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ENTHALPHIC CALIBRATIONS OF A DTA APPARATUS

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ABSTRACT

This paper proposes a method of attack and a technique of calculation in calibrating DTA apparatus for calorimetric applications. The equations are intended to be applicable only to the instrument on which they were taken and at the time they were taken.

The equations reported, perfectly reasonable predictors for the specific instrument used and over the range for which they were obtained, are satisfactory provided they are not extrapolated beyond the limits of any of the variables or even interpolated between the various R and W values. No attempt is made to compare the two equations since there is no reason to believe that the instrument should produce the same results after change or repair of a part.

INTRODUCTION

A differential thermal analytical apparatus (DTA) makes use of thermal resistances to establish ΔT readings. When one wishes to calculate thermodynamic and kinetic quantities, a calibrating parameter, E, in units of millicalories per degree-minute is required in order to convert the ΔT output of the instrument to calorimetric units. This parameter is a function of temperature and, consequently, not a true constant. The calibration is performed usually by measuring either the enthalpies of fusion of a number of very pure metals[1] or the heat capacity of a material whose C_p values have been established over the range of temperature desired. For a high degree of precision the fusion method may be preferable but for a wide range of temperature there are advantages to the heat capacity method. The current paper illustrates the latter technique, notes the strong influences of rate of heating, sample weight and temperature, and indicates further that recalibration is absolutely essential whenever any component of the instrument is modified, replaced, or repaired. The apparatus used was a DuPont 900 readout and programming console with a DSC sample cell chamber.

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EXPERIMENTAL

Samples of sapphire (Al_2O_3) were weighed into the aluminum sample pans to one hundredth of a milligram and, when so specified, were of identical weight (within the abilities of the experimenter and the balance used). Results are reported for two separate calibrations because certain parts of the instrument were repaired in the interim. In the first calibration program both sample weights and rates of heating were changed, the weights being either 12 milligrams or 18 milligrams and the rates of heating being either 10 degrees per minute or 20 degrees per minute. In the second, only rate of heating was changed, the two rates being the same as in the first experiment. In the first, temperature was programmed from 67° to 567°C, while in the second, readings were also started at 67°C but were terminated at 367°C. Heat capacities were used to calculate the calibrating constant at arbitrary intervals as noted in Table I.

TABLE I

SELECTED POINTS FOR TEMPERATURE READINGS (°C)

Set 1		*Set 2*	
t	*Coded t*	*t*	*Coded t*
67	−230	67	−131.4
87	−210	92	−106.4
117	−180	117	−81.4
167	−130	142	−56.4
217	−80	167	−31.4
267	−30	192	−6.4
317	20	217	18.6
367	70	242	43.6
417	120	267	68.6
467	170	292	93.6
517	220	317	118.6
567	270	342	143.6
		367	168.6
t_0 = 297		t_0 = 198.4	

In the first program, the rates and weights were replicated at two levels each, effecting a 2^2 factorial design with two replications at each position in factor space. The 12 temperature points in each of the 8 runs thus provided a total of 96 points. In the second program, sample weights were not varied, but 10 and 20°/min were again used for heating rates. There were 6 replications at each heating rate, providing a total of 12 readings at each of 13 temperature points or a total of 156 points. Those familiar with statistical designs will readily recognize the split plot character of these runs.

EXPERIMENTAL RESULTS

In the first calibration program there was strong statistical evidence for both rate and weight effects as shown by the analysis of variance in Table II. These effects seem quite reasonable. Transients must exist through the sample and will be affected

TABLE II
PARTIAL ANALYSIS OF VARIANCE—SET 1

Source of variation	*SS*	*d.f.*	*M.S.*
R	41.91	1	41.91[a]
W	116.01	1	116.01[b]
RW	289.22	1	289.22[c]
RW—error	40.32	4	10.08
T—error	196.31	44	3.83
Between replicated	208.89	48	4.35

[a]Significant at 15% point, approximately. [b]Significant at 5% point, approximately. [c]Significant at ½% point, approximately.

either by a change in weight (*i.e.*, thickness) or by a change in the rate of heat input. It is therefore implied that the user should calibrate his instrument for the rate and for the approximate sample size intended in cases where calorimetric interpretations are required. The analysis of variance for the calibration at the second set of conditions is shown in Table III. It is clear that only temperature effects are detected. Moreover, the rate–error interaction is extremely high, making very difficult the detection of rate effects, if any exist. The sample weights used in this set of results, when listed as being identical, may have been less well replicated than were those in the first test; or, the instrument, after being repaired, may have been incapable of reproducing data as well as in the first instance. If at each temperature the differences between the average

TABLE III
ANALYSIS OF VARIANCE—SET 2

Source of variation	*SS*	*d.f.*	*M.S.*
R	121.02	1	121.02
R–error	3208.00	10	320.80
T	20910.84	12	1742.57[a]
RT	28.11	12	2.34
T–error	450.53	120	3.75
Total replications	3658.53	130	28.14

[a]Obviously significant. No other important effects detected, primarily due to large size of *R*–error.

values at the low and high levels of rate are used as paired comparisons, the conclusion that rate is significant will be erroneously obtained. The deception is due to the low value of the $R \times T$ interaction which automatically is used as an estimate of error in a paired comparison test.

GENERAL FORM OF REGRESSION EQUATIONS

In order to use DTA data to provide estimates of thermodynamic and kinetic parameters, it is convenient to represent E as a function of the variables measured. The general function

$$E = f(W, R, T)$$

has been written in linear form

$$E = b_0 + b_R R + b_W W + b_T T + b_{RW} RW + \ldots + b_{TT} T^2 + \ldots + \\ + b_{RTT} RT^2 + b_{WTT} WT^2 + \ldots \quad (1)$$

for terms through the fourth power of T.

In each set of results, the input conditions were coded as

$W = +1$, 12 mg; $W = -1$, 18 mg

$R = +1$, 10 deg/min; $R = -1$, 20 deg/min

$T_i = (t - t_0)$, (°C), where t_0 is an arbitrary value near the average.

The regression equations derived are then adequate for interpolation in t but apply only to the rates and weights used, since there is no indication of the form of the function between the terminal points. However, this limitation is not serious. As noted, each experimenter should calibrate his instrument for the conditions under which it is to be used. If variation in sample weights is important, he must investigate the effects produced by more than two sample sizes. The point to emphasize here is the dependence or potential dependence on rate and weight and the unquestionable dependence upon temperature at any instantaneous configuration of the instrument.

The data for the two sets of experiments were fitted to the best regression equation which could be found for the rate and temperature effects as well as, in the first run, difference in sample weight. The computer program used was that noted by Daniel and Wood[2] (deposited in the SHARE library, No. 360D-13.6.008). The equations reported below use features included in that program and described in the text, particularly the new Mallows' criterion for selecting the number of terms in the "best equation" (see p. 86 of ref. 2).

EQUATIONS FOR SPECIFIC TESTS REPORTED

A number of choices from which to select the final equation for the first calibration program are presented in Table IV. The data in this table indicate the form

TABLE IV

COEFFICIENTS OF VARIABLES AND CORRESPONDING VALUES OF t FROM EQUATION (1)

	Pass 5		*Pass 6*		*Pass 7*	
	β	t	β	t	β	t
R	—	—	—	—	—	—
W	0.352	0.9	—	—	0.623	1.8
$T/10$	23.98	48.1	23.98	52.2	23.98	53.8
RW	1.699	5.7	1.699	6.2	1.699	6.4
RT	−1.120	5.7	−1.029	6.1	−1.029	6.3
WT	—	—	—	—	—	—
T^2	4.186	29.0	4.186	31.5	4.186	32.4
RT^2	−0.548	1.8	−0.198	2.5	−0.198	2.6
WT^2	—	—	—	—	—	—
RWT^2	—	—	—	—	—	—
T^3	0.755	7.3	−0.755	7.9	−0.755	8.1
RT^3	—	—	—	—	—	—
WT^3	—	—	0.107	3.0	0.122	3.4
RWT^3	—	—	—	—	—	—
T^4	—	—	—	—	—	—
RT^4	0.066	1.2	—	—	—	—
WT^4	0.0578	3.0	0.0507	3.4	0.0288	1.5
RWT^4	—	—	—	—	—	—
b_0	161.97	—	161.97	—	—	—
RMS	4.26655	—	3.5977	—	3.4084	—
v	38	—	39	—	38	—
p	10	—	9	—	10	—
Fit	ok	—	<ok	—	ok	—
P-plot	ok	—	<ok	—	poor	

of the equation, the residual mean square (RMS) and its attendant degrees of freedom (v) for the number of parameters (p) in the equation. The last two lines are subjective judgements as to adequacy of the fit and to the possibility that the residuals are reasonably normally distributed. Information related to an equation which appears entirely adequate is labelled Pass 6. The equation (with variables still in coded form) is

$$E = 161.97 + 1.699\,RW + 0.2398\,T - 0.01029\,RT + 4.186 \times 10^{-4}\,T^2 - \\ -0.198 \times 10^{-4}\,RT^2 - 0.755 \times 10^{-6}\,T^3 + 0.107 \times 10^{-6}\,WT^3 + \\ +0.00507 \times 10^{-8}\,WT^4 \qquad (2)$$

The residual mean square of 3.5977 is less than the error mean square for temperature (3.8312) estimated from the replicates, the number of parameters required is less than either of the other alternatives, and the form of the probability plot is good. In addition, the variables were chosen in accord with the Mallows' criterion.

The choice of the second equation was complicated by the clear lack of rate effects and very large differences between the total mean square error of 28.14 and the mean square error for temperature effects of 3.75 which latter figure is similar to that obtained with the other set of data. To produce a fit which seemed satisfactory for a mean square error of 3.75, the following equation was required:

$$E = 117.47 + 0.604R + 0.820T + 5.72 \times 10^{-4}T^2 + 1.59 \times 10^{-6}T^3 - \\ -0.973 \times 10^{-8}T^4 + 0.38 \times 10^{-4}RT^2 \qquad (3)$$

The solid lines in Fig. 1 were calculated using this equation.

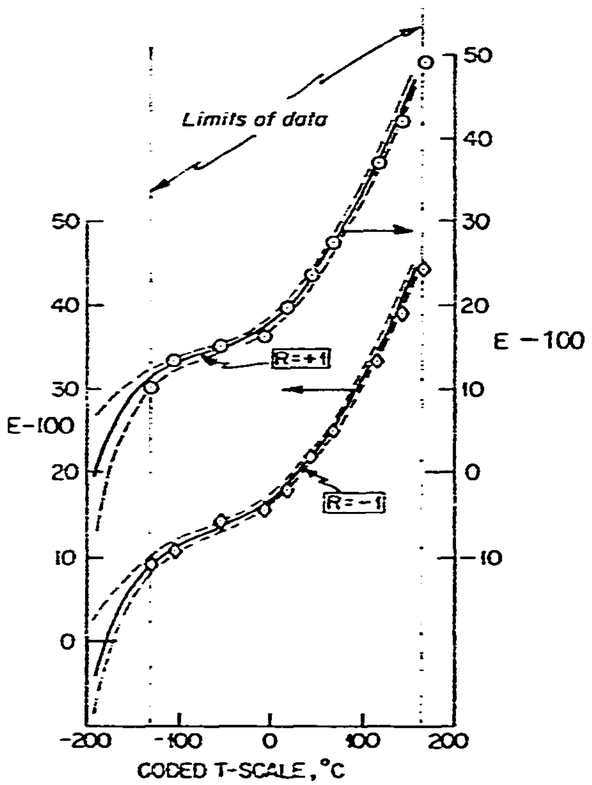

Fig. 1. Calculated values and confidence limits for the calorimetric calibration parameter, E, as a function of temperature. $R = +1$ (10 deg/min), $R = -1$ (20 deg/min).

However if one merely wishes to satisfy by the fitted equation an average error mean square of 27.04 and knows from prior information that rate effects are not significant, the following equation is adequate:

$$E = 117.32 + 0.0799T + 5.97 \times 10^{-4}T^2 + 1.72 \times 10^{-6}T^3 - 1.074 \times 10^{-8}T^4. \qquad (4)$$

The residual mean square for this equation is approximately 8.5 which is certainly adequate in comparison to the pooled mean square of 28.14 for the entire set of data.

Confidence intervals

The variance expected at any point, E_0, would always be estimated by

$$\text{var}(E_0) = X_0^T(X^TX)^{-1}X_0s^2$$

where

s^2	is the estimated error variance assuming that the fitted model is adequate,
X_0	is the p-dimensional vector of variables in the fitted equation representing the conditions at which E_0 is to be estimated; p is the number of parameters in the fitted model,
$(X^T X)^{-1}$	is the usual inverse of $X^T X$ where X is an $n \times p$ matrix of points for the n points used in establishing the calibration.

Predicted lines, and a set of "95% confidence intervals" for Eqn. (3) are shown in Fig. 1. The two solid lines represent the predicted best fit. The points marked are for the averages of six measurements each. The lines for the 10°/min and 20°/min data (coded $R = +1$ and $R = -1$) are not exactly identical as indicated by the second term in Eqn. 3. The estimated lines are therefore represented separately along with appropriate "95% confidence intervals" as calculated by the program referred to by Daniel and Wood (*loc cit.*).

Several items on these curves are worthy of special note. First the ordinates are dislocated to prevent overlapping of the data. Second, the expected rapid increase in confidence intervals outside the range of the data is apparent in the low ends of each curve. Third, the confidence intervals are calculated using $\pm t$ (0.025.8) and have consequently been placed in quotation marks since some authorities believe that the multiplier should be the Scheffé factor[3] and not student-t. A line and confidence intervals were calculated for $R = +3$ but are not reported since the extrapolation is clearly not justified. Fourth, it is important to realize that the confidence intervals are for the predicted line based on all points and not applicable to individual measurements at any point or even to averages of 6 at any point. To obtain the latter the variable at any temperature point should be increased by $s^2/6$ before multiplying by t.

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