Thermodynamic properties of cycloketones: A DSC study

Anne Gonthier-Vassal, Henri Szwarc[*]

Laboratoire de Chimie Physique des Matériaux Amorphes, URA D 1104, CNRS, Bâtiment 490, Université Paris Sud, 91405 Orsay, France

Abstract

In this paper, we describe the study of the thermodynamic properties of all cycloketones, from cyclobutanone to cyclododecanone, through DSC measurements in order to reveal possible new glassy crystalline phases. This work presents revised phase diagrams of the four previously known plastic crystals of the series, namely cyclohexanone, cycloheptanone, cyclooctanone, and cyclononanone. In particular, it has been shown that the last three crystals exhibit two phase sequences, a stable one and a metastable one, which could be attained through reproducible heat treatments. Contrary to what could be expected by comparison with the cyclo-alcohol series, only two compounds, namely cyclooctanone and cyclononanone, exhibit glassy crystalline phases. Finally, the thermodynamic data related to the various phase transitions of all these compounds have been determined. © 1998 Elsevier Science B.V.

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1. Introduction

From the time Seki et al. [1] demonstrated that a transition observed at 150 K in rapidly cooled crystalline cyclohexanol was basically a glass transition, a number of glassy crystals have been discovered [2]: these are crystals from the structural point of view and glasses from the thermodynamic one. To obtain a glass transition, it is necessary to 'freeze' a large amplitude motion and the obvious candidates for yielding glassy crystals are the so-called plastic crystals within which large molecular reorientational motions are usually observed. Moreover, it has been shown that some 'symmetry departure' is necessary to generate enough disorder to lead to a glassy phase [3,4]. Derivatives of moderate-sized cycloalkanes are globular enough to give plastic crystals and un-symmetric enough to generate disorder. As a matter of fact, homologous cyclo-alcohols, from cyclobutanol to cyclooctanol, all lead to glassy crystals [5] and several other derivatives of cyclohexane also do the same [6].

The present work was meant to discover whether members of the cycloketone series (from cyclobutanone to cyclododecanone) also yield glassy crystals. It led to the discovery of two new glassy crystalline phases and to the determination of four phase diagrams, not to mention that of a number of thermodynamic data.

In what follows, in agreement with Seki et al. [1], we will call 'glass' an amorphous solid obtained by freezing a liquid phase and 'glassy crystal' or 'glassy crystalline phase' an out-of-thermodynamic-equilibrium crystalline phase obtained by freezing a plastic crystal (or phase). This latter belongs to the general class of orientationally disordered crystals (ODIC).

*Corresponding author. E-mail: szwarc@cpma.u-psud.fr

2. Experimental

All products were purchased from Aldrich; purification and purities will be specified in every case. Purity was generally checked on cycloketone solutions in ether by means of gas-phase chromatography at 473 K using a 12 m OY1 (methylsilicone) column under a 40 kPa helium pressure. It is to be noted that the retention time increases linearly with the number of carbon atoms from cyclopentanone to cyclododecanone.

A few milligrams of the product (1–10 mg) were sealed in aluminium capsules under a nitrogen atmosphere inside a glove box. Scanning calorimetry measurements were performed in the 100–350 K range by means of a Perkin–Elmer DSC-2C apparatus equipped with a TADS-3600 thermal analysis data station and a homemade cooling attachment [7]. The temperature and enthalpy scales were calibrated with respect to the II→I phase transition and the melting point of cyclohexane [8,9] using the same heating rate as in the ensuing measurements (10 K min^{-1}, unless otherwise specified). The accuracy and reproducibility of the onset temperatures were better than 1 K and the relative accuracy of enthalpy determinations was 5%.

The cooling rates, given below, refer to the values displayed on the control panel. The displayed, namely 320, 160, 80, 40, and 20 K min^{-1}, cooling rates are effective only down to ca. 203, 152, 121, 106, and 98 K, respectively.

3. Results

3.1. Cyclobutanone

The product of 99% initial purity was purified by bulb-to-bulb distillation. Gas-phase chromatography could not detect any impurity, so that the purity was certainly better than 99.5%.

Five different samples were studied with weights ranging from 0.82 to 10.3 mg. Ten measurements were performed to determine the melting temperature, which was determined at (220.5±0.5) K. According to the value of the entropy of melting, 48.8 J K^{-1} mol^{-1}, crystalline cyclobutanone is not plastic.

It is very difficult to quench liquid cyclobutanone to a glassy phase. It usually crystallizes during the cooling procedure. It was found that it crystallized at 190 and 184 K, when cooled at rates of 10 K min^{-1} and 80 K min^{-1}, respectively. It was necessary to dip it in liquid nitrogen to observe a glass transition at T_g~125 K with a heat capacity increment equal to ~3.5 J K^{-1} mol^{-1}.

3.2. Cyclopentanone

The product of 99% initial purity was purified by distillation by means of a rotating band column. No impurity could be detected by gas-phase chromatography.

Four different samples were studied with weights ranging from 1.67 to 10.22 mg. Seven measurements were performed to determine the melting temperature which was found to be (221.2±0.2) K. This is in good agreement but slightly lower than the values previously reported [10–13] which range from 221.7 to 222.2 K. Sixteen measurements were performed to determine the melting enthalpy which leads to a melting entropy value, $\Delta_m S$=(51.3±0.4) J K^{-1} mol^{-1}, which shows that cyclopentanone is not plastic.

No phase transition was observed in agreement with previous studies. Liquid cyclopentanone is very difficult to quench to a glassy state. On cooling at the rates of 1.25, 10, and 320 K min^{-1}, cyclopentanone crystallizes at 181, 178, and 147 K, respectively. Only once, after dipping a sample in liquid nitrogen, did we observe a very small thermal anomaly near 125 K, which could correspond to a glass transition in a partially quenched system. The data for cyclobutanone and cyclopentanone are recorded in Table 1.

3.3. Cyclohexanone

The product of 99.8% initial purity was purified by two distillations by means of a rotating band column. No impurity could be detected by gas-phase chromatography.

Three different samples were studied with weights ranging from 4.57 to 14.39 mg. Fifteen measurements were performed to determine the melting temperature which was found to be (242.6±0.5) K. This value agrees with those previously reported for this product

Table 1
Thermodynamic data for melting and glass transition of cyclobutanone and cyclopentanone as determined by DSC measurements

	Cyclobutanone	Cyclopentanone
T_{fus}/K	220.5±0.5	221.2±0.2
$\Delta_{fus}H$/(kJ mol^{-1})	10.8	11.35±0.08
$\Delta_{fus}S$/(J K^{-1} mol^{-1})	48.8	51.3±0.4
T_g/K	∼125	∼125[a]
$\Delta_g C_p$/(J K^{-1} mol^{-1})	∼3.5	

[a] A thermal event which could correspond to a glass transition was observed only once (see text).

which have been extensively studied [11–20]. The reported values range from 241 to 242.4 K, except for that given by Nakamura et al. [20], as being 245.21 K, which was determined by adiabatic calorimetry and corresponds to an extrapolation to 100% purity. We see no explanation for this discrepancy. The melting enthalpy was determined in the same fifteen measurements [$\Delta_{fus}H$=(1.25±0.03) kJ mol^{-1}] and agrees with the values previously reported, which range from 1 to 1.3276 kJ mol^{-1}, except the value 3.1 kJ mol^{-1} given by Nitta and Seki [14], whose method of determination is not described. The very low value of the melting entropy ($\Delta_{fus}S$= (5.2±0.1) J K^{-1} mol^{-1}) shows that cyclohexanone

phase I is plastic, but we were unable to quench it fast enough to obtain a glassy crystalline phase.

Two very close crystal–crystal phase transitions were observed at (221.0±0.5) K (17 measurements) and 223.5 K. The latter was observed only once after a heat treatment which will be described below. As its intensity is small ($\Delta_{trs}H$ ∼0.5 kJ mol^{-1}), and as there was only one measurement made, the determination of Δ_{trs} and $\Delta_{trs}H$ is not accurate. However, there is no doubt about its existence. By cooling the crystal (previously heated to 223 K for half a minute or so) at −20 K min^{-1}, we observed two exothermic peaks with minima at 215.6 and 197.2 K, which prove the occurrence of the two transitions (Fig. 1). The transition at 221 K was removed by heating the crystal up to 224 K for ca. 30 s, cooling it down to 190 K at −20 K min^{-1}, and recording the scan at 10 K min^{-1}. Fig. 2 shows this scan (a) as compared with scan (b), which exhibits the usual two-transition peak and the melting transition. This is in agreement with the observation of Nakamura et al. [20], according to which the transition they observed at 220.83 K proceeds in two steps and with the measurements of Würflinger and Kreutzenbeck [13] which show that two solid–solid transition lines in the p vs. T diagram coalesce near atmospheric pressure at 220.3 K. The
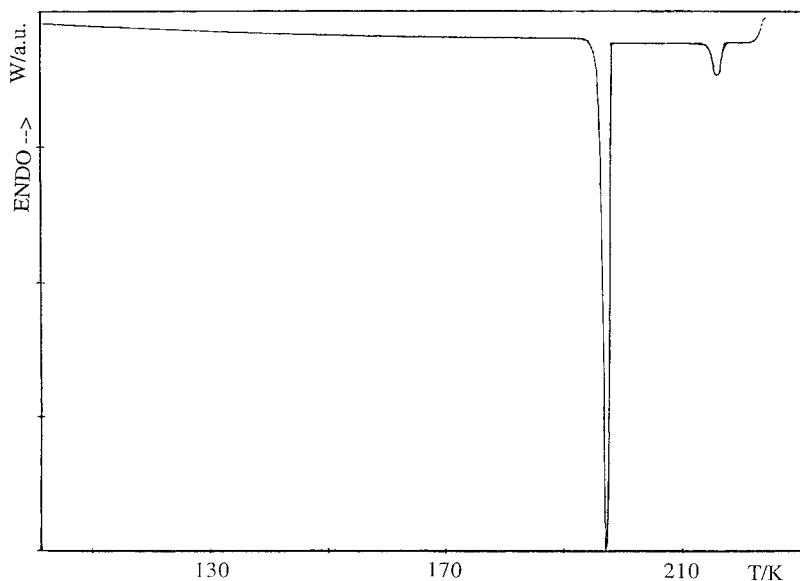

Fig. 1. Cyclohexanone: DSC scan recorded at −20 K min^{-1} on cooling from 223 K down to 100 K a crystalline sample annealed in phase I. The minina of the 2 exothermal peaks lie at 215 and 197 K, respectively.
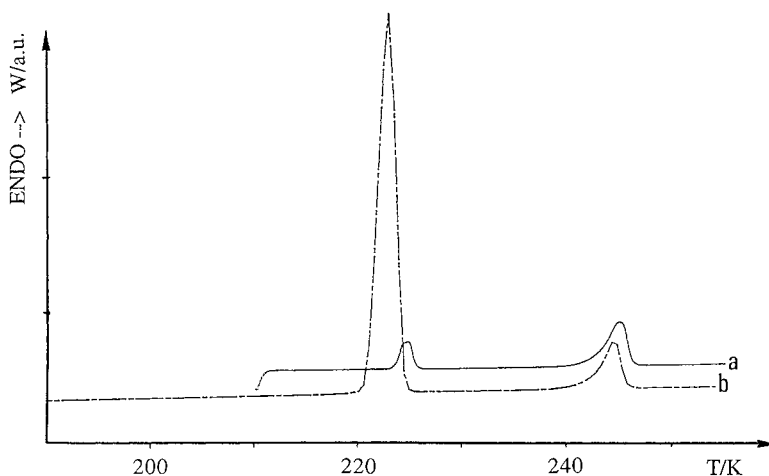
Fig. 2. Cyclohexanone: DSC scans recorded at 10 K min^{-1}: (a) after heating the crystal at 224 K for ∼30 s and cooling it back down to 190 K at −20 K min^{-1}; and (b) after cooling from the liquid phase down to 100 K.

values that the latter authors determined for the transition enthalpies (that are 0.6 and 8.1 kJ mol^{-1}, respectively) closely coincide with our values. It is noteworthy that the existence of the second transition was suggested by Crowe et al. [15] and also by van Miltenburg [21].

Liquid cyclohexanone is very difficult to quench to a glassy state. On cooling at 10, 20, and 320 K min^{-1} rates, cyclohexanone crystallized in the 230–240, 210–220, and 225 K ranges, respectively. Only once, after dipping a sample in liquid nitrogen, was a very small thermal anomaly observed near 132 K, which could correspond to a glass transition in a partially quenched system. Table 2 shows the phase diagram of cyclohexanone.

3.4. Cycloheptanone

The product of 99% initial purity was purified by bulb-to-bulb distillation; thereafter, gas-phase chromatography could not detect any impurity.

Four different samples were studied with weights ranging from 6.17 to 8.02 mg. Seventeen measurements were performed to determine the melting temperature which was found to be T_m=(259.3±0.4) K. This is notably higher than the value resulting from a previous determination [19], 252 K. According to the very low value of the melting entropy, $\Delta_{fus}S$= (5.4±0.1) J K^{-1} mol^{-1}, crystalline cycloheptanone

Table 2
Phase diagram of cyclohexanone and corresponding thermodynamic data as determined by DSC measurements

T/K	221.0±0.5	∼223.5		242.6±0.5
ΔH/(kJ mol^{-1})	8	∼0.5		1.25±0.03
ΔS/(J K^{-1} mol^{-1})	←—38.5±0.4—→ [a]			5.2±0.1
Phases	III	II	I	liq

Only the sum of the entropy increments for transitions III→II and II→I can be determined with some accuracy.

is plastic. This is in agreement with Fried's NMR work [19], according to which quasi-isotropic reorientation and translational diffusion of the molecules occur in phase I.

At first sight, cooling to temperatures <190 K reveals four exothermal peaks which correspond to crystallization and to three solid–solid transitions at ca. 220, 205 (this one being very broad), and 188 K (Fig. 3, scan (a)). The ensuing heating scan (Fig. 3, scan (b)) exhibits a large peak at ∼225 K (with a small shoulder on the lower temperature side), a small one at ∼232 K and the melting peak at 259 K. If the scan was recorded when using a lower heating rate, the large endothermal peak was followed by a small exothermal feature and the last two peaks as above. In Fig. 4, scans (a and b) show the pertinent temperature range for the rates of 10 and 2.5 K min^{-1}, respectively.

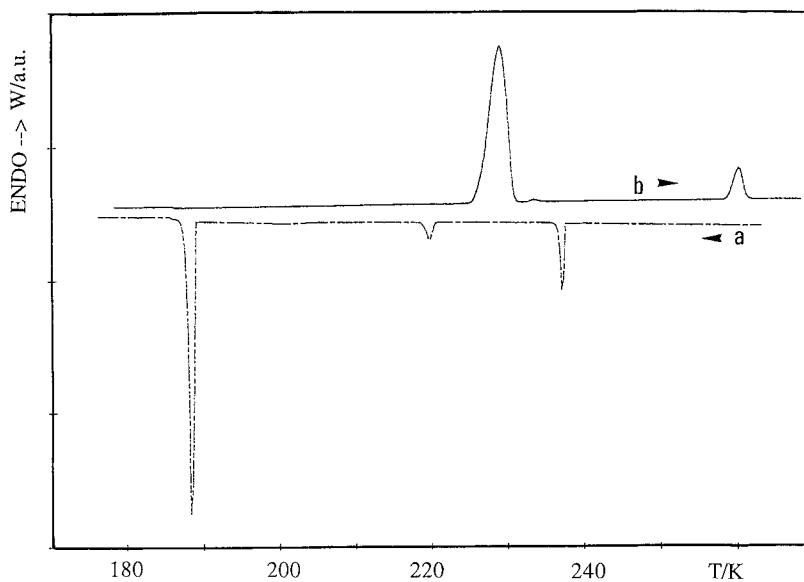When cooling was stopped at ∼200 K, the low-temperature limit of the broad feature of the previous

Fig. 3. Cycloheptanone: DSC scans recorded at: (±) 10 K min⁻¹; (a) on cooling to a temperature <190 K; and (b) on heating back.
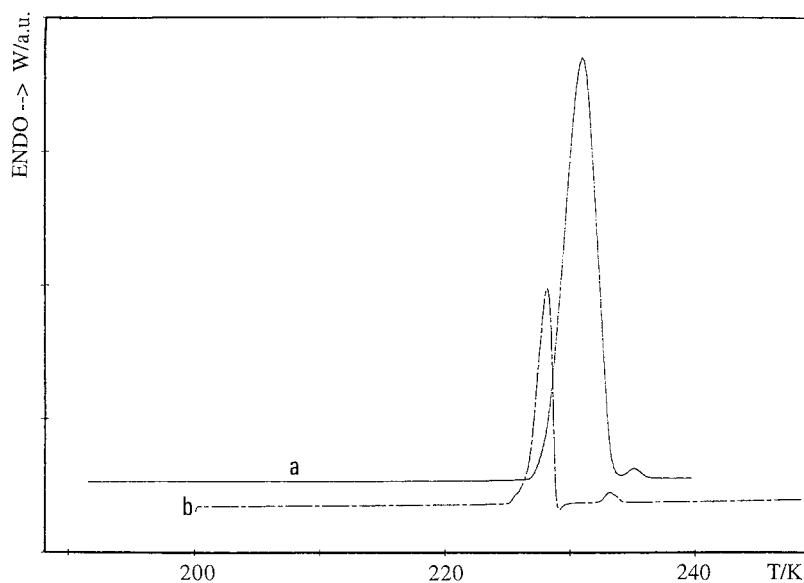

Fig. 4. Cycloheptanone: DSC scans recorded on heating; (a) at 10 K min⁻¹, and (b) at 2.5 K min⁻¹.

scan, the heating diagram exhibited three endothermal peaks (Fig. 5, scan (a)) within the solid domain with onsets at ca. 198, 223 and 232 K, respectively, (the 198 K value comes from several experiments). The first two did not exist in the previous experiment. (In

Fig. 5, scan (b) reproduces the pertinent part of scan (Fig. 3(b)) using the same intensity scale: the transition at 232 K which is, in fact, transition II→I, seems less intense than on scan (Fig. 5(a)) because part of it has been 'eaten' by the exothermal phenomenon
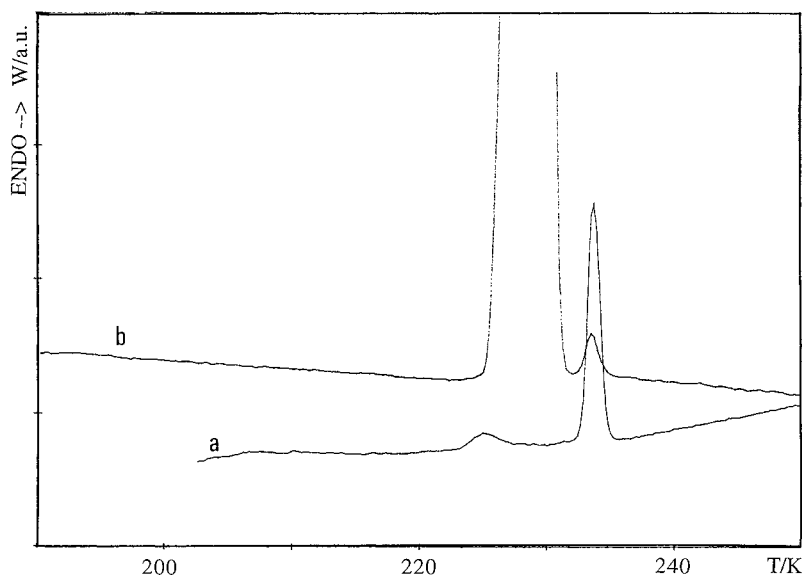
Fig. 5. Cycloheptanone: DSC scans recorded at 10 K min⁻¹ (a) after cooling down to $T>200$ K (the endotherm beginning near 200 K is smeared out over 10–15 K), and (b) after cooling down to $T<190$ K.

which exists on the higher temperature side of the large endotherm at ~225 K.) They probably correspond to the very broad peak recorded at ~205 K on cooling down to temperatures lower than 190 K.

This can be understood only in terms of two phase sequences, a stable one, featured by scan Fig. 5(b), and a metastable one, represented by scan Fig. 5(a) which are reported in Table 3 (the notation proposed in the case of thiophene [23] are used). The exothermal peak at 188 K of Fig. 3(a) corresponds to the

irreversible transformation of the metastable sequence into the stable one.

The large endothermal peak at ~225 K (Fig. 5(b)) encompasses the overall transformation V→II. We have to assume the existence of phase III because of the exothermal transformation which can be observed at low heating rates of the stable sequence on the higher temperature side of the above intense endotherm (Fig. 4(b)). A sensible explanation is that the involved large-enthalpy transformation proceeded

Table 3
The two-phase sequences of cycloheptanone and corresponding thermodynamic data as determined by DSC measurements

Phases	V	IV	III	II	I	liq
Stable sequence						
T/K	225	226.8	228	232.6±0.5	259.3±0.4	
ΔH/(kJ mol⁻¹)		←—12.4±0.5 [b]—→		0.43±0.02	1.39±0.02	

Phases	II₂ [a]	II₁	II	I	liq
Metastable sequence					
T/K	198		223.1	232.6±0.5	259.3±0.4
ΔH/(kJ mol⁻¹)	~0.17		~0.11	0.43±0.02	1.39±0.02

[a] At temperatures near 195 K, metastable phase II₂ undergoes a spontaneous exothermal transformation into stable phase V.
[b] Only the enthalpy increment for the overall transformation V→II can be determined (see text).

directly for a part from phase IV to phase II, which is still metastable below ca. 228 K. The exothermic feature would be due to the transformation of metastable phase II into phase III which was stable between 226.8 and ~228 K. Obviously, this value is an approximation because it cannot be directly observed by means of a kinetic method like DSC.

The foregoing phase behaviour is far more complicated than that presented by Gaümann et al. [22], which consists only of a phase transition at (221.5±2.5) K, or that, which results from Fried's NMR measurements that can be understood in terms of two transitions at ca. 220 and 235 K (see Fig. 3 of Ref. [19]).

Even when dipping samples in liquid nitrogen, it was impossible to observe glassy or glassy crystalline states.

3.5. Cyclooctanone

The product of 98% initial purity was purified by two successive sublimations at room temperature; thereafter, gas-phase chromatography could not detect any impurity. A third sublimation did not lead to any improvement of the purity according to DSC measurements.

As cyclooctanone sublimes very easily and tends to deposit on the cover of the aluminium pan, which retards heat transfer within the sample, the samples were encapsulated between two pan bottoms in order to allow them very little empty space. In this way, scans recorded before, and after, melting the samples were the same.

Nine different samples were studied with weights ranging from 0.8 to 7.5 mg. Nineteen measurements were performed to determine the melting temperature which was found to be T_{fus}=(318.7±0.3) K. This value is in good agreement with that reported by Rudman and Post [24], that is 315 K. According to the low value of the melting entropy (8 measurements), $\Delta_{fus}S$=(9.0±0.3) J K^{-1} mol^{-1}, (to be compared with ca. 8 J K^{-1} mol^{-1} [24]), crystalline cyclooctanone is plastic. This is in agreement with Fried's NMR work [19], according to which quasi-isotropic reorientation occurs in phase I and translational diffusion of the molecules becomes observable before phase I melts.

Liquid cyclooctanone crystallizes readily into phase I. With cooling rates of 10 and 320 K min^{-1}, crystal-
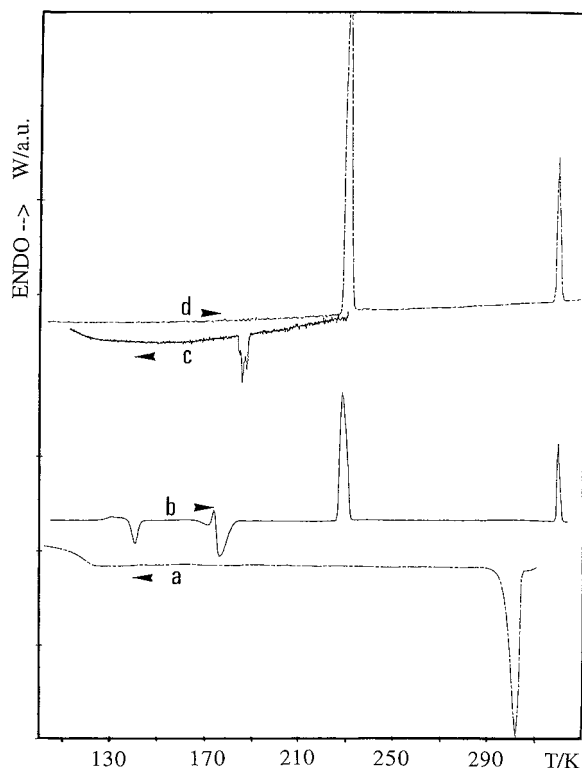

Fig. 6. Cyclo-octanone: DSC scans recorded for different heat treatments; (a) cooling from the liquid at −320 K min^{-1} down to 100 K, (b) heating the former sample at 10 K min^{-1}, (c) cooling from phase I at −0.6 K min^{-1}, and (d) heating back at 10 K min^{-1}.

lization occurs at ca. 300 and 290 K, respectively. It was, therefore, impossible to obtain a glass by quenching the liquid phase.

The DSC scans recorded on cooling the liquid down to 100 K, then on heating up to ~320 K, depend strongly on the cooling rate which was used. Fig. 6 sketches typical scans obtained (a) on cooling a cyclooctanone sample at ~−320 K min^{-1} down to 100 K, then (b) on heating at 10 K min^{-1}. The cooling curve only exhibited one exothermal peak which corresponds to solidification. This agrees with the observation of Burer and Gunthard [25], according to which there is no phase transformation on cooling down to 93 K. The heating curve shows a step increase near 127 K, an exothermal peak at ~138 K, an endothermal peak near 173 K, immediately followed by an exothermal event at 177–178 K, a strong endothermal peak at ~227 K and, finally, the endothermal melting peak at
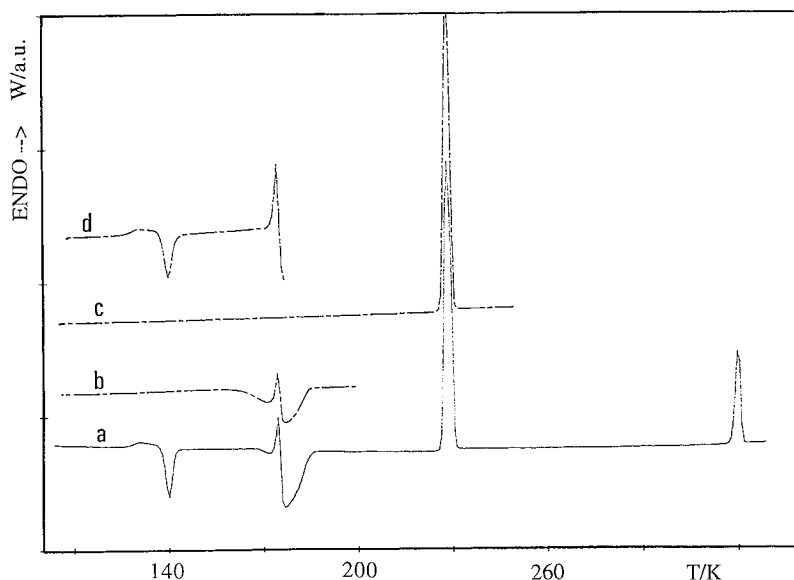
Fig. 7. Cyclooctanone: DSC scans recorded at 10 K min^{-1}; (a) after cooling to 100 K from the melt at -320 K min^{-1}, (b) after stopping the previous heating process at 160 K and cooling back to 100 K, (c) after stopping the previous run at 200 K and cooling back to 100 K, and (d) after stopping the previous run at 250 K and cooling back to 100 K.

318.7 K. Except the step increase near 127 K, this scan is analogous to that which was recorded by Rudman and Post [24] and was assigned to transformations between three crystalline phases they named I, II, and III, the exothermal peak at $\sim$177 K being considered as an evidence for 'extensive recrystallization' accompanying the so-called III$\rightarrow$II transition.

The corresponding scans, however, recorded for a 0.6 K min^{-1} cooling rate were quite different. The cooling curve of Fig. 6(c), exhibited the exothermal solidification peaks and a jagged exotherm at lower temperature. The heating curve (Fig. 6(d)) only reveals two endothermal peaks featuring a solid–solid transition (undoubtedly, Rudman and Post's I$\rightarrow$II transition) and melting.

A series of thermal treatments allowed assigning all the remaining peaks of the heating curves of Fig. 6. In Fig. 7, all heating scans were recorded at 10 K min^{-1} after cooling the sample at -320 K min^{-1}.

- Scan (a) was sketched previously in Fig. 6(b) and exhibits all the features already described.
- Scan (b) was recorded after stopping the heating process at 160 K, that is after the exothermal peak at 138 K has occurred, and cooling back to 100 K:

the step increase and the previous peak disappeared, which shows that they were related to metastable states. There remains, ca. 170 K, the previously observed endothermal peak and the exothermal one, the latter now encompassing the former.
- Stopping the heating at 200 K in the previous run, cooling back to 100 K, and heating anew leads to scan (c), which only exhibits the 227 K endothermal peak. This proves that the thermal events around 170 K were related to metastable states.
- The previous run was stopped at 250 K, that is in phase I. The sample was then cooled back to 100 K, and heated anew. This led to scan (d) in which the peaks related to the metastable states reappeared. Therefore, these states resulted from the quenching of phase I and from the ensuing transformations.

It is now possible to assign all the transformations which occur in crystalline cyclooctanone.

The shape of the step increase which occured at $\sim$127 K (Fig. 7, scans (a and d)) is characteristic of a glass transition. As it results from the quenching of phase I to low temperatures (Fig. 7d), it indicates the change of a glassy crystalline phase, I_g, into phase I

Table 4
Phase transformations of cyclo-octanone after cooling from the liquid phase down to 100 K at 320 K min^{-1} and heating back at 10 K min^{-1}

T/K	127.4±0.5	138.2±0.4	173	~177	226.8±0.5	318.7±0.3	
Type of transition	T_g	→	⇔	→	⇔	⇔	
Phase	I_g	I	A_2	A_1	II	I	liq

which is metastable at the above temperature. The latter irreversibly transforms near 138 K into a metastable phase, designated A_2, which exhibits a crystal–crystal phase transition towards another metastable phase, A_1, which finally transforms irreversibly into stable phase II near 177 K. Phase II transforms at 226.8 K into phase I which melts at 318.7 K. Rudman and Post [24] also noted, "...that phase I can be retained even below −105°C if cooled with sufficient speed." However, they could not perform thermodynamic measurements below 150 K and, thus, could not observe the glass transition and the irreversible transformation into phase A_2. The overall sequence corresponding to Fig. 7(a) is recorded in Table 4.

Starting from 100 K, the sequence of stable phases consists only of phases II, I, and the liquid. It is represented by the heating scan (b) of Fig. 6. Phase III, which according to Ref. [24], is stable below 183 K corresponds in fact to phases A_2 and A_1 of the metastable sequence. This latter sequence can only be obtained through an irreversible transformation from phase I and transforms back to the stable sequence through another irreversible transformation. Thus, no relationship (e.g. in cycloheptanone) can be made between the two phase sequences and, there is no conventional way for naming the above metastable phases. The names have been chosen arbitrarily.

On scans (a and b) of Fig. 7, it can be seen that the exothermal peak ca. 175 K and the endothermal $A_2 \rightarrow A_1$ transformation may overlap. This means that phase A_2 may transform into phase II before the above transformation occurs. In some runs, the endothermal peak disappeared altogether and only an exothermal peak (featuring the resultant enthalpy of simultaneous transformations $A_2 \rightarrow II$, $A_2 \rightarrow A_1$, and $A_1 \rightarrow II$) could be observed.

The quenching of phase I at low temperatures occurs easily for a 320 K min^{-1} cooling rate, but it is no longer complete at −80 K min^{-1}. For slower cooling, one can observe cracks developing in an otherwise transparent material. These cracks are prob-

ably the origin of the jagged exotherm of the cooling scan (b) of Fig. 6 which indicates the crystallization of phase II as witnessed by the ensuing heating scan. This shows that phase II crystallizes readily. For instance, the crystallization is complete in <1 h at 168 K. This indicates that the X-ray profile that Rudman and Post recorded at the above temperature and assigned to their phase III is to be attributed to phase II instead.

Expansivity measurements, performed by means of a Perkin–Elmer TMA7 dilatometer, somewhat support this conclusion. Fig. 8 shows the thermal expansion curve (a) and its derivative (b) as a function of temperature. Curve Fig. 8(b) is very similar to the scan observed after rapid quenching of cyclooctanone (Fig. 7(a)) with its succession of glass transition, recrystallizations and phase transitions. On the thermal linear expansion curve (Fig. 8(a)), it can be seen that the thickness of phase A_2 around 170 K is about 1% larger than that of phase I near 120 K or phase II in the 200–220 K range, which means that its density is ~3% smaller. According to our measurements, the volume increment, $\Delta V/V$, at the II→I is (10±1)% which is near the 11.4% density variation between 168 K (phase II) and 298 K (phase I) as measured by X-ray methods [24]. Thus, we conclude that the monoclinic structure, determined by Rudman and Post at 168 K, is to be assigned to phase II instead of the so-called phase III and the structures of metastable phases A_1 and A_2 are still unknown.

The linear expansion coefficients of metastable phase I, below 130 K, and phase II are $(1.0\pm0.3)\times10^{-4}$ and $(0.5\pm0.2)\times10^{-4}$ K^{-1}, respectively. It was impossible to measure the thermal expansion of phase I above the II→I transition, because the plastic phase is really plastic from the mechanical point of view and deforms under the dilatometer rod even with the smallest load. Rudman and Post have found the value $(2.18\pm0.02)\times10^{-4}$ K^{-1} for phase I in its stability range which is coherent with the usual variation of expansivity of a plastic crystal in such a large temperature range.
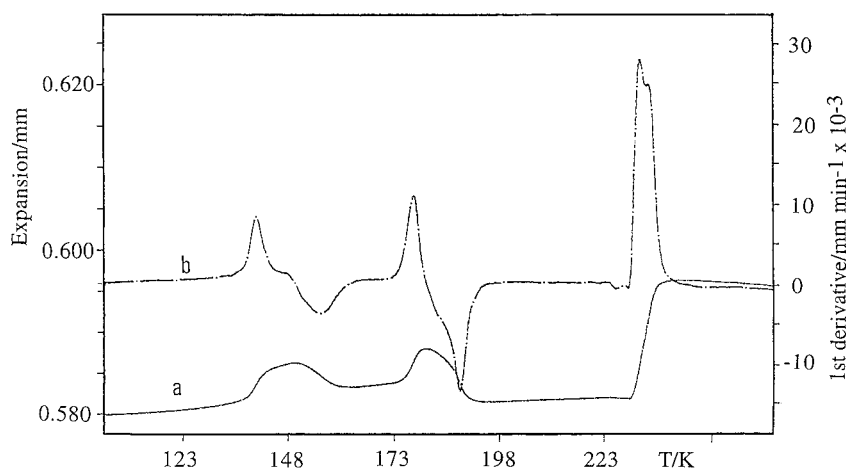
Fig. 8. Cyclooctanone: (a) thermal expansion, and (b) first derivative of the previous curve.

Table 5
Phase diagram of cyclo-octanone and corresponding thermodynamic data, as determined by DSC measurements

Transition	$I'_g \to I$	$I \to A2$	$A2 \to A1$	$A1 \to II$	$II \to I$	$I \to liq$
T'_g/K	127.4±0.5 (133±2)*					
T/K		138.2±0.4	173	177–178	226.8±0.3 (228±1) [a]	318.7±0.3
$\Delta H/(J\ mol^{-1})$		−1980±120	5060	−9200	13 800	2870±110
$\sum \Delta H/(J\ mol^{-1})$			∼4000 [b]			
$\Delta S/(J\ K^{-1}\ mol^{-1})$		14.4±0.9			60.8	9.0±0.3
$\Delta C_p/(J\ K^{-1}\ mol^{-1})$	73±7					

[a] From nine thermal expansivity measurements.
[b] This enthalpy increment corresponds to the transformation $A_2 \to II$.

The thermodynamic data for cyclooctanone are presented in Table 5. The data for the $A_2 \to A_1$ and $A_1 \to II$ transformations are to be considered as approximate because they result from 'guessed' shapes of the peaks of two simultaneous transformations. The overall enthalpy for the two transformations (i.e. ∼4000 J K^{-1} mol^{-1}) is very close to the value (4300 J K^{-1} mol^{-1}) estimated previously [24]. As to transition $II \to I$, more than 20 measurements were performed which yield a mean enthalpy near 11 kJ mol^{-1}. However, two experiments led to the value 13.8 kJ mol^{-1}, that we consider the best, because it is the higher one and is recorded in Table 5. It is to be compared with the ∼17 kJ mol^{-1} value which was cited by Rudman and Post [24]. A possible explanation for the difference between our higher

values and the lower ones is that the crystallization of metastable phase I into the other low-temperature phases is usually not complete because of the kinetic character of the DSC experiment. The remaining phase I part will obviously not contribute to the enthalpy of the endothermal transformation at 227 K.

3.6. Cyclononanone

The product of stated 95% initial purity was purified by bulb-to-bulb distillation at ca. 335 K. According to gas-phase chromatography the purity was better than 99%.

Five different samples were studied with weights ranging from 2.23 to 8.58 mg. The very broad melting peaks of both products rather look like liquidus curves
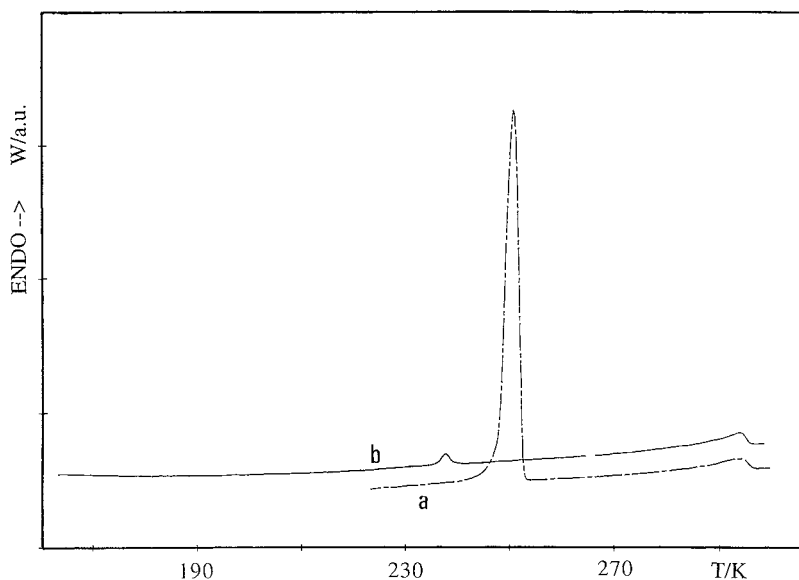
Fig. 9. Cyclononanone: DSC scans recorded at 10 K min^{-1} (a) after cooling a sample to 100 K, heating back to 240 K at 10 K min^{-1}, annealing for 5 min at 240 K, and cooling down to $T<220$ K, and (b) after cooling from the melt down to 160 K.

(Fig. 9(a)) as if some impurity was involved and the melting temperature ranges from 293 K for the so-called purified product to 298–299 K for the non-purified one, while Ziegler and Aurnhammer [26] determined the value 301 K. The melting enthalpy was determined as (1.3 ± 0.2) kJ mol^{-1} for the so-called purified product and (1.6 ± 0.2) kJ mol^{-1} for the non-purified one, which gives a melting entropy of ~5 J K^{-1} mol^{-1} to be compared with $\Delta_{fus}S=6.3$ J K^{-1} mol^{-1} as cited previously [24].

In spite of these variations for the melting temperature, both products behaved in a similar way with respect to the solid–solid transitions.

The cooling scan did not depend markedly on the cooling rate (from 320 to 10 K min^{-1}). It exhibited an exothermal peak near 255 K which corresponded to solidification and a step near 130 K which featured a glass transition (Fig. 10(a)). The ensuing heating scan (Fig. 10(b)) shows a step increase at 133 K (the reverse glass transition), a very broad two-or-three component exothermal feature stretching from 180 to 230 K, a small endothermal peak at ~235 K, a large peak at 247 K and, finally, the broad melting peak. The small endotherm did not show up when previous cooling to 100 K had been performed at -10 K min^{-1}. Otherwise, it could be removed altogether by stopping
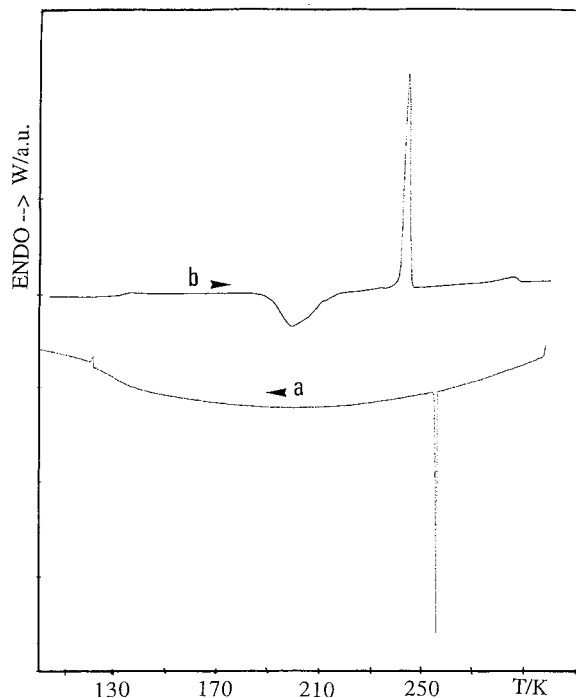

Fig. 10. Cyclononanone; DSC scans recorded (a) at 320 K min^{-1} from the melt, and (b) at 10 K min^{-1} after the previous run.

the previous heating process at 240 K for ∼5 min, cooling down to 220 K, or any lower temperature down to 100 K, and heating back up to melting. Under these conditions, only the large peak at 247 K and melting are observed (Fig. 9(a)).

If the cooling process from the liquid phase is stopped at a temperature higher than that of the glass transition, say 160 K, the ensuing heating scan exhibited only a small peak near 235 K (two or three times larger than that observed previously at the same temperature) and the melting peak. The large transition at 247 K disappeared completely (Fig. 9(b)).

It is now possible to assign all transformations to definite phase changes. Scan (b) of Fig. 10 shows that the phase formed during the cooling to 160 K or during the short annealing at this temperature transforms into phase I at 235 K. But this transition can be suppressed by annealing at 240 K to yield a more stable phase which transforms into phase I at 247 K. Therefore, this new phase is phase II of the sequence of stable phases. The phase which transforms at 235 K belongs to a sequence of metastable phases and will be called I_1 according to the same conventions as before. Hence, the phases reported in Table 6.

Let us now consider scan (b) of Fig. 10. As the glass transition at ∼130 K follows the crystallization into crystalline phase I, it corresponds to the freezing of the latter phase into a glassy crystalline phase, I_g. On heating, scan (b) of Fig. 10 reveals successively:

- the transformation, through the above glass transition at (133 ± 1) K, of phase I_g into phase I with a heat capacity increment ΔC_p equal to 105 J K^{-1} mol^{-1};
- the irreversible transformation of phase I into phase II from 180 to 230 K;

- the transformation into phase I at 235.5 K of a small amount of phase I_1 which has formed either in the cooling process or simultaneously with the above irreversible transformation;
- the transition II→I at 247 K;
- and finally melting of phase I at 298 K.

The scan (b) of Fig. 10 reveals the presence of some amount of phase I_1 which could have been formed during cooling. Thus cooled, phase I_1 may participate in the glass transition. To check this point, we performed a treatment leading to pure phase I_1 (by cooling a sample down to 160 K and heating it back to 222 K) and then tried to quench it down to 100 K at −320 K min^{-1}, but the ensuing heating scan was the same as scan (b) of Fig. 10: most of phase I_1 had transformed into phase I during the cooling process, so that there is no way to know whether quenched phase I_1 led to some glassy crystal. However, the enthalpy increment at the I_1→I transition is weak and it is to be expected that phase I_1 also would be plastic: for a fast enough cooling process, it should lead to a glassy crystal.

3.7. Cyclodecanone, cycloundecanone, cyclododecanone

All these compounds were purified by bulb-to-bulb distillation and the purities checked by gas-phase chromatography on L31 columns. As specified in Table 7, cyclodecanone was still impure and the DSC scan showed a premelting phenomenon which stretched over ∼25 K. For the other two compounds, GPC revealed no impurity. Two, two and six different samples were studied with weights ranging from 3.71 to 4.41 mg, 3.97 to 4.54 mg, and 1.39 to 5.35 mg, for these three compounds, respectively. As shown by the large values of the melting entropies (Table 7), none of these compounds was plastic so that no glassy crystal was expected.

Quenching the compounds into liquid nitrogen did not enable freezing of the liquids into glasses. Small exothermal peaks were sometimes observed with cyclodecanone and cycloundecanone indicating that the crystallization of the liquids was not complete and the heating scans of cycloundecanone and cyclodecanone revealed, at least once for each compound, some anomaly which could have been a glass transi-

Table 6
The two phase sequences of cyclononanone and corresponding thermodynamic data as determined by DSC measurements

Stable sequence				
Phases	II		I	liq
T/K		247.0±0.3	298	
ΔH/(kJ mol^{-1})		14.7±0.5	1.6±0.2	
Metastable sequence				
Phases	I_1		I	liq
T/K		∼0.4	1.6±0.2	
ΔH/(kJ mol^{-1})		235.5	298	

Table 7

Thermodynamic data for melting and glass transition of cyclodecanone, cycloundecanone, and cyclododecanone as determined by DSC measurements

	Cyclodecanone	Cycloundecanone	Cyclododecanone
Purity/%	∼97.5	>99.5	>99.5
T_m/K	294.9±0.4	287.7±0.2	336.3±0.2
	298.2 [a]	283 [b]	332-4 [c]
$\Delta_{fus}H$/(kJ mol^{-1})0	24.3	23.0±0.3	16.6±0.4
$\Delta_{fus}S$/(J K^{-1} mol^{-1})	82.3	80.5±1.2	50±1
Exothermal peak T/K (see text)	230–250	250–270	—
T_g/K	—	185 (?)	240(?)

[a] In Beilstein, 7(2) 36.
[b] In Beilstein, 7(2) 45.
[c] In Beilstein, 7(2) 48.

tion corresponding to the freezing of a small part of the liquid phase. All the results are recorded in Table 7.

4. Conclusions

Our results show that, in the series from cyclobutanone to dodecanone, only four cycloketones, namely cyclohexanone, cycloheptanone, cyclooctanone, and cyclononanone, exhibit plastic phases. Moreover, with the cooling rates which can be achieved with our experimental system, only two compounds, cyclooctanone and cyclononanone, lead to glassy crystalline phases. This series is different from the cyclo-alcohol one in which the five studied compounds exhibit plastic phases leading to glassy crystalline ones [5]. These differences are likely to be related to the existence of hydrogen bonding arising from the OH groups.

The present work has also allowed to revise the phase diagrams of the four cycloketones with plastic phases which have been studied previously. Intricate heat treatments are involved. It has been shown that:

- cyclohexanone crystal undergoes two crystal–crystal phase transitions, at 221 and 223.5 K, which was previously suspected;
- cycloheptanone exhibits two phase sequences, a stable one and a metastable one, so that this compound leads to seven different phases from 100 K to melting;
- cyclooctanone also exhibits two phase sequences, but the metastable one cannot be related to the

stable one by a reversible phase transition. Anyway, quenching of phase I leads to a glassy crystalline phase;
- cyclononanone is another example of two phase sequences which are related through a reversible phase transition. Phase I leads to a glassy crystalline phase and metastable phase I$_1$, which is plastic could also do.

A number of thermodynamic data have been determined but it must be kept in mind that the accuracy achieved is only that which is possible with a method like DSC. To obtain reference values, it would be necessary to perform adiabatic calorimetry measurements.

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