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INTERPRETATION OF DSC CURVES OF THE INDIUM MELTING PROCESS AND DETERMINATION OF THE THERMAL RESISTANCE R, THERMAL TIME CONSTANT RC_s AND LEAST SEPARATION TEMPERATURE L *

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ABSTRACT

Analogous DSC curves of the indium melting process obtained from five different types of apparatus are presented in this paper. The initial part of the DSC curve of the melting of indium is a straight line; an equation is established and through this the thermal resistance R of the apparatus can be derived. The end point of the melting of indium is located at the maximum of the DSC curve; after this exponential damping occurs and the thermal time constant RC_s can be derived. When two adjacent peaks are 50% apart, the temperature separation is

$$L = (0.693RC_s + 0.5t_{\max})\frac{dT_r}{dt}$$

The R value has no effect on peak area, but it does influence peak shape to a large extent: the smaller the R value, the narrower and steeper the peak and the better the separation of the adjacent peaks. Therefore the values R, RC_s and L are three important indications of performance of a DSC apparatus.

INTRODUCTION

Differential scanning calorimetry (DSC) is a widely used thermal analytical technique which has been rapidly developed. According to our statistics, from 1973 to 1983, the literature on the DSC technique appearing in the Thermal Analysis Abstract (TAA) (sponsored by the International Confederation for Thermal Analysis) increased some 3.5 times. During this period, more factories produced DSC apparatus, and the technique was improved daily. However, since Watson and O'Neill (Perkin-Elmer, U.S.A.) invented the DSC apparatus in 1964 [1,2], only Gray [3] has proposed a

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DSC curve equation for power compensation. However, he did not prove it experimentally. A graph of the DSC curve of the melting of indium appeared in the article by McNaughton and Mortimetry [4] (Perkin-Elmer) in 1975. The researchers pointed out that the initial part was a straight line (slope, $1/R \cdot \mathrm{d}T_r/\mathrm{d}T$) and that the value of the melting point could be derived from the extrapolation of the initial temperature of the peak. However, the meaning of the maximum and its relation to the back side of the curve downward to baseline remain unexpressed. In 1984, we obtained an analogous DTA curve [5]; the method used and the conclusions reached were approximately the same as the DSC results reported in this paper.

We assume the following: C_s is the heat capacity of the sample and its container and holder (unit, cal $°\mathrm{C}^{-1}$), C_r is the heat capacity of the reference sample and its container and holder, T_s is the temperature of the sample and its container and holder, T_r is the temperature of the reference sample and its container and holder, T_p is the temperature of the heat source, R is the thermal resistance between the heat source and the sample or the reference sample, both are equal (unit, $°\mathrm{C}$ s mcal^{-1}), $\mathrm{d}Q_s/\mathrm{d}t$ is the amount of heat transferred to or from the sample in unit time (unit, mcal s^{-1}), $\mathrm{d}Q_r/\mathrm{d}t$ is the amount of heat transferred to or from the reference sample in unit time (unit, mcal s^{-1}), $\mathrm{d}H_r/\mathrm{d}t = 0$ (no thermal effect on reference), $\mathrm{d}H/\mathrm{d}t$, i.e. $\mathrm{d}H_s/\mathrm{d}t$ is the enthalpy change of the sample in unit time, $\mathrm{d}T_s/\mathrm{d}t = \mathrm{d}T_r/\mathrm{d}t$ is the temperature change of the sample or reference sample in unit time, i.e. heating rate, t is the time (counted from the initial temperature of the peak and $t_{\max}$ is the time for the maximum of the peak.

According to the law of conservation of energy, the equation of heat transfer and the principle of keeping "null balance", i.e. $T_s = T_r$, in the DSC

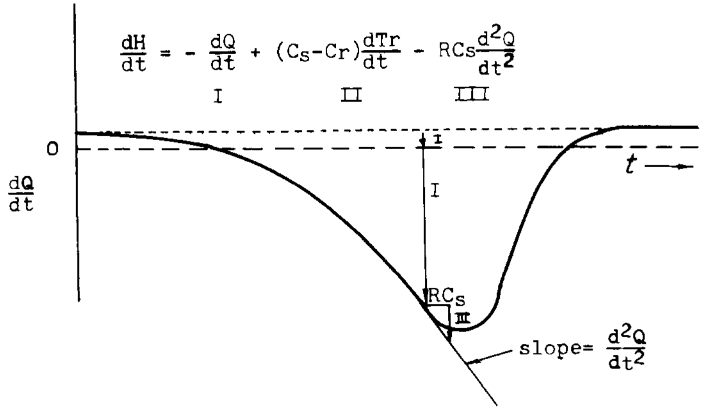

Fig. 1. Graphical determination of $\mathrm{d}H/\mathrm{d}t$ from experimental DSC curve.

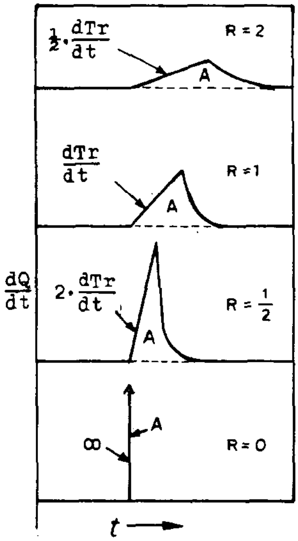

Fig. 2. Effect of *R* on peak shape and area.

apparatus, the DSC curve equation can be derived as follows [3]

$$\frac{\mathrm{d}H}{\mathrm{d}t} = -\frac{\mathrm{d}Q}{\mathrm{d}t} + (C_s - C_r)\frac{\mathrm{d}T_r}{\mathrm{d}t} - RC_s\frac{\mathrm{d}^2Q}{\mathrm{d}t^2} \tag{1}$$

Figure 1 is a graphical determination of $\mathrm{d}H/\mathrm{d}t$ from the DSC curve. Figure 2 shows the relationship between thermal resistance *R* and the DSC curve. Resistance *R* has no influence on DSC peak area, but it does affect the peak shape.

SIMILARITIES IN THE INITIAL PARTS OF THE DSC CURVES OF THE INDIUM MELTING PROCESS AND DETERMINATION OF THE THERMAL RESISTANCE *R*

According to the law of heat transfer, in unit time the rate of heat transfer is directly proportional to the temperature difference of heat transfer, and is inversely proportional to thermal resistance, i.e.

sample side

$$\frac{\mathrm{d}Q_s}{\mathrm{d}t} = \frac{(T_p - T_s)}{R} \tag{2}$$

reference side

$$\frac{\mathrm{d}Q_r}{\mathrm{d}t} = \frac{(T_p - T_r)}{R} \tag{3}$$

then

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = \frac{\mathrm{d}Q_s}{\mathrm{d}t} - \frac{\mathrm{d}Q_r}{\mathrm{d}t} = \frac{(T_p - T_s)}{r} - \frac{(T_p - T_r)}{R} = -\frac{(T_s - T_r)}{R} \tag{4}$$

that is

$$-\frac{dQ}{dt} \cdot R = T_s - T_r \tag{5}$$

During the melting of the metal, the temperature of the sample remains constant, i.e. $T_s = T_m$ (melting point), $dT_s/dt = 0$, and the reference sample is heated under the original constant heating rate, i.e.

$$T_r = T_r^{\ominus} + \frac{dT_r}{dt} \cdot t \tag{6}$$

Then, we obtain the equation

$$T_s - T_r = T_m - \left(T_r^{\ominus} + \frac{dT_r}{dt} \cdot t\right) = T_m - T_r^{\ominus} - \frac{dT_r}{dt} \cdot t \tag{7}$$

where t is the time counted from the initial temperature of the peak and $T_r^{\ominus}$ is the reference temperature at the occurrence of the peak. Since $T_m - T_r^{\ominus} = R(C_s - C_r)(dT_r/dt)$, i.e. the baseline equation, then

$$T_s - T_r = R(C_s - C_r)\frac{dT_r}{dt} + \frac{dT_r}{dt} \cdot t \tag{8}$$

Rearranging eqns. (5) and (8), we obtain

$$\frac{dQ}{dt} = (C_s - C_r)\frac{dT_r}{dt} + \frac{1}{R} \cdot \frac{dT_r}{dt} \cdot t \tag{9}$$

Since

$$\frac{dT_r}{dt} = \frac{dT_p}{dt}$$

then

$$\frac{dQ}{dt} = (C_s - C_r)\frac{dT_p}{dt} + \frac{1}{R} \cdot \frac{dT_p}{dt} \cdot t \tag{10}$$

The first term on the right-hand side of eqn. (10) is the baseline deviation resulting from the unmatched heat capacity of the sample and reference: it is constant in a single DSC measurement, i.e. $dQ/dt \sim t$ is a linear relationship; the slope is $(1/R)(dT_p/dt)$, where dT_p/dt is the known DSC heating rate; the value of R can thus be derived.

The DSC curves of the melting of high purity indium (99.999%) were obtained with five different apparatuses, as follows.

1. Perkin-Elmer (U.S.A.) DSC-2c, 1983 (referred to as apparatus I).
2. Perkin-Elmer (U.S.A.) DSC-2b, 1979 (apparatus II).
3. Beijing Optics I.F. (China) SR-1, 1982 (apparatus III).
4. Rigaku (Japan) Thermoflex TG-DSC, 1983 (apparatus IV).
5. Rigaku (Japan) Thermoflex TG-DSC, 1974 (apparatus V).

The heating rate used for all apparatuses was 10 °C min^{-1} i.e. 0.16667 °C s^{-1}; the other operating conditions were almost the same. Table 1 shows the

TABLE 1

Data from the initial part of the DSC curve and derivation of thermal resistance R

App. I	t(s)	0 1.25 2.5 3.75 5.0 6.25 7.5 8.75 10.0
	$\mathrm{d}Q/\mathrm{d}t$(mCal s^{-1})	0 0.0455 0.1818 1.1363 2.0453 3.0906 3.8633 4.8177 5.7722
	Linear reg.	$a = -1.2644$, $b = 0.6904$, $r = 0.9943$, $R = 0.2414$ (°C s mcal^{-1})
App. II	t	0 0.375 0.75 1.125 1.50 1.875 2.25 2.625 3.00 3.375 3.75
Test 1	$\mathrm{d}Q/\mathrm{d}t$	0 0.16 0.24 0.38 0.56 0.92 1.08 1.34 1.58 1.98 2.2
	t	4.125 4.5 4.875 5.25 5.625 6.0 6.375
	$\mathrm{d}Q/\mathrm{d}t$	2.46 2.7 2.88 3.08 3.40 3.70 3.80
	Linear reg.	$a = -0.2291$, $b = 0.6376$, $r = 0.9967$, $R = 0.2614$
App. II	t	0.75 1.5 2.25 3.0 3.75 4.5 5.25 6.0 6.75
Test 2	$\mathrm{d}Q/\mathrm{d}t$	0.18 0.5 0.94 1.5 2.0 2.5 2.96 3.5 3.84
	Linear reg.	$a = -0.3988$, $b = 0.637333$, $r = 0.9988$, $R = 0.2615$
App. III	t	0 1 2 3 4 5 6 7 8 9 10
	$\mathrm{d}Q/\mathrm{d}t$	0 0.06 0.2 0.48 0.8 1.2 1.66 2.16 2.56 2.96 3.15
	Linear reg.	$a = -0.3759$, $b = 0.3517$, $r = 0.9872$, $R = 0.4739$
App. IV	t	0 1.5 3.0 4.5 6.0 7.5 9.0
	$\mathrm{d}Q/\mathrm{d}t$	0 0.096 0.672 1.248 1.888 2.432 2.864
	Linear reg.	$a = 0.4426$, $b = 0.3764$, $r = 0.9986$, $R = 0.4428$
App. V	t	0 1.5 3.0 4.5 6.0 7.5 9.0 10.5 12.0
	$\mathrm{d}Q/\mathrm{d}t$	0.032 0.064 0.112 0.184 0.272 0.352 0.424 0.496 0.576
	t	13.5 15.0 16.5 18.0
	$\mathrm{d}Q/\mathrm{d}t$	0.656 0.736 0.816 0.896
	Linear reg.	$a = 0.03503$, $b = 0.051319$, $r = 0.9995$, $R = 3.2477$

data for the initial part of the curve and the derivation of R from the DSC curves of the indium melting process.

The linear relationship of the initial part of the DSC curve can be extrapolated to the maximum, which is the end point of the melting process. This agrees with the results of DTA curves of the same measurement. Figure 3 shows the DSC curve of the melting of indium. Figure 4 shows the initial

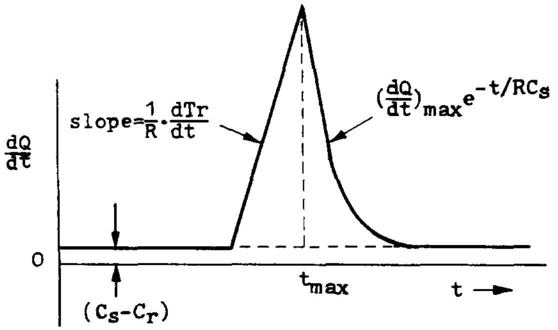

Fig. 3. The DSC curve of the melting of indium.

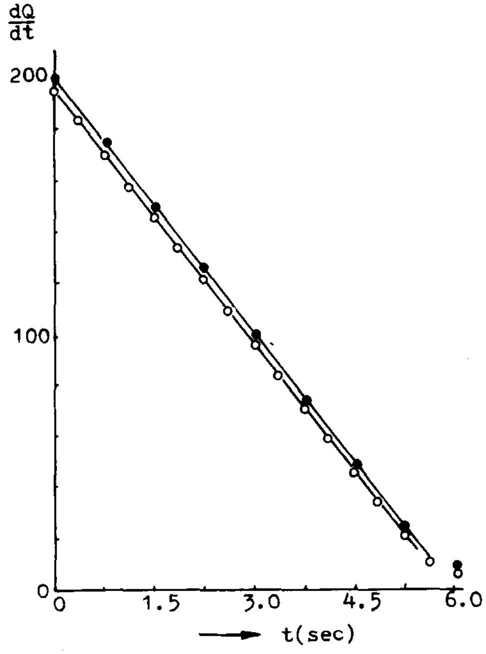

Fig. 4. Initial part of the DSC curve obtained using Perkin-Elmer DSC-2b (App. II). ○, Test 1; ●, test 2.

part of the DSC curve obtained using apparatus II and Fig. 5 presents the same for apparatus V.

THE EXPONENTIAL DAMPING OF THE DSC CURVES OF THE MELTING OF INDIUM AND DERIVATION OF THE THERMAL TIME CONSTANT RC_s

The whole sample changes into liquid after the end point of the melting process (i.e. the maximum of the DSC curve) is reached. Then no more

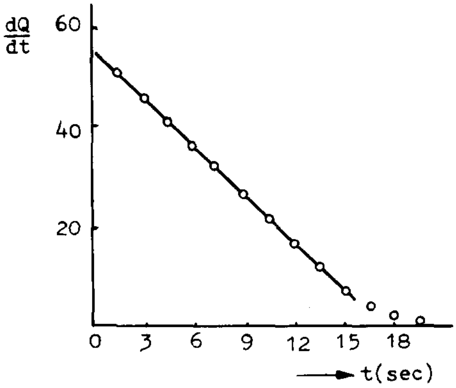

Fig. 5. Initial part of the DSC curve obtained using Rigaku DSC (App. V).

latent heat is released and thus $\mathrm{d}H/\mathrm{d}t = 0$, i.e. the right-hand side of eqn. (1) equals zero

$$-\frac{\mathrm{d}Q}{\mathrm{d}t} + (C_s - C_r)\frac{\mathrm{d}T_p}{\mathrm{d}t} - RC_s\frac{\mathrm{d}^2Q}{\mathrm{d}t^2} = 0 \qquad (11)$$

Rearranging eqn. (11), we obtain

$$\frac{\mathrm{d}^2Q}{\mathrm{d}t} = \frac{1}{RC_s} - \frac{\mathrm{d}Q}{\mathrm{d}t} + (C_s - C_r)\frac{\mathrm{d}T_p}{\mathrm{d}t} \qquad (12)$$

Let $y = \mathrm{d}Q/\mathrm{d}t$ and $a = (C_s - C_r)(\mathrm{d}T_p/\mathrm{d}t)$; rewriting eqn. (12), we obtain $y' = (1/RC_s)(-y + a)$, i.e. $(RC_s\,\mathrm{d}y)/(a - y) = \mathrm{d}t$. Rearranging to give $-RC_s[\mathrm{d}(a - y)/(a - y)] = \mathrm{d}t$ and integrating when $t = 0$ and $y = (\mathrm{d}Q/\mathrm{d}t)_{\max}$ we obtain

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = a + \left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)_{\max} \exp\left(-\frac{t}{RC_s}\right) \qquad (13)$$

Substituting $a = (C_s - C_r)(\mathrm{d}T_p/\mathrm{d}t)$ into eqn. (13), then

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = (C_s - C_r)\frac{\mathrm{d}T_p}{\mathrm{d}t} + \left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)_{\max} \exp\left(-\frac{t}{RC_s}\right) \qquad (14)$$

This equation shows that the end point of the melting process is exactly the maximum of the DSC peak; its ordinate $(\mathrm{d}Q/\mathrm{d}t)_{\max}$ is a constant. After this exponential damping occurs (generally the baseline deviation is neglected) then [3]

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = \left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)_{\max} \exp\left(-\frac{t}{RC_s}\right) \qquad (15)$$

Taking a logarithm

$$\ln\frac{\mathrm{d}Q}{\mathrm{d}t} = \ln\left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)_{\max} - \frac{t}{RC_s} \qquad (16)$$

that is

$$\ln\left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)_{\max} - \ln\left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right) = \frac{1}{RC_s}\cdot t \qquad (17)$$

Plotting $\ln(\mathrm{d}Q/\mathrm{d}t)_{\max} - \ln(\mathrm{d}Q/\mathrm{d}t)$ vs. t gives a linear relationship whose

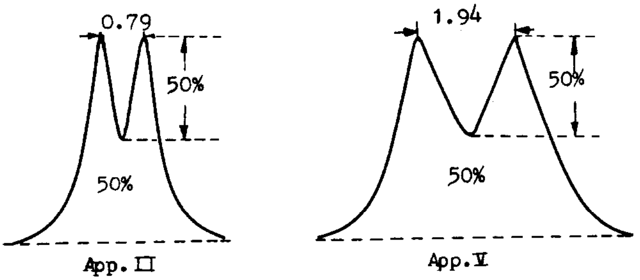

Fig. 6. Scheme of least separation temperature L of two DSC apparatuses.

TABLE 2

Data on the exponential damping of the DSC and DTA curves and derivation of RC_s

App. II	$t - t_{max}$ (s)	0	0.357	0.75	1.125	1.5	1.875	2.25	2.625	3.0	3.375	
DSC	dQ/dt	190.5	184	174	151	138	115	90	72	52	42	
Test 1	$\ln(dQ/dt)$	5.249	5.2149	5.159	5.0172	4.927	4.7449	4.4998	4.2766	3.912	3.737	
	$\ln Q'_{max} - \ln Q'$	0	0.0341	0.090	0.2318	0.322	0.5041	0.7492	0.9724	1.2978	1.512	
cont.	$t - t_{max}$	3.75	4.125	4.5	4.875	5.25	5.625	6.0				$r = 0.9913$
	dQ/dt	30	22	16	12	9.5	7	5.5				$a = -0.58126$
	$\ln(dQ/dt)$	3.401	3.090	2.7725	2.4849	2.251	1.945	1.7047				$b = 0.66878$
	$\ln Q'_{max} - \ln Q'$	1.848	2.159	2.4765	2.7641	2.998	3.304	3.5443				$RC_s = 1.4953$
App. II	$t - t_{max}$	0	0.75	1.5	2.25	3.0	3.75	4.5	5.25	6.0	6.75	$r = 0.9938$
DSC	dQ/dt	192	176	140	100	53	27	14	8	4	2.1	$a = -0.84314$
Test 2	$\ln(dQ/dt)$	5.257	5.170	4.942	4.605	3.970	3.2958	2.639	2.079	1.386	0.7419	$b = 0.77252$
	$\ln Q'_{max} - \ln Q'$	0	0.087	0.315	0.652	1.287	1.9612	2.618	3.178	3.871	4.5151	$RC_s = 1.2945$
App. V	$t - t_{max}$	0	1.5	3.0	4.5	6.0	7.5	9.0	10.5			$r = 0.9677$
DSC	dQ/dt	56	49	44	31.5	22	10	4	2			$a = -0.8518$
test	$\ln(dQ/dt)$	4.025	3.8918	3.784	3.4499	3.0910	2.303	1.386	0.6931			$b = 0.37005$
	$\ln Q'_{max} + \ln Q'$	0	0.1332	0.241	0.5751	0.934	1.725	2.639	3.3319			$RC_s = 2.702$
App. V	$t - t_{max}$	0	1.5	3.0	4.5	6.0	7.5	9.0	10.5	12.0	13.5	15.0
DTA	dQ/dt	152	120	89	70	50	40	30	25	18	14	11
test	$\ln(dQ/dt)$	5.024	4.787	4.488	4.248	3.912	3.689	3.401	3.219	2.890	2.639	2.397
	$\ln Q'_{max} - \ln Q'$	0	0.237	0.536	0.776	1.112	1.335	1.623	1.805	2.134	2.385	2.627
cont.	$t - t_{max}$	16.5	18.0	19.5	21.0	22.5	24.0	25.5	27.0			$r = 0.9996$
	dQ/dt	9	6	5	3.5	2.8	2.1	1.6	1.25			$a = -0.014967$
	$\ln(dQ/dt)$	2.197	1.792	1.609	1.253	1.029	0.742	0.470	0.223			$b = 0.178251$
	$\ln Q'_{max} - \ln Q'$	2.832	3.232	3.415	3.771	3.995	4.282	4.554	4.801			$RC_s = 5.610$

$Q'_{max} = (dQ/dt)_{max}$, $Q' = (dQ/dt)$.

slope is $1/RC_s$; the value of RC_s can thus be derived easily. The experimental data are listed in Table 2 and Fig. 6. The DTA curves of the indium melting process obtained using the Rigaku apparatus also show the relationship $\Delta T = (\Delta T)_{\max} \exp(-T/RC_s)$ [5], and the following equation can be derived

$$\ln(\Delta T)_{\max} - \ln(\Delta T) = \frac{1}{RC_s} \cdot t \tag{18}$$

The original data [5] and the calculated results are listed in Table 2.

THE INFLUENCES OF THE THERMAL RESISTANCE R AND THE THERMAL TIME CONSTANT RC_s ON THE DSC AND DTA PEAK SHAPES AND LEAST SEPARATION TEMPERATURE L

On the basis of the data of six DSC measurements and one DTA measurement carried out using five different apparatuses and Gray's definition of the least separation temperature L

$$L = (0.693RC_s + 0.5t_{\max})\frac{dT_r}{dt} \tag{19}$$

Substituting the parameters of the six related tests into eqn. (19), we obtain $L_1 = 1.27$, $L_2 = 0.79$, $L_3 = 1.17$, $L_4 = 1.63$, $L_5 = 1.94$ and $L_6 = 3.40$. The net results are listed in Table 3.

Although one DSC or DTA peak is sufficient to obtain the value of L, as in the case of testing only indium melting in this paper, RC_s and $T_{\max}$ can be measured and substituted into eqn. (19) to derive the value of L (the values are 0.79 °C and 1.94 °C for apparatus II and V respectively). This means, for apparatus II, when two adjacent peaks are of the same size, the smallest temperature separation between their maxima is 0.79 °C; then the valley formed between these two peaks can reach up to 50% of the total peak

TABLE 3

The influences of R and RC_s on peak shape and L

App.	Test	R (°C s mcal^{-1})	RC_s (s)	$t_{\max}$ (s)	Peak base width		L (°C)
					Time (s)	Temp. (°C)	
App. I	DSC	0.2414	1.940	12.5	22.5	3.75	1.27
App. II	DSC	0.2615	1.395	7.5	15.0	2.5	0.79
App. III	DSC	0.4739	2.379	10.0	30.0	5.0	1.17
App. IV	DSC	0.4428	1.143	18.0	33.0	5.5	1.63
App. V	DSC	3.248	2.702	19.5	33.0	5.5	1.94
App. V	DTA		5.610	33.0	67.5	11.3	3.40

height. For apparatus V, the smallest temperature separation would be at least 1.94°C to reach the same level (see Fig. 6). For the DTA curve, the smallest temperature separation would be 3.4°C. Of course the resolution of the peaks from all the apparatuses will be correspondingly lowered. From eqn. (19) we can see that the value of L is proportional to the heating rate; a lowering of the heating rate promotes the resolution.

RESULTS AND DISCUSSION

(1) Experiments prove that the initial part of the DSC curve of the indium melting process is a straight line, only slightly deflected at both ends; its slope is $(1/R)(\mathrm{d}T_p/\mathrm{d}t)$; the value of the thermal resistance R can be derived therefrom. Every point on this straight line represents the temperature $T_s = T_m$ of the indium sample in the melting process. The value is constant and is equal to the extrapolated initial temperature $T_e = 156.4 \pm 0.2$°C of the DSC peak. This is similar to the DTA curve for the same test [5].

(2) Exponential damping occurs after the maximum of the DSC curve. This can be proved by the linear relationship $\ln(\mathrm{d}Q/\mathrm{d}t)_{\max} - \ln(\mathrm{d}Q/\mathrm{d}t) \sim t$. From the slope of this linear relationship, RC_s can be derived easily; its value agrees with the relationship between thermal resistance R and peak width, peak shape etc. This method, in comparison with the original method of making $(\mathrm{d}Q/\mathrm{d}t) \sim t$ and analysing the data by linearized non-linear regression, yields better results and the derivation of RC_s is easier. The results are compared in Table 4. Data are listed as correlation coefficients r. This method and the solution for RC_s are as we proposed.

(3) Thermal resistance R has no effect on peak area, but it does influence peak shape to a large extent. The smaller the R value, the narrower and steeper the peak and the better the separation of adjacent peaks. So the R value is an important indication of the performance of a DSC apparatus. In comparison with the DTA technique, DSC is superior in showing peak width and has a narrower peak shape. DSC is also better in giving the least

TABLE 4

Comparison of the two methods for the determination of the exponential damping of the DSC and DTA curves

App.	Curve	r of $(\mathrm{d}Q/\mathrm{d}t) \sim$ t	r of $\ln(\mathrm{d}Q/\mathrm{d}t)_{\max} - \ln(\mathrm{d}Q/\mathrm{d}t) \sim t$
App. II	DSC	0.9850	0.9938
App. II	DSC	0.9868	0.9913
App. V	DSC	0.9524	0.9837
App. V	DTA	0.9997	0.9996

separation temperature. In DSC the R value has no effect on baseline deviation, it does not change with temperature and does not influence the peak area, etc.

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