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THERMODYNAMICS OF GEOTHERMALLY IMPORTANT
AQUEOUS ELECTROLYTES

John Christopher Peiper
(Ph.D. Thesis)

February 1983

MASTER

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Thermodynamics of Geothermally Important Aqueous Electrolytes

John Christopher Peiper

Abstract

Thermodynamic measurements at temperatures between 273 and 323 K for the system (Na^+ , CO_3^{2-} , HCO_3^- , OH^- , Cl^- , CO_2 , H_2O) are correlated using the mixed-electrolyte-solution equations developed by Pitzer. $\text{CO}_3^{2-}(\text{aq})$ hydrolysis and $\text{HCO}_3^-(\text{aq})$ disproportionation are explicitly recognized and their effects on activity coefficients, enthalpy, and heat capacity are included. The resulting consistent set of ion-interaction parameters reproduce measurements essentially to within experimental error and may be reliably used in correlations for more-complex systems. Tables of thermodynamic properties are included.

In a separate analysis, a large array of thermochemical data for $\text{NaCl}(\text{aq})$ at temperatures to 623 K are correlated using Pitzer's equations. This analysis complements earlier work on $\text{NaCl}(\text{aq})$ volumetric properties; combining the results from these investigations yields an equation of state valid for $273 \text{ K} \leq T \leq 573 \text{ K}$, $1 \text{ bar} \leq P \leq 1 \text{ kbar}$ and $0 \leq m \leq 6 \text{ mol kg}^{-1}$. The equations may be extrapolated, but with reduced accuracy, to molalities greater than 6 mol kg^{-1} and to temperatures slightly above 573 K. Uncertainties are estimated for many thermodynamic quantities at selected temperatures, pressures and compositions. Extensive tables of thermodynamic properties are given in the appendix to chapter 2.

Finally, a flow microcalorimeter designed to measure the heat capacity of fluids at temperatures to 573 K and pressures to 1 kbar is described in chapter 3. This instrument is a reconstruction of the device used earlier in this laboratory to measure the $\text{Na}_2\text{SO}_4(\text{aq})$ heat capacity. The new instrument includes several improvements. In addition, a problem associated with the calibration of flow calorimeters for power losses is addressed. A new technique which circumvents this problem is proposed and shown to yield accurate results. Estimates of experimental precision are given.

Dedication

I puzzled over this dedication for some time, unable to choose between the many friends, family members, and chemistry faculty who lent their love and support during this endeavor. I can deny no-one his contribution in this work, and to each my deepest thanks. One only stands head-and-shoulders above the rest. His initials, uncoincidentally, are also J.C.

Acknowledgment

I thank Professor K. S. Pitzer for his patient support throughout this project. As an educator, Professor Pitzer teaches the fundamentals of chemistry and chemical research; he also promotes that integrity and professionalism which are the hallmarks of excellence, whatever the discipline. I owe him a great debt.

I thank Professor R. N. Roy, Dr. R. H. Busey and their associates for making data available in advance of publication.

Finally, I thank Mrs. C. Yoder for her patience and expertise in typing this thesis, and especially for attending to the many details which I overlooked.

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Preface

The evaluation of thermodynamic properties for aqueous electrolytes has recently received much attention from workers in the fields of electric power production, mining technology and hydrothermal energy, as well as in the basic chemical and physical sciences. Many of the problems faced by these workers concern systems under extreme conditions and of great compositional complexity. Natural waters are perhaps the most complex of electrolyte solutions, with highly variable compositions dependent upon local geology, atmospheric conditions, biologic activity, etc., and may include neutral species such as gases and some organics. To understand properly the chemistries of these and related systems, it is necessary to have some knowledge of their thermodynamic properties.

Electrolyte solution properties have been of great theoretical importance for many years.^{1,2} Recently, Friedman³ has advanced electrolyte solution theory far beyond the original work of Debye and Hückel.⁴ However, the mathematical infrastructure is very complex and does not lend itself as a practical tool. Pitzer,⁵ noting this and other theoretical work and drawing on a large base of precise experimental data, proposed an ion-interaction model for electrolyte solution behavior. His equations have since been applied with success to aqueous mixed electrolytes⁶ and to single-solute systems at high temperatures.⁷

The first two chapters of this thesis use Pitzer's equations in thermodynamic analyses of the systems (Na^+ , CO_3^{2-} , HCO_3^- , OH^- , Cl^- , CO_2 , H_2O) and (Na^+ , Cl^- , H_2O). The former system is one of great geological importance, but has not been accurately characterized because of its complexity. Chapter 1 presents a thorough thermodynamic analysis of this system, including activity, enthalpy and heat capacity data, for

temperatures between 273 and 323 K. The analysis presented in Chapter 2 for NaCl(aq) extends to 573 K and completes work begun by Rogers and Pitzer.⁸ The equations given here incorporate recent precise measurements of the NaCl(aq) enthalpy and heat capacity at high temperatures and pressures. In combination with Rogers' and Pitzer's results, an equation of state valid for $273\text{ K} \leq T \leq 573\text{ K}$ and $1\text{ bar} \leq P \leq 1000\text{ bar}$ is obtained. NaCl(aq) serves as a model solution in many geochemical and engineering applications.

The ability to correlate published data is but one aspect of the problems referred to in the first paragraph. For many systems, particularly those at elevated temperatures and pressures, experimental data are sparse or lacking entirely. Chapter 3 presents details of a flow microcalorimeter designed to measure the heat capacity of fluids to 573 K and 1 kbar. With information gathered from this or a similar instrument, the enthalpy and Gibbs energy may be computed from well-known thermodynamic formulae. One of the problems of flow calorimetric measurement has centered on calibrations for power losses.⁹ A new calibration technique which eliminates the need for a chemical standard in calibration is advocated.

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* See LBL-12725 for information contained on pages 1 thru 47.

† See LBL-15512 for information contained on pages 50 thru 182.

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Chapter 1

Thermodynamic Properties of (Na^+ , CO_3^{2-} , HCO_3^- , OH^- , Cl^- , CO_2 , H_2O)

The contents of this chapter, excepting the appendix, are essentially that of Report LBL-12725 which has now been published in the Journal of Chemical Thermodynamics, volume 14, pages 613-38, 1982. Consequently this material (pp. 1-46) is not duplicated here. The appendix is included on the following pages.

8. Appendix

This appendix presents the calculation of higher-order electrostatic terms discussed in the main body of this chapter.

Using the notation of Pitzer^{11,20,21}, the mixing parameter $\theta_{i,j}$ may be decomposed into electrostatic and short-range contributions, $E_{\theta_{i,j}}$ and $S_{\theta_{i,j}}$. The former term has an ionic strength derivative $E'_{\theta_{i,j}}$ whereas $S_{\theta_{i,j}}$ is assumed independent of I . Both terms possess temperature derivatives to all orders, but these are small and in all but work of the highest precision may be neglected. The electrostatic terms may be calculated from formulae given by Pitzer¹¹:

$$E_{\theta_{i,j}} = \frac{z_i z_j}{4I} [J(x_{i,j}) - \frac{1}{2} J(x_{i,i}) - \frac{1}{2} J(x_{j,j})] \quad (\text{A1a})$$

$$E'_{\theta_{i,j}} = -\frac{E_{\theta_{i,j}}}{I} + \frac{z_i z_j}{8I^2} [x_{i,j} J'(x_{i,j}) - \frac{1}{2} x_{i,i} J'(x_{i,i}) - \frac{1}{2} x_{j,j} J'(x_{j,j})] \quad (\text{A1b})$$

where z_i and z_j are the charge magnitudes, in protonic units, on ions i and j ; I is the molal ionic strength. The univariant function J is obtained from cluster-integral theory³¹ with omission of short-range forces. The variable $x_{i,j}$ is defined by

$$x_{i,j} = 6z_i z_j A_\phi I^{1/2} \quad (\text{A2})$$

The functions J and J' are given by Pitzer^{11,20} in integral and series form. The latter is useful only for $x_{i,j} \leq 0.10$, which fortuitously is the region where numerical integration is difficult. Dropping the subscripts on x , one obtains

$$J(x) = - \sum_{p=3} (\ln x + K_p) \frac{x^{p-1} p^{p-3}}{p! (p-3)!} . \quad (A3)$$

The quantities K_p are constants given as sums involving Euler's constant, $\ln p$ and integral fractions; the first few values are $K_3 = 0.41970$, $K_4 = -0.292608$, $K_5 = -0.369464$, $K_6 = -3.00381$. From eq. (A3) one obtains

$$J'(x) = - \sum_{p=3} [1 + (p-1)(\ln x + K_p)] \frac{x^{p-2} p^{p-3}}{p! (p-3)!} , \quad (A4)$$

$$J''(x) = - \sum_{p=3} [(2p-3) + (p-1)(p-2)(\ln x + K_p)] \frac{(xp)^{p-3}}{p! (p-3)!} . \quad (A5)$$

The error in truncating these series at $p = 6$ for $x = 0.10$ is less than 1.0 percentum.

For $x > 0.10$ numerical methods are most precise. The integral given by Pitzer for $J(x)$ may be rearranged to the form

$$J(x) = \frac{x}{4} - 1 + \int_0^1 \frac{\ln t}{q} (1 - e^q) dt , \quad q = \frac{xt}{\ln t} . \quad (A6)$$

A variety of methods may be used to compute its value; a 200-point Gauss-Legendre method was used in this work. The derivatives of eq. (A6) are given by

$$\begin{aligned} J'(x) &= \frac{1}{4} + \int_0^1 \frac{t}{q^2} [1 - (1-q)e^q] dt , \\ J''(x) &= \frac{2}{x} \int_0^1 \frac{t}{q^2} [1 - (1 - q + \frac{q^2}{2})e^q] dt , \end{aligned} \quad (A7)$$

and were also computed using the Gauss-Legendre method. Figure A1 shows the functions J , J' and J'' .

Figure A-1. The functions J , J' and J'' .

Chapter 2

Thermodynamic Properties of Aqueous Sodium Chloride Solutions

The contents of this chapter are essentially the same as that of LBL report # 15512 which is being issued simultaneously. Consequently this material (pp. 50-182) is not duplicated here.

CHAPTER 3

Measurement of Heat Capacities by Flow Microcalorimetry

1. Introduction

Many geochemical processes of great significance in mineral transport, and deposition, hydrothermal energy and other areas involve aqueous solutions under extreme conditions. Minerals dissolve to form primarily ionic solutions, but neutral species including gases and some organics may be present as well. The composition of these solutions is highly variable, being dependent upon local geology, atmospheric conditions at present and in the recent past, biologic activity and so forth. At high temperature, many minerals become more soluble while others become less so, and a chemistry very different from that at low temperatures may ensue. Thus it is necessary, if one is to properly understand the chemistry of these geologic systems, to have some knowledge of their thermodynamic properties.

One approach to this problem is the systematic and precise measurement and evaluation of thermodynamic properties for solutions of the major components in geologic waters. The previous chapter of this work correlates a great number of these measurements for NaCl(aq) . Precise thermodynamic measurements are difficult for temperatures above 373 K, and doubly so if the pressure is significantly increased. Many techniques originally devised under room conditions become inadequate or even impossible at higher temperatures and pressures. Consider, for example, the determination of solvent or solute activity. Precise e.m.f. techniques may be used to temperatures of 348 K or thereabouts, but beyond this temperature only the hydrogen electrode has a proven

reliability. Concentration cells might be used, but interpretation of these data requires a knowledge of transference numbers which are difficult to obtain under extreme conditions. Solubility measurements are occasionally but not generally useful, and vapor pressure methods are limited to pressures along the liquid-vapor saturation curve. This stalemate has recently generated much interest along the lines of "correcting" precise low-temperature, low-pressure information to more extreme conditions via a knowledge of the temperature and pressure derivatives of the Gibbs energy. The aqueous solution volume,¹ enthalpy²⁻⁴ and heat capacity⁵⁻⁷ are measurable, with some difficulty, to high temperature and pressure.

This chapter is concerned with the construction, testing and operation of a flow microcalorimeter for use in measuring the heat capacity at temperatures to 573 K and pressures to 1 kbar. The flow microcalorimetric technique was originally pioneered by Picker, et al.,⁸ at low temperature. Subsequently, it was extended to high temperature and pressure by Rogers and Pitzer⁵ and Wood and co-workers.^{6,7} The calorimeter discussed herein is a reconstruction of the calorimeter used by Rogers, but incorporates several improvements. In addition, a new technique of measurement, which has advantages in calibrating the instrument for power losses, is investigated and preliminary power loss measurements are reported. Finally, the limitations of the instrument in determining the specific heat capacity of a sample solution are discussed.

2. Principles of Operation and Equations

The technique introduced by Picker, et al.,⁸ is one whereby the temperature rises in the working and reference loops of a twinned flow

microcalorimeter are matched by adjustment of the electrical current through the working loop heater. Calibration using pure water allows the determination of power loss for each loop since the heat capacity of water is known.

A balancing of heat gained through electrical heating and heat lost through sample flow, radiation, conduction, etc., leads to the simple equation

$$P - L = P(1 - L/P) = rc_p \Delta T \quad (1)$$

wherein P is the total power dissipated by the heating element, L is the power lost to radiation, conduction, etc., so that $(P-L)$ is the power transferred to the fluid, r is the mass flow rate of the fluid and c_p is its specific heat capacity, and ΔT is the rise in fluid temperature on heating. If the temperature rises are matched exactly then two of equations (1) may be equated and the solution heat capacity related to that of the solvent. Recognizing that the mass flow rate of solution, r_s , is related to the mass flow rate of water, r_w , and the densities of solution and water, ρ_s and ρ_w , by $r_w/\rho_w = r_s/\rho_s$, Fortier, *et al.*,⁹ obtain (subscripts s and w refer to solution and water, respectively)

$$\frac{c_{p,s}}{c_{p,w}} = \left[1 + f \left(\frac{P_s}{P_w} - 1 \right) \right] \left(\frac{\rho_w}{\rho_s} \right)_{T_r} \quad (2)$$

Densities are required only at the reference bath temperature T_r (Fig. 2) since a volume of solution is displaced by an equal volume of water. The factor f accounts for power losses but is not easily related to the absolute loss L . Its value is determined by calibration with pure water and is assumed to be independent of solution composition. Rogers⁵ uses the more direct equation

$$\frac{c_{p,s}}{c_{p,w}} = \left(\frac{P_s - L_s}{P_w - L_w} \right) \left(\frac{\rho_w}{\rho_s} \right)_{Tr} \quad (3)$$

with the assumption that $L_s = L_w$, i.e., the absolute magnitude of the power loss depends primarily upon the temperature rise and only negligibly upon the power and other factors. This differs from the treatment of Fortier, et al., who find that the relative loss L/P is independent of P . White and Wood,⁷ in their detailed evaluation of eqs. (2) and (3) at temperatures to 600 K, found that taking $L_s = L_w$ underestimates $c_{p,s}$ and they recommend eq. (2). However, it is important to realize that the three calorimeters, although based on similar operating principles, are of independent and very different designs, so that assuming $L_s = L_w$ may be reasonable in some instances but not in others.

The attraction of the temperature-matching technique is due largely to the ease with which the matching process may be automated. For a low-temperature calorimeter such as described by Picker, et al., where temperature fluctuations are small and easily controlled, automation is easily accomplished. At higher temperatures, however, fluctuations of long and short duration increase and automatic power control becomes quite complex. Manual temperature matching is a tedious and occasionally time-consuming process due to instrument lag time, which is 5-10 s for the calorimeter described here. Determination of the specific heat capacity at a level of precision of 0.1% requires the matching error to not exceed ± 0.001 K.

In our experience it is experimentally simpler and more accurate to measure the temperature rise directly; in one sense this represents a return to a more traditional heat capacity measurement. If the efficiency of the working loop is given by $\epsilon = (1 - L/P)$, in accordance with

Fortier, et al., and White and Wood, eq. (1) may be rewritten

$$\Delta T = \epsilon P / rc_p. \quad (4)$$

Calibrations using pure water are sufficient to determine the dependence of ϵ upon total power and heat capacity flux (rc_p). Once this information is known, eq. (4) may be inverted so that $c_{p,s}$ may be computed for a sample solution. Note that this is not trivial since ϵ itself depends on the value of $c_{p,s}$. Fortunately this dependence is not large, so one may take $c_{p,s} = c_{p,w}$ when computing ϵ . If the data are sufficiently precise, the value of $c_{p,s}$ thus obtained may be used to compute a new value for ϵ , and the calculation repeated until agreement is satisfactory. One or two repetitions should be sufficient.

A distinct advantage of this method in addition to its experimental simplicity is the ease and precision with which the efficiency (or, equivalently, the power loss) may be measured as a function of the two variables P and (rc_p). This is not the case for temperature-matching instruments, as pointed out both by Fortier, et al., and by White and Wood. Thus, the need for a chemical standard is eliminated. The calorimeter described here may be used as a temperature-matching or direct-temperature-rise instrument.

3. Experimental Design

The calorimeter used in this work is a reconstruction of that described by Rogers and Pitzer⁵ which incorporates several improvements over the original design.

The calorimeter proper remains essentially the same in physical layout, twinning of working and reference sides and choice of heating and temperature sensing elements. The stainless steel tubing used by

Rogers was replaced with tubing of Hastelloy C-276 (of the same dimensions) as corrosion of the former in the calorimeter hot zone was evidenced. This tubing was annealed as directed by the manufacturer after cold-working to the required form. During the annealing process, heating elements and wells for temperature sensors were brazed onto the Hastelloy tubing with Wilbraz 7008 alloy (70% Au, 8% Pd, 22% Ni). Two nearly-identical solution loops are mechanically supported on a large copper block which serves as thermal mass and a portion of the adiabatic shield. To insure independent operation of working and reference loops, a barrier of thin copper sheet was positioned between the loops but not in contact with them. Mounted directly on the copper block, this barrier serves primarily to eliminate radiative heat transfer between the loops. After electrical connections are made (described below) the remainder of the adiabatic shield is attached and the entire apparatus placed inside a stainless steel vacuum jacket as indicated in Figure 1.

The calorimetric assembly is immersed in a thermostatted, fluidized-sand bath with stability better than ± 1.0 K. Because of the large thermal mass of stainless steel vacuum jacket and copper adiabatic shield these fluctuations are reduced by an order of magnitude in the interior of the calorimeter. During the course of a heat capacity measurement, the calorimeter temperature rarely varies by more than 0.2 K, measured using a $1000\ \Omega$ platinum thermometer implanted in the adiabatic shield. Since working and reference loops of the calorimeter are equally affected by these fluctuations, the temperature difference between the loops is stable to ± 0.001 K. Oxidation of component parts

Figure 1. The Flow Microcalorimeter. The working loop of the calorimeter is indicated by solid lines, the reference loop by dashed lines.

- A. Stainless steel vacuum jacket.
- B. Copper adiabatic shield.
- C. Calorimeter block.
- D. Heating element (wound about solution tubing).
- E. Thermometer well (containing platinum resistance thermometer).
- F. Support tube containing electrical leads and vacuum connection.

and electrical leads in the high-temperature zone is inhibited by maintaining a vacuum of at least 40 μ m Hg with a mechanical pump.

Plumbing is as indicated in Figure 2. Tubing external to the high-temperature bath is of 0.0625 in. o.d., 0.020 in. wall stainless steel. Connections are made with Swagelok compression fittings. There are two major improvements over Rogers' design.⁵ First, a length of flattened stainless steel tubing (0.0625 in. o.d.) is used as a back-pressure regulator. Fluid flow through this type of regulator varies with the length of flattened tubing and pressure drop across the device and inversely with the fluid viscosity. Several regulators of different lengths were constructed, thus allowing some choice in the flow rate. Since a sample solution will in general have a viscosity different from that of the pure solvent, it is necessary to insert a delay loop as indicated in Figure 2. To assure optimal operation, regulator and delay loop are thermostatted at 298.15 K. Second, a ballast of $\sim 20 \text{ cm}^3$ volume is inserted as shown to dampen out pressure fluctuations. The ballast is pressurized at the initiation of a measurement to a maximum of 100 bars with an inert gas. The combination of a constant (metered) solvent flow, achieved with an Attex model 100 reciprocating, dual-piston HPLC pump, and back-pressure regulator further compresses the gas until a steady-state pressure is reached. The fluid pressure, measured with a transducer calibrated against a Bourdon-tube gauge (Ashcroft Digigauge model 7781), fluctuates by less than 1 bar (the precision of measurement). The remainder of the plumbing is as described by Rogers.

Electrical connections to heating and temperature sensing elements are of the four-lead type. Platinum lead wires of 0.010 in. diameter and 20 cm. length are silver-soldered to these elements. This length of

Figure 2. Plumbing for the Flow Calorimeter. A, High pressure sample injection valve. B, Sample loop. C, Delay loop. BPR, Back-pressure regulator.

platinum wire is sufficient to pass through the adiabatic shield (B in Figure 1) and into the support tube (F). At this point, copper leads of 0.032 in. diameter are silver soldered to the platinum. These pass upwards out of the high-temperature bath and through a vacuum seal (Conax PL series) to the external circuitry.

All measurements are made with a Leeds & Northrup type K-3 potentiometer and Keithly model 147 null detector. Electrical circuits are shown in Figure 3. All power supplies are of the constant-current type with continuously adjustable output; current stability is better than 10 ppm.

The temperature sensing circuit (Fig. 3a) is composed of 1000 Ω platinum thermometers $R_{P,1}$ and $R_{P,2}$ (mounted in the thermometer wells of the calorimeter proper, E of Fig. 1), 1000 Ω standard resistors $R_{S,1}$ and $R_{S,2}$, matching resistors $R_{M,1}$ and $R_{M,2}$ and block thermometer R_{Blk} . The matching resistors are required since the thermometers do not have identical resistances; $R_{M,1} \approx 12.1 \Omega$ and $R_{M,2}$ is a 25 Ω , ten-turn potentiometer. The thermometers themselves were calibrated against a platinum thermometer purchased from Rosemount, Inc. (Model 162-CE), with calibration traceable to NBS standards. Two chart recorders, measuring the balance potential, E_{Bal} , and the bridge potential, E_{Br} , are included, as are potential leads for measuring the e.m.f.'s across the standard resistors and platinum thermometers. The standard and matching resistors are immersed in a thermostatted oil bath. The electrical currents i_1 and i_2 are independently and continuously adjustable from 0 μA to 300 μA . Use of this circuit is described below.

The heating circuit (Fig. 3b) is composed only of 40 Ω standard resistors, $R'_{S,1}$ and $R'_{S,2}$, and heating elements, $R'_{H,1}$ and $R'_{H,2}$, connected so that conventional four-lead potential measurements may be made. The

Figure 3. Electrical Circuitry for the Flow Calorimeter. The temperature-sensing circuit is given in (a) and the heating circuit in (b). The working and reference loops are indicated by subscripts 1 and 2, respectively. R_S is a standard resistor, R_M a matching resistor, R_P a platinum thermometer, R_H a heating element and R_{Blk} the block thermometer.

heating elements are $50\ \Omega$ inconel-clad nichrome wires 1 m in length wound about the Hastelloy C-276 tubing in the manner described by Rogers;⁵ see also Figure 1. As before, the standard resistors are immersed in an oil bath and the electrical currents i_1' and i_2' are independently and continuously adjustable from 0 mA to 100 mA. The upper current limit produces a temperature rise of ~ 10 K for a fluid flow rate of 0.7 g/min.

The efficiency of the working loop is determined by reference to the known heat capacity of water.¹⁰ With a fixed pressure and water flow rate through the working loop (the latter determined by selection of the appropriate back-pressure regulator), the calorimeter is allowed to stabilize for two to four hours. Stable operation is indicated by a smooth, non-cyclic trace of the bridge potential, E_{Br} (Fig. 3a), which is proportional to the difference in temperature between working and reference loops. No power is dissipated in either heating element at this time. When Stable operation has been assured, the currents i_1 and i_2 are adjusted so that a null is obtained for the balance potential, E_{Bal} . Then the matching resistor $R_{M,2}$ is adjusted to null the bridge potential E_{Br} . With the temperature-sensing circuit properly balanced, power is applied to the working heater and measurement of E_{Blk} , E_{Std} , E_H' , E_{Std}' and E_{Br} begun. The standard bath temperature and system pressure are noted also. On completion of these measurements, the power dissipated by the heater is increased and a new set of potentials obtained. This sequence is repeated a total of four or five times, covering temperature rises to 0.75 K. The dependence of ϵ on the heat capacity flux, rc_p , is obtained by repeating this sequence of measurements using a different back-pressure regulator.

Specific heat capacity measurements are performed in a very similar manner, only the sample solution flows through the working loop in place of pure water. One sequence of measurements at a single mass flow rate but varying power is sufficient.

The flow rate is required in the determination of ϵ . This is measured by massing the water collected at the terminus of the flow system in a given length of time. A 10 cm³ vial with rubber serum cap is used to prevent evaporation. By this method the flow rate may be determined to a precision of 0.1%.

The NaCl(aq) solutions studied in this report were prepared by mass from Malincrodt reagent-grade NaCl(<0.03% total impurities, by weight) and distilled water. All masses were corrected for air buoyancy.

4. Results and Discussion

The major goals of this work are to i) construct and test a flow microcalorimeter for use in measuring the heat capacity of liquids to 573 K and 500 bar, and ii) determine the dependence of the calorimetric efficiency, ϵ , on the absolute temperature, the temperature rise and the heat capacity flux. In addition, the heat capacity of NaCl(aq) at 3.0 mol kg⁻¹, the molality at which White and Wood⁷ made detailed measurements, has been measured at a few temperatures. Construction details are given in the previous section.

The calorimetric efficiency for the working loop is determined from temperature-rise measurements with pure water. Measurements were made at 360, 374, 475, and 554 K and either 100 or 250 bars, and interpreted using eq. (4) and the known heat capacity of water.¹⁰ Plots of ΔT vs P/rc_p exhibit no detectable curvature for temperature rises to 0.9 K; Figure 4 shows data collected at 475 K. Therefore, ϵ is independent of

Figure 4. Dependence of the Temperature Rise on the Power Dissipated in the Working Heater at 474 K. The slope of the line is the calorimetric efficiency, ϵ , defined by eq. (4).

the temperature rise. For larger P and ΔT (assuming constant rc_p), it is likely that ϵ will decrease somewhat as radiative and conductive effects become more important. By making several series of measurements with pure water at different mass flow rates, the dependence of ϵ on the heat capacity flux may be determined. Two series of measurements were conducted at 374, 475, and 554 K wherein the heat capacity flux was varied by 10% to 15%. This is roughly the difference in rc_p between a moderately concentrated electrolyte solution and pure water. A least-squares analysis of these data finds no significant dependency of ϵ on rc_p . Table 1 presents a summary of these data.

Such a dependency must, however, exist. Consider the operating extremes for constant power dissipation: In the limit of zero flow rate, hence zero heat capacity flux, only power which is transferred (chiefly by conduction along the tubing and by radiation) from heating to temperature-sensing elements will be detected. The detected temperature rises will be small but nonzero, and will increase with increasing power dissipated in the heating so that ϵ will also be small but nonzero. In this limit, eq. (4) is not valid. At the opposite extreme of large heat capacity flux, power losses due to radiation and conduction are small in comparison to the power transported by fluid flow, and ϵ may be expected to approach unity or some value only slightly less. For the calorimeter described here, ϵ will always be less than one since a short (<1 cm) length of heating element required for lead attachment is not in thermal contact with the tubing. Picker's design⁸ is an example wherein ϵ may be expected to approach unity.

To estimate the dependence of ϵ on rc_p , two series of measurements were made at widely varying flow rates and 360 K. A summary of these measurements is given in Table 1. The flow rates chosen are roughly one-half and twice, respectively, that which would be used in an actual heat capacity experiment conducted with our instrument, and therefore represent heat capacity fluxes far outside the normal experimental range. Under the (rash) assumption that ϵ varies linearly with rc_p , a value may be computed for a flow rate of 0.020 g sec^{-1} which may be compared with an extrapolation of values at higher temperatures. As may be seen in Figure 5, where the triangles represent data corrected to $r = 0.020 \text{ g sec}^{-1}$, agreement is not exact, but remains encouraging. There is no reason to believe ϵ will vary linearly with the temperature (at a given flow rate); rather, one might expect a slightly downward curvature due primarily to increased radiative losses at the higher temperatures.

In sum, these calibrations indicate that variations of the heat capacity flux between pure water and a sample solution are not large enough to produce significant effects upon the calorimetric efficiency, to the level of precision indicated in Table 1. However, for more precise measurements or for variations in rc_p greater than 15%, this may not be correct. Additional studies are underway to determine more precisely the dependence of ϵ on rc_p at each experimental temperature. The present measurements also confirm the results of White and Wood⁷ with regard to the dependence of power losses on rc_p .

A final check on calorimetric operation is obtained through measurement of the NaCl(aq) heat capacity. Comparison may be made with the equations of the previous chapter which are based, in part, on the

Table 1. Results of Calibration

Temperature K	Pressure bars	Flow Rate g sec^{-1}	ϵ	Number of Measurements
359.9	201	0.007071	$0.8918 \pm 0.3\%$	4
	201	0.02745	$0.9711 \pm 0.3\%$	4
374.4	264	0.01301	$0.9167 \pm 0.3\%$	8
475.0	100	0.019-0.022	$0.9201 \pm 0.4\%$	8
555	100	0.020-0.023	$0.9013 \pm 0.6\%$	8

Figure 5. Dependence of the Calorimetric Efficiency on the Absolute Temperature for a Flow Rate of 0.020 g/sec. The triangles represent data at other flow rates corrected to 0.020 g/sec.

results of White and Wood.⁷ Data taken at 374, 475, and 554 K are given in Table 2. The direct temperature-rise technique described above was used. The errors indicated at 475 and 555 K are large due to an experimental oversight: These heat capacities were computed from temperature-rise measurements not exceeding 0.6 K, which is much too small for precision measurement with this instrument. The temperature rise may be measured with an error of $\pm 0.001 - 0.002$ K, which is independent of the magnitude of the temperature rise. Thus measurements with ΔT ranging up to 1.5 K would be far more precise than those given in Table 2. The measurements at 374 K were made with larger temperature rises, as the precision level indicates. In all, the measured and computed heat capacities are in good agreement.

5. Estimation of Uncertainties

The major limitations to precision measurement with this instrument are i) the ability to determine the temperature rise only to $0.001 - 0.002$ K and ii) ensuring a constant and measurable mass flow rate. For the former, errors may be reduced to 0.1% by adjusting the power dissipated in the heating element so that the temperature rise is 1.5 - 2.0 K. However, one must be careful in applying eq. (4) to large temperature rises, particularly at high experimental temperatures, since the calorimetric efficiency will likely decrease at high P due to radiative and conduction losses.

With the technique described above, the mass flow rate may be determined to 0.1%, although some practice is required. The major problem arises from the presence of particulates in the fluid. If particulates are large enough, they will block the entrance to the back pressure

Table 2. Specific Heat Capacity of $2.997_g \text{ mol kg}^{-1} \text{ NaCl(aq)}$

Temperature K	Pressure bars	Measured c_p $\text{Jg}^{-1} \text{ K}^{-1}$	Computed c_p^{10} $\text{Jg}^{-1} \text{ K}^{-1}$
374.4	264	3.563 ± 0.007	3.561 ± 0.002
475.0	100	3.661 ± 0.02	3.637 ± 0.005
554.9	100	3.95 ± 0.03	3.863 ± 0.07

regulator and consequently change the flow rate. It appears that particles larger than a few microns are of sufficient size to cause irregularities. Therefore it is important to filter both solvent and sample solution as well as possible. Nevertheless, irregularities occur and are betrayed by a discrete jump in the measured flow rate.

There are other contributing errors which largely cancel out in a heat capacity measurement. An example of this sort are inaccuracies in the working thermometer calibration which appear in the determination of ϵ but not the heat capacity (since the known heat capacity of water is used to calibrate the instrument). The power may be measured with a precision of 20 ppm, so contributions from this source are insignificant. The overall precision of a heat capacity measurement obtainable with this instrument is no larger than 0.2% for a temperature rise of 1.5 - 2.0 K. The calorimetric efficiency may be determined to within 0.3%.

6. Conclusion

A flow microcalorimeter after the design of Picker, et al.,⁸ and Rogers and Pitzer⁵ was constructed and tested. This instrument incorporates several improvements in electrical and mechanical design which better allow for stable and precise operation as well as longer instrument life at high temperatures and pressures. A new method is advocated for determining the calorimetric efficiency (or, equivalently, the power loss) and solution heat capacity. This direct temperature-rise measurement is shown to be both experimentally simple and more advantageous than the original temperature-matching technique in the determination of power losses.

The results are presented of a preliminary investigation into the effects of variances in the heat capacity flux on the calorimetric efficiency. It is found that changes of 15% in rc_p have no detectable effect on the efficiency, but it is also shown that such an effect must exist and the ground work is laid for its precise determination.

Finally, a few measurements on NaCl(aq) solutions were performed. These measurements are consistent with previously reported values for the NaCl(aq) heat capacity, but are not of the highest precision obtainable from this instrument. Various sources of error are discussed and it is found that determination of the temperatures rise and of the mass flow rate are the largest contributors.

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