A Proposed Unified Approach to the Thermochemistry of Fluids

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November 1990

A practical approach is proposed to thermochemistry, which would be based on a unified model of physical, transport, thermal, and chemical behavior of fluids. The model would provide a bridge between the microscopic and macroscopic properties. The model microscopic behavior of individual fluids would be used as a basis for determining the properties of reacting mixtures.

INTRODUCTION

The macroscopic physical, transport, thermal, and chemical properties of fluids (liquids and gases) are considered to be manifestations of microscopic properties. When viewed from this perspective, these properties are not seen as unrelated or independent. Typically the macroscopic properties of pure non-reacting fluids are approximated by empirical relationships, which may or may not be based on a conceptual model of the microscopic. Mixtures of reacting fluids are often approximated by empirical relationships, which are drawn from laboratory experiments. By necessity these laboratory experiments involve only select proportions of specific groups of fluids. Because of the increased complexity of reacting mixtures compared to pure non-reacting fluids, these latter empirical relationships are often quite simplified and rarely traceable to a microscopic model.

The proposed approach would be to develop (or select an existing) model, which could relate the microscopic and macroscopic properties of a wide range of fluids. The microscopic properties of the individual fluids would then be used to approximate the interactions and mixture properties. The thermochemical aspects of the mixture would be considered to be a subset of the mixture properties.

In this sense the proposed approach would be similar to a corresponding states model except that the parameters of correspondence would be taken at the microscopic level (e.g. collision diameter and mean free path) rather than at the macroscopic level (e.g. critical temperature and pressure). Because such an approach would provide a methodology by which to approximate the behavior of reacting mixtures based on the properties of the reactants and the products individually, the amount of empirical data required to drive the model for a given mixture would be greatly reduced. Furthermore, because the approach would provide a unified model of the properties, the number of simplifications required in order to compute such things as composition would be reduced (i.e. the simplifications would be at a lower level—in the model—rather than in the empirical forms, making them fewer in number, more easily identifiable, and testable).

ASSUMPTIONS

In order to develop a model for the behavior of fluids it is necessary to make certain assumptions. Part of the testing and improving of the model would be the further inspection of the assumptions. The assumptions can be broken into categories as follows:

The Macroscopic Continuum Assumption

It is recognized that there is an irresolvable degree of secular and spatial uncertainty inherent in any physical system. It is also recognized that there is a fuzzy threshold below which a continuum cannot be reasonably assumed to exist. Nevertheless, for most physical systems there is a secular and spatial scale at which for practical purposes the behavior can be viewed from a macroscopic perspective. A corollary to this assumption would be that the calculus of continuous functions may be applied to such systems under appropriate conditions.

The Reduction Assumption

It is assumed that macroscopic properties are manifestations of microscopic ones. A corollary to this assumption would be that if one were able to mathematically describe microscopic behavior, then through the devices of integral calculus, one should, at least in theory, be able to describe the macroscopic behavior. Conversely, if one were able to mathematically describe macroscopic behavior then through the devices of differential calculus, one should, at least in theory, be able to describe the microscopic behavior. A consistent model would be a bridge between the two perspectives.

The Extended Gibbs Rule

If it can be assumed that macroscopic properties are manifestations of microscopic ones, and it is recognized that there is a limited number of mechanisms by which the microscopic members of a system interact, then it is reasonable to deduce that the number of independent macroscopic properties of a system is limited by the number of interaction mechanisms. A practical example of this deduction would be the following. The pressure of a pure non-reacting fluid is uniquely determined by the temperature and density. In order to determine the enthalpy, entropy, free energy, and celerity for such a fluid, it is only necessary to add the specific heat at zero pressure (as a function of temperature). A corollary to this assumption would be that in order to determine the viscosity, thermal conductivity, and self-diffusion coefficient it should be necessary to add only one other parameter such as the viscosity at zero pressure (as a function of temperature) provided that there is only one additional significant interaction mechanism responsible for these macroscopic manifestations.

The Louisville Theorem and Equilibrium

The Louisville Theorem is the most basic statement of the concept of equilibrium. It can be summarized as follows: the ultimate macroscopic description of any isolated system will be independent of time. Stated in a different way, any isolated system will proceed to a state, which is not only stable, but terminal. This condition will persist until there is some interaction with the surroundings, in which case the system would no longer be isolated. It is also recognized here that there can be different time scales associated with an evolving system. Diffusion, convection, chemical reactions, and nuclear reactions may occur in the same system at similar or vastly different time scales. These time scales are, of course, dependent on the individual controlling mechanisms.

The Gibbs Condition and Equilibria

Gibbs reasoned that the ultimate state postulated by the Louisville Theorem would be that which corresponded to the minimum free energy (which is equivalent to the maximum entropy in the case of an isolated system). Chemical equilibria are computed based on this postulate. The elemental abundance constraints and the Gibbs Condition form a set of simultaneous equations

whose solution is the equilibrium molar abundances. There are several methods for solving this set of equations having various computational performance. All of these methods require assumptions about the nature of the reacting fluid mixture; because they all require the computation of the free energy. The proposed model would, of course, be required to supply functional relationships for the free energy.

Reaction Rate and Path

The Gibbs Condition is not sufficient to provide a basis for determining reaction rate or the path taken from the initial conditions to the ultimate state. Free energy is a point function (ie. the difference in the free energy of a system between two states depends only on the endpoints and is independent of the path). Work and heat are path functions (ie. the quantity associated with a transformation of the system depends on the path taken between the endpoints). From the perspective of calculus, point functions are represented by exact differentials; whereas path functions are represented by inexact differentials. There are an infinite number of paths between any two points. If work, heat, or reaction rate are desired results from a model, then it must provide some means of prescribing the path.

If it can be assumed that the driving force for a reaction is proportional to the excess free energy (ie. the difference between the current free energy and the final free energy) then it could reasonably be presumed that the path would follow the gradient. The gradient of the free energy at the ultimate state is zero; thus this path would be consistent with the final destination. This path would be analogous to the mathematical method of steepest descent for solving nonlinear equations. The method of steepest descent is not necessarily the shortest path to the final destination nor does it necessarily arrive at the final destination in the fewest number of steps; nevertheless, each step represents a reduction in the residual. For an evolving thermochemical system, this gradient following would mean that the transformation would take a path, which always reduces free energy. Such a path would be consistent with the Second Law of thermodynamics. In fact, the only other type of path that would be consistent with the Second Law would be one that followed down gradient for a span, then followed along a contour of constant free energy, then resumed down gradient.

THE CONCEPTUAL MODEL

The model could be described by a series of statements identifying a conceptual microscopic mechanism and its corresponding macroscopic manifestations.

The Limiting Volume

If a system consisting of a fixed number of stable members is isothermally compressed, there exists a fuzzy volume at which the pressure increases dramatically with decreasing volume. For some equations of state this is not a clearly identifiable value; whereas for others it is a singularity. For the Lennard-Jones potential, for instance, this would be the bottom of the free energy well. For the van der Waals equation of state, this would be the parameter "b". The limiting volume is presumed to be an indication of the size of the individual particles, which make up the fluid. The inter-particle forces and transfer via collisions—from which arise macroscopic properties such as pressure and viscosity—would be related to this limiting volume. The behavior of reacting a mixture should also depend on the limiting volumes of its members. Therefore, the equation of state—which would be part of the model-should involve a clearly identifiable limiting volume.

The Limiting Rate of Propagation

The limiting rate of propagation of an infinitesimal disturbance in a fluid is one definition of the celerity. The celerity is completely determined by the equation of state. If the celerity were presumed to be equal to the mean effective particle velocity, then there would be another link between the microscopic and macroscopic properties. Furthermore, if the speed distribution were assumed to be normal, then the total energy can be separated into kinetic and all other contributing mechanisms. This last deduction will be used later to determine mixture properties.

The Mean Free Path

The mean free path is the average distance traveled by a particle before a collision. It has long been recognized that the viscosity is related to the mean free path. Diffusion is proportional to the mean free path and the mean particle velocity. Thermal conductivity is proportional to the specific heat, the density, the mean free path, and the mean particle velocity. Thus there would be additional links between the microscopic and macroscopic properties.

THE PROPERTIES OF THE MIXTURE

In order to address thermochemical reactions, the model must describe the behavior of mixtures. Some success has been achieved in the past using the model of corresponding states. For many substances, the model of corresponding states based on critical properties is sufficiently accurate to determine compressibility, enthalpy, entropy, viscosity, and thermal conductivity. The proposed model would be similar to the model of corresponding states. The major difference being that instead of basing the correspondence and weighting on macroscopic critical properties, the proposed model would be based on microscopic properties. Because the proposed model links the microscopic and macroscopic properties, the required microscopic properties—which cannot be directly measured and are not readily available—can be computed from macroscopic properties—which can be measured and are readily available.

Limiting Volume of the Mixture

If the limiting volume of the constituents is known, as is the number of moles of each; and it could be presumed that the limiting volumes are unaffected by the presence of the other constituents (this is not typically true of other mixture properties); then the limiting volume of the mixture can be computed directly. This is the first step in determining the equation of state for the mixture.

Specific Heat of the Mixture

The total energy of a mixture can be divided into three categories: that due to structure (viz. the heat of formation), that due to kinetics, and that due to inter-particle fields. The heat of formation must be supplied as an experimentally determined value. At zero pressure, it is reasonable to assume that the inter-particle fields are responsible for only a negligible fraction of the total energy. The specific heat at zero pressure for the individual constituents must be supplied as experimentally determined values. It might well be assumed that the specific heat of the mixture at zero pressure can be approximated by the mole weighted average of the constituents. The specific heat and energy at any conditions other than zero pressure can be computed from the equation of state. This leaves only the energy due to inter-particle fields, which, by definition, is the only remaining unknown.

Celerity of the Mixture

Because the celerity can be computed from the equation of state, and the presumption has been made that the kinetic energy is directly related to the celerity, this brings a closure on the celerity, specific heat, and the equation of state.

The Mean Free Path of the Mixture

The effective mean free path of the mixture would be presumed to be determined by the density, the limiting volume, and the celerity. The viscosity, thermal conductivity, and self diffusion coefficient for the mixture would then be determined as before, except with the computed microscopic mixture quantities.

Free Energy of the Mixture

Once the equation of state and specific heat for the mixture is determined then the free energy of the mixture and each of its constituents is determined. Thus the state satisfying the Gibbs condition and the presumed direction of the path along the gradient to this state is determined and the reaction can be solved.

Free Energy of Precipitates

Precipitates are often presumed not to participate in the reaction once they are formed. This follows logically from the presumption that the gradient of the free energy of the mixture is independent of the molar abundance of the precipitates. This presumption, however, precludes stable computation of the chemical equilibria. A more advantageous and consistent presumption would be that the precipitates continue to contribute to the gradient of the free energy by virtue of their limiting volumes as long as they remain dispersed throughout the mixture.

REACTION RATE

Given that the ultimate result of any reaction is determined by the Gibbs Condition, and that this state can be computed from the free energy and its various partial derivatives, and that these may be in turn computed from the previously described equation of state, and presuming that the path of the reaction is as described previously along the gradient of the free energy, and that the driving force for the reaction is proportional to the excess free energy, then the only parameter remaining is the constant (or constants) of proportionality. These must be determined from experimental data, but should be dependent on the microscopic properties already computed (ie. mean free path, celerity, and self diffusion coefficient). These data already exist and are an integral part of purely empirical reaction rate models. Thus the necessary constants of proportionality could presumably be extracted from existing data rather than resorting to additional laboratory experiments. Provided that the basis of the model is sound, these constants of proportionality should be more clearly and easily describable than empirical relationships for reaction rate which are not based on a unified model.

SUMMARY

In summary, a unified model for the behavior of reacting mixtures has been proposed for the computation of thermochemical processes including chemical reactions. This proposed model of reacting mixtures would be based on the concept of adding microscopic building blocks rather than macroscopic ones. All of the properties of the mixture—including free energies, which determine the outcome of chemical reactions—would be obtained from the mixture model through the devices of differential calculus. The proposed model would require less empirical

data than a model based predominantly on empirical correlations. The proposed model would involve simplifications—as do all practical models; however, these simplifications would be at a lower level—in the model—rather than in the empirical forms, making them fewer in number, more easily identifiable, and testable. The proposed model would provide a means by which to extend the zone of applicability beyond that specifically tested by laboratory experiment.

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