is not always possible. If no chemical reaction is being considered, the mole number is not necessary to a thermodynamic analysis.

This set of six thermodynamic properties will be basic to the discussion in the following chapters. A number of intensive variables are omitted that can be defined simply as ratios of the extensive variables (e.g., bulk density, defined as