A New Tool for an Old Job: Using Fixed Cell Scanning Calorimetry to Investigate Dilute Aqueous Solutions -The Hugh M. Huffman Memorial Award Lecture -

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The development of fixed twin cell temperature scanning calorimeters has enabled the more efficient determination of heat capacities of dilute aqueous solutions with a precision comparable to that of the Picker flow heat capacity calorimeters developed nearly 40 years ago. Experiments require less than 0.5 cm^3 of solution, and results can be obtained routinely over the temperature range (278 to 395) K at pressures up to a few bars. Multiple scanning of samples at both increasing and decreasing temperature allows assessment of instrument drift, solute stability, and reproducibility of the results. Chemical calibration is essential to take full advantage of the precision and sensitivity of fixed cell calorimeters, and solution densities are needed to transform the results into heat capacities per unit mass of solution. Examples of solutes we have investigated include a variety of inorganic and organic compounds that dissolve to give simple ionic or neutral species, or that produce complexes or other species that exist in equilibrium distributions that can change as the temperature is scanned. Appropriate selection of the results from experiments on combinations of solutes allows calculation of standard state (m = 0) thermodynamic quantities for useful chemical processes and reactions over the ranges of temperatures scanned. Results will be presented and discussed for some classes of solutes we have investigated during the past few years.