Extrapolation of Thermal Functions to 0° K. Using Unconstrained Nonlinear Optimization

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This paper deals with the extrapolation of thermal functions and subsequent entropy calculation in the temperature region below experimental measurement capability. The problem involves the use of nonlinear optimization to express experimental heat capacity–temperature data as a linear combination of nonlinear Debye and Einstein heat capacity functions. The optimization technique used, a combination of conjugate gradient and steepest descent methods, is briefly described. Examples of application are illustrated for a variety of compounds.

THE GIBBS free energy of a reaction is used to determine if a reaction is possible and to what extent it will proceed under equilibrium conditions. Thus:

$$\Delta G_T^0 = \Delta H_T^0 - T\Delta S_T^0 \tag{1}$$

where ΔG_T^0 is the free energy, ΔH_T^0 the heat of reaction, T the temperature of reaction in ° K., and ΔS_T^0 the entropy of reaction. The entropy of reaction is obtained from the third law entropies of the reactants and products which for a liquid is:

$$S_T^0 = \int_0^{T_1} \frac{C_p \text{ (crystal)}}{T} dT + \int_{T_1}^{T_M} \frac{C_p \text{ (crystal)}}{T} dT + \frac{\Delta H_M}{T_M} + \int_{T_M}^{T} \frac{C_p \text{ (liquid)}}{T} dT \tag{2}$$

where C_p is the molar heat capacity and ΔH_M the heat of melting. Each quantity but the first may be experimentally determined in a low temperature calorimeter. Approximation of the first integral is not difficult if T_1 is low enough (say 4° K.) but becomes increasingly difficult and less accurate at higher temperatures depending upon the particular material being studied.

This paper illustrates a mathematical representation of the experimental heat capacities with a linear combination of theoretically based Debye and Einstein heat capacity functions. With these analytical functions, dependable extrapolations to 0° K. are obtained, and the first integral of Equation 2 can be evaluated. The use of empirical approximating curves, such as least squares and orthogonal polynomials, is not applicable to this problem because of the great uncertainty involved when these equation forms are used for extrapolation. The Debye and Einstein functions for a particular set of experimental heat capacity data are characterized by various nonlinear parameters, θ's. The determination of these θ's and the optimal linear combination of the Debye and Einstein functions is formulated as a problem in unconstrained nonlinear optimization. The particular optimization procedure used, a combination of steepest descent and conjugate gradient techniques, is discussed with some results achieved with its use.

PROBLEM FORMULATION

The problem of selecting Debye and Einstein thetas for a set of experimental heat capacity measurements over a selected temperature range requires an unrestricted minimum of a complicated function:

$$F(\theta_{D_i}, \theta_{E_i}, b_i, c_i) \text{ for } i = 1,2, \ldots ,p \tag{3}$$

where p, in this study, has a maximum value of 3. Using a least squares criteria, the function F may be written as the sum of squared absolute or relative differences between observed and calculated heat capacity values of m experimental measurements:

$$F = \sum_{k=1}^{m} (\text{calcd. } C_k - \text{obsd. } C_k)^2 \tag{4}$$

or

$$F = \sum_{k=1}^{m} [1 - (\text{obsd. } C_k/\text{calcd. } C_k)]^2 \tag{5}$$

The calculated C_k value for each T_k is the resultant of an analytical function consisting of a prescribed linear combination of Debye and Einstein functions.

The physical and mathematical features of the Debye heat capacity theory are described in detail elsewhere (*4*) as well as complete tables (*8*) listing heat capacity as a function of temperature and θ_D. The single degree Debye contribution (D_k) to the molar heat capacity of a material is expressed as:

$$D_k = 3R\left(\frac{1}{x}\right)^3 \int_0^x \frac{x^4 e^x}{(e^x - 1)^2} dx \tag{6}$$

$$= 3R\left[\frac{4}{x^3} \int_0^x \frac{x^3}{e^x - 1} dx - \frac{x}{e^x - 1}\right] \tag{7}$$

where $x = (\theta_D/T_k)$ and R is the universal gas constant.

The integral portion of Equation 7 can not be analytically integrated but may be estimated by the formula of Debye (*4*):

$$\frac{\pi^4}{15} - x^4 \sum_{n=1}^{\infty} e^{-nx} \left[\frac{1}{nx} + \frac{3}{n^2x^2} + \frac{6}{n^3x^3} + \frac{6}{n^4x^4}\right] \tag{8}$$

In the selected optimization procedure, a simpler analytical representation of the Debye function is desirable. Therefore, an empirical polynomial curve of the form:

$$\ln D_k = a_0 + a_1 x + \ldots + a_n x^n$$

was determined using the Debye function tables (*8*). The technique for this orthogonal polynomial type of curve fitting is described (*12*). The form and coefficients of the equation are given in Table I. For a system of 100 points of x where $0 \leqq x \leqq 60$ and using a 12th degree polynomial, the resulting agreement between the calculated table and

Table I. Transformed Polynomial Determination of Debye Function

$$\ln D_k = a_o + \sum_{l=1}^{12} a_l \left(\frac{x - 30}{31.5}\right)^l \text{ where } x = \frac{\theta_D}{T_k}$$

a_0	=	−2.962260	a_7	=	13.745102
a_1	=	−3.175212	a_8	=	59.402574
a_2	=	1.482403	a_9	=	−18.722584
a_3	=	−0.481934	a_{10}	=	−74.543524
a_4	=	4.035179	a_{11}	=	10.716087
a_5	=	−5.728326	a_{12}	=	31.522597
a_6	=	−19.803321			

polynomial values was ±0.05%, which is well within the range of the allowable experimental error of heat capacity measurements. For use with the optimization procedure described later this polynomial description could be considered uniformly monotonic. Thus the analytical Debye function is expressed in F as:

$$D\left(\frac{\theta_D}{T_k}\right) = \exp\left[h_o + h_1 \frac{\theta_D}{T_k} + \ldots + h_{12} \left(\frac{\theta_D}{T_k}\right)^{12}\right] \tag{9}$$

The theory and development of the Einstein function and its contribution to the total heat capacity is described (*5*) and tabular values are available (*11*). The value of the function for a single degree of freedom is:

$$E_k = R \frac{x^2 e^x}{(e^x - 1)^2} \tag{10}$$

where

$$x = \frac{\theta_E}{T_k}$$

Here, the total calculated heat capacity corresponding to each experimental temperature comprises a linear combination of Debye and Einstein functions so that:

$$\text{total calcd. } C_k = b_1 D(\theta_{D1}, T_k) + b_2 D(\theta_{D2}, T_k) + b_3 D(\theta_{D3}, T_k) + c_1 E(\theta_{E1}, T_k) + c_2 E(\theta_{E2}, T_k) + c_3 E(\theta_{E3}, T_k) \tag{11}$$

The linear constants b_i and c_i are greater than or equal to zero and integral in value. Using either Equation 4 or Equation 5, it is possible to select the linear coefficients and corresponding Debye and Einstein thetas for a given set of temperature-heat capacity measurements. The algorithmic procedure is presented below. Having made the optimal selection, the determination of the low temperature entropy of Equation 2:

$$S_T^0 = \int_0^{T_1} \frac{C_p}{T} dT \tag{12}$$

becomes the simple problem of evaluating the integral using the analytical form of Equation 11 from zero to a specified temperature T_1, which represents the temperature of the lowest measured heat capacity. The accuracy of the calculated S_T^0 is directly dependent on the extrapolation of Equation 11 which is a function of the goodness of fit indicated by the final value of Equation 4 or 5 after optimization.

TECHNIQUE DESCRIPTION

The function given by Equation 11 for each T_k is continuous for the various thetas and linear constants. Thus the total summed function F, given by Equation 4 or 5, over m measurements can be evaluated at all points. The total derivatives of F with respect to the various parameters are analytically defined consisting of a summation of m individual point derivatives. These characteristics make the optimization problem suitable for sequential optimization techniques, such as the gradient methods. The procedure used in this study is a combination of one of the recent conjugate gradient methods and the classical steepest descent technique.

The optimization procedure follows a brief discussion of the particular gradient methods. Consider a general function F of n variables whose value $F(z)$ and gradient vector $g(z)$ can be evaluated at any n dimensional point z. Using a Taylor series, the function F may be expanded near the required minimum point $\bar{a}$ and approximated by the quadratic form:

$$F(z) = F(\bar{a}) + \tfrac{1}{2}(z - \bar{a})^T G(z - \bar{a}) \tag{13}$$

where G is a symmetric and positive definite matrix of second-order partial derivatives. It is desired to generate the minimum point $\bar{a}$ as the limit of a sequence of points $z_0, z_1, \ldots, z_i, \ldots, \bar{a}$ where z_0 is the initial estimate of the minimum. Thus, a systematic procedure is needed to indicate the directions and amounts of change to each of the n components of a current z_i vector to arrive at a new vector z_{i+1} where $F(z_{i+1}) < F(z_i)$. These directions from z_i form an n dimensional vector d_i so that a general step is given by the recursive relationship:

$$z_{i+1} = z_i + \alpha_i d_i \tag{14}$$

where α_i is a positive scaler quantity. To be efficient $F(z_{i+1})$ should not only be less than $F(z_i)$ but be a minimum with respect to α_i along the line $z_i + \lambda d_i$. The manner of determination of d_i gives rise to the several different classes of gradient methods.

The classical steepest descent techniques, based on the calculus, demonstrate that the negative gradient of a function $F(z_i)$ evaluated at z_i indicates the best local (infinitesimal) direction of change of z that will decrease the value of $F(z)$. Thus:

$$d_i = -g_i \tag{15}$$

which is the basis of one part of the two stage optimization procedure used in this paper. However, this determination of d_i, while appealing in its simplicity, slowly converges for the second and most time consuming part of the optimization procedure of this study. Thus, a more efficient method was needed, and a recent conjugate gradient method was chosen.

Convergence with the gradient directions of Equation 15 is uncertain and difficult to estimate, even for so-called well behaved functions. With the conjugate gradient methods, the convergence pattern to a solution $\bar{a}$ is much more rapid and is convergent in n steps if $F(z)$ of Equation 13 is an exact quadratic function in n dimensions. The above pattern, as well as the nature of the conjugate gradient techniques, has been demonstrated (*6, 11*).

Most of the earlier gradient techniques do not provide for such a guaranteed convergence pattern. For the usual case of more general functions that are not quadratic—for example, the Debye and Einstein functions of this study—the quadratic Taylor series representation becomes increasingly descriptive during the final stages in the optimization process. An efficient approximation of quadratic convergence is thus provided. Even in regions far removed from a minimum of a general function, the quadratic representation improves convergence by using directional moves based on knowledge of the rate of curvature of the function as compared with gradient directions alone. Of course, all the gradient techniques are only applicable for finding a local optimum of a function. If a function has a number of optimal solutions, the particular solution generated depends on the initial estimate of the variables involved.

The problem with using the conjugate gradient method is the generation of a set of *G*-conjugate directions. Several approaches have been proposed and tested (*1, 6, 7, 9, 15, 17*) with the algorithm developed by Fletcher and Powell (*6*) being the most powerful and used in this study. Their work consists, in part, of a reformulation of a technique originated by Davidon (*3*). In the Fletcher and Powell algorithm, the *G*-conjugate directions d_i are given by:

$$d_i = -H_i g_i \tag{16}$$

where H_0, H_1, ... is a sequence of symmetric positive definite matrices corresponding to the points z_0, z_1, ... In this study H_0 is initially taken to be the unit matrix, so that the first directional change is taken along the line of steepest descent. Later H_{i+1} matrices are recursively generated as functions of d_i, H_i, g_i, and g_{i+1}. Thus, information on the function curvature gained in the previous steps is included in the direction determination d_i from a point z_i. As z_i approximates $\bar{a}$, the matrix H_i tends to G^{-1} so that the method completely describes the curvature of the function $F(z)$ at its minimum (*6*).

The relationship for determining H_{i+1} is:

$$H_{i+1} = H_i + \frac{s_i s_i^T}{s_i^T c_i} + \frac{-H_i c_i c_i^T H_i}{c_i^T H_i c_i} \tag{17}$$

where $s_i = \alpha_i d_i$ and $c_i = g_{i+1} - g_i$. The derivation of Equation 17 and the proof that Equation 16 does indeed generate *G*-conjugate directions are presented by Fletcher and Powell (*6*). An important characteristic of the method is that it uses the gradient of *F* to estimate second order information of the function. The ability to use this pseudo second order information in the d_i determination accounts for the speed of the procedure. However, from the nature of Equation 17, the advantage is gained only when an accurate evaluation of the function gradient at any *z* is possible. This effectively leads to the requirement of supplying analytical derivatives as part of the solution procedure.

The optimal determination of the Debye and Einstein thetas with corresponding integer constants (Equation 11) is essentially a repetitive two stage problem. The function *F* to be optimized is given by either Equation 4 or Equation 5 with variables b_i, c_i, θ_{Di}, θ_{Ei} for $i = 1, 2, 3$. For reasons explained below, the choices of the various constants b_i and c_i in Equation 11 are not usually known *a priori* for any given set of experimental temperature–heat capacity data and must be integral in value. The problem of optimally selecting the thetas for a given set of *b*'s and *c*'s can be handled by the use of the continuous variable conjugate gradient technique described earlier. However, the additional requirement that the various b_i and c_i constants also be optimally chosen poses an interesting problem because of the integral requirement. Changing the value of these constants presents problems of continuity and further depends on the selection of thetas corresponding to each set of *b*'s and *c*'s. Thus the need for a repetitive two stage procedure is apparent. The first is necessary for optimally changing the current *b*'s and *c*'s, while the second stage determines the optimal theta values for the current set of linear constants.

The criterion for changes in either stage is a decreased value of the *F* of Equation 4 or 5. The general step in the optimization procedure consists of changing one b_i or c_i at a time, and following this change, the set of associated optimal thetas for a minimal *F* is found (assuming the current set of *b*'s and *c* 's to be temporarily constant). The particular linear constant b_i or c_i to be changed, always either increased or decreased by one, is that constant having the largest gradient in magnitude using Equation 4 or 5. This criterion for selecting the direction of change in the linear constants is essentially a univariate form of the classical gradient directions method and is sufficient. The above two stage process of changing one of the linear constants and then finding the corresponding minimal value of *F* by optimally changing the thetas is repeated until no further reduction in *F* is possible.

The use of the function gradient to change the linear constants indicates only the "best" infinitesimal change of any constant. Since these constants are not changed in a continuous manner, a new set with one changed b_i or c_i might give an *F* higher in value after selecting the new thetas than the previous set of constants with its thetas. In this case, the procedure returns to the previous set of *b*'s, *c*'s, and thetas and changes that constant having the next largest gradient component. This situation occurs only in the final stages of the optimization procedure or where a change in a constant will violate the imposed nonnegativity constraints. The procedure is terminated at the point where no integral change in the linear constants leads to an improved value of *F*. Any one or more of the linear constants can be fixed during the entire procedure.

The selection of the thetas for any given set of linear combinations by the conjugate gradient method seldom requires more iterations than the number of thetas in Equation 11. This indicates the value of the quadratic approximation and convergence pattern discussed earlier.

The entire procedure has been programmed in Algol-60 for the Burroughs B-5500 computer system. The program provides for many various input-output and calculating options. The data to be supplied consist of the specified number and starting estimates of the various linear constants and thetas, the set of temperature–heat capacity measurements, and control cards. The program has an option, discussed in the next section, which will automatically estimate a starting set of constants and thetas.

EXPERIMENTAL EXAMPLES

Historically, the problem of analyzing low temperature heat capacity data has required a combination of the knowledge of a skilled investigator with tedious trial and error calculations. Analyses involving the study of translational, rotational, and vibrational degrees of freedom with other contributions such as $C_p - C_v$ corrections are usually too difficult to make purely theoretical predictions practical. Most investigators simply use Debye and Einstein tables (*8, 11*) and a trial and error procedure of matching heat capacity data with Debye and Einstein thetas. Another procedure is the graphical method of Kelley and King (*13*). In this section, the use of an efficient and direct algorithmic approach to the problem will be illustrated for a number of examples.

Equation 11 shows that up to three separate Debye and three separate Einstein functions can be used for fitting. The linear constants preceding each function are degrees of freedom which thus lead to the integral requirement discussed earlier. For the Debye portion, either the conventional three degree Debye function or three single degree Debye contributions can be used. The limit of three Einstein parameters was established for computational economy reasons. While it may be advisable to use up to 3 × (number of atoms −1) Einstein degrees of freedom, the curve fitting flexibility resulting from using the complete number of degrees of freedom available and/or from using more than three Einstein functions has not been necessary in the low temperature range.

There are a number of ways in which the optimization procedure may be used by an investigator. One way would be to supply initial estimates of the thetas and linear constants and optimally select the thetas for the data set holding all the linear constants fixed. A second way could

Table II. Heat Capacity Data[a]

T_i	Obsd. C_i	Calcd. C_i	Error, %	T_i	Obsd. C_i	Calcd. C_i	Error, %
	DIETHYL ETHER (*14*)[b]				VINYL BROMIDE (*14*)[c]		
11.28	0.800	0.760	−5.1	13.19	1.452	1.482	2.1
12.79	1.018	1.044	2.5	13.64	1.620	1.590	−1.8
14.05	1.309	1.302	−0.6	15.48	2.026	2.040	0.7
15.67	1.601	1.656	3.4	15.57	2.076	2.062	−0.7
16.62	1.838	1.872	1.8	17.72	2.615	2.591	−0.9
18.34	2.269	2.277	0.3	17.93	2.604	2.642	1.5
18.84	2.363	2.399	1.5	20.06	3.187	3.161	−0.8
20.42	2.802	2.788	−0.5	20.21	3.197	3.197	0.0
20.91	2.980	2.912	−2.3	22.15	3.677	3.659	−0.5
22.54	3.355	3.329	−0.8	22.21	3.739	3.674	−1.7
23.17	3.548	3.495	−1.5	24.38	4.181	4.177	−0.1
24.59	3.850	3.868	0.5	24.60	4.203	4.227	0.6
25.30	4.058	4.058	0.0	26.85	4.701	4.728	0.6
26.83	4.502	4.472	−0.7	27.32	4.797	4.830	0.7
27.78	4.769	4.729	−0.8	29.66	5.301	5.321	0.4
29.63	5.248	5.232	−0.3				
31.49	5.713	5.738	0.4				
33.48	6.218	6.273	0.9				
35.68	6.783	6.853	1.0				
	METHYL ETHYL KETONE (*18*)[d]				VINYLIDENE CHLORIDE (*10*)[e]		
13.12	0.984	0.982	−0.2	12.67	1.043	1.053	0.9
13.21	0.941	1.002	6.5	12.81	1.105	1.087	−1.6
14.33	1.344	1.275	−5.1	14.83	1.601	1.626	1.6
14.56	1.349	1.335	−1.0	14.90	1.687	1.646	−2.4
15.58	1.620	1.613	−0.4	16.77	2.196	2.199	0.1
16.20	1.745	1.791	2.6	16.78	2.172	2.202	1.4
16.98	2.194	2.023	−7.8	18.70	2.768	2.786	0.7
17.86	2.283	2.292	0.4	20.85	3.420	3.428	0.2
18.53	2.566	2.501	−2.5	20.90	2.432	3.442	0.3
19.59	2.833	2.835	0.1	23.54	4.206	4.179	−0.7
20.37	3.033	3.082	1.6	23.69	4.186	4.218	0.8
21.37	3.412	3.398	−0.4	26.48	4.923	4.910	−0.3
22.36	3.567	3.707	3.9	26.60	4.948	4.938	−0.2
23.29	4.025	3.993	−0.8	29.60	5.708	5.580	−2.3
24.45	4.233	4.341	2.5	29.68	4.744	5.595	−2.6
25.27	4.592	4.580	−0.3				
26.53	4.772	4.936	3.4				
	2,5-DIMETHYLTHIOPHENE (*2*)[f]				1,2,4-TRIMETHYLBENZENE (*16*)[g]		
12.05	1.281	1.281	0.0	14.77	1.901	1.911	0.5
13.50	1.651	1.652	0.0	15.80	2.188	2.188	−0.0
15.04	2.072	2.067	−0.2	16.96	2.518	2.506	−0.5
16.67	2.528	2.525	−0.1	18.40	2.914	2.910	−0.1
18.36	3.009	3.013	0.1	20.36	3.472	3.468	−0.1
20.11	3.513	3.524	0.3	22.82	4.165	4.169	0.1
21.99	4.067	4.075	0.2	25.46	4.900	4.909	0.2
24.12	4.688	4.690	0.0	28.16	5.626	5.636	0.2
26.52	5.370	5.362	−0.2	30.91	6.360	6.333	−0.4
29.16	6.089	6.064	−0.4				

[a] Units are temperature in ° K., heat capacity in calories per mole-degree, and entropy in calories per mole-degree. [b] Final function value = 0.006175; standard error of estimate = 0.04312; starting variable vector = $3D(101.81/T) + 1E(83.66/T) + 2E(83.66/T) + 3E(83.66/T)$; final variable vector = $3D(93.20/T) + 3E(149.74/T) + 3E(186.12/T)$; total entropy at 15° K. = 0.5813. [c] Final function value = 0.001671; standard error of estimate = 0.03335; starting variable vector = $3D(94.21/T) + 1E(86.85/T) + 2E(86.85/T) + 3E(86.85/T)$; final variable vector = $3D(82.15/T) + 3E(142.69/T)$; total entropy at 15° K. = 0.7940. [d] This work: Final function value = 0.01813; standard error of estimate = 0.09041; starting variable vector = $3D(109.68/T) + 1E(93.65/T) + 2E(93.65/T) + 3E(93.65/T)$; final variable vector = $3D(105.83/T) + 2E(93.53/T) + 1E(127.96/T)$; total entropy at 15° K. = 0.4747. Sinke and Oetting (*18*): Function value = 0.03147; variable vector = $6D(124.70/T)$; Total entropy at 15° K. = 0.5249. [e] This work: Final function value = 0.002732; standard error of estimate = 0.06384; starting variable vector = $3D(103.57/T) + 1E(89.30/T) + 2E(89.30/T) + 3E(89.30/T)$; final variable vector = $3D(98.69/T) + 2E(89.29/T)$; total entropy at 15° K. = 0.5704. Hildenbrand *et al.* (*10*): Function value = 0.01763; variable vector = $3D(90.00/T) + 3E(118.00/T)$; total entropy at 15° K. = 0.6517. [f] This work: Final function value = 0.00004102; standard error of estimate = 0.01247; starting variable vector = $3D(90.63/T) + 1E(81.61/T) + 2E(81.61/T) + 3E(81.61/T)$; final variable vector = $3D(80.64/T) + 2E(121.35/T) + 2E(139.52/T)$; total entropy at 15° K. = 0.8398. Carlson and Westrum (*2*): Total experimental entropy at 15° K. = 0.868. [g] This work: Final function value = 0.00007875; standard error of estimate = 0.01562; starting variable vector = $3D(93.44/T) + 1E(91.60/T) + 2E(91.60/T) + 3E(91.60/T)$; final variable vector = $3D(82.21/T) + 1E(121.33/T) + 3E(137.41/T)$; total entropy at 15° K. = 0.8000. Putnam and Kilpatrick (*16*): Function value = 0.005293; variable vector = $5D(103.70/T)$; total entropy at 15° K. = 0.7286. Stull, Westrum, Sinke (*19*): Function value = 0.002665; variable vector = $3D(80.50/T) + 6E(155.00/T)$; total entropy at 15° K. = 0.8327.

be to estimate again initial values of the thetas and linear constants and let the optimization procedure optimally determine the thetas and the best linear combination. Any particular constants may be fixed during optimization. A third and most convenient way is to let the procedure start with a standard set of linear constants, estimate the initial corresponding thetas, and then optimally determine the set of thetas and constants for the particular data set. This last option completely removes the burden of estimation from an investigator and, in the authors' studies, has consistently given curve fits that are at least as good, from a statistical point of view, as any fits resulting from trial and error procedures of a skilled investigator. All the examples given in this paper use this option.

In this last use, the procedure generates a starting set of parameters of the form:

$$\text{cal. } C_k = 3D(\theta_{D1}, T_k) + 1E(\theta_{E1}, T_k) + 2E(\theta_{E2}, T_k) + 3E(\theta_{E3}, T_k) \qquad (18)$$

This estimate of the thetas is based upon the assignment of 75% Debye character to the lowest observed C_k plus sufficient Einstein character split up among the specified degrees of freedom to make up the remaining 25% of the lowest C_k value. To accomplish this, a brief table of Debye and Einstein functions *vs.* (θ/T) was included in the procedure along with a table look-up scheme. This assignment of heat capacity, although strictly arbitrary, serves the purpose well as will be illustrated in the following six examples.

The criteria for judging the goodness of fit and comparisons between investigations is the final value of the F in Equation 5. This function represents the sum of the squared deviations of relative differences between observed and calculated heat capacity values. The relative deviate basis is chosen since the variables determined are to be used for extrapolation purposes from the smaller valued end of the heat capacity-temperature data set. Also associated with each determination is the usual standard error of estimation. Once the optimal selection of parameters is made, the low temperature entropy, S_T^0, is directly determined from the integral of Equation 12 using the analytical form of Equation 11.

Diethyl ether and vinyl bromide were recently measured (*14*) by one of the authors in an adiabatic low temperature calorimeter. Table II lists the results of the optimization procedure and the subsequent entropy determination.

Methyl ethyl ketone (*18*) and vinylidene chloride (*10*) are examples of previous measurements taken in the Dow Chemical Thermal Laboratory. They were included as examples to test the optimization procedure against manual curve fitting of experienced investigators. The improvement in F over the original investigator's parameter selection is not large, but the automatic technique used in this paper has the obvious advantages of having made its selection in a direct algorithmic manner.

The compound 2, 5-dimethylthiophene was included (*2*) to test the optimization procedure on data from a laboratory with good quality 5° K. capabilities. The original investigators' data in the range from 12° to 30° K. was used to compare an entropy value at 15° K. obtained by extrapolation with an entropy value at the same temperature determined essentially experimentally. The entropy values differ by approximately 3%, which is considered good for this type of estimation.

The data for 1,2,4-trimethylbenzene as measured by Putnam and Kilpatrick (*16*) was chosen for inclusion in a new monograph by Stull, Sinke, and Westrum (*19*). This example illustrates the differences that can arise when experienced investigators attempt to fit a difficult case. The range of the estimated total entropy is relatively large being from 0.73 to 0.83 cal. per mole-degree. The estimated entropy given by the procedure of this study (0.80) is obviously the most reliable figure considering the size of the various function values indicating goodness of fit.

CONCLUSION

The repetitive two stage optimization procedure described in this paper is an extremely useful and efficient technique for determining entropy in the temperature region below experimental capability. It is an automatic and direct algorithmic approach requiring little specialized effort by a potential user. The optimization procedure has a convergence pattern that leads to consistently better estimates of the unknown variables involved thus eliminating trial and error type calculation. The results achieved with its use are at least as good or better than those arrived at by other means.

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