

capacity of water is well documented, the absolute heat capacity of the sample can be readily calculated.

In describing the experimental procedure of the invention, it is noted that this procedure is the same for a water baseline scan or a sample scan. The stainless steel ampoules 12 are removed from the calorimeter, washed and dried and loaded using a syringe and hypodermic needle. The total mass of sample or water is determined by weighing (to ± 0.00001 g) the ampoule before and after filling with 0.6 to 1 cc of material. The ampoules 12 are pressurized if desired, and tightly sealed to prevent evaporation and hence large anomalous heating effects. The ampoules are placed into the calorimetric cells through the fill holes provided, the copper plugs 44 are positioned into the heat sink openings, and the insulation plugs 46 are inserted. The calorimeter is usually loaded in this way at room temperature or above to prevent possible water vapor condensation inside the opened calorimeter at low temperatures. If data is required below room temperature, the refrigerated water bath 176 is turned on to circulate cold water through the cooling coils 30, 32 in order to cool the calorimeter down to the desired starting temperature. During this cool down period, dry nitrogen gas is usually bled into the air space between the heat sink 16 and the adiabatic shield 22 to maintain a dry atmosphere within the heat sink 16 and to thereby prevent water condensation and subsequent evaporation during a scan.

Thermal equilibrium of the heat sink contents at or near the thermostat controlled bath setting is determined by a negligible voltage reading from the thermopiles. At this time the scanning experiment is initiated by shutting off the cooling water bath 176 and turning on the voltage regulated power supply 162 at a voltage level required to give the desired scanning rate; e.g., 13 watts provides a scan rate of 15° C./hr. There is an approximate 15-20 minute start-up period before the voltage signal reaches its steady-state value. Typically, the start-up exhibits a rapid departure from zero voltage and asymptotically approaches the steady state value (determined by the masses of material in each cell and the scanning rate) after 15-20 minutes. Only after attainment of steady state conditions do the assumptions used in deriving the relevant equations hold. This lag time before collection of data can begin means that it is necessary to initially cool the calorimeter below the desired minimum temperature for heat capacity data; approximately 4° to 5° C. when $\alpha = 15^\circ$ C./hr. During this time the dry nitrogen gas flow is shut off, and the precision temperature controller 156 driving the adiabatic shield 22 has more than ample time to adjust the shield temperature to that of the heat sink. The sink heater power supply and shield controller then remain without any further adjustment for the duration of the scanning experiment.

When the desired high temperature of the scan is reached in the heat sink 16, the experiment is terminated by shutting off the sink heater power supply 162, the precision temperature controller 156, and the data collection devices. The calorimeter can then be cooled down by activating the refrigerated water bath 176.

During data analysis, the experimental data (T, V, t) is read into a file on a time shared computer for analysis. The data is then processed in one of three selected modes of operation of the program "SCAN". The water baseline data, i.e. the values of T, α , V, dV/dt , V_2 , and dV_2/dt where T is the heat sink temperature, α is its time derivative, dT/dt , V and dV/dt refer to the

differential thermopile voltage, and V_2 and dV_2/dt refer to the calculated values of the reference cell thermopiles, at every calculated 0.1 deg interval of the sample cell temperature, are stored in a baseline file. For a scanning rate α of 15° C./hr, $V_2 \approx 12$ mV while $V = V_{AC} - V_{BC} \pm 50 \mu V$. The stored values are calculated from a least squares fit of the values of T, V, and V_2 as second order polynomial functions with time over an approximate 2 degree range of temperature centered around the calculated time at which the cell temperature was the desired value.

The second operational mode is for analysis of data obtained from a scanning experiment in which the experimental solvent (buffer) is loaded in the sample ampoule. The solvent heat capacity is calculated and stored in another computer file for every 0.1° C. in order to subtract that portion of the experimental heat capacity due to the solvent from the solution of interest.

The third operational mode is for analysis of the heat capacity of a solute in the experimentally scanned solution. In this mode, the values T, V, V_2 and each respective time derivative are also calculated from sliding second order polynomials centered around each 0.1° C. cell temperature over an appropriate temperature range. The experimental heat capacity is then calculated by comparing these solution variables with those of the preceding water baseline values stored in the computer file. The instrumental parameters such as ϵ and τ for each cell are calculated at the appropriate temperature using stored coefficients of second order polynomial fits of each parameter with temperature, as determined from a previous series of electrical calibrations at different temperatures. After subtracting the value of the solvent heat capacity contribution, the remaining calculated heat capacity in calories/degree is divided by the known mass of solute and printed out as solute heat capacity in calories per gram-degree at every 0.1° C. interval of sample cell temperature. The essence of the computer operation is the subtraction of the instrumental baseline, and then the transformation of the voltage as a function of time into heat capacity as a function of temperature.

An example of the data analysis is shown in FIG. 7, where a single data transformation is shown. The curve labeled 184 corresponds to differential thermopile voltage data collected every 13 sec for a water baseline scan with the power supply 162 delivering 13 watts of power to the heater elements 146, 148 and 150, resulting in a calorimetric scanning rate (α) of 15° C./hr. The curve labeled 184 is a simulation of the heat capacity of an unknown sample obtained by repeating the scan of curve 182 while adding heat to the sample cell through the 50Ω sample cell calibration heater. This heat is generated from an external regulated constant current (D.C.) source with a precise timing control, and for curve 184 was turned on (t_1 on FIG. 7) at 4 mA; seven minutes later (t_2 on FIG. 7) the heater was automatically shut off. Therefore, the difference between curves 184 and 182 is the differential thermopile voltage generated by a constant heat effect of $+0.2$ mcal/sec inside the sample cell for the seven minutes between times t_1 and t_2 (total heat input = 85 mcal) and a zero heat effect elsewhere. Curve 184 was computer analyzed as described using program "Scan" in the solvent mode, with the previously calculated data from curve 182 stored in the baseline file. The results of this calculation are shown for every 0.1° C. of the sample cell as an apparent heat capacity in curve 186 in FIG. 7. The calculated