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Database of Thermodynamic Properties for Aqueous Organic Compounds[1]

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Results are presented from a project undertaken to develop a database for properties of organic compounds relevant for geochemistry and environmental chemistry. The database includes critically assessed standard thermodynamic properties in aqueous solution, properties of pure compounds at ambient conditions, and bibliographic references. All information stored in the databases is accessible through a web interface, which includes calculation modules for evaluating properties at elevated temperatures and pressures. The basic structure of the databases and the web interface design are described.

KEY WORDS: aqueous solutions; database; data compilation; organic compounds; pure compounds; thermodynamic properties; thermodynamic properties of hydration.

1. INTRODUCTION

While there is an abundance of comprehensive general-purpose databanks of thermophysical and thermodynamic properties of individual organic and inorganic compounds (TRC SOURCE [1], TRC Table [2], DIPPR [3] are the largest), a concise source of information on the thermodynamic properties of compounds in aqueous media at ambient and elevated

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temperatures and pressures is a challenge to find. Nevertheless, such information is often crucial for geochemistry, microbial ecology, and environmental projects. At present, the volume of published experimental data and the state of thermodynamic theory for aqueous solutions allow a systematic generalized collection and evaluation of the mutually consistent data at ambient and elevated temperatures for many classes of organic compounds.

We present results of a project dedicated to developing and maintaining a framework for analysis, storage, and treatment of literature data on the properties of organic compounds important for geochemistry and environmental chemistry. Two databases—the Database of Organic Compounds (DOC) and the Database of Bibliographic References have been created. The primary focus of DOC is compiled and critically evaluated thermodynamic properties of hydration of organic compounds. Other properties include standard thermodynamic functions of formation in aqueous solution, second cross virial coefficients, properties of solutes along the vapor-liquid equilibrium (VLE) line of pure water, and auxiliary physical and thermodynamic properties of pure compounds. The Database of Bibliographic References is not limited to the properties of compounds stored in DOC, but covers a much wider spectrum of substances and their properties (for future evaluation) which can be searched independently.

The databases are accessible through a web interface at http://webdocs.asu.edu. The web server manages search and retrieval of the information from the databases and accesses several calculation modules. The modules (for calculations at elevated temperatures and pressures) enable calculations of the thermodynamic functions of hydration, second cross virial coefficients, vapor-liquid distribution constants, fugacity coefficients, Henry's law constants, and apparent Gibbs energies of solutes in aqueous solution, as well as vapor pressures, second virial coefficients, and ideal gas heat capacities of pure compounds.

2. DESCRIPTION OF THE DATABASE OF ORGANIC COMPOUNDS

The Database of Organic Compounds is a relational Microsoft SQL Server database containing over 200 common organic substances grouped in classes. The "class" is defined as a homologues series of organic compounds of the same chemical structure and bonding types. At present the database includes normal and branched alkanes; alkenes and dienes; alkynes and diynes; alkylbenzenes; cycloalkanes; cycloalkenes; normal, isomeric, unsaturated, and cyclic alcohols; ketones; aliphatic ethers; esters; monoterpenes; inorganic gases; and miscellaneous compounds. The quantity and quality of stored data vary greatly among the most and the least

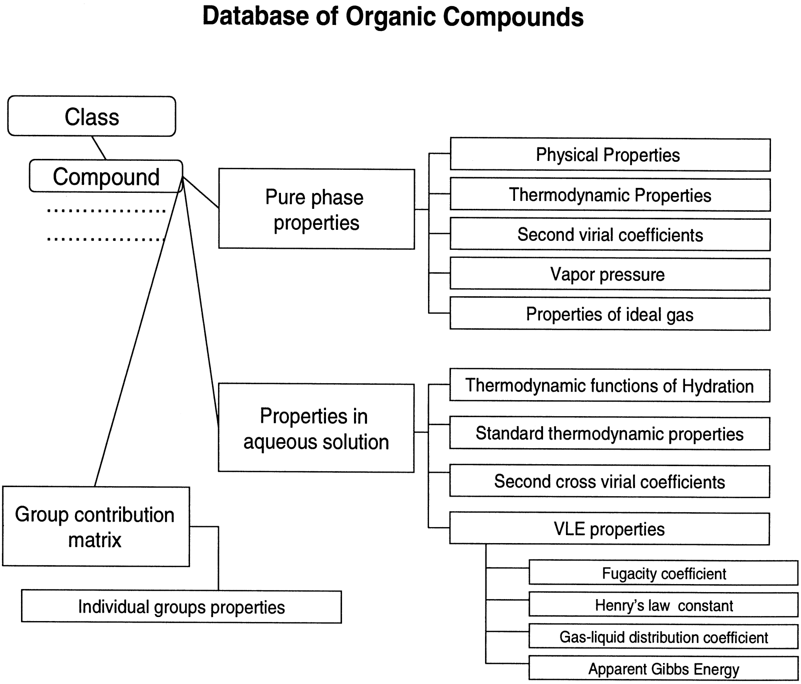

Fig. 1. Structural diagram of the Database of Organic Compounds.

studied compounds in the database, reflecting the current state of exploration of the properties under consideration. The set of data for each compound consists of properties in aqueous solution, properties of pure phases, and a group contribution matrix (see Fig. 1).

3. DATA COMPILATION AND EVALUATION OF PROPERTIES

3.1. Thermodynamic Properties of Aqueous Organic Compounds at 298.15 K, 0.1 MPa

The properties of primary interest in this project are the partial molar properties of hydration of organic solutes at infinite dilution at 298.15 K and 0.1 MPa, called, for brevity, thermodynamic functions of hydration. Thermodynamic functions of hydration represent the change of the thermodynamic functions for the process of transferring one mole of a solute from the ideal gas state to a standard aqueous solution. The standard state conventions adopted in the database are those defined by CODATA [4]: "the standard state for a pure gaseous substance is that of the substance as a (hypothetical) ideal gas at the standard-state pressure" of $P^{\otimes} = 0.1$ MPa; "the standard state for a pure liquid substance is that of the liquid under the standard-state pressure;" "the standard state for an undissociated substance in aqueous solution is the hypothetical state of the pure substance dissolved in pure water without dissociation at unit molality to give an ideal solution, under the standard-state pressure."

3.1.1. *Standard Thermodynamic Functions of Hydration*

Presently, the functions of hydration included in the DOC are the Gibbs energy, $\Delta_h G^0$; enthalpy, $\Delta_h H^0$; entropy, $\Delta_h S^0$; heat capacity, $\Delta_h Cp^0$; and volume, $\Delta_h V^0 \equiv V_2^0$. We are planning to include values of the isothermal compressibility, $\Delta_h k^0 \equiv k_2^0 = -(\frac{\partial V_2^0}{\partial P})_T$, in a future update.

Each value of the thermodynamic functions of hydration is critically assessed using primary literature publications containing experimental data (partial and excess enthalpies, heat capacities and volumes of aqueous mixtures, Henry's and gas-water distribution constants, activity coefficients at infinite dilution and mutual solubility data). Values from secondary sources of data (literature compilations), as a rule, are not included. Procedures used to convert published data into the values of the thermodynamic functions of hydration at 298.15 K, including the necessary temperature corrections, are described in Refs. 5 and 6. DOC includes summaries of the primary data sources employed in the compilation. In the case of compounds with little or no literature data available, we present values of the functions of hydration obtained by the group contribution method [6].

3.1.2. *Thermodynamic Properties in the Standard Aqueous Solution*

Combining values of the functions of hydration of a solute with thermodynamic properties of an organic compound in the ideal gas state, we calculate the partial molar thermodynamic functions of formation of the solute in the standard aqueous solution. As an example, the Gibbs energy of formation is given by

$$\Delta_f G^0(aq) = \Delta_h G^0 + \Delta_f G^0(g). \quad (1)$$

3.2. Thermodynamic Properties of Aqueous Organic Compounds Along the Vapor-Liquid Equilibrium of Pure Water

The database contains parameters for calculating values of the standard chemical potential of a solute (given as the vapor-liquid distribution constant; Henry's constant; fugacity coefficient in the vapor phase; or the partial molar Gibbs energy of formation in aqueous solution) at the saturated water vapor pressure using methods developed in this research group ([5, 7]). Each of these representations of the chemical potential is discussed in this section.

The vapor-liquid distribution constant, K_{D}, is defined as $K_{\mathrm{D}} = \lim_{x\to 0} \frac{y}{x}$, where y and x stand for the mole fraction concentrations of a solute in vapor and liquid phases of water, respectively. Values of K_{D} can be calculated from the triple point to the critical point of water, using algorithms for single compounds or for the group contribution method proposed in Ref. 7. Our correlating equation for K_{D} is consistent with the asymptotic form in the neighborhood of the critical point of water required by theory (see Ref. 8). The values of the Krichevskii parameter (see Ref. 9) for aqueous solutes, which are necessary for many thermodynamic and technological applications at near-critical conditions, are available for most organic compounds (and functional groups of organic compounds) in our database.

Henry's constant, k_{H}, is defined as $k_{\mathrm{H}} = \lim_{x\to 0} \frac{f_2}{x}$, where f_2 represents the fugacity of a solute in the vapor phase. Values of k_{H} (MPa units) are calculated from the vapor-liquid distribution constants, K_{D}, using the relation $k_{\mathrm{H}} = K_{\mathrm{D}}\Phi_2^0 P_1^0$, where Φ_2^0 and P_1^0 represent the fugacity coefficient of a solute and the saturated vapor pressure of water, respectively.

Values of Φ_2^0 are calculated by two methods. First, we use the virial equation of state truncated at the second term [10]: $\ln \Phi_2^0 = (2B_{12} - B_{11})\frac{P_1^0}{RT}$ with B_{11} being the second virial coefficient of pure water from the IAPWS-95 formulation [11] and B_{12} being the second cross virial coefficient for interactions between water and a solute, evaluated as suggested in Ref. 5. Second, we employ the Peng–Robinson [12] equation of state as modified [13] to calculate Φ_2^0. In general, values of Φ_2^0 calculated using these two methods do not coincide. As a compromise, we use an empirical weighting procedure that at temperatures below (550 to 600) K strongly favors values of the fugacity coefficient from the truncated virial equation of state and approaches ones calculated from the Peng–Robinson–Stryek–Vera equation at temperatures between 600 and 623 K. This step can be justified by the fact that two-parameter cubic equations of state are not capable of accurate representation of second virial coefficients for either pure compounds or mixtures. Calculations of k_{H} are stopped at 623 K because of large uncertainties of Φ_2^0 values at higher temperatures.

The partial molar Gibbs energies of formation of a solute in aqueous solution are obtained using Eq. (1) at temperatures between 273.15 and 623.15 K at the saturated water vapor pressure using values of the Gibbs energies of hydration of a solute calculated from Henry's constants as

$$\Delta_h G^0 = RT \ln\left(\frac{k_{\mathrm{H}}}{P^{\otimes}}\frac{M_{\mathrm{w}}}{1000}\right)$$

where $P^{\otimes}$ is the ideal gas standard state pressure and $M_{\mathrm{w}} = 18.0153\ \mathrm{g \cdot mol^{-1}}$ is the molar mass of water.

3.3. Other Thermodynamic Properties of Aqueous Organic Compounds at Elevated Temperatures

Approximate values of the second cross virial coefficients for interactions between water and many organic compounds at 250 to 1200 K are calculated by either the group contribution method or the empirical estimation of the mixture-specific parameter k_{12} in the Tsonopoulos [14] corresponding-state correlation (see Ref. 5 for details). The database stores k_{12} values for individual compounds and square-well potential parameters for functional groups of organic compounds.

For a few compounds values of the thermodynamic functions of hydration can be calculated over wide temperature and pressure ranges in the framework of the fluctuation solution theory-based correlating model [15, 16] (an optimistic estimation suggests that calculations are meaningful up to 1300 K and densities of pure water up to $1000\ \mathrm{kg \cdot mol^{-1}}$). Currently, such calculations are possible for methane, hexane, ethane, benzene, toluene, cyclohexane, methanol, ethanol, propanol, and some inorganic solutes (Ar, Xe, CO_2, H_2S, NH_3). We follow the IAPWS recommendations [17] for the properties of water at elevated temperatures and pressures used in the calculation procedure.

3.4. Auxiliary Properties of Organic Compounds in Pure Phase States

3.4.1. Physical Properties

The set of physical properties for an individual compound in the database includes critical properties (temperature, pressure, and molar volume), normal boiling point, dipole moment, acentric factor, radius of gyration, and melting temperature. We reference the IUPAC ([18–20] and others) recommendations for the critical properties where available or use published experimental data; other properties are taken from Refs. 3 and 21. The selection of the physical properties listed in the database is influenced by their necessity in evaluating other properties.

3.4.2. Thermodynamic Properties

The database contains the standard thermodynamic functions of formation of pure compounds in their stable physical state at 298.15 K, thermodynamic functions of vaporization for liquid compounds, and thermodynamic properties of formation in the ideal gas state. The temperature dependence of the ideal gas heat capacity is taken from Ref. 22 or estimated using the group contribution method [21].

3.4.3. *Second Virial Coefficients*

Calculation of the second virial coefficients over a wide temperature range is based on the corresponding-states correlations by Tsonopoulos [14] and Hayden and O'Connell [23]. All the necessary parameters are stored in the database.

3.4.4. *Vapor Pressure*

The vapor pressure of pure compounds within their VLE temperature interval is evaluated with either the Wagner equation ([21, 24]) or the Antoine equation [21]. For an individual compound the database indicates the type of equation to be used and contains the necessary parameters. Primary experimental data are accessible in the database for some classes of compounds.

4. DATABASE OF BIBLIOGRAPHIC REFERENCES

The Database of Bibliographic References is a separate SQL Server database. It includes over 3000 literature references dedicated to the study of organic compounds and their properties. Each record consists of a unique abbreviation (the year of publication, first three letters of the last names of the first two authors separated by a slash, and a numeric index if required, for example 2000PLY/SHO, 2000PLY/SHO1), authors, title, publisher, key words, substances studied, and corresponding Chemical Abstract (CAS) numbers. The CAS numbers are used as search keys when searching for references available for a particular compound.

5. WEB INTERFACE AND SOFTWARE

We use the Microsoft SQL Server 2000 software for database management. This project was designed as an open internet-accessible source of information for any interested group or individual. The database connections, search, and retrieval of the information are handled by Java servlets with Macromedia's JRun4 software as a Java servlet engine for the Microsoft IIS6 web server. Servlets are also used as online calculators of properties at elevated temperatures and as image processors. JSP (Java Server Pages) technology is employed for directing a client's requests and formatting the response pages sent to the client.

The calculations of the functions of hydration at elevated temperatures and pressures require properties of water vapor at given conditions. We rely on the NIST/ASME STEAM Properties database adopting the IAPWS formulation for thermodynamic properties of water [17]. The set of FORTRAN source files provided by NIST were recompiled, together with the C++ computation module for the thermodynamic functions of hydration, into a single Windows binary, COM (Component Object Model) server object. The COM server object receives input parameters from the web server, performs actual calculations of the properties of hydration, "runs" the FORTRAN code to obtain the properties of water, and sends the resulting arrays of data back to the web server. To handle the COM-Java connection, a COM client and a helper Java Native Interface class were developed.

The web interface to the project (Fig. 2) located at http://webdocs.asu.edu provides a tree view of the Database of Organic Compounds which enables easy browsing, and a "Compound Search" form to conduct searches by CAS number, compound name (including synonyms), or formula. Critically-assessed standard thermodynamic and physical properties are provided with literature references links and comments. The

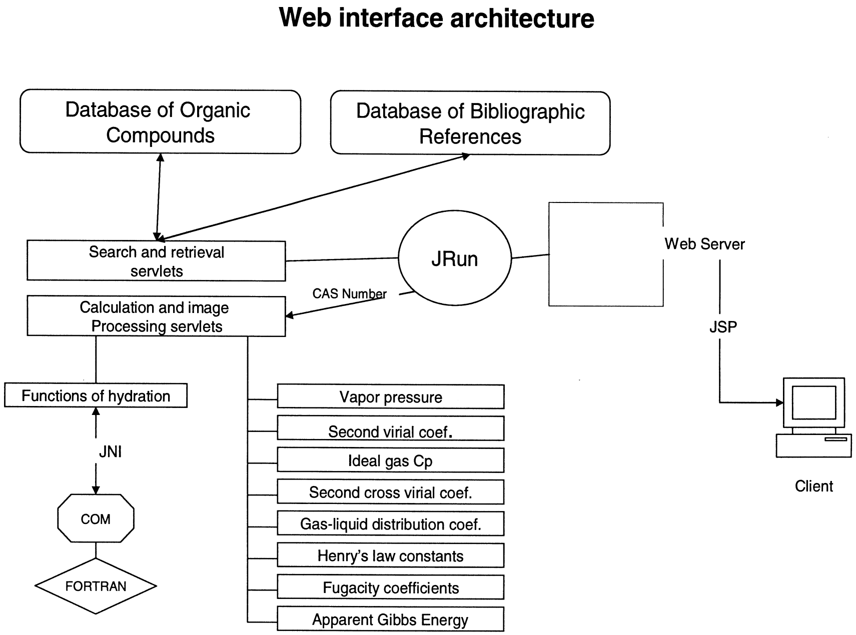

Fig. 2. Web interface architecture diagram of the project.

compiled values of the standard functions of hydration are referenced by links to primary experimental data pages where available.

The menus on top of the page provide access to online calculators of properties at elevated temperatures, and results are presented in tabular and/or graphic format that can be exported to MS Excel or saved in a plain text file. Primary experimental data, if available, for vapor pressures and second virial coefficients are presented in a linked table view and/or plotted on the images. The images in jpeg format are generated by Java servlets at run time from the results of calculations and can be saved.

The Database of Bibliographic References is accessible through the links from compound properties pages. In addition, independent reference searches can be conducted from the "Reference Search" form by author, title, reference abbreviation, substance name or CAS Number, key words, and publisher.

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