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COMPUTER ANALYSIS OF RESISTANCE–TIME TEMPERATURE–TIME THERMOGRAMS

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ABSTRACT

Two computer programs, one for the calibration experiment and the second for the reaction experiment of an isoperibol solution calorimeter have been written. The programs, written in the Fortran IV, level G language, analyze the thermograms using (*a*) a straight line approximation between the main period experimental data points, and (*b*) Dickinson's method to establish corrected temperature or resistance changes. Computer calculated values of corrected resistance changes (ΔR_{cor}) agree within 0.5% with the values obtained using the graphical methods of Regnault–Pfaundler and Dickinson. A program to calculate ΔH per mole has also been written.

INTRODUCTION

Analysis of isoperibol calorimetric data requires lengthy graphical procedures and/or tedious calculation to obtain corrected resistance changes** for the reaction and calibration experiments. The reaction experiment graphically resolves into two linear portions, the initial rating period (IRP), and the final rating period (FRP), connected by a curve for which no analytical equation is known. Similarly the "thermogram" representing the calibration experiment consists of three linear portions, the IRP, FRP, and linear main period during which electrical heat is introduced.

A computer program was desired that would minimize the amount of graphing required. A search of the literature did not yield any computer method applicable to the data collection methods used in our laboratory. Computer calculated values of the corrected resistance change would be acceptable, it was decided, if the deviation from graphical results was no greater than ±0.5%.

The computer analysis of the experimental data was consistent with the following scheme: The equations of the linear IRP and FRP portions are established from a least-square application to the experimental data. The end points of the IRP and FRP are known in the calibration experiment; for the reaction experiment they are

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**If temperature is measured directly, or a sensor is used which has a positive temperature coefficient, a minor modification of the programs is required. Instructions are included with the Fortran statements.

not known. By application of a deviation squared limit to the IRP and FRP data of the reaction experiment, the beginning and end parts of the main period can be found. Assuming that the main period can be considered to be a series of straight line segments connecting experimental points, the mean temperature during the main period can be found and the corrected temperature rise established. Results of the computer programs were compared to the graphical values obtained using the two generally accepted graphical techniques, Dickinson's method and the Regnault–Pfaundler method.

Separate programs were written for the calibration and the reaction experiments. A program was also written to obtain ΔH per mole. All programs were written in the Fortran IV, level G language and run on the Wayne State University IBM System 360 Model 65 computer. Exhaustive output information is preprogrammed to aid the investigator in interpretation of results and allow checking of input information.

Description and operation of solution calorimeter

The isoperibol solution calorimeter (isothermally jacketed calorimeter), was built at Wayne State University. The calorimeter vessel consists of a sealed capsule containing the solid reactant which is suspended in the solution reactant. This is contained within a silvered Dewar flask which is submerged in the isothermal water jacket. Time and resistance readings are recorded until the change in resistance with respect to time becomes a constant (or nearly so). At this point, the vessel and contents are in thermal equilibrium with the surroundings (the initial rating period). The capsule is now opened and the time recorded. The solid reacts in the solution and the time and resistance readings continue to be made until the change in resistance with respect to time becomes a constant (the final rating period). The vessel and contents are now again in thermal equilibrium with the surroundings.

All experiments referenced in this work were run near 25°C. A Leeds and Northrup platinum resistance thermometer was used as a calibration reference. To achieve higher thermal sensitivity, an 83 ohm thermistor was employed. Resistance readings referred to throughout are those of the thermistor.

THE CALIBRATION EXPERIMENT PROGRAM

Programming considerations

All portions of the calibration thermogram are considered linear. The experimental data consists of resistance and time data for the initial and final rating periods (IRP and FRP), the heater start and stop times, and the current-potential measurements during the heating period.

The following steps are involved in the calculation of the corrected resistance change, ΔR_{cor}:

(*I*) Application of a least-square fit to the IRP and FRP data to obtain the equations of the least-square lines for each. The calculation of slope (m) and intercept (*b*) of these lines is given by the following general formulas

$$m = \frac{n \sum_{i=1}^{n} x_i y_i - \sum_{i=1}^{n} x_i \sum_{i=1}^{n} y_i}{n \sum_{i=1}^{n} x_i^2 - \left(\sum_{i=1}^{n} x_i \right)^2} \tag{1}$$

$$b = \frac{\sum_{i=1}^{n} y_i - m \sum_{i=1}^{n} x_i}{n} \tag{2}$$

where n = the number of data points, the coordinates of the *i*th point being, x_i, y_i.

It should be pointed out that the least-square method minimizes the deviation of only y values from the least-square line. The deviation is defined as follows:

$$\text{deviation} = y_{\text{obs}} - m x_{\text{obs}} - b. \tag{3}$$

The deviation squared is useful since it is always positive.

(*2*) Resistance corresponding to the known heater start and stop times are found by solving the linear equations of the IRP and FRP respectively.

(*3*) Determination of ΔR_{obs} the observed change in resistance.

(*4*) Determination of the mean time during the main period.

(*5*) Determination of ΔR_{cor}, the corrected change in resistance, by solving the linear equations of the IRP and FRP for resistance values at the mean time and taking the difference of the resistance values.

TABLE I

COMPARISON OF COMPUTER AND GRAPHICAL VALUES OF ΔR_{cor} CALIBRATION EXPERIMENT

Experiment code	ΔR_{cor}		*Deviation (ohms)*	*Percentage deviation*
	Graph	*Computer*		
083168[a]	0.1698	0.1688	−0.00092	−0.53[b]
083168[a]	0.1694	0.1688	−0.00052	−0.32
083168[a]	0.1704	0.1688	−0.00152	−0.83[b]
083168[a]	0.1700	0.1688	−0.00112	−0.66[b]
071469	0.2713	0.2709	−0.0004	−0.15
071569	0.2780	0.28451	+0.00651	+2.32[b]
869137A	0.5486	0.54957	+0.0010	+0.17
869142A	0.4776	0.47847	+0.00073	+0.18
022070[a]	0.5342	0.53285	+0.00135	+0.27
022070[a]	0.5319	0.53285	+0.0010	+0.18
021970[a]	0.4503	0.44995	−0.00025	−0.07
022770[a]	0.38754	0.38755	+0.00001	0.00
091065[a]	0.20725	0.20724	−0.00001	0.00
071569	0.2832	0.28451	+0.0013	+0.45

[a] Data graphed by authors. [b] Data exceeding desired percentage deviation (see text).

RESULTS

A comparison of the ΔR_{cor} for a series of calibration experiments obtained graphically and via the computer program is summarized in Table I. Column headings indicate the experiment date code, the ΔR_{cor} obtained graphically, the ΔR_{cor} found using the computer program, the deviation of the computed value of ΔR_{cor} from the graphical value, and the percent deviation assuming the graphical value is correct. Repetition of the date codes indicates multiple graphing was performed; the purpose of this is discussed fully in the following section. Data not marked with a superscript *a* refer to graphical information, furnished by a member of our research group[1], for which the graphical precision is unknown. The graphical values of codes marked with a supercript *a* were obtained by the authors. Experiment codes ending with '65' refer to calibration experiments run in an Oak Ridge National Laboratory calorimeter[2]; all others were run in our laboratory.

Discussion of results

Values in Table I which exceeded the bench mark percentage deviation of 0.5 are marked with a superscript *b*. Experiments 083168 and 071569 were re-graphed, and both were then within the desired percentage deviation.

An investigation was made into one of the factors that could affect graphically determined values of ΔR_{cor}. Variations were made in the drawing of lines through the experimental points of the IRP and FRP. Figs. 1(a) and 1(b) show two lines for each of IRP and FRP drawn through the experimental points of experiment number 083168. Since these lines are extrapolated, the effect upon the value of resistance at the heater start and stop times becomes significant, as indicated in Table II (extrapolation could not be shown in Fig. 1 (a, b) due to page size limitations). It can be concluded that the location of the lines representing the linear rating periods then accounts for the variation in percentage deviation of ΔR_{cor} graphical values for experiment 083168. One of the advantages of the computer least-square routine is the elimination of any "personal bias" in the plotting of the linear rating period.

TABLE II

COMPARISON OF RESISTANCES AT HEATER START AND STOP

From Fig. 1 (a, b) (Run 083168)

IRP	*FRP*	R_{Heater}		ΔR_{cor}
		Start	*Stop*	
—	—	84.6375	84.4675	0.1700
—	—	84.6379	84.4681	0.1698
—	—	84.6375	84.4681	0.1694
—	—	84.6379	84.4675	0.1704
Computer program		84.6376	84.46872	0.1689

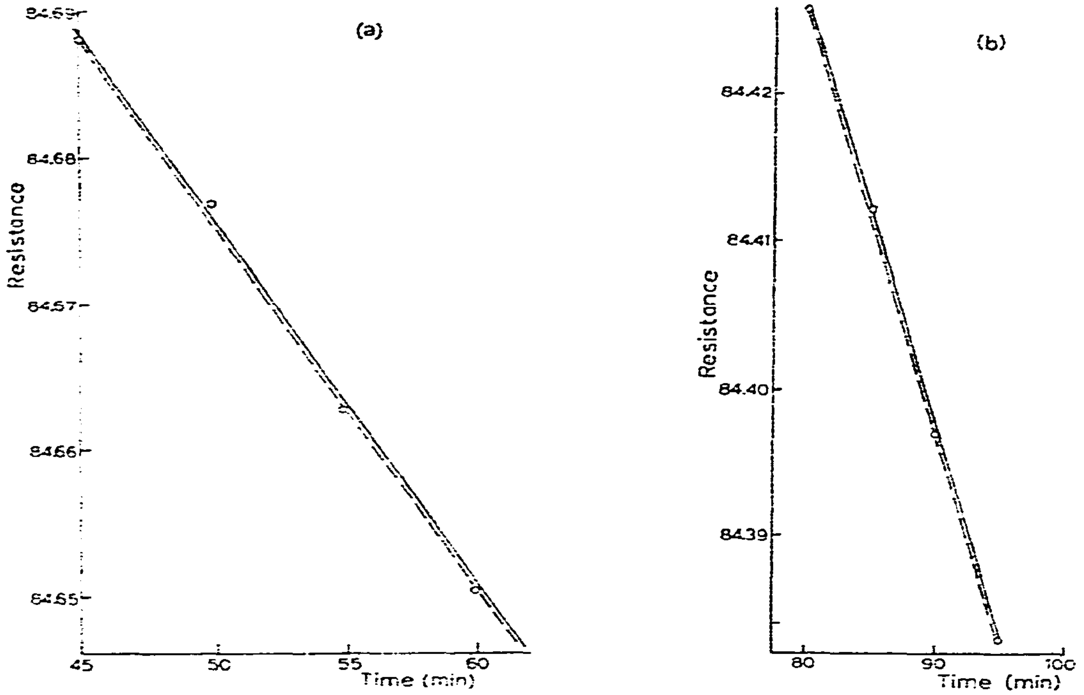

Fig. 1. Plot of resistance *vs.* time for Expt. No. 083168 during (a), initial rate period and (b), final rate period.

TABLE III

COMPARISON OF GRAPHICAL PRECISION AND PERCENTAGE DEVIATION OF ΔR_{cor}

Experiment code	*Graph scale (ohm/cm)*	*Graphical precision (ohms)*	*Percentage deviation*[a]
022070	0.0080	±0.00040	−0.27
022070	0.0040	±0.00020	+0.18
021970	0.0040	±0.00020	−0.07
022770	0.0004	±0.00002	0.00
091065	0.0004	±0.00002	0.00

[a] From Table I

The effect of the size of the graph upon percentage deviation is shown in Table III. As can be seen, agreement between the graphical and computer calculated values increases with increasing graphical precision. Assuming the average ΔR is 0.3000 for a reaction, a graph with a precision ±0.00002 would require an abscissa 750 cm (300 in) in length. Obviously, graphs of this size are impractical, and normally graphs are made with a precision of ±0.0002. The computer, however, easily achieves a precision of ±0.00002. Thus, the computer is the method of choice for the calculation for ΔR_{cor} of calibration experiments.

One word of caution is in order; the program does not distinguish between "good" rating period data and "bad" rating period data. It is the responsibility of the experimenter to obtain good rating period data and to avoid the conclusion that the least-square routine will average out poor experimental data. In practice this means that the jacket temperature must remain constant and that the change of resistance with respect to time during the rating periods be nearly constant. A "buffer" is included in the routine to handle an occasional erratic experimental point. The output also shows the calculation of deviation and deviation squared, point by point, from the calculated least-square line. These devices have been found to be useful in spotting erroneous data.

To test the accuracy of the calibration program, a series of "ideal" data points were calculated. All points were exact coordinates of lines representing the IRP or FRP.

It was anticipated that the deviations of individual experimental points from the least-square lines would be about 10^{-7}, assuming the computer could carry seven significant figures[3,4]. Actually, output from the computer showed that the deviations were not better than 10^{-5}, and the computed slope and intercept values were in error by as much as 1%, which was completely unacceptable.

The problem can be understood if one considers the functioning of the IBM system 360/65. Normally, using single precision, the decimal registers of the 360 are 4 bytes long and can contain 8 number characters in scientific notation. The first two are used for the sign of the number and the experiment. The remaining six are the significant figures. Since there is no exact conversion from decimal numbers less than one to binary, the last character position is inaccurate; therefore, five significant figures are carried.

For the text data used, the numerator in the least-square calculation;

$$n \sum_{i=1}^{n} x_i y_i - \sum_{i=1}^{n} x_i \sum_{i=1}^{n} y_i \tag{4}$$

would numerically evaluate to $0.60290656 \times 10^4 - 0.60290856 \times 10^4 = -0.00000200 \times 10^4$. The error introduced by rounding occurs in the sixth decimal place, and in this case significantly affects the calculation. The resulting error introduced causes the discrepancy in the least-square calculation.

To overcome this the programs were converted to double (extended) precision. The computer utilizes a full 8 bytes in this case and accuracy more than doubles. After this was done, the deviation values for the selected data dropped to 10^{-13} and the slope and intercept values were accurate to 0.005% for the ideal data.

REACTION EXPERIMENT PROGRAM

Programming considerations

The initiation and termination of the main (reaction) period is indicated by a deviation of the resistance rate change from, and return to, quasi-linear or linear character, respectively. A requisite of the program routine is that the data reflect

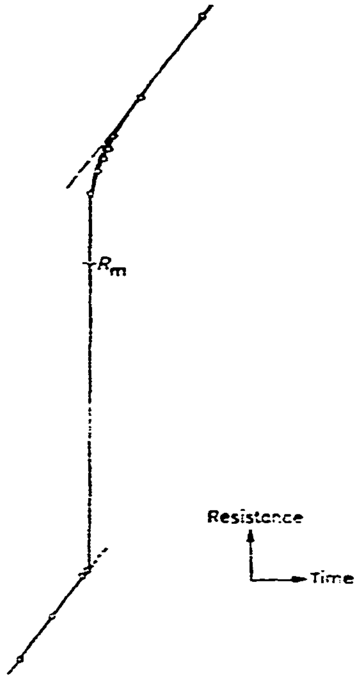

Fig. 2. Comparison of straight-line and smooth-curve approximation to main period.

true thermal equilibrium conditions for the last three drifts of the initial and final rating periods.

Comparison of the graphs used according to the Dickinson method leads to the conclusion that R_m, median resistance occurs in the near linear portion of the main period curve as shown in Fig. 2. The approximation that the experimental data points in the main period could be connected by a series of straight lines rather than a smooth curve yielded ΔR_{cor} values within ±0.5% of the values obtained in the usual graphing manner.

The straight-line approximation to the main period curve was chosen for the computer program. This is not an unrealistic approximation, as the Regnault–Pfaundler method determines the area beneath the curve using a trapezoidal method which, in essence, approximates the curve using straight lines[5].

In contrast to the electrical calibration experiment, the times at which the main period begins and ends are unknown in the reaction experiment. Although the time at which the capsule is opened is known, the reaction may not start immediately. As a result, the start and stop times must be determined during the course of the calculation. The reaction start and stop times were established by comparing successive experimental points to the linear equations of the rating periods. Significant deviation of two successive experimental points from either the IRP or FRP linear equations results in the last point, within a deviation-squared limit, to be chosen as the reaction start or stop point of the respective rating period.

The deviation-squared limit is arrived at by one of two methods. In the first method a predetermined value is programmed. This predetermined value (1×10^{-7}) was arrived at experimentally by comparing the average values of deviation squared of the IRP and FRP of many calibration experiments. The second method is based upon the last three points of the IRP and last three points of the FRP. An average deviation squared of these points is calculated, and if it exceeds the predetermined limit the average deviation squared is substituted as the new limit, otherwise the present limit continues to be used. This choice in determining the limit was found to be necessary after running a variety of data through the program routine. For several cases, the predetermined-limit method did not allow enough flexibility in the program.

The basic sequence of steps used to calculate ΔR_{cor} for the reaction experiment follows:

(*1*) The first three data sets have the least-square analysis applied to them.

(*2*) An average deviation square of the first three points is calculated.

(*3*) Successive data sets have deviation squares calculated from the least-square line equation of the first three points.

(*4*) If the value of the deviation squared of a data set is less than or equal to the average deviation square of step (*1*), the data set is in the initial rating period, and the next data set is considered.

(*5*) If two successive data sets exceed the average deviation square of step (*1*), the last data set within the average deviation square is established as the initial point in the main period.

(*6*) If one point exceeds the average deviation square and the next does not, the former is deleted from the least-square calculation.

(*7*) After the IRP least-square calculation is complete, that is, after the first point in the main period is established, the routine starts reading the last data point, then the second last, etc. Steps (*1*)–(*6*), inclusive, are repeated until the last point in the main period is established.

(*8*) ΔR_{obs} is calculated from the difference between the resistances at the reaction start and stop points.

(*9*) It is determined whether or not the reaction is exothermic or endothermic.

(*10*) The mean resistance is calculated from $R_m = 0.63\ \Delta R_{obs}$.

(*11*) The mean time, t_m, is found.

(*12*) Corresponding values of resistance during the initial and final rating periods at t_m are found, using the equations of each established by the appropriate least-square routines.

(*13*) ΔR_{cor} is calculated.

Results

In Table IV ΔR_{cor} values obtained via Dickinson's graphical method are compared with those calculated using the computer program for the reaction experiments. The deviation and the percentage deviation are calculated using the ΔR_{cor} value of the graphical procedure as the correct value. Where available the graphical precision is

TABLE IV

COMPARISON OF ΔR_{cor} VALUES OBTAINED VIA DICKINSON'S AND COMPUTER METHODS. REACTION EXPERIMENT

Experiment code[b]	*ΔR_{cor}*		*Deviation*	*Percentage deviation*	*Graphical precision*
	Dickinson	*Computer*			
869143	0.7828	0.7817	−0.0011	−0.14	n.a.
083168[c]	0.2669	0.26569	−0.0012	−0.41	n.a.
071569	0.2780	0.27721	−0.0008	−0.28	n.a.
071469	0.3432	0.34278	−0.00052	−0.11	n.a.
091065[a]	0.02765	0.02758	−0.00007	−0.25	±0.00005
090565[a]	0.05590	0.05588	−0.00002	−0.03	±0.00005
090365[a]	0.06612	0.06606	−0.0006	−0.10	±0.00005
081269	0.3684	0.3675	−0.0009	−0.21	n.a.
072169	0.3046	0.3044	−0.0002	−0.06	n.a.
071669	0.1952	0.1959	+0.0007	+0.35	n.a.

[a] Data graphed by authors. [b] Experiment codes ending with '65' refer to heats of solution experiments run at Oak Ridge National Laboratories[2] on K_2ReCl_6. [c] Code number 083168 is a reaction involving the solution of KCl. All others involve the solution of TRIS, (tris-hydroxyaminomethane) in NaOH. The KCl and TRIS experiments were run at Wayne State University[1].

TABLE V

COMPARISON OF ΔR_{cor} VALUES OBTAINED VIA REGNAULT–PFAUNDLER AND COMPUTER METHODS

Experiment code[a]	*ΔR_{cor}*			*Deviation*	*Percentage deviation*
	Computer	*R.–P. Eqn. (5)*	*R.–P. Eqn. (6)*		
091065	0.02758	0.02751		+0.0007	+0.25
091065	0.02758		0.02776	+0.0018	+0.65
090565	0.05588	0.05589		$\sim$0	$\sim$0
090565	0.05588		0.05589	$\sim$0	$\sim$0
090365	0.06606	0.06599		+0.00007	+0.10
090365	0.06606		0.06593	+0.00013	+0.20

All data graphed by the authors. [a] See footnote *b* in Table IV.

reported. Experiment codes marked with a superscript *a* indicate those data graphed by the authors, all others were graphed by P. S. Kothari.

Some of the experiments had long enough main periods to use the Regnault–Pfaundler semigraphical method for the calculation of ΔR_{cor}. Comparisons between the values of ΔR_{cor} found using the Regnault-Pfaundler[5] equations, (5) and (6), and the computed values, are presented in Table V[5].

$$\Theta = \Delta T - [g_i - K(T_m - T_i)]\Delta t \tag{5}$$

$$\Theta = \Delta T - [g_f - K(T_m - T_f)]\Delta t \tag{6}$$

where Θ = the corrected temperature change, ΔT = the observed temperature change,

g_i = mean value initial period slope, g_f = mean value final period slope, K = calorimeter constant, T_m = mean temperature during main period, T_i = mean temperature during initial period, T_f = mean temperature during final period, and Δt = time length of the mean period. All values in this table were calculated by the authors. The results of using Eqns. (5) and (6) should be invariant with respect to each other.

TABLE VI

CORRELATION OF R_m VALUES AND ΔR_{cor} PERCENTAGE DEVIATION

Experiment code[a]	R_m		ΔR_{cor} *Percentage deviation*
	Computer	*Graph*	
091065	104.7066	104.7066	−0.25
090565	104.6540	104.6540	−0.03
090365	104.6827	104.6828	−0.10
072169	83.2059	83.2065	−0.06
081069	83.9291	83.9295	−0.21

[a] See footnote *b* in Table IV.

R_m values obtained using Dickinson's method are compared with those using the computer program in Table VI. The significance of this comparison is discussed in the following section.

Discussion of results

All computer calculated results are within the desired percentage deviation of the ΔR_{cor} values obtained using Dickinson's graphical method. With the exception of experiment code 091065, the computer program results also agree, within the desired accuracy, with the values of ΔR_{cor} calculated via the Regnault–Pfaundler technique. Since the values for ΔR_{cor} using Eqns. (5) and (6) do not agree, it must be concluded that the resulting values of ΔR_{cor} should not be relied upon. This particular experiment was regraphed three times; however, the disparity between ΔR_{cor} using Eqns. (5) and (6) still existed.

There are two sources of discrepancy between the computer method and Dickinson's method that would cause the ΔR_{cor} values to differ. One is the establishment of the linear IRP and FRP curves. The second is the construction of linear line segments through experimental data, in the establishment of a smooth curve through manually graphed data of the main period. Table VI is an attempt to determine which of the two sources of discrepancy predominates. Where the R_m values obtained graphically and via the program agree exactly, the graphical curve and the computer-generated line segments are coincident. Any discrepancy between the ΔR_{cor} is due solely to the different methods used to obtain the IRP and FRP lines. Where the R_m values are not identical, the difference is assigned to a combination of both sources of discrepancy. No clear conclusion is evident as to which discrepancy predominates, since no correlation between percentage deviation of the ΔR_{cor} values and R_m values is apparent.

It is noteworthy that computer calculated values of ΔR_{cor} fall between those of the Regnault–Pfaundler and the Dickinson method.

ΔH PROGRAM

Discussion

The enthalpy of a reaction program uses, (*a*) ΔR_{cor} and R_{m} values obtained from the reaction and calibration experiment programs; (*b*) the values of potential, current and time of heating during the calibration experiment; and (*c*) the gram-molecular weight, and weight of the sample used.

The electrical energy introduced into the calorimeter is given by

Power (joules) = potential (volts) × current (amps) × time (sec)

The specific heat of the calorimeter is determined from

$$C_{\mathrm{p}} = \text{power}/R_{\mathrm{cor}} \text{ (calibration)}$$

ε is defined by

$$\varepsilon = C_{\mathrm{p}} \times R_{\mathrm{m}} \text{ (calibration)}$$

ε is used to account for differences in the R_{m} values of the calibration experiment(s) and the reaction experiment. Literature data indicate that some experimenters[6] choose to use the ε correction. The program calculates ΔH per mole both with and without the ε correction.

ΔH per mole is calculated in the usual manner,

$$\Delta H \text{ (joules per mole)} = \varepsilon \times \Delta R_{\mathrm{cor}} \text{ (reaction)} \times \mathrm{g/GMW} \times R_{\mathrm{m}} \text{ (reaction)}$$

If more than one calibration experiment per reaction experiment is performed, an average ΔH can be reported. The program will also calculate this average ΔH if data are supplied, and will calculate a ΔH for the reaction based upon each calibration run separately. This feature is useful to detect the subtle differences that exist in the thermal characteristics of the solution reactant and solid reactant, and the final product.

Detailed output information is also provided in this program.

The above described programs with instructions are available on request from: Karl H. Gayer, Department of Chemistry, Wayne State University, Detroit, Michigan 48202, U. S. A.

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