Thermochimica Acta, 150 (1989) 53–61
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

A COMPUTING METHOD FOR DRAWING THE DSC BASELINE

GAO XIANG and LAO YUNLIANG

Department of Dynamical Engineering, Beijing Institute of Technology, P.O. Box 327, Beijing (China)

(Received 10 January 1989)

ABSTRACT

When a sample is investigated by DSC (differential scanning calorimetry), the rates of evolved heat of the initial and final states are frequently different, so that it is difficult to determine the heat of transition and the evoked heat-rate values. This paper presents a theoretical analysis of this problem. A computing method has been derived for determining the heats of transition and the true values of the rate of evolved heat, and a corresponding FORTRAN program has been composed with which several common reaction mechanism have been modelled. The results show that the computing method has high reliability and good accuracy.

INTRODUCTION

In DSC, the reaction mechanism and the kinetic parameters, as well as the heat of transition of a pure substance are determined from the data under the differential power–time curve. It is often found that the evolved heat-rate values of the initial and final states are different because the differences between the thermal capacity of the sample before and after transition are either ignored [1–4], arbitrarily posited [5,6] or are based on the authors' conception of the reaction process [7–10]. In general, the change in the evolved heat rate caused by this difference in thermal capacities is small compared with the true evolved heat rate and heat of transition, so that the method used to draw the baseline may not be critical within the limits of experimental accuracy for available instruments. However, the advance in DSC instrumentation should increase the precision of the heat measurements, and thus make the correct determination of the baseline significant. Furthermore, there are some cases where the heat capacity of the sample before the transition differs considerably from its heat capacity after the transition. Such reaction processes may involve the evolution of a gaseous product or the vaporization of the sample itself and the correct drawing of the baseline is important in these cases.

0040-6031/89/$03.50

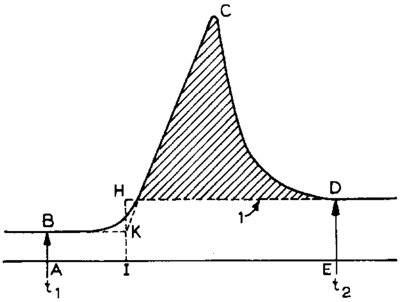

Fig. 1. Drawing of a baseline 1.

Guttman and Flynn have introduced a method for drawing the baseline [11]. They suggested that the correct baseline can be obtained by extrapolating the heat capacities of the initial and final temperature to the thermodynamic transition temperature, see Fig. 1

$$\text{Area (ABCDE)} = h(t_2) - h(t_1) = \int_{T_{1s}}^{T_{ts}} C_{p_1}\,\mathrm{d}T + \int_{T_{ts}}^{T_{2s}} C_{p_2}\,\mathrm{d}T + h_f \tag{1}$$

where T_{ts} is the transition temperature, C_{p_1} and C_{p_2} designate the heat capacity of the two different states, 1 and 2, and h is the transition heat. The steady state true temperature of the sample at t_1 is T_{1s}, and that at t_2 is T_{2s}. T_{1s}, and T_{2s}, as well as T_{ts}, are true thermodynamic temperatures. Finally

$$h_f = \text{Area (ABCDE)} - \text{AREA (IHDE)} - \text{Area (ABKI)} \tag{2}$$

where K is the transition point. Because these states are removed from any kinetic phenomena associated with the transition, this method may yield an accurate transition heat, but cannot give the true values of the evolved heat rate, which involves the kinetic phenomena. From the kinetic point of view, the transition degree of the sample increases continuously from state 1 to state 2 with time. Before point B, there has been no transition; after point D, the sample has changed completely to state 2.

In order to determine the reaction mechanism and the kinetic parameters it is necessary to introduce a new method of baseline determination.

PRINCIPLE AND METHOD

If, during the whole transition process, there is only one reaction, T_i is in the temperature range of transition, $q_i = (\mathrm{d}H/\mathrm{d}t)_i$ is the evolved heat rate at T_i, $q_0 = (\mathrm{d}H/\mathrm{d}t)_0$ is that for state 1 and $q_N = (\mathrm{d}H/\mathrm{d}t)_N$ is that for state 2, the degree of conversion at T_i is α_i.

Based on the law of energy conservation

$$q_{fi} = q_i - (1 - \alpha_i)q_0 - \alpha_i q_N \tag{3}$$

where q represents the true evolved reaction heat.

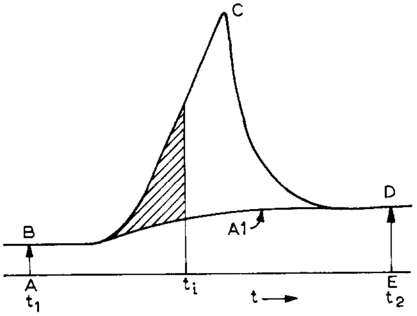

Fig. 2. Drawing of a baseline A1.

It can be seen from eqn. (3) that $(1-\alpha_i)q_0$ represents the contribution of the reactant thermal capacity to the evolved heat rate and $\alpha_i q_N$ represents that of the product thermal capacity to the evolved heat rate. The contribution of the product thermal capacity increases while that of the reactant decreases as the degree of conversion increases. Equation (3) can be rewritten as

$$(\mathrm{d}H/\mathrm{d}t)_{\mathrm{f}i} = (\mathrm{d}H/\mathrm{d}t)_i + \left[(\mathrm{d}H/\mathrm{d}t)_0 - (\mathrm{d}H/\mathrm{d}t)_N\right] - (\mathrm{d}H/\mathrm{d}t)_0 \tag{4}$$

Because the reaction is a simple one

$$\alpha_i = H_{\mathrm{f}i}/\Delta H_{\mathrm{f}} \tag{5}$$

$$H_{\mathrm{f}i} = \int_{t_1}^{t_i} (\mathrm{d}H/\mathrm{d}t)_{\mathrm{f}i}\,\mathrm{d}t \tag{6}$$

$$\Delta H_{\mathrm{f}} = \int_{t_1}^{t_2} (\mathrm{d}H/\mathrm{d}t)_{\mathrm{f}i}\,\mathrm{d}t \tag{7}$$

where $H_{\mathrm{f}i}$ is the transition heat before T_i and ΔH_{f} is the total transition heat of the sample. Therefore, there are four parameters to be determined by four equations which is a soluble problem.

In eqn. (4), α_{i} represents the degree of conversion, i.e. the ratio of the shaded area to the overall area of the transition range (see Fig. 2). A1 represents the correct baseline. The effect of the difference between the final and initial states can be removed by a combination of two convex functions, $(1-\alpha_i)(\mathrm{d}H/\mathrm{d}t)$, and $\alpha_i(\mathrm{d}H/\mathrm{d}t)_N$. Equations (4)–(7) are a non-linear group of equations; $(\mathrm{d}H/\mathrm{d}t)_i$ is a point on the experimental curve and has no known function. The determination of $(\mathrm{d}H/\mathrm{d}t)_{\mathrm{f}i}$ and the calculation of the transition heat ΔH_{f} require the use of a numerical method. The authors propose the following computational solution.

In the determination of the initial values, there are two choices. One is to allow $(\mathrm{d}H/\mathrm{d}t)^1_{\mathrm{f}i}$ to be $(\mathrm{d}H/\mathrm{d}t)_i - (\mathrm{d}H/\mathrm{d}t)_0$; another is to allow $(\mathrm{d}H/\mathrm{d}t)^1_{\mathrm{f}i}$ to be $(\mathrm{d}H/\mathrm{d}t)_i - (\mathrm{dH/dt})_N$. $(\mathrm{d}H/\mathrm{d}t)_{\mathrm{f}i}$ is in the range $[(\mathrm{d}H/\mathrm{d}t)_i - (\mathrm{d}H/\mathrm{d}t)_0, (\mathrm{d}H/\mathrm{d}t)_i - (\mathrm{d}H/\mathrm{d}t)_N]$. The iteration process starts at the two sides

TABLE 1

True, perturbated and computed values

Temp.	True values		Perturbated values		Computed values	
	dH/dt	H	dH/dt	H	dH/dt	H
$n=1$						
664.12	0.0173	0.2421	2.0185	0.2421	0.0182	0.0564
668.24	0.0229	0.3244	2.0245	0.3244	0.0238	0.1425
670.99	0.0275	0.3934	2.0295	0.3934	0.0284	0.2140
675.11	0.0362	0.5238	2.0388	0.5238	0.0370	0.3482
677.86	0.0433	0.6327	2.0465	0.6327	0.0442	0.4595
681.99	0.0566	0.8374	2.0608	0.8374	0.0574	0.6679
684.73	0.0675	1.0075	2.0725	1.0075	0.0683	0.8403
688.86	0.0876	1.3254	2.0942	1.3254	0.0884	1.1618
691.60	0.1040	1.5880	2.1119	1.5880	0.1048	1.4268
695.73	0.1340	2.0761	2.1444	2.0761	0.1348	1.9185
698.47	0.1584	2.4771	2.1707	2.4771	0.1591	2.3218
702.60	0.2026	3.2176	2.2187	3.2176	0.2033	3.0658
705.34	0.2380	3.8219	2.2571	3.8219	0.2388	3.6724
709.47	0.3018	4.9300	2.3265	4.9300	0.3025	4.7840
712.22	0.3524	5.8274	2.3815	5.8274	0.3531	5.6837
716.34	0.4420	7.4587	2.4793	7.4587	0.4427	7.3185
719.09	0.5120	8.7677	2.5558	8.7677	0.5127	8.6298
723.21	0.6338	11.1223	2.6894	11.1223	0.6344	10.9878
725.96	0.7268	12.9898	2.7917	12.9898	0.7275	12.8576
730.08	0.8843	16.3034	2.9659	16.3034	0.8850	16.1745
732.83	1.0009	18.8921	3.0954	18.8921	1.0015	18.7652
736.95	1.1904	23.4037	3.3075	23.4037	1.1911	23.2796
739.70	1.3238	26.8579	3.4581	26.8579	1.3244	26.7355
743.82	1.5268	32.7344	3.6905	32.7344	1.5274	32.6140
746.57	1.6577	37.1122	3.8433	37.1122	1.6583	36.9927
750.69	1.8331	44.3193	4.0547	44.3193	1.8337	44.2004
753.44	1.9258	49.4903	4.1733	49.4903	1.9264	49.3712
757.56	2.0095	57.6286	4.2977	57.6286	2.0101	57.5084
760.31	2.0175	63.1724	4.3334	63.1724	2.0181	63.0509
764.43	1.9431	71.3737	4.2999	71.3737	1.9437	71.2500
767.18	1.8321	76.5728	4.2150	76.5728	1.8327	76.4475
771.30	1.5794	83.6377	3.9976	83.6377	1.5801	83.5108
774.05	1.3655	87.6911	3.8039	87.6911	1.3661	87.5640
778.17	1.0102	92.5949	3.4732	92.5949	1.0108	92.4692
780.92	0.7749	95.0452	3.2502	95.0452	0.7755	94.9217
785.04	0.4645	97.5763	2.9523	97.5763	0.4651	97.4577
787.79	0.3023	98.6208	2.7954	98.6208	0.3029	98.5059
791.91	0.1357	99.4928	2.6332	99.4928	0.1363	99.3836
794.66	0.0706	99.7689	2.5694	99.7689	0.0711	99.6631
$n=2$						
667.52	0.0217	0.3077	2.0232	0.3077	0.0227	0.1178
675.04	0.0358	0.5196	2.0384	0.5196	0.0367	0.3372
680.05	0.0496	0.7318	2.0532	0.7318	0.0504	0.5543
687.57	0.0798	1.2096	2.0858	1.2096	0.0806	1.0396
692.58	0.1086	1.6784	2.1170	1.6784	0.1095	1.5134

TABLE 1 (continued)

Temp.	True values		Perturbated values		Computed values	
	$\mathrm{d}H/\mathrm{d}t$	H	$\mathrm{d}H/\mathrm{d}t$	H	$\mathrm{d}H/\mathrm{d}t$	H
700.10	0.1699	2.7102	2.1835	2.7102	0.1707	2.5529
705.11	0.2263	3.6974	2.2448	3.6974	0.2271	3.5454
712.63	0.3403	5.8034	2.3693	5.8034	0.3410	5.6594
717.64	0.4389	7.7482	2.4776	7.7482	0.4396	7.6097
725.16	0.6220	11.7110	2.6806	11.7110	0.6227	11.5801
730.17	0.7642	15.1800	2.8401	15.1800	0.7649	15.0534
737.69	0.9910	21.7770	3.0999	21.7770	0.9916	21.6547
742.70	1.1345	27.1107	3.2701	27.1107	1.1351	26.9895
750.22	1.3019	36.3187	3.4835	36.3187	1.3026	36.1960
755.23	1.3620	43.0156	3.5771	43.0156	1.3626	42.8905
762.75	1.3565	53.3090	3.6230	53.3090	1.3572	53.1797
767.76	1.2917	59.9648	3.5915	59.9648	1.2924	59.8336
775.28	1.1272	69.0987	3.4727	69.0987	1.1279	68.9672
780.30	0.9925	74.4160	3.3646	74.4160	0.9931	74.2862
787.81	0.7845	81.0924	3.1899	81.0924	0.7851	80.9673
792.83	0.6550	84.6955	3.0785	84.6955	0.6556	84.5743
800.34	0.4870	88.9673	2.9318	88.9673	0.4875	88.8525
805.36	0.3945	91.1701	2.8504	91.1701	0.3951	91.0596
812.88	0.2841	93.7013	2.7526	93.7013	0.2846	93.5968
817.89	0.2269	94.9769	2.7018	94.9769	0.2274	94.8761
825.41	0.1612	96.4222	2.6433	96.4222	0.1616	96.3265
830.42	0.1281	97.1440	2.6138	97.1440	0.1285	97.0514
837.94	0.0907	97.9585	2.5805	97.9585	0.0912	97.8701
842.95	0.0721	98.3648	2.5639	98.3648	0.0725	98.2790
850.47	0.0512	98.8239	2.5453	98.8239	0.0516	98.7417
855.48	0.0408	99.0537	2.5361	99.0537	0.0412	98.9737
863.00	0.0292	99.3143	2.5257	99.3143	0.0295	99.2375
868.01	0.0234	99.4454	2.5206	99.4454	0.0237	99.3706
875.53	0.0168	99.5950	2.5148	99.5950	0.0172	99.5231
880.54	0.0135	99.6706	2.5119	99.6706	0.0139	99.6006
888.06	0.0098	99.7575	2.5086	99.7575	0.0101	99.6901
893.07	0.0079	99.8018	2.5069	99.8018	0.0083	99.7361
900.59	0.0058	99.8529	2.5051	99.8529	0.0061	99.7897
905.60	0.0047	99.8791	2.5041	99.8791	0.0050	99.8175
$n = 3$						
673.35	0.0319	0.4615	2.0342	0.4615	0.0329	0.2660
686.70	0.0747	1.1358	2.0804	1.1358	0.0756	0.9570
695.60	0.1277	2.0180	2.1378	2.0180	0.1286	1.8516
708.95	0.2675	4.5619	2.2903	4.5619	0.2683	4.4162
717.85	0.4124	7.5558	2.4502	7.5558	0.4131	7.4240
731.20	0.6942	14.8875	2.7686	14.8875	0.6948	14.7695
740.10	0.8810	21.9204	2.9906	21.9204	0.8815	21.8013
753.45	1.0477	35.0017	3.2227	35.0017	1.0484	34.8674
762.35	1.0478	44.3930	3.2698	44.3930	1.0485	44.2478
775.70	0.9166	57.6357	3.2047	57.6357	0.9173	57.4850
784.60	0.7882	65.2320	3.1143	65.2320	0.7889	65.0849
797.95	0.5959	74.4485	2.9682	74.4485	0.5966	74.3125

TABLE 1 (continued)

Temp.	True values		Perturbated values		Computed values	
	dH/dt	H	dH/dt	H	dH/dt	H
806.85	0.4849	79.2459	2.8811	79.2459	0.4856	79.1184
820.20	0.3514	84.7857	2.7754	84.7857	0.3520	84.6707
829.10	0.2828	87.5973	2.7207	87.5973	0.2833	87.4896
842.45	0.2043	90.8196	2.6584	90.8196	0.2048	90.7217
851.35	0.1649	92.4563	2.6272	92.4563	0.1654	92.3641
864.70	0.1203	94.3436	2.5920	94.3436	0.1207	94.2589
873.60	0.0978	95.3106	2.5744	95.3106	0.0982	95.2304
886.95	0.0722	96.4368	2.5544	96.4368	0.0726	96.3626
895.85	0.0593	97.0201	2.5444	97.0201	0.0596	96.9496
909.20	0.0443	97.7066	2.5329	97.7066	0.0447	97.6412
918.10	0.0367	98.0661	2.5270	98.0661	0.0370	98.0037
931.45	0.0278	98.4937	2.5203	98.4937	0.0281	98.4356
940.35	0.0232	98.7199	2.5168	98.7199	0.0235	98.6645
953.70	0.0178	98.9916	2.5127	98.9916	0.0180	98.9399
962.60	0.0149	99.1368	2.5106	99.1368	0.0152	99.0875
975.95	0.0116	99.3129	2.5081	99.3129	0.0118	99.2668
984.85	0.0098	99.4078	2.5068	99.4078	0.0100	99.3638
998.20	0.0077	99.5239	2.5053	99.5239	0.0079	99.4828
1007.10	0.0065	99.5871	2.5045	99.5871	0.0067	99.5478
1020.45	0.0052	99.6650	2.5035	99.6650	0.0054	99.6282
1029.35	0.0044	99.7077	2.5030	99.7077	0.0046	99.6726
1042.70	0.0035	99.7608	2.5023	99.7608	0.0037	99.7279
1051.60	0.0031	99.7902	2.5020	99.7902	0.0032	99.7587
1064.95	0.0025	99.8269	2.5016	99.8269	0.0026	99.7975
1073.85	0.0021	99.8473	2.5014	99.8473	0.0023	99.8192
1087.20	0.0017	99.8731	2.5011	99.8731	0.0019	99.8468
1096.10	0.0015	99.8875	2.5010	99.8875	0.0016	99.8624

of the range; assuming $(\mathrm{d}H/\mathrm{d}t)_{\mathrm{f}i}^{k}$, α_i^k, $H_{\mathrm{f}i}^k$ and ΔH_{f}^k are obtained after the Kth interation, the results of the $(K+1)$th iteration are taken from

$$(\mathrm{d}H/\mathrm{d}t)_{\mathrm{f}i}^{(k+1)} = (\mathrm{d}H/\mathrm{d}t) - (\mathrm{d}H/\mathrm{d}t)_0(1-\alpha_i^k) - (\mathrm{d}H/\mathrm{d}t)_n\alpha_i^k \tag{8}$$

$H_{\mathrm{f}i}^{(k+1)}$, $\Delta H_{\mathrm{f}}^{(k+1)}$ and $\alpha_i^{(k+1)}$ are calculated by inserting $(\mathrm{d}H/\mathrm{d}t)_{\mathrm{f}i}^{(k+1)}$ into eqns. (5)–(7).

There are two criteria for determining whether or not the equations have been solved by iteration.

$$|H_{\mathrm{f}i}^{(k+1)} - H_{\mathrm{f}i}^{k}| < \epsilon_1 \tag{9}$$

$$|(\mathrm{d}H/\mathrm{d}t)_{\mathrm{f}i}^{(k+1)} - (\mathrm{d}H/\mathrm{d}t)_{\mathrm{f}i}^{(k+1)}| < \epsilon_2 \tag{10}$$

If eqns. (9) and (10) are satisfied, the iteration is stopped and the results from the $(k+1)$th iteration are taken to be the solution of the equations.

For eqns. (6) and (7), the DSC curve is divided into several parts. Each part consists of five points. A fourth-order polynomial gives an accurate solution to the integration.

To verify the reliability and accuracy of this computing method, the baseline of a theoretical DSC curve has been drawn by this method.

RESULTS AND DISCUSSION

Based on the classical laws of kinetics the rate of chemical reaction heat evolved is

$$\mathrm{d}H/\mathrm{d}t = kf(\alpha)\ \Delta H \tag{11}$$

where k is the rate constant and $f(\alpha)$ is some function of the degree of conversion. For a single reaction $\alpha = H/\Delta H$ and $k = A\ \exp(-E/RT)$. Taking $f(\alpha)$ as $f(\alpha) = (1-\alpha)^n$, eqn. (11) can be written as

$$\mathrm{d}H/\mathrm{d}t = A\ \exp(-E/RT)(1-\alpha)^n \Delta H \tag{12}$$

Substituting x for $-E/RT$ into eqn (12), after integration, an expression relating the degree of conversion to temperature or to the variable x is obtained

$$(1-\alpha) = ((n-1)\phi + 1) \quad \text{for } n \neq 1 \tag{13}$$

$$(1-\alpha) = \exp(-\phi) \quad \text{for } n = 1 \tag{14}$$

where $\phi = AEP(x)/(BR)$, and $P(x)$ is an exponential function defined by Doyle [12] as

$$P(x) = -\exp(-x)x + \int_{-x}^{x} \exp(-x)/x\ \mathrm{d}x \tag{15}$$

As there is no exact analytical solution for $Px/$, a number of approximate expressions and semi-empirical formulae have been developed. Van Tets' approximation [13] was chosen

$$P(x) = \exp(-x)(x+1)/((x+3)x) \tag{16}$$

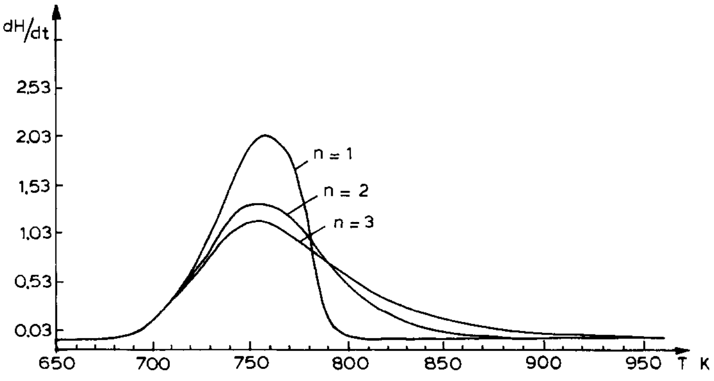

Fig. 3. DSC curves synthesized using true values.

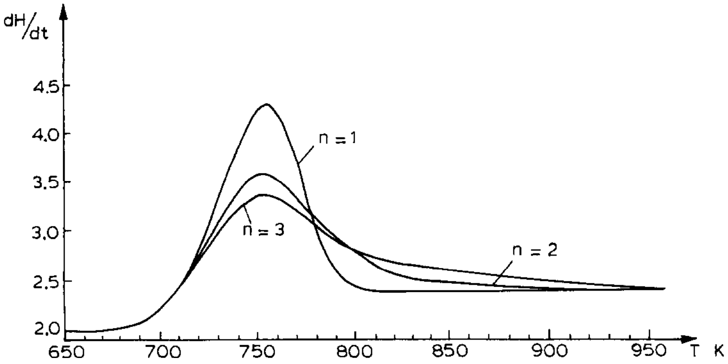

Fig. 4. DSC curves synthesized using perturbated values.

To obtain the DSC curves, the values of activation energy $E = 251.16$ kJ mol^{-1}, pre-exponential factor $A = 10^{15}$ s^{-1} and heating rate $B = 0.1$°C s^{-1} were taken. R is the Avogadro constant. The reaction order n is choosen as 1, 2 and 3, and $\Delta H = 100$ J g^{-1}.

After $\mathrm{d}H/\mathrm{d}t$, H, ΔH, α and T were determined by eqns. (12)–(16), the thermal capacity of the sample is assumed to change after reaction, the difference being 0.5 J g^{-1} K^{-1} ($\mathrm{d}H/\mathrm{d}t$) of DSC curve, then

$$(\mathrm{d}H/\mathrm{d}t)_i = \mathrm{d}H/\mathrm{d}t - 0.5H/\Delta H + (\mathrm{d}H/\mathrm{d}t)_0 \tag{17}$$

$(\mathrm{d}H/\mathrm{d}t)_i$ was used to synthesize the DSC curve and the computing method above was used to see if the true $\mathrm{d}H/\mathrm{d}t$ values could be derived.

Table 1 lists the true values, the values after perturbation, and the derived values. Figures 3–5 are the corresponding curves.

It can be seen that the derived values are very close to the true values, which indicates that this computing method is reliable and accurate.

The method is a semi-empirical one based on the concepts of physics and chemistry. It can be easily verified that when the criteria of iteration are

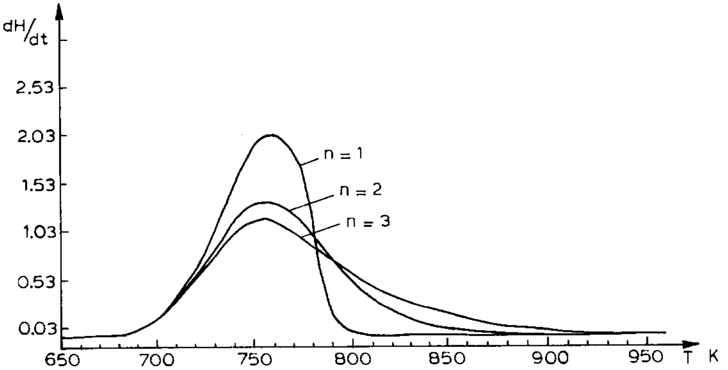

Fig. 5. DSC curves synthesized using computed values.

satisfied, the values by iteration are very near to the true values. However, the convergence of eqn. (8) and the conditions under which it is applicable need further investigation: this work is in progress.

REFERENCES

1 E.S. Watson, M.J. O'Neill, J. Justin and N. Brenner, Anal. Chem., 36 (1964) 1233.
2 M.J. O'Neill, Anal. Chem., 36 (1964) 1238.
3 A.P. Gray, in R.S. Porter and J.R. Johnson (Eds.), Analytical Chemistry, Plenum Press, New York, 1968, p. 209.
4 Thermal Analysis Newsletter, Analytical Division, Perkin–Elmer Corp., Norwalk, Conn., Nos. 1–9, 1965–70.
5 H.G. McAdie, Report of the Committee on Standardization, Abstracts of the 3rd Int. Conf. Therm. Anal., Davos, Switzerland, August 1971, p. 11.
6 R.C. Mackenzie, Report of the Nomenclature Committee, 3rd Int. Conf. Therm. Anal., Davos, Switzerland, 1971, p. 3.
7 W.P. Brennan, B. Miller and J.C. Whitwell, Ind. Eng. Chem. Fundam., 8 (1969) 314.
8 W.P. Brennan, PhD. Thesis, Princeton University, 1970.
9 G. Adam and F.H. Muller, Kolloid-Z.Z. Polym., 192 (1963) 29.
10 A. Engelter, Kolloid-Z.Z. Polym., 205 (1964) 102.
11 M. Guttman, J.H. Flynn, Anal. Chem., 45 (1973) 408.
12 C.D. Doyle, J. Appl. Polym. Sci., 5 (1961) 285.
13 A. Van Tets, Thermochim. Acta, 17 (1976) 372.