LETTERS TO THE EDITOR

COMMENTS ON "INCONSISTENCIES IN THERMODYNAMIC ANALYSES OF THE LONG-TERM ISOLATION OF HIGH-LEVEL WASTE"

Schweitzer[1] questions the value of a thermodynamic approach to interpret why some reactions having negative free energy changes do not occur. He acknowledges studies that indicate that reactions that are important for assessing the performance of nuclear waste repositories, such as

$$2Cu + H_2SO_4 + 3Fe_2SiO_4 \Leftrightarrow Cu_2S + 3Fe_2O_3 + 3SiO_2 + H_2O \ , \quad (1)$$

are kinetically hindered by the slow rate of inorganic sulfate reduction at temperatures less than ~200°C. However, he suggests that interpretations of reactions using a thermodynamic/kinetic framework, such as Eq. (1), may not always be valid because of what he perceives as a limitation in the meaningful application of thermodynamic quantities, such as entropy and chemical potential, in systems involving very low concentrations of the reacting species.

Schweitzer's premise is a result of two misconceptions. First, the assertion that thermodynamic relationships are not valid for equilibria involving very low concentrations of reacting species is incorrect. Equilibrium relationships are theoretically valid for all concentrations, even when the concentrations may be too low to have much physical significance. Second, the potential for reactions to occur, relative to a given set of environmental conditions (temperature, pressure, compositions, etc.), is given quantitatively by the chemical affinity, and not by the sign and magnitude of the standard molal Gibbs free energies of reaction. There are additional errors or misstatements in the paper, but most can be traced back to these two basic misconceptions.

The discussion of "thermodynamic artifacts" is based on the misconception concerning the validity of thermodynamics applied to equilibria involving low concentrations. Schweitzer states that "...equilibria that require activities corresponding to concentrations of single molecules in large volumes (10^{-23} M/ℓ) cannot be considered thermodynamically meaningful," and "entropy, chemical potential, and temperature concepts are statistical concepts applying to assemblies and ensembles in which the number of identical particles (N) must be very large." He contends that potential failure mechanisms of copper containers in high-level nuclear waste repositories [such as reaction (1)] should be considered "thermodynamic artifacts," because the concentrations of one or more species in the reaction are so low at equilibrium that they are not meaningful in natural systems. Schweitzer suggests that slow rates of reaction cannot always be used to explain apparent disequilibrium, because this presupposes that an equilibrium state exists and can be achieved given enough time or the presence of a suitable catalyst.

We reiterate that the statistical interpretation of thermodynamic quantities is not based on the existence of a large number of identical particles (or atoms, molecules, etc.), but by the number of possible microstates accessible to a system. Entropy, for example, is proportional to the number of possible microstates in which the macroscopic (i.e., observable) state of the system can be found at a given time. The relationship can be expressed quantitatively by (see, for example, Denbigh[2])

$$S = k \ln \Omega \ , \quad (2)$$

where

S = entropy of the system

k = Boltzmann constant

Ω = number of microstates.

The latter quantity is given by

$$\Omega = \Omega(U, V, N_i) \ , \quad (3)$$

where U and V represent the internal energy and volume of the system, respectively, and N_i stands for the number of molecules of the i'th kind. Entropy therefore varies according to the appropriate functional form of the relationship given by Eq. (3) and is not necessarily simply proportional to, nor limited by, the numbers of particular species in the system.

Changes in entropy resulting from a spontaneous process will reflect an increase in the total number of microstates accessible to the system. For adiabatic mixing involving two components in an ideal solution, for example, the functional representation of Eq. (3) is

$$\Omega_{mix} = (N_1 + N_2)/(N_1|N_2|) \ , \tag{4}$$

and the entropy of mixing, from Eq. (2), is then given by

$$\Delta S_{mix} = -k(N_1 \ln x_1 + N_2 \ln x_2) \ , \tag{5}$$

where x_1 and x_2 are the mole fractions of the two components, 1 and 2, in the mixture (see, for example, Lewis and Randall[3]). This illustrates that statistical interpretations of changes in entropy are also not based simply on the presence of a very large number of identical particles, but rather on the manner in which the particles may be distributed among the various possible microstates. Irreversible processes can be interpreted as an evolution wherein the macroscopic state of the system more and more frequently is found in one of a large number of indistinguishable microstates. As expressed by Lewis and Randall,[3] "... With an infinite number of molecules, or with any number of molecules taken at an infinite number of times, the probability that the macroscopic state of the system will lie within this group [of most probable microstates] is infinitely greater than the probability that it will lie outside of that group."

Thermodynamic analyses may indicate that the concentrations of some species in a reaction are so low at equilibrium that they cannot have much physical significance. This does not invalidate a thermodynamic approach, but simply indicates that alternative ways of writing reactions should be found to characterize the system in terms of species that are present in detectable concentrations at equilibrium. Stumm,[4] for example, points out that aqueous electrons should be considered only as a phase rule component in redox calculations, because as an aqueous species they do not, in a practical sense, have an existence of their own (see also Hostettler[5] and Thorstenson[6]). Thermodynamic components are abstract quantities and need not represent compositions of real entities in a system, provided the compositions of all species can be described in terms of the components selected for a thermodynamic analysis. Equilibrium relationships involving electron transfer reactions are not invalidated by the virtual absence of aqueous electrons. The measurable concentrations of redox-sensitive species are fixed at equilibrium and can be ascertained by calculation.

Lewis and Randall[3] also address the thermodynamic significance of low concentrations calculated from an equilibrium analysis of solubility or vapor pressures. They conclude that while concentrations "... are sometimes obtained which are so small as to seem ridiculous to the uninitiated... such figures, when properly interpreted, have as definite a significance, and often as high an accuracy, as others which are capable of direct measurement."

Schweitzer is correct, therefore, in recognizing the lack of physical significance of concentrations on the order of 10^{-23} M/ℓ, but is incorrect in asserting that a thermodynamic analysis of equilibria involving such low concentrations is not meaningful. We disagree with his conclusion that a lack of physical significance provides a basis for rejecting a kinetic interpretation to explain why reactions such as reaction (1) can fail to achieve equilibrium over very long periods of time.

Schweitzer also introduces the concept of "free ride reactions," which is based on the incorrect use of standard Gibbs free energies of reactions as a measure of reaction potential for systems containing reactants and products that are not in their standard states. The criterion for determining whether a reaction j will spontaneously occur is correctly given by the chemical affinity A_j and not by the standard Gibbs free energy of reaction. The chemical affinity is given by (see, for example, Helgeson[7])

$$A_j = -RT \ln(Q_j/K_j) \ , \tag{6}$$

where

K_j = equilibrium constant

Q_j = activity product for the j'th reaction, given by

$$Q_j = \Pi a_i^{\nu_{i,j}} \ . \tag{7}$$

In Eq. (7), a_i represents the activity of the i'th species and $\nu_{i,j}$ corresponds to the stoichiometric reaction coefficient for the i'th species in the reaction (positive for products of the reaction and negative for reactants).

The relationship between the chemical affinity and the standard molal Gibbs free energy of reaction, ΔG_r^0, is given by

$$\Delta G_r^0 = -RT \ln K_j \tag{8}$$

and

$$\Delta G_r = -A_j = -RT \ln K_j + RT \ln Q_j \ . \tag{9}$$

Reaction j will spontaneously occur (i.e., irreversible formation of products from the reactants) when $\Delta G_r < 0$ (i.e., when $A_j > 0$). The reaction will not occur spontaneously if $\Delta G_r > 0$. The reaction is reversible at equilibrium when $\Delta G_r = 0$, and then $Q_j = K_j$. The potential for an irreversible reaction to occur depends, therefore, on the values of the activities of the reactants and products, at given temperature and pressure, and is measured relative to the standard molal Gibbs free energy of reaction, calculated using data for a system in which all reactants and products are in their standard states (e.g., at the temperature and pressure chosen for the standard state, with unit activity for pure solids and liquids, ideal gas behavior for gas species at a pressure of 0.1 MPa, and a hypothetical ideal 1 molal solution for aqueous species).

Schweitzer uses ΔG_r^0 (termed ΔG, but identified in the second paragraph under the heading "Conclusions," and by inference from his calculations, as the standard molal Gibbs free energy of reaction, calculated from standard free energies of formation of reactants and products), instead of the chemical affinity, as a measure of reaction potential. He identifies a free ride reaction as a reaction having a negative ΔG_r^0 value, which is formulated as the sum of two or more subordinate reactions, one (or more) of which may have a positive ΔG_r^0 value. A subordinate reaction having a positive ΔG_r^0 value is therefore given an algebraic free ride, according to Schweitzer, by its combination with a reaction having a larger negative ΔG_r^0, resulting in a negative ΔG_r^0 for the composite reaction. However, because standard Gibbs free energies of reaction are used by Schweitzer, all reactants and products must be assumed to exist in their standard states. This approach, therefore, cannot provide a basis for determining reaction potential in systems (for example, those existing in a repository) that are not at standard-state conditions. In addition, it is unclear how Schweitzer uses these fixed standard-state values for ΔG_r^0 to assess the effect of variable concentrations of reactants and products [e.g., in Eqs. (4), (19), and (20)]. Evaluation of variations in aqueous compositions is prohibited by the assumptions and structure of Schweitzer's formulations. The correct evaluation of the spontaneity of irreversible reactions is given by Eq. (9).

Based on the arguments given above, we conclude that "thermodynamic artifacts" and "free ride reactions" are misconceptions that invalidate Schweitzer's assertion that a kinetic interpretation cannot be used to explain the presence of coexisting minerals, or concentrations of aqueous species and gases, that are incompatible with conditions of equilibrium.

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RESPONSE TO "COMMENTS ON 'INCONSISTENCIES IN THERMODYNAMIC ANALYSES OF THE LONG-TERM ISOLATION OF HIGH-LEVEL WASTE'"

Arthur and Apted[1] claim that the premises in my paper[2] are based on two misconceptions. One is associated with their assumption that equilibria apply to single molecules in large volumes and the other is associated with their assumption that the potential for a reaction to occur cannot be given by the standard Gibbs free energy change because it applies only to materials in their standard states. I believe they are incorrect on both counts.

In my paper, I have argued that single molecules in large volumes should not be considered thermodynamic systems in equilibrium because concepts such as entropy, chemical potential, temperature, etc., are ill-defined for single molecules. These are statistical concepts applying to assemblies in which the number of identical particles (N) must be very large.

Arthur and Apted disagree, claiming that "equilibrium relationships are theoretically valid for all concentrations, even when the concentrations may be too low to have much physical significance." They then proceed to argue

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> where U and V represent the internal energy and volume of the system, respectively, and N_i stands for the number of molecules of the i'th kind.

The above discussion is not valid for a single molecule in a large volume. A single molecule is not a "system" to which an internal energy (U) can be assigned with justification nor is it a system that contains a number (N_i) of molecules of the i'th kind. The authors are treating the concept of possible microstates available to a system and the mathematical foundations on which the Boltzmann entropy are justified in too simplistic a fashion.

The Boltzmann entropy is, by definition, the number of *a priori* equally probable complexions of an *assembly* having given values of U, V, and N. For a single molecule, it is not possible to defend the concept of a microstate nor is it possible to support claims as to which microstates are equally probable. It is also not possible to justify assumptions that the assignment of temperature or internal energy to the possible "microstates" of a single molecule is valid.

The Boltzmann entropy is calculated from

$$\Omega = \sum_n N! \Big/ \prod_i n_i! \ ,$$

$$\left[\sum_i n_i = N\right] \ ,$$

and

$$\left[\sum_i n_i u_i = U\right] \ ,$$

under the restrictions that

$$n_1 + n_2 + n_3 \ldots + n_i = \sum_i n_i = N$$

and

$$n_1 u_1 + n_2 u_2 + n_3 u_3 \ldots + n_i u_i = \sum_i n_i u_i = U \ .$$