

**DETERMINATION OF THE PARTIAL MOLAL HEAT CAPACITIES OF DILUTE D-GLUCOSE AT ELEVATED TEMPERATURES RELEVANT TO LOW GRADE HYDROTHERMAL ACTIVITY.** A. F. Bennett<sup>1</sup>, M. D. Schulte<sup>1</sup>, and J. C. Seitz<sup>2</sup>; <sup>1</sup> Department of Geological Sciences, 101 Geology Building, University of Missouri, Columbia, MO 65211, [ariel.bennett@mizzou.edu](mailto:ariel.bennett@mizzou.edu), [schultemd@missouri.edu](mailto:schultemd@missouri.edu); <sup>2</sup>Department of Earth & Environmental Sciences, California State University, East Bay, 25800 Carlos Bee Blvd., Hayward, CA 94542, [jeff.seitz@csueastbay.edu](mailto:jeff.seitz@csueastbay.edu).

**Introduction:** The search for extraterrestrial life is limited by what is currently known about life in analogous environments on Earth. Thus it is necessary to define quantitatively habitable zones as those meeting the minimum requirements of all living organisms: sufficient geochemical energy for reactions to proceed spontaneously, building materials for biosynthesis, and an aqueous medium in which reactions may occur.

Submarine hydrothermal systems are geochemically reactive environments that are thought to have hosted the first organisms on Earth. Many current theoretical and experimental studies are aimed at elucidating potential mechanisms leading to the emergence of life. However, relatively little is known about the nature of early life, from the first metabolic pathways to the temperatures of its emergence. In addition, it was previously held that the upper temperature limit for life was 120°C due to lack of data and incorrect assumptions about the behavior of organic compounds above these temperatures. However, the hyperthermophilic archaeon, *Methanopyrus kandleri* strain 116, isolated from deep sea hydrothermal vents, has recently been found to grow up to 122°C [1] leading to reconsideration of currently held assumptions regarding the upper limits possible. Genetic studies also indicate that the last universal common ancestor was thermophilic or hyperthermophilic. Difficulties in being able to evaluate which chemical reactions may have led to the emergence of life include the relative paucity of studies investigating the reaction properties of biologic molecules and their inorganic precursors at elevated temperatures. Determining reaction properties of simple organic compounds is needed to understand the potential for abiotic formation of these compounds in the environments thought to have hosted the emergence of life. Therefore, the immediate aim of this study is to determine experimentally the thermodynamic reaction properties of molecules fundamental to biological processes. We have chosen to begin our studies with determination of the partial molal heat capacity of aqueous glucose.

Glucose is the most ubiquitous monosaccharide in biological systems. It is essential to most primary metabolic pathways by serving as the main source of energy in the Krebs and the reverse citric acid cycles. Through the Embden-Meyerhof pathway, it is oxidized to pyruvic acid thus initiating a metabolic cycle that ultimately yields ATP, the energy currency of all living organisms. Previous studies have determined the reac-

tion properties of aqueous glucose up to 120°C and 0.35 MPa. However, the thermodynamic properties of aqueous glucose at higher temperatures have not been experimentally determined. Estimates of the properties are available [2], and one of our goals is to test these estimates. Because the temperature limit of life is not known, extending the temperature range of thermodynamic properties of aqueous biomolecules will ultimately help elucidate whether the chemistry of these compounds led to the emergence of life at higher temperatures through geochemical models of these environments.

**Experimental Methods:** Apparent molal heat capacities for solutions of D-glucose were obtained using Thermal Analysis (TA) Instruments Nano DSC model 6300 twin, fixed cell differential, temperature scanning calorimeter. This instrument is capable of measuring heat capacities of fluids up to 433.15 K and 0.7 MPa. The fundamental equation used to determine the apparent molal heat capacity,  $c_{p,\Phi}$  ( $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ ) is:

$$c_{p,\Phi} = M \cdot c_{p,s} + \{ 1000 \cdot (c_{p,s} - c_{p,r}) / m \},$$

where  $M$  is the molar mass of the solute,  $c_{p,s}$  and  $c_{p,r}$  are the apparent molal heat capacities of the solute and solvent solution, respectively, and  $m$  is the molality of solution. The apparent molal heat capacity of the solute,  $c_{p,s}$ , is calculated with the equation:

$$c_{p,s} = k_c \cdot (\Delta P_s - \Delta P_w) / \rho_s + c_{p,w} \cdot \rho_w / \rho_s.$$

where  $\rho_w$  and  $\rho_s$  are the densities of water and the solution, respectively,  $\Delta P$  represents the difference in power output necessary to maintain the temperature between a cell containing the solution and a water-filled reference cell, and  $k_c$  represents the temperature and pressure dependent calibration constant determined with standard NaCl solutions and their properties based on the equations of state of Archer (1990) [3].

Solutions of D-glucose (Sigma, >99% pure) were prepared by mass in distilled, deionized, degassed water and stored in 60 ml glass bottles sealed with PTFE butyl septa. Solutions were extracted for use with gas tight syringes to prevent fluid loss and minimize reintroduction of atmospheric gases prior to obtaining measurements. The apparent molal heat capacity was determined by performing a series of ten alternating

heating and cooling scans from 288.15 K to 433.15 K, at 0.7 MPa, at a scan rate of  $16.7 \text{ mK}\cdot\text{s}^{-1}$ . Reference scans were run between every solution experiment to account for any small drift in the instrument's baseline performance. Solution densities needed to calculate the massic heat capacities were obtained experimentally by our lab group and others [4-6].

**Results:** Previous studies report the apparent molal heat capacities of D-glucose up to 393.15 K at 0.35 MPa with experimentally determined densities measured up to 368.15 K and 0.35 MPa. In combination with the volumetric work performed by Seitz et al. (2010) we have successfully extended the database for partial molal heat capacities to 433.15 K at 0.7MPa.

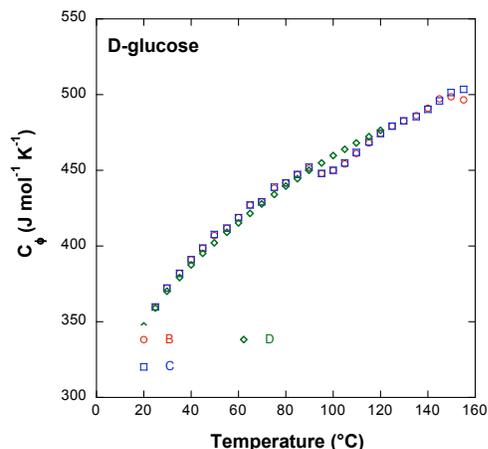


Figure 1 shows the apparent molal heat capacities of D-glucose determined experimentally in this study.

Comparisons of these data show a high degree of agreement our values and those from the literature. The data from this study extend the available calorimetric data for dilute glucose solutions to elevated temperatures, and will allow us to incorporate D-glucose into more accurate geochemical models of hydrothermal environments.

**References:** [1] Takai, K et al. (2008) *Proceedings of the National Academy of Sciences*, 105, 10949-10954. [2] Amend, J. P. and Plyasunov, A. V. (2001) *Geochimica Et Cosmochimica Acta* 65, 3901-3916. [3] Archer, D. G. (1992) *J. Phys. Chem. Ref. Data*, 21, 793-826. [4] Kishore et al. (1993) *J. Chem. Thermodynamics*, 25, 847-859. [5] Origlia M. L. et al. (2000) *J. Chem. Thermodynamics*, 32, 847-856. [6] Seitz J. C. et al., (2010) Astrobiology Science Conference abstract