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Note

Simple procedure for calibrating cells for calorimetry and related purposes; a new standard of internal consistency in measurements of temperature differences with thermistors

LEONARDO LAMPUGNANI and LOUIS MEITES
Department of Chemistry, Clarkson College of Technology, Potsdam, N.Y. 13676 (U. S. A.)

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Constant-temperature–environment calorimetry, thermometric titrations, and differential thermometric studies of reaction enthalpies, rates, and equilibria require the evaluation of two parameters characterizing the apparatus used. One of these is the effective thermal capacity Q (cal/deg) of a reaction vessel and its contents; the other is the Newtonian heat-exchange constant ε (sec^{-1}) that describes its rate of exchange of heat with its surroundings.

Both may be evaluated from the temperature–time curve obtained when a known amount of heat is liberated in the reaction vessel[1–6]. This may be done by electrical resistance heating, in which case it is generally necessary to evaluate ε from data obtained during the re-establishment of thermal equilibrium after the flow of current has been stopped, and then to compute and apply corrections based on its value to the data obtained during the heating interval in order to find ΔT_{corr}, the rise of temperature that would have resulted in the absence of heat exchange. An alternative procedure is to mix known amounts of a strong acid and a strong base, or of some other reactants for whose reaction the value of ΔH is accurately known; if the reaction is sufficiently fast ΔT_{corr} may be obtained from a short extrapolation. As against the more complex and tedious calculations entailed by the electrical procedure, the chemical one is more difficult to employ in work involving non-aqueous solutions in which the enthalpy changes for suitable reactions may be unavailable, and in addition it involves the tacit assumption that the specific heat of a solution is independent of its composition so that the value of Q may be applied to solutions very different from the one in the calibration experiment.

With the aid of multiparametric curve-fitting[7], however, it is easy to evaluate both ε and Q from data obtained during electrical heating of a reaction mixture. Defining ΔT as the difference between the temperatures of the mixture and its surroundings, one has

$$\frac{d(\Delta T)}{dt} = -\varepsilon(\Delta T) + \frac{0.239 I^2 R}{Q} \tag{1}$$

where I is the current (A) flowing through a resistance heater having a resistance of R ohms. Integration gives

$$\Delta T = \frac{0.239\, I^2 R}{\varepsilon Q}(1 - e^{-\varepsilon t}). \tag{2}$$

Values of ΔT and t will be available from the recorded temperature–time curve, and I and R will be known; the problem is to select the values of ε and Q that provide the best fit of Eqn. (2) to the data.

Experimental data were obtained with a differential thermometric apparatus built around a locally constructed differential twin calorimeter fabricated from a Lucite cylinder approximately 25 cm in diameter. A Lucite support inside the calorimeter holds two 50-ml Teflon cups, each containing a magnetic stirring bar. The bars are rotated synchronously by magnets mounted below the calorimeter and driven by a variable-speed motor through a gear train. Each cup also contains a resistance heater made from 0.003-in platinum wire and having a resistance of approximately 9 ohms and one of a pair of carefully aged and matched glass-bead 100,000-ohm thermistors (Type 51A1, Victory Engineering Corp., Springfield, N.J.)[5], and provision is made for adding reagents to the two cups by externally actuated syringes. A Metrohm E211 "Coulometer" (Metrohm AG, Herisau, Switzerland) was used to pass an accurately known constant current through the heater in the vessel being calibrated; the resistance of the heater was measured with a Hewlett–Packard Model 3450 A digital voltmeter. The calorimeter is submerged in a Tronac Model 1005 constant-temperature bath equipped with a Tronac Model 1040 controller (Tronac, Inc., Orem, Utah) and with a cooling coil connected to an external refrigerator-circulator that provides a fixed rate of heat loss; over a 3-hour period this provides an environment whose temperature is constant within about ±100 μdeg. The thermistors are connected to a fixed-arm dc Wheatstone bridge energized by a 2.7-V mercury battery producing a power level of 18 μW in each thermistor. In aqueous solutions this is low enough to minimize thermal convection at the thermistor-solution interfaces and to give remarkably clean differential temperature–time curves. The unbalance voltage from the bridge is amplified by an Analog Devices, Inc. (Cambridge, Massachusetts) Model 260K low-noise MOSFET-chopper and recorded on a Hewlett-Packard Model 7000 AM recorder operated in the Y–T mode. Careful shielding and grounding was employed throughout, but there is no damping at any point.

The chart deflections listed in the second column of the body of Table I were obtained in a typical experiment employing an 0.5 F solution of sodium acetate; the "bridge sensitivity" appearing in the heading has the units of unbalance voltage per degree per volt energizing the bridge, or deg^{-1}, and was used in this form because the voltage of the mercury battery was checked at the time of each experiment. Minor changes were made in the program previously described[7] to (1) accept input and provide printout in the form shown, (2) compute ΔT at each point from the measured chart deflection, the bridge and recorder sensitivities, the bridge voltage, and the amplifier gain, and (3) reject from further consideration any point for which the

TABLE I

COMPUTER PRINTOUT OF THE RESULTS OF MULTIPARAMETRIC CURVE-FITTING OF DIFFERENTIAL THERMOMETRIC DATA OBTAINED IN AN ELECTRICAL CALIBRATION EXPERIMENT

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RUN
ELECTRICAL CALIBRATION OF CUP N, DATE & CODE 7/8/72 A
HEATER RESISTANCE, OHMS? 9.338
HEATER CURRENT, MA? 10.00
BRIDGE SENSITIVITY, PER DEG? 1.1471E-2
BRIDGE VOLTAGE, V? 2.7021
RECORDER SENSITIVITY, MICROV/CM? 100
AMPLIFIER GAIN? 101
NO. OF DATA POINTS? 15
EXPECTED RANGES OF HEAT-EXCHANGE CONST.? 5E-4, 3E-3
                              THERMAL CAPACITY? 40,42

7 CYCLES

HEAT-EXCHANGE CONST. = 1.908269E-3
THERMAL CAPACITY = 40.35343
SUM (DEV.) ↑ 2 = 5.440657

TIME,      DEFLECTION,          DIFF(T), MICRODEG              DEV., M-C,
SEC        CM                   MEAS.          CALC.           MICRODEG

3          .54                  17.25073       16.54438         .7063563
13         2.23                 71.23914       71.01318         .2259530
23         3.91                 124.9081       124.4525         .4556241
33         5.55                 177.2992       176.8816         .4175618
43         7.17                 229.0514       228.3198         .7316321
53         8.74                 279.2063       278.7856         .4206813
63         10.28                328.4028       328.2976         .1052249
73         11.78                376.3215       376.8736        -.5521979
83         13.26                423.6013       424.5317        -.9303476
93         14.72                470.2422       471.2888        -1.046574
103        16.18                516.8831       517.1621        -.2790766
113        17.61                562.5656       562.1684         .3972164
123        19                   606.9702       606.3239         .6463088
133        20.36                650.4165       649.6449         .7716562
143        21.65                691.6266       692.1469        -.5203256

STAND. DEV. OF 1 VALUE = .6022545 MICRODEG

READY
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experimental value of ΔT differed from that calculated from the best values of ε and Q obtained in any cycle by more than twice the standard deviation calculated in that cycle. Points so rejected were invariably found to have been afflicted by errors of reading or transcription.

The program accepted crude initial estimates of ε and Q and proceeded in the fashion previously described[7] to refine these estimates so as to improve the goodness of fit, stopping when the sum of the relative range widths, (A4 + B4 − 2) in the previous rotation, decreased to 0.001 or less. At this point neither of the values would be changed by as much as 0.1% on further computation. Execution on a Digital Equipment Corp. PDP8/I minicomputer operated in POLYBASIC (Digital Equipment Corporation Users' Society, Maynard, Massachusetts) typically consumed about 3 min.

These calculations not only facilitate the evaluation of parameters needed for further experimentation but also provide a direct check on the internal consistency of the data obtained. From Table I it appears that this internal consistency corresponds to a standard deviation of ±0.6 μdeg, which is almost a full order of magnitude smaller than the values ±3.5 μdeg obtained by Dohner, Wachter, and Simon[8] and Smith, Barnes, and Carr[9]. Measurements with thermistors of temperature differences having internal consistencies or precisions between the latter value and about ±20 μdeg have been reported by numerous authors during the last few years, but it is evident that this is by no means the limit to what can be accomplished in this direction. Our figure, ±0.6 μdeg, corresponds to an uncertainty of ±0.2 mm in reading the pen deflection from the recorded chart, for the overall sensitivity of the electrical circuitry used in this work can be stated as 3.194 μdeg/mm.

Five replicate experiments (under conditions different from those used to obtain the data in Table I) gave values of Q ranging from 45.11 to 45.65 cal deg^{-1} and values of ε ranging from 3.9×10^{-4} to 4.49×10^{-4}, the relative standard deviations being ±0.48% and ±5.5%, respectively. These reproducibilities are consistent with the precision of the recorder used to obtain the temperature–time curves.

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