"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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REFERENCES

1. D. G. SCHWEITZER, "Inconsistencies in Thermodynamic Analyses of Long-Term Isolation of High-Level Waste," *Nucl. Technol.*, **84**, 88 (1989).

2. K. DENBIGH, *The Principles of Chemical Equilibrium*, 3rd ed., Cambridge University Press, London (1978).

3. G. N. LEWIS and M. RANDALL, *Thermodynamics*, 2nd ed., revised by K. S. PITZER and L. BREWER, McGraw-Hill Book Company, New York (1961).

4. W. STUMM, "Interpretation and Measurement of Redox Intensity in Natural Waters," Comment to T. FREVERT, "Can the Redox Conditions in Natural Waters be Predicted by a Single Parameter?," *Schweiz. Z. Hydro.*, **46**, 2, 291 (1984).

5. J. D. HOSTETTLER, "Electrode Electrons, Aqueous Electrons, and Redox Potentials in Natural Waters," *Am. J. Sci.*, **284**, 734 (1984).

6. D. C. THORSTENSON, "The Concept of Electron Activity and its Relation to Redox Potentials in Aqueous Geochemical Systems," Open-File Report 84-072, U.S. Geological Survey (1984).

7. H. C. HELGESON, "Mass Transfer Among Minerals and Hydrothermal Solutions," *Geochemistry of Hydrothermal Ore Deposits*, 2nd ed., H. L. BARNES, Ed., John Wiley & Sons, New York (1979).

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

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])

$$S = k \ln \Omega$$

where

S = entropy of the system

k = Boltzmann constant

Ω = number of microstates.

The latter quantity is given by

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

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

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

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

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

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

The evaluation of Ω in closed algebraic form from this expression is impossible unless N is very large. Neither $\sum_i n_i$ nor $\sum_i n_i u_i$ can be justified as an applicable factor describing or distinguishing equally probable microstates of a single molecule.

The authors seem to believe that statistical support for equilibria applied to one molecule can be obtained from the notion that the number of particles and the number of possible equally probable microstates available to an assembly are independent concepts. They are not. *The number of available microstates is determined by the number of ways of dividing N particles into groups that contain $n_1, n_2, \ldots, n_i$ particles. The N particles are identical. The groups differ from each other in that each group has a different energy.*

The number of microstates, i.e, the number of ways of dividing N identical particles into i groups containing n_1, n_2, $n_3, \ldots, n_i$ particles (Ω) cannot be evaluated for small N and, as such, has no meaning for a single molecule. For large N, it is possible to show that only the largest term in the summation defining Ω makes a significant contribution to its value. It is the value of this term that is used in calculations as a test to justify that the hypotheses used in the statistical mechanical definition of entropy agree with the observations obtained from the chemical operational definition

$$dS = DQ_{rev}/T \ .$$

The Lewis and Randall quote used by Arthur and Apted deals with macroscopic states that imply assemblies, i.e., "...the probability that the *macroscopic* state of the system..." and has no meaning for a single molecule.

The concept of imagining a time average of one molecule traversing N (or Ω) "states" over time has no theoretical support as an alternative for conventional statistical evaluation of thermodynamic equilibrium properties. The states are not physical entities. They are configurations obtained by arranging a very large number of identical particles into a large number of distinguishable groups with different group properties.

There are other problems with assuming that equilibria apply to single molecules *even if time averaging statistics were acceptable as a substitute for large N statistics and even if the temperature were not ill-defined.* For example, the entropy changes at constant temperature in first-order phase transitions (i.e., melting-freezing equilibria) are not meaningful for single molecules. There is no defensible method to declare that a single molecule can be associated with either the liquid or solid state at a temperature where both can coexist.

Arthur and Apted, in postulating their view that "equilibrium relationships are theoretically valid for all concentrations, even when the concentrations may be too low to have much physical significance," are ignoring several pertinent limitations of statistical mechanics and entropy calculations. In general, it is not possible to justify, other than through the mathematics of large N statistics, that a single term can be used to replace the sum that defines the number of available microstates. In general, it is also not possible to define, through independent theory, the number of equally probable microstates. It is an underlying hypothesis of statistical mechanics that all conceivable states of an assembly with the same values of U, V, and N are equally probable. *If the "assembly" cannot be assigned a value of U and V and N, it cannot be assigned a defensible value of entropy.*

I find the example of electron transfer reactions and the absence of aqueous electrons given by Arthur and Apted unrelated to the points raised in my paper. It is well known that a classic approach to the concept of dynamic equilibrium invokes the hypothesis that equilibrium is achieved for a given set of reactants and products when the kinetic rates of the forward and back reactions become equal. The assumption that the forward and back kinetic reactions at equilibrium may involve small concentrations of activated species or high-energy intermediates does not invalidate thermodynamic treatments of the relationships between the macroscopic activities of the postulated or measured reactants and products. These are predicted from measurements used to develop the free energy of formation tables and the derived internally consistent thermodynamic data bases. If such predictions do not match observation, then it is generally assumed that the postulated reaction does not include the correct naturally occurring species and was written with either too few or too many species. Thermodynamic properties of kinetic intermediates do not enter into equilibrium calculations.

I find the discussion by Arthur and Apted on the "differences" between the chemical affinity and the standard Gibbs free energy pedantic, simplistic, and irrelevant to the points made in my paper. Their discussion on the limitations of the standard Gibbs free energy is incorrect.

After claiming that the correct criterion for determining whether a reaction *"will spontaneously occur"* is the chemical affinity and not the standard Gibbs free energy, they proceed to offer the classic relationships (available in most freshman texts on thermodynamics) between the standard Gibbs free energy and the equilibrium constant and/or chemical affinity. They attribute a "misconception" to me by claiming

> 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.

The authors seem to have a distorted view of the logic and manner in which speculations are made on possible changes in activities of species in postulated reactions. The prime sources of data for such speculations are measurements yielding the free energy of formation of compounds from elements. These data are given in the form of standard Gibbs free energies at given temperatures. Simple algebraic manipulation of these source reactions allows one to obtain the free energy change associated with the conversion of reactants in their standard states to products in their standard states. This value of the standard free energy change is then used to calculate the numerical value of the equilibrium constant for the appropriate temperature. The form of the equilibrium constant involves functions of the thermodynamic activities of the postulated species. The individual functions are determined from the correctly balanced postulated reaction.

To speculate on what value the activity of a given species will have at equilibrium, the values of the activities of the other species at equilibrium must be known or assumed.

The point to be made is that, with very few exceptions, neither the equilibrium constant nor the activity product are available as prime sources of data for speculation. In the absence of specific equilibrium measurements dealing with

the reaction as postulated, the equilibrium constant is calculated from the standard free energy change for the postulated reaction. The thermodynamic activities of the other reactants and products must be assumed or obtained from independent measurement or independent theory.

The magnitude of the Gibbs free energy change for reactants in their standard states converting to products in their standard states at a given temperature is the basic data source for determining the quantitative value of the relationship between reactants and products for what can be an infinite number of activity and concentration sets that are stable and will not change at that temperature. The claim that its use is valid only for materials in their standard states is as misleading and as incorrect as is the claim that canaries were used in coal mines only as a source of music.

By itself, the sign and numerical value of the standard free energy for reactants and products in their standard states is a direct and classic indicator for estimating relative differences in the equilibrium activities of the numerator and denominator of the equilibrium constant. If desired, it can be used to calculate the quantitative value of the equilibrium constant. It is not restricted to situations where the reactants and products must be in their standard states.

I do not believe that this approach is a misconception on my part. What I do believe is that the claim by Arthur and Apted that "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" is naive and erroneous.

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REFERENCES

1. R. C. ARTHUR and M. J. APTED, "Comments on 'Inconsistencies in Thermodynamic Analyses of the Long-Term Isolation of High-Level Waste,'" *Nucl. Technol.*, **86**, 313 (1989).

2. D. G. SCHWEITZER, "Inconsistencies in Thermodynamic Analyses of Long-Term Isolation of High-Level Waste," *Nucl. Technol.*, **84**, 88 (1989).

COMMENTS ON "AMERICIUM FILTRATION IN GLAUCONITIC SAND COLUMNS"

The recent paper by Saltelli et al.[1] presents the migration characteristics of polydispersed ^{241}Am colloid in sand columns. In this paper, the nature of the colloid migration was explained as convection, filtration, and sorption of the polydispersed colloid in solution. The sorption saturation mechanism was interpreted with a Langmuir isotherm.

The most interesting observation in this work is that the plateau of americium concentration in the column was generated rapidly (within 28 days) and did not seem to increase with time. This phenomenon was explained as not due to the colloid filtration, but due to the adsorption of the colloid on the packing material under a Langmuir-type isotherm. Considering this observation, polydispersed colloid migration in the porous media was modeled and it showed a good agreement with experimental results. However, if we look into this model, it shows an inconsistency with the observation: Even though it was explained that the plateau was not thought to be affected by colloid filtration, Eq. (17) included the filtration term. Thus, in Figs. 8, 9, and 10, the americium plateaus from modeling increase with time.

In summary, the modeling through observation does not seem to be proper.

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REFERENCE

1. A. SALTELLI, A. AVOGADRO, and G. BIDOGLIO, "Americium Filtration in Glauconitic Sand Columns," *Nucl. Technol.*, **67**, 245 (1984).

RESPONSE TO "COMMENTS ON 'AMERICIUM FILTRATION IN GLAUCONITIC SAND COLUMNS'"

I have read Dr. Choi's letter and am puzzled by his concluding remark.

Of course my Eq. (17) includes a filtration term; the point we are making in the paper is that the filtration term is not responsible for the plateau at early times, which—I believe—we have shown.

Is the apparent plateau in Figs. 8, 9, and 10 increasing? This does not seem to be the case at all. What is increasing is the overall colloid concentration in the column, which is superimposed on the plateau; in Fig. 10 the plateau is no longer visible.

We encourage Dr. Choi to verify the above by testing the model without the sorption term, in order to verify the influence of filtration alone.

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