**Grantee:** Washington University
Department of Earth & Planetary Sciences
St. Louis, MO 63130

**Grant:** DE-FG02-92ER14297

**Title:** Development of an Experimental Database and Theories for Prediction of Thermodynamic Properties of Aqueous Electrolytes and Nonelectrolytes of Geochemical Significance at Supercritical Temperatures and Pressures

**Time Period:** 15 Sept 01 – 31 May 02

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**OBJECTIVES:** The objectives of this research are to combine new experimental measurements on heat capacities, volumes, and association constants of key compounds with theoretical equations of state, and with first principals quantum mechanical predictions, to generate estimates of thermodynamic properties of aqueous solutes. The resulting thermodynamic data allow quantitative models of geochemical processes at high temperatures and pressures.

**PROJECT DESCRIPTION:** This project is part of ongoing collaboration between Prof. Everett Shock of Washington University and Prof. Robert Wood of the University of Delaware, which involves 1) experimental measurements on key compounds 2) making substantial improvements in theoretical equations of state for aqueous nonelectrolytes and electrolytes based largely on these experimental measurements 3) pursuing novel applications of these equations of state to the study of high temperature/pressure geochemical processes involving aqueous fluids, and 4) developing and using *ab initio* quantum calculations with molecular dynamics simulations to predict chemical potentials of aqueous solutes where experimental measurements are impossible or not available. The experimental work is conducted at the University of Delaware. Geochemical applications of the data are done at Washington University. Efforts to improve the equations of state and develop predictive methods are shared between the two labs, because this task in particular requires close collaboration between the Principal Investigators.

**RESULTS:** Progress continues with analysis and critique of thermodynamic data, development of estimation methods, and exploration of new equations of state for nonelectrolytes. Recently, Dr. Andrey Plyasunov has completed a study of second cross virial coefficients and cross Joule-Thomson coefficients for interactions involving water. This project involved assembling all of the relevant experimental data from which these coefficients can be calculated, developing methods to extrapolate and estimate these coefficients, and working out a group contribution scheme for aqueous organic

nonelectrolytes. Two papers were completed and submitted (Plyasunov and Shock, 2002; and Plyasunov et al., 2002).

We have also concentrated on further developments of our Fluctuation Solution Theory (FST) based models for aqueous species. In their current form these formulations can be applied to neutral solutes, given values of the second cross virial coefficient with water. Now that such coefficents can be more reliably estimated, we expect renewed progress with the FST approach.

In addition, work has begun on methods to predict vapor-liquid distribution constants up to the critical temperature of water for many aqueous solutes. For many geochemical applications, values of the vapor-liquid distribution constants are needed for quantitative modeling of the fate of chemical constituents when fractionation between liquid and vapor phases occurs. There are many suggestions in the literature that boiling can have dramatic effects on the evolution of hydrothermal solutions, but sound numerical approaches are uncommon. We intend to calculate the distribution constants for many inorganic species and obtain values for organic functional groups as well. Then we plan to pursue geochemical applications to geothermal systems. These efforts will be complimentary to a new project by Shock, Prof. Dennis Bird of Stanford and Prof. Stefan Arnorsson of the University of Iceland to quantify trace element mobility in Icelandic geothermal and hydrothermal systems.

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**Key Words**: thermodynamic properties of geologic fluids, aqueous solution chemistry, supercritical fluids, volumes, heat capacity, high temperature, estimation methods, predictions.

27 June 2002

# Development of an Experimental Database and Theories for Prediction of Thermodynamic Properties of Aqueous electrolytes and Nonelectrolytes of Geochemical Significance at Supercritical Temperatures and Pressures

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DOE Grant: DE-FG03-02ER15361

## PROGRESS REPORT FOR 2003

Research funded by this grant involves the development of new theoretical equations of state for aqueous solutions of nonelectrolytes, methods to estimate thermodynamic data not available from experiments, summary and critique of available data, and development of an online database of properties of organic aqueous compounds. Results of this research have been reported in several presentations in seminars as well as national and international meetings. This report summarizes research highlights of the last year (2003) and gives a complete list of papers published, accepted, or submitted during the year.

## COMPILATION, CORRELATION AND ESTIMATION OF SECOND CROSS VIRIAL COEFFICIENTS FOR INTERACTIONS INVOLVING WATER AND VOLATILE NONELECTROLYTES

Thermodynamic properties of neutral aqueous compounds in low-density gas-like $H_2O$ can be rigorously calculated from the virial equation of state, provided that the necessary values of the virial coefficients between water and compounds under consideration are known. This circumstance explains our interest to know the values of the second cross virial coefficients, $B_{12}$, for interactions between water and other compounds. First, we compiled or evaluated from existing experimental data (specifically: PVT properties and excess enthalpies of gas mixtures, solubility of the condensed phases of liquid water or ice in compressed gases) values of $B_{12}$ for interactions of water with about 30 compounds, which differ greatly in size, polarity, and strength of water-solute interactions (inert gases, nonpolar, polar and "hydrogen-bonding" solutes) (Plyasunov and Shock, 2003a). This inventory provides a strong foundation for a search for correlations to estimate $B_{12}$ values. We propose two ways to predict/estimate values of $B_{12}$ (Plyasunov et al., 2003). First, it appears possible to estimate the mixture-specific parameter of the Tsonopoulos correlation, the knowledge of which (together with the properties of pure compounds) allows predictions of $B_{12}$ values over a wide range of temperatures. Second, there is strong empirical evidence that a group contribution approximation is applicable to cross virial coefficients for interactions between water and members of homologous series of organic compounds.

# ESTIMATION OF THE KRICHEVSKII PARAMETER FOR VOLATILE NONELECTROLYTES IN WATER

Our strategic goal is the development of equations of state for aqueous solutes over wide ranges of temperatures and densities. However, the overwhelming majority of experimental data are obtained at high densities in liquid-like $H_2O$. Establishing second cross virial coefficients between water and other compounds puts rigorous constrains on the properties of aqueous solutes at very low densities in gas-like $H_2O$. Still, there is a gap in the availability of data in the intermediate $H_2O$ density range, say between 200 and 600 $kg \cdot m^{-3}$. In order to fill this gap and obtain additional constraints on the thermodynamic properties of aqueous compounds we devised a method of estimating the Krichevskii parameter for compounds in water (Plyasunov and Shock, 2003b). This parameter is given by the relation $A_{Kr} = \left(\dfrac{\partial P}{\partial x}\right)^c_{T,V,x=0}$, with P and V standing for the pressure and volume of a system; the superscript c indicates that the evaluation is done at the critical point of the pure solvent. The Krichevskii parameter appears ubiquitously in most applications of near-critical theory and governs such seemingly different problems as the initial coordinates of the critical lines, the sign and magnitude of the partial molar properties of a solute at near-critical conditions, etc. As shown by Levelt Sengers and coworkers, values of the Krichevskii parameter can also be determined from variations of the vapor-liquid distribution constants for a solute, $K_D$, according to the relation: $RT \ln K_D = 2A_{Kr} \dfrac{\rho - \rho_c}{\rho_c^2}$, where $K_D = \lim\limits_{x_1 \to 0} \dfrac{y_2}{x_2}$, $y_2$ and $x_2$ represent the vapor and liquid mole fractions of the solute; $\rho$ and $\rho_c$ stand for the liquid-phase density at saturation and the critical density of the solvent, respectively; R indicates the gas constant. This method can be used even if $K_D$ values are measured at temperatures 100-150 K *below* the critical temperature of water.

We concentrated our efforts on estimating $K_D$ values at temperatures up to 550 K based on available information on thermodynamic properties of aqueous solutes at the reference isotherm 298.15 K (Plyasunov and Shock, 2003c). Once $K_D$ values at 500-500 K are known then the reliable values of the Krichevskii parameter can easily be calculated. The method of estimating $K_D$ values explores the link between Henry's constant, fugacity of a solute in the gaseous phase and the thermodynamic functions of hydration in liquid phase of $H_2O$. In brief, we evaluate the needed values of the fugacity coefficients of solutes in the vapor phase of $H_2O$ through the knowledge of the second cross virial coefficient between $H_2O$ and solutes (a reasonable approximation at temperatures below 600 K), and extrapolated the values of Henry's constants of aqueous solutes to elevated temperatures assuming a linear temperature dependence of the heat capacity of hydration of solutes, $\Delta_h C_p^o(T)$. This approximation appears reasonable over the temperature range 273-550 K, *i.e.*, far away from the critical region of water. To make this approach workable, we devised an empirical method to estimate the temperature change of the heat capacity of hydration of solutes based on values of $\Delta_h C_p^o$ and the Gibbs energy of hydration, $\Delta_h G^o$, for solutes at 298.15 K (these properties are taken to be approximations of the strength of water-solutes interactions and the sizes of compounds). The analysis of the results

shows that the values of the Krichevskii parameter for aqueous solutes follow group additivity systematics, and we derive a set of corresponding group contribution values for a large number of functional groups of organic compounds (Plyasunov and Shock, 2003b). A byproduct of this line of research is a model for predicting the temperature dependence of the vapor-liquid distribution constants for many inorganic and organic neutral compounds in water over the whole temperature range of the existence of the vapor-liquid equilibrium of water, *i.e.* up to 647.1 K.

## DEVELOPMENT OF AN ONLINE DATABASE OF THERMODYNAMIC PROPERTIES FOR AQUEOUS ORGANIC COMPOUNDS

The results of our DOE-sponsored research have been streamlined into a software database system designed for developing and maintaining a framework for storage, evaluation, and presentation of the data on properties of organic compounds. The primary focus of the database system is our critically-evaluated thermodynamic properties of organic compounds in aqueous solution (standard partial molar Gibbs energy, enthalpy, and heat capacity of hydration, partial molar volumes, all at 298.15 K, 0.1 MPa, standard thermodynamic functions of formation in aqueous solution at 298.15 K, 0.1 MPa, second cross virial coefficients up to 1200 K, properties of solutes along the vapor-liquid equilibrium (VLE) curve for pure $H_2O$ up to the critical point). We also include auxiliary physical and thermodynamic properties of pure compounds (enthalpy, Gibbs energy and heat capacity of vaporization; thermodynamic functions of formation; gas-liquid critical properties; second virial coefficients for pure compounds; vapor pressure of pure compounds, etc).

We have developed three MS SQL Server databases: 1) critically-evaluated properties, 2) primary data used in the evaluation of the functions of hydration, and 3) relevant bibliographic references (Plyasunova et al., 2003). The databases are freely accessible on the internet through the web interface at http://webdocs.asu.edu. The web interface is highly interactive and designed for easy browsing, and search and retrieval of the information stored in the databases. Several computational modules have been written allowing a user to perform online calculations and store the results in tabular and/or graphic format. The calculations include temperature and pressure dependence of the functions of hydration, as well as temperature dependence of other properties of aqueous solutes, and pure compound (in the ideal gas state).

At present properties of 255 compounds grouped by classes (normal and branched alkanes; alkenes and dienes; alkynes and diynes; alkylbenzenes; cycloalkanes; cycloalkenes; normal, isomeric, unsaturated, and cyclic alcohols; ketones; aliphatic ethers; esters; monoterpenes; some inorganic gases; and miscellaneous compounds) are included in the database system. Each property value is critically assessed and accompanied by cross-linked literature references and our comments, so that it can be 'transparent', easily understandable by the end user and modifiable if necessary.

One of the advantages of the software database system is the possibility of dynamic evaluation of the properties of organic compounds based on basic thermodynamic relations. This approach minimizes errors associated with data input and automates checks for data consistency.

Currently we have developed an algorithm for dynamic evaluation of thermodynamic properties of pure compounds, thermodynamic properties of hydration, and properties of formation in aqueous solution.

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Abstracts of Presentations:

N.V. Plyasunova, A.V. Plyasunov, E.L. Shock. Database of properties for aqueous organic compounds. Presented on 15th Symposium on Thermophysical Properties (June 22-27, 2003, Boulder CO). Special session: Database Demonstration

A.V. Plyasunov, E.L. Shock. Prediction of the Krichevskii parameter for volatile nonelectrolytes in water. Presented on 15th Symposium on Thermophysical Properties (June 22-27, 2003, Boulder CO). Special session: Properties of Aqueous Systems.

A.V. Plyasunov, N.V. Plyasunova, E.L. Shock. Group contribution values at 298.15 K, 0.1 MPa for thermodynamic functions of hydration of ethers and esters. Presented on 15th Symposium on Thermophysical Properties (June 22-27, 2003, Boulder CO). Special session: Properties for Environmental Applications.

A.V. Plyasunov, E.L. Shock. Second cross virial coefficients for interactions involving water: Compilation and correlation of data. Presented on 15th Symposium on Thermophysical Properties (June 22-27, 2003, Boulder CO). Special session: Properties of Aqueous Systems.