

HEAT CAPACITY MEASUREMENTS BY COMPUTER-INTERFACED DSC

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A computer assisted heat capacity measuring system has been designed from commercial components. A differential scanning calorimeter of type Perkin-Elmer DSC-2 forms the basis for measurements from 100 to 1000 K. A Hewlett-Packard calculator (minicomputer) of type 9821 is the data handling system. The data are collected and permanently stored on teletape. The program has been written to govern measurement and final computation, tabulation, plotting, and curve fitting. Calibration is done by comparison with benzoic acid or aluminium oxide (sapphire). Zinc heat capacities have been measured as an example and for evaluation of accuracy. Accuracies of better than $\pm 0.5\%$ have been achieved, an improvement of approximately a factor 3 to 5 over a similar system without computer assist. The system will be used mainly for heat capacities of linear macromolecules.

The heat capacity is the key thermal property of a material. Through its knowledge, the enthalpy, entropy, and free energy can be calculated and used for discussion of interactions, degree of disorder, and stability, respectively. The use of heat capacities for description and understanding of matter has been neglected somewhat in the past due to difficulties in measuring heat capacities [1]. Presently, this difficulty has been removed by the development of differential scanning calorimeters (DSC) of sufficient speed and accuracy to make heat capacity measurements routine [2].

In the here described work a computer program has been developed for the rapid determination of heat capacity. Thermal analysis data (dQ/dt vs. T) are generated by the DSC. The analogue output from the DSC is converted into digital form through an interface system and recorded on paper punch tape for permanent record. Although the program does not directly control the operation of the DSC, it oversees the entire run through a series of questions and directions which are displayed on the console of the calculator.

The details of the program are given and method of generation and treatment of data are described in Ref. [3]. Measurements of heat capacity of zinc are reported to illustrate the capability of our DSC-computer system.

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The major advance in heat capacity measurement is the increase in accuracy over normal operation of the DSC. Without change in calorimetric equipment, an increase in accuracy by a factor 3 to 5 over prior manual evaluation described in Ref. [2] has been achieved. Coupled with the wide range of temperature possible, the value of heat capacity data by DSC can approach and exceed those of adiabatic calorimetry.

Experimental

A differential scanning calorimeter (Perkin-Elmer DSC-2) is used for thermal analysis of all the samples. An enclosed, air cooled refrigeration unit (Perkin-Elmer Intracooler II) is attached to the DSC, which permits operation down to 210 K. With liquid nitrogen as coolant the range can be extended to 100 K. The upper limit of the calorimeter is 1000 K. The DSC output is recorded on the standard recorder equipped with temperature marker. Continuous transformation

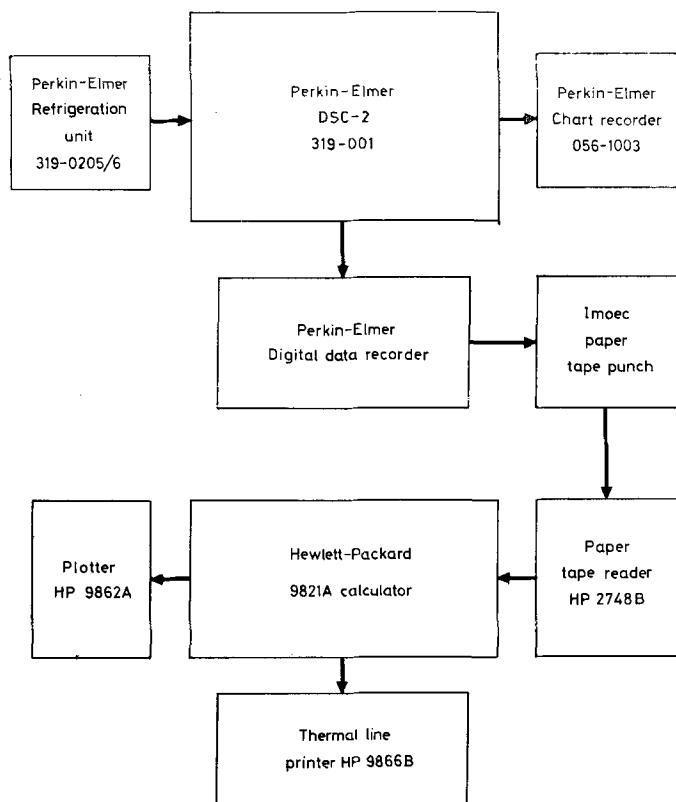


Fig. 1. Flow diagram of the DSC-Computer set-up.

of the output amplitudes into digital form suitable for further analysis is accomplished through the use of an analog/digital converter (Perkin-Elmer Digital Data recorder). The digital output from the digitizer is fed into a paper tape punch machine (Iomec Inc.). The range of digital output is 0 to 10,000 which is set by calibration to correspond to full scale displacement of the DSC recorder. The sampling interval between amplitude recordings can be present to any convenient value from a low of 0.6 seconds to a high of 99 minutes. The run on the DSC and the recording of amplitudes are started simultaneously to make the temperature markers of the DSC agree with the corresponding sequence number of the recorded amplitudes.

Heat capacity calculations from the recorded amplitudes are done on a Hewlett-Packard 9821A calculator system programmable in algebraic language. The calculator has an available memory for programming and data storage of 929 registers and is equipped with a digital cassette tape deck which gives access to another 6000 registers. The programs for computations and operation of the computer are stored in various files on the digital cassette tape. Files are loaded into the memory of the calculator automatically to carry out a given set of operations. The information on the paper tape (DSC output) is read by an optical tape reader (HP 2748B) and assimilated into the calculator which then proceeds to determine the heat capacities. The output of the program is obtained using a page printer (HP 9866A) and plots of the data and output are obtained using a plotter (HP 9862A). Figure 1 gives a block diagram of the DSC-Computer setup.

This facility is installed in a separate laboratory which is maintained at a constant temperature of $23 \pm 1^\circ$ using dual heating/air conditioning system.

High purity zinc of calibration standard quality (Perkin-Elmer 319-0018) was used for all the heat capacity measurement reported here. Sapphire (specific heat kit, Perkin-Elmer 219-0136) was used as calibration standard in all the measurements. Samples were encapsulated in aluminum pans. Hermetically sealed sample pans were used. All weighings were done on a Cahn microbalance with a sensitivity of 0.01 mg and an accuracy of about $\pm 0.01\%$.

Before measurements, the baseline of the DSC was optimized over the operating temperature region (310 to 750 K). Baseline flatness was optimized to vary within 1% of the full scale deflection of the recorder. The temperature scale was calibrated using standards to be within ± 0.2 K [4].

Heat capacity program

The program defines a system for automatic evaluation and reporting of heat capacities. Heat capacities may be determined for any temperature range in the region of 100 K to 1000K (the limits of the operation of the DSC). The temperature range was chosen to be in multiples of ten degrees and the absolute values of the lower and upper limits should also be multiples of ten degrees. The regions where phase transition occur (i. e., glass transition, melting crystallization, etc.) should

be avoided so as to obtain a continuous function of variation of heat capacity with temperature. However, the program can calculate nonaveraged heat capacities in the regions where phase transitions take place. A separate program for transitions has been developed and is used for heat of transition measurements [5].

The temperature range of interest is divided into intervals of 30 to 50 degrees and separate heat capacity runs are made for each interval. Heat capacities measured over these intervals are then combined to give a continuous function of heat capacity vs. temperature.

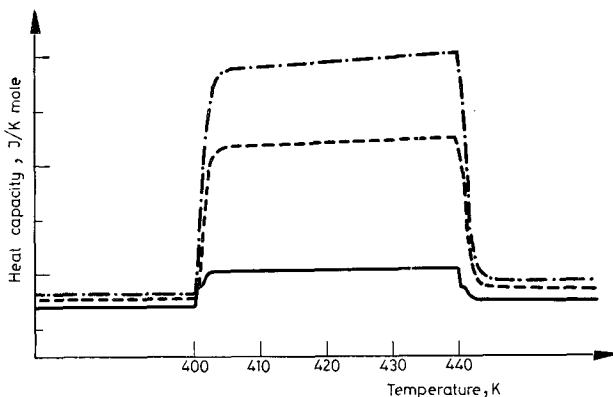


Fig. 2. DSC curves for baseline, standard, and sample scan (Print-out of data tapes). Lowest curve: baseline scan; Middle curve: sample scan; Top curve: standard scan (Al_2O_3). The left horizontals are the starting isotherms, followed by heating from 400 to 440 K. The right horizontals are the ending isotherms.

Sample: zinc. Standard: sapphire.

A measurement of heat capacity consists of three parts: a) Baseline scan b) Standard scan c) Sample scan. The baseline scan is obtained by scanning a weighed empty pan in the sample holder and an unweighed reference empty pan in the reference holder. The latter pan is the same used for standard and sample scans. To obtain positive displacements for the baseline scan, our reference pan is slightly lighter than the sample pan. The baseline scan is used to compensate for differences in weights and heat losses of the sample and reference calorimeter and also to determine the heat capacity contribution of pan material. The standard scan is obtained by scanning the encapsulated heat capacity standard against the reference pan which was used in the baseline scan. The standard scan is used to calibrate the instrument amplitude for the actual heat capacity measurement. Sapphire is used as a calibrating standard in the temperature range of 200–1000 K and benzoic acid is used below 200 K. Benzoic acid is used as a calibrating standard in the low temperature region because of the strong temperature dependence of heat capacity of sapphire in this region. Benzoic acid is not used above

200 K due to its high vapor pressure. The sample scan is obtained by scanning the encapsulated sample against the same prior used reference pan. All the three scans are performed using the same settings of the instrument (heating rate and range). If baseline and standard scans are not run with every sample, a prior-determined best data set may be used after proof of constancy of baseline and amplitude has been brought.

The DSC-curve of baseline, standard, and sample runs consists of three part a) the starting isotherm b) the programmed heating portion and c) the ending isotherm (see Fig. 2). The ending isotherm is extrapolated to the end of the programmed heating and an extrapolated baseline is obtained for all the three curves by connection with the starting isotherm at the start of the program as shown in Fig. 2. Ordinate displacements at selected temperatures are measured from the extrapolated baselines to the recorded curve; corrected standard and sample scan amplitudes are obtained by subtracting baseline scan displacements from standard and sample displacements respectively. These amplitudes are further corrected for the differences in weights of standard and sample pans. The heat capacities at selected temperatures are calculated using the equation:

$$C_p^{\text{sample}} = \frac{W_{\text{standard}}}{W_{\text{sample}}} \times \frac{D_{\text{sample}}}{D_{\text{standard}}} \times C_p^{\text{standard}} \quad (1)$$

where

- C_p^{sample} = Heat capacity of sample
- C_p^{standard} = Heat capacity of the standard
- W_{sample} = Weight of sample
- W_{standard} = Weight of standard
- D_{sample} = Baseline scan corrected sample amplitudes
- D_{standard} = Baseline scan corrected standard amplitude

The program consists of fourteen files which are listed below. The first line of each file directs that the file name be displayed on the calculator console, thereby providing the operator information about the contents of the various files.

<i>File No.</i>	<i>File name</i>
0	Baseline scan
1	Analysis of baseline tapes
2	Standard scan
3	Analysis of standard tapes
4	Sample scan
5	Analysis of sample tapes
6	Heat capacity calculation
7	Heat capacity temperature plot
8	Curve fitting/plotting $Y = Ax + B$

9 Curve fitting/plotting
 $Y = Ax^2 + Bx + C$
 10 Curve fitting/plotting
 $Y = Ax^2 + Bx + C$
 11 Curve fitting
 $\ln Y = A \ln x^3 + B \ln x^2 + C \ln x + D$
 12 Curve plotting
 $\ln Y = A \ln x^3 + B \ln x^2 + C \ln x + D$
 13 Plot of data tapes

If a particular operation of the program is not desired, the corresponding file can be bypassed. A flow diagram of the program is given in Fig. 3. Listing and detailed descriptions of all the files is given in Ref. [3]. A sample print-out of a complete heat capacity run is given in Fig. 4.

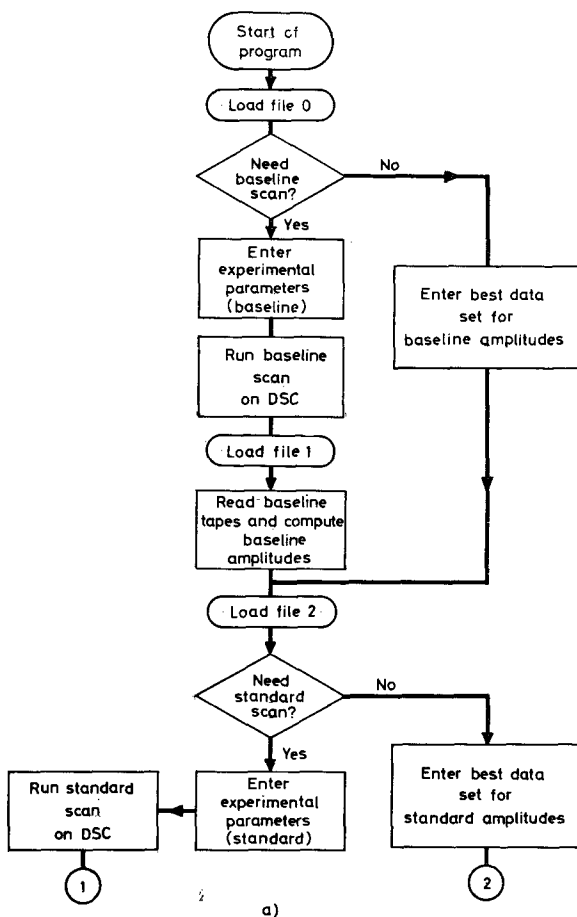


Fig. 3. Flow diagram of the heat capacity program

Heat capacity measurements on zinc

Heat capacity of zinc has been measured from 410 to 520 K using various experimental parameters to determine instrument settings for our DSC-computer system (see Figs 4 and 5).

Heat capacities were computed in ten degrees intervals. These experimental values at every ten degrees were smoothed by an inverse quadratic least square curve fitting ($C_p = AT^{-2} + BT + C$) to obtain a set of smoothed data (see Fig. 6). The experimental and smoothed data were then compared to literature values. These were obtained by curve fitting of all reported values of heat capacity of zinc in the range 410–520 K into the function $C_p = AT^{-2} + BT + C$. Table 1

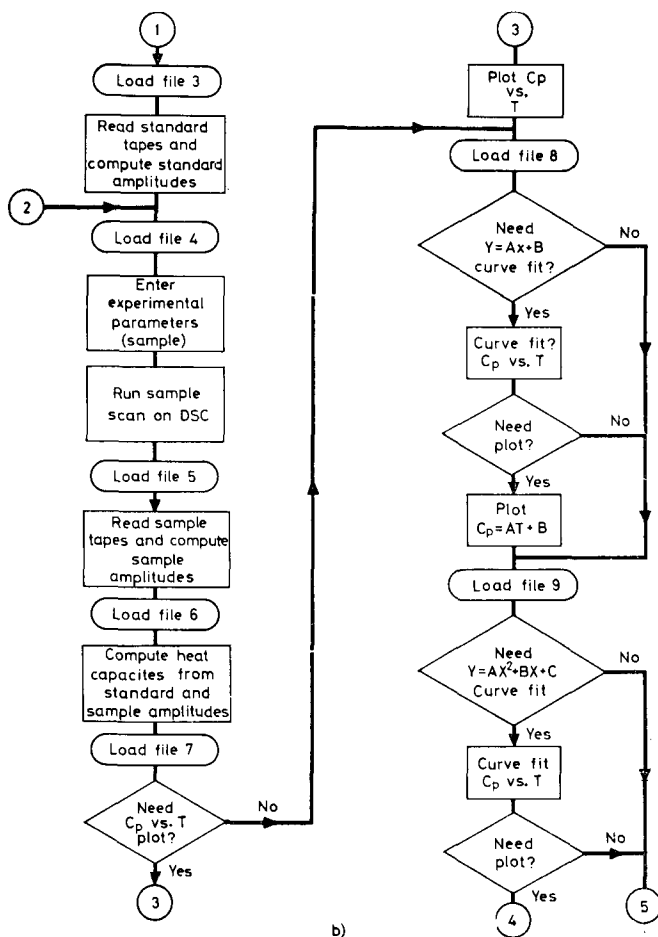


Fig. 3.

lists all the reported heat capacities and the curve fitted function. All the reported and curve fitted values agree within 1%.

Table 2 lists seven measurements of heat capacities of zinc which were made using combinations of instrument and run parameters. These measurements illustrate the effect of the various parameters on the quality of heat capacity data obtained.

Table 3 gives the experimentally obtained heat capacities over the region 410–520 K for all seven measurements. The coefficients obtained by curve fitting the experimental values into the function $C_p = AT^{-2} + BT + C$ are given in Table 4. Maximum deviations (in per cent) and standard deviations (in absolute values) are also listed. The smoothed values for all seven measurements are listed along

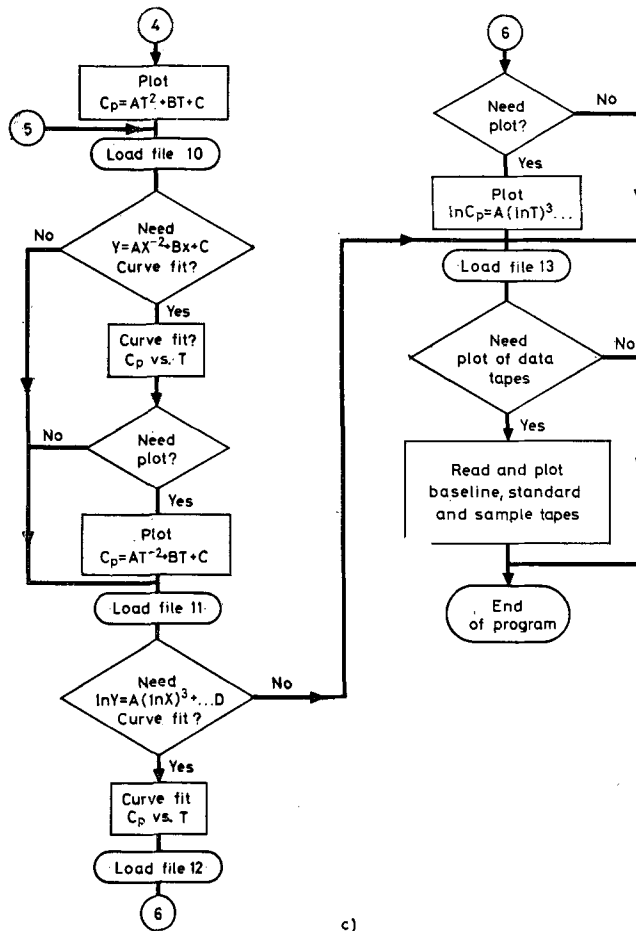


Fig. 3. Flow diagram of the heat capacity program.

BASELINE SCAN

DATE 8.09.1976
OPERATOR 1

EXPERIMENTAL PARAMETERS

PAN MATERIAL = ALUMINIUM
 WEIGHT OF THE PAN+COVER = 26.33 MG
 PURGE GAS PRESSURE = 20 PSI
 HEAD TEMPERATURE = 210 K
 HEATING RATE = 10.00 DEG/MIN
 RANGE = 5.0 MCAL/SEC
 ZERO = 465.0
 INTERVAL BETWEEN POINTS ON DATA TAPE = 1.2 SEC

RUN NUMBER LOWER LIMIT (K) UPPER LIMIT (K)
 712 400.0 480.0
 713 400.0 480.0
 714 400.0 480.0

BASELINE AMPLITUDES

TEMPERATURE (K) AMPLITUDES (DIGITAL UNITS)
 410.0 2.0734E 03
 420.0 3.2756E 03
 430.0 3.7430E 03
 440.0 3.9740E 03
 450.0 3.9740E 03
 460.0 3.4488E 03
 470.0 3.3428E 03
 480.0 3.2405E 03
 490.0 3.2405E 03
 500.0 3.2405E 03
 510.0 3.2405E 03
 520.0 3.2405E 03

SAMPLE SCAN

DATE 8.09.1976
OPERATOR 1

EXPERIMENTAL PARAMETERS

MOLECULAR WEIGHT = ZINC = 65.37
 WEIGHT OF THE PAN = 13.04 MG
 WEIGHT OF THE PAN+COVER = 26.33 MG
 WEIGHT OF THE SAMPLE = 12.22 MG
 WEIGHT OF THE PAN+COVER = 26.76 MG
 PURGE GAS PRESSURE = 20 PSI
 HEAD TEMPERATURE = 210 K
 HEATING RATE = 10.00 DEG/MIN
 RANGE = 5.0 MCAL/SEC
 ZERO = 465.0
 INTERVAL BETWEEN POINTS ON DATA TAPE = 1.2 SEC

RUN NUMBER LOWER LIMIT (K) UPPER LIMIT (K)
 721 400.0 480.0
 722 400.0 480.0
 723 400.0 480.0

SAMPLE AMPLITUDES

TEMPERATURE (K) AMPLITUDES (DIGITAL UNITS)
 410.0 1.2627E 03
 420.0 1.2627E 03
 430.0 1.1277E 03
 440.0 1.1277E 03
 450.0 1.1277E 03
 460.0 1.2299E 03
 470.0 1.2299E 03
 480.0 1.2299E 03
 490.0 1.2299E 03
 500.0 1.2299E 03
 510.0 1.2299E 03
 520.0 1.2299E 03

STANDARD SCAN

DATE 8.09.1976
OPERATOR 1

EXPERIMENTAL PARAMETERS

STANDARD = SAPPHIRE
 WEIGHT OF THE PAN = 12.21 MG
 WEIGHT OF THE PAN+COVER AND STANDARD = 55.23 MG
 WEIGHT OF THE STANDARD = 29.11 MG
 WEIGHT OF THE PAN+COVER = 26.29 MG
 PURGE GAS PRESSURE = 20 PSI
 HEAD TEMPERATURE = 210 K
 HEATING RATE = 10.00 DEG/MIN
 RANGE = 5.0 MCAL/SEC
 SLOPE = 465.0
 ZERO = 465.0
 INTERVAL BETWEEN POINTS ON DATA TAPE = 1.2 SEC

RUN NUMBER LOWER LIMIT (K) UPPER LIMIT (K)
 715 400.0 480.0
 716 400.0 480.0
 717 400.0 480.0

STANDARD AMPLITUDES

TEMPERATURE (K) AMPLITUDES (DIGITAL UNITS)
 410.0 2.0734E 03
 420.0 3.2756E 03
 430.0 3.7430E 03
 440.0 3.9740E 03
 450.0 3.9740E 03
 460.0 3.4488E 03
 470.0 3.3428E 03
 480.0 3.2405E 03
 490.0 3.2405E 03
 500.0 3.2405E 03
 510.0 3.2405E 03
 520.0 3.2405E 03

HEAT CAPACITY CALCULATIONS

SAMPLE = 65.37

TEMPERATURE (K)

410.00
 430.00
 440.00
 450.00
 460.00
 470.00
 480.00
 490.00
 500.00
 510.00
 520.00

HEAT CAPACITY (J/OLE-K/MOLE)

56.43
 56.43
 56.43
 56.43
 56.43
 56.43
 56.43
 56.43
 56.43
 56.43
 56.43

LEAST SQUARES

Y=AX+Z+BX+C
 A = 1.5944E-04
 B = 1.0530E-02
 C = 1.1951E-01

% DEVIATION

X= 4.10000E 02
 4.20000E 02
 4.30000E 02
 4.40000E 02
 4.50000E 02
 4.60000E 02
 4.70000E 02
 4.80000E 02
 4.90000E 02
 5.00000E 02
 5.10000E 02
 5.20000E 02

Y=

54249E 01
 54724E 01
 55773E 01
 57219E 01
 58612E 01
 59572E 01
 71820E 01
 72746E 01
 73344E 01
 73884E 01
 74305E 01

Y(CALC)=

54249E 01
 54724E 01
 55773E 01
 57219E 01
 58612E 01
 59572E 01
 71820E 01
 72746E 01
 73344E 01
 73884E 01
 74305E 01

STD DEVIATION= 3.01017E-02

Fig. 4. Sample print-out of the heat capacity program. (Measurement 6, see Table 2). Upper left of the figure is the printout for the baseline scan (files 0 and 1); upper right, for the standard scan (files 2 and 3); lower left, for the sample scan (files 4 and 5); lower right for the heat capacity calculations (files 6 and 10).

Table 1
Heat capacities of zinc in the range 410–520 K reported in the literature

Temperature, K	Heat capacity J mol ⁻¹ K ⁻¹ (reported)	Heat capacity, J mol ⁻¹ K ⁻¹ (calculated) ^a	% Deviation	Reference
410.0	24.49	26.48	-0.1	5
420.0	26.59	26.55	-0.2	5
423.0	26.34	26.57	0.9	6
423.0	26.75	26.57	-0.7	9
430.0	26.69	26.62	-0.2	5
438.0	26.50	26.69	0.7	6
440.0	26.79	26.70	-0.3	5
450.0	26.89	26.78	-0.4	5
453.0	26.64	26.80	0.6	6
473.0	26.89	26.97	0.3	6
473.0	27.27	26.97	-1.0	7
473.0	26.87	26.97	0.4	8
498.0	27.13	27.17	0.2	6

^a Data smoothed by curve fitting into the function

$$C_p = 21.586 + 1.034 \times 10^{-2}T + 1.095 \times 10^5 T^{-2}$$

(standard deviation 0.17)

with the literature values in Table 5. In Table 6 a comparison of the quality of the experimental and smoothed data with literature values is given. Also listed are maximum percent departure and standard deviation for all seven measurements.

Table 2
Instrument and run parameters used in various measurements

Experimental variable	Heat capacity measurement						
	1	2	3	4	5	6	7
Weight of sample, mg	13.84	22.69	22.69	42.22	42.22	42.22	42.22
Heating rate, deg/min	5	5	10	5	5	10	10
Range sensitivity,* mcals/sec	5	2	5	5	2	5	5
Heating interval, degrees	40	40	40	0	40	40	120
Sampling interval, sec	1.2	1.2	0.6	1.2	1.2	1.2	1.2
No. of data points per degree	10	10	10	10	10	5	5

* mcals/sec for full scale deflection

Table 3
Heat capacities of zinc, experimentally measured

Temperature K	Heat capacity, Joules K ⁻¹ mole ⁻¹							
	Reported value	Heat capacity measurement						
		1	2	3	4	5	6	7
410	26.48	24.00	26.42	26.26	26.48	26.79	26.43	26.37
420	26.55	24.26	26.52	26.44	26.61	26.78	26.47	26.46
430	26.62	24.55	26.64	26.52	26.68	26.85	26.57	26.54
440	26.70	25.89	26.56	26.54	26.81	26.78	26.68	26.58
450	26.78	26.15	26.79	26.74	27.07	27.03	26.72	26.70
460	26.86	25.58	26.93	26.76	27.14	27.20	26.86	26.81
470	26.94	25.02	26.93	26.78	27.24	27.20	26.96	26.92
480	27.02	—	26.77	26.81	27.21	27.16	27.05	27.00
490	27.11	—	27.21	27.11	26.92	27.31	27.18	27.07
500	27.19	—	27.41	27.23	27.08	27.18	27.27	27.18
510	27.28	—	27.58	27.42	27.09	27.09	27.33	27.22
520	27.37	—	27.37	27.60	27.10	26.91	27.39	27.27

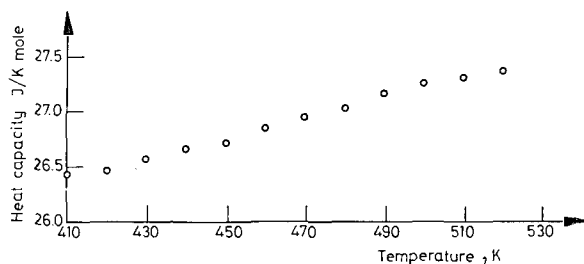


Fig. 5. Final data plot (Measurement 6 see Table 4 and Fig. 4); Plot carried out using file 7).

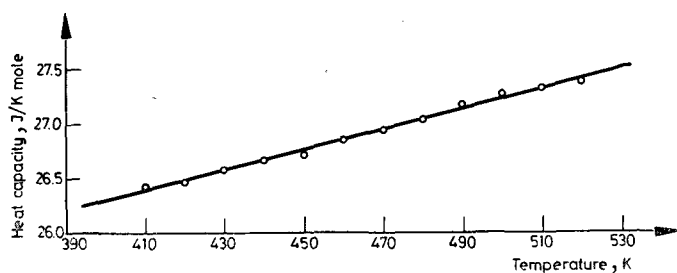


Fig. 6. Data and function plot $C_p = AT^{-2} + BT + C$ (Measurement 6 see Table 5); Plot carried out using file 10.

Table 4

Coefficients for curve fitting experimental data into the polynomial $C_p = AT^{-2} + BT + C$

Measurement number	Coefficient A	Coefficient B	Coefficient C	Maximum % deviation	Standard deviation
1	8.8084×10^5	3.6664×10^{-2}	4.398	$\pm 3.5\%$	0.52
2	4.8811×10^5	1.9915×10^{-2}	15.371	$\pm 1.0\%$	0.14
3	8.2975×10^5	2.7864×10^{-2}	9.992	$\pm 0.6\%$	0.08
4	-1.8236×10^6	-3.1777×10^{-2}	50.304	$\pm 0.5\%$	0.11
5	-1.4775×10^6	-2.6755×10^{-2}	46.410	$\pm 0.8\%$	0.11
6	4.3315×10^4	1.025×10^{-2}	21.941	$\pm 0.2\%$	0.03
7	-1.247×10^5	6.0973×10^{-2}	24.594	$\pm 0.2\%$	0.03

Table 5

Heat capacities of zinc obtained by curve fitting the experimental data

Temperature, K	Heat capacity, Joules K ⁻¹ Mole ⁻¹							
	Reported value	Heat capacity measurements						
		1	2	3	4	5	6	7
410	26.48	24.67	26.44	26.35	26.43	26.65	26.40	26.35
420	26.55	24.79	26.50	26.40	26.62	26.80	26.49	26.45
430	26.62	24.93	26.58	26.46	26.78	26.91	26.58	26.54
440	26.70	25.08	26.66	26.54	26.90	27.01	26.67	26.63
450	26.78	25.25	26.74	26.63	27.00	27.07	26.77	26.72
460	26.86	25.43	26.84	26.73	27.07	27.12	26.86	26.81
470	26.94	25.62	26.94	26.84	27.11	27.15	26.95	26.90
480	27.02	—	27.05	26.97	27.14	27.15	27.05	27.98
490	27.11	—	27.16	27.10	27.14	27.15	27.14	27.06
500	27.19	—	27.28	27.24	27.12	27.12	27.24	27.14
510	27.28	—	27.41	27.39	27.09	27.08	27.33	27.22
520	27.37	—	27.53	27.55	27.04	27.03	27.43	27.30

Table 6

Comparison of experimental and curve fitted data with literature values

Measurement number	% Deviation of experimental data from literature values	Standard deviation	% Deviation of smoothed data from literature values	Standard deviation
1	-10% to -2%	1.92	-6% to -4%	1.73
2	$\pm 1.1\%$	0.14	$\pm 0.6\%$	0.07
3	$\pm 0.9\%$	0.15	$\pm 0.7\%$	0.13
4	$\pm 1.1\%$	0.20	$\pm 1.2\%$	0.18
5	$\pm 1.7\%$	0.26	$\pm 1.3\%$	0.24
6	$\pm 0.3\%$	0.05	$\pm 0.3\%$	0.05
7	$\pm 0.4\%$	0.07	$\pm 0.5\%$	0.07

Discussion and conclusions

In a review of a large body of heat capacities of linear macromolecules, for which our system is primarily designed, adiabatic calorimeters were found to be accurate to only 3% or less [11]. This relatively low accuracy for linear macromolecules is mainly due to sample variation and metastability. In a separate study [2] in which three commercial dynamic differential calorimeters were compared, it was found that an accuracy of the order of magnitude of $\pm 3\%$ is attainable also from dynamic differential calorimeters. In the measurements reported here on zinc, we have found an accuracy of up to $\pm 0.3\%$ using the most appropriate instrument and run parameters.

The most important run parameter is the ordinate displacement. This is evident by comparing heat capacity data obtained from measurements using various sample weights (measurements 1 and 4 and 2 and 5). Larger samples give better heat capacities accuracy (see Table 4). Sample scans which do not differ in amplitudes from the baseline scan by at least 500 digital units give rise to erratic data (see data from measurement 1). The minimum amount of sample required can be determined from its approximate heat capacity and the heating rate and range sensitivity. Too large a sample would give rise to noise in the sample scan if not packed uniformly and would cause excessive temperature gradients in the sample if it is a poor thermal conductor.

Ordinate displacements can also be increased by using higher sensitivities and faster heating rates. Higher sensitivity gives rise to inherent noise in the signal which results in a slight depreciation in quality of the data obtained (measurements 4 and 5). Since higher sensitivity and weights of the sample used give both rise to noise in the signal, changing of sensitivity and weight, keeping approximately the same ordinate displacement, do not change the quality of data obtained by a large amount (measurements 2 and 5).

Faster heating rates give higher ordinate displacement and result in better heat capacity values (measurements 4 and 6). The effect of increased heating rate is still pronounced if the sensitivity is decreased to get comparable amplitudes (measurement 5 and 6). Heating rates faster than 10 degrees per minute result in larger temperature gradients in the sample and later attainment of steady state amplitudes. For faster heating rates one would also be limited by our data collection system.

In measurements 1 to 5, data sampling rates of 10 data points per degree have been used. In the 6th measurement, 5 data points per degree were recorded, which did not result in any depreciation in quality of heat capacity values obtained. A more detailed analysis of the sampling rate was possible in a study of heats of transition where larger changes in amplitude occur over a small temperature range [5].

Finally, the programmed heating interval of 40 degrees has been used in the first six measurements. Using the instrument settings of the 6th measurement (which gave best heat capacity data) and 120 degrees programmed heating interval,

the heat capacity values obtained were equally good. This increase in heating interval depends upon the quality of the instrument baseline. When this measurement was made, the instrument had the best baseline possible. However, the baseline changes slightly from day to day and thus programmed heating interval of 30–50 degrees are found more reliable.

These instrument settings are difficult to generalize. If adequate ordinate displacements are obtained (> 1000 digital units or over 10% of full scale deflection) the routine accuracy of our DSC-computer system is of the order of 1%. However, by careful selection of the right combination of experimental and run parameters, the accuracy can be improved to better than 0.5%.

This scanning calorimeter system allows thus a complete evaluation of heat capacities to an accuracy comparable to adiabatic calorimeters. The temperature range is much larger than can normally be covered with an adiabatic calorimeter. The efficient data handling permits measurements to be completed in times shorter than one week, including duplicate runs; a considerable time savings over adiabatic calorimetry. Finally, the cost of the installation in time and money is only a fraction of that needed for adiabatic calorimetry.

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RÉSUMÉ — Un dispositif a été conçu à partir de composants commerciaux pour la mesure des chaleurs spécifiques et a été associé à un ordinateur. Un analyseur calorimétrique différentiel à compensation de puissance, de type Perkin-Elmer DSC-2, constitue l'élément de base pour les mesures entre 100 et 1000 K. Le traitement des données s'effectue avec un ordinateur du type Hewlett-Packard 9821 (mini-ordinateur). Celui-ci assure l'acquisition des données et leur conservation permanente sur télé-bande. Le programme a été conçu pour contrôler la mesure et le calcul final, la mise en tableaux, le tracé des courbes et leur ajustement. L'étalonnage s'effectue par comparaison avec l'acide benzoïque ou l'oxyde d'aluminium (saphir). A titre d'exemple, la chaleur spécifique du zinc a été mesurée afin d'évaluer l'exactitude. Celle-ci est meilleure que $\pm 0,5\%$ c'est-à-dire qu'elle est 3 à 5 fois supérieure à celle d'un système similaire sans ordinateur. Le dispositif sera surtout utilisé pour la détermination des chaleurs spécifiques des macromolécules linéaires.

ZUSAMMENFASSUNG — Ein mit einem Komputter ausgestattetes Wärmekapazitäts-Mess-System wurde aus handelsüblichen Bestandteilen gebaut. Ein Differential-Scanning Kalorimeter vom Typ Perkin-Elmer DSC-2 bildet das Grundgerät für Messungen zwischen 100 und 1000 K. Ein Hewlett-Packard Kalkulator (Mini-Komputer) des Typs 9821 ist das Datenbehandlungssystem. Die Daten werden gesammelt und laufend am Tele-Band gespeichert. Das Programm eignet sich zur Steuerung der Messung und zur Endauswertung, Tabulierung, Berechnung von Zusammenhängen und Anpassung an Kurven. Geeicht wird mittels Vergleichen mit Benzoesäure oder Aluminiumoxid (Saphir). Die Wärmekapazitäten von Zink wurden als Beispiel und zur Bewertung der Genauigkeit gemessen. Die Genauigkeiten erwiesen sich besser als $\pm 5\%$, also 3 bis 5-mal so gut wie bei einem ähnlichen System ohne Komputter. Das System wird hauptsächlich zur Messung der Wärmekapazitäten linearer Makromoleküle eingesetzt.

Резюме — Из производимых компонентов была сконструирована система для измерения теплоемкости с участием ЭВМ. Дифференциальный сканирующий калориметр типа Перкин—Эльмер ДСК-2 являлся основой для измерения от 100 до 1000 К. Системой сбора данных служил Хьюлетт—Паккард калькулятор (мини-ЭМВ) типа 9821. Данные собирались и постоянно хранились на телетайпе. Была написана программа для управления измерений и конечных вычислений, табулирования, записи и построения кривой. Калибровка была проведена по отношению к бензойной кислоте и окиси алюминия (сапфир). С целью определения точности в качестве примера были определены теплоемкости цинка. Достигнутые точности были лучше чем $\pm 0,5\%$, что приблизительно составляло улучшение фактора от 3 до 5 по сравнению с системой без ЭВМ. Система была использована главным образом для определения теплоемкостей линейных макромолекул.