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# QUANTITATIVE DETERMINATION OF SPECIFIC HEAT BY DIFFERENTIAL SCANNING CALORIMETRY

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The influence of some experimental parameters on the quantitative determination of specific heats by DSC is discussed. Conditions allowing measurement of the specific heat with a maximum relative error of 1.5% are proposed. The specific heats of NaA zeolite, $C_p = 0.227 \pm 0.003$ cal.°C$^{-1}$.g$^{-1}$, and AgA zeolite $C_p = 0.205 \pm 0.003$ cal.°C$^{-1}$.g$^{-1}$ have been determined.

Specific heat can be relatively simply determined by DSC. Scanning of an external standard (usually synthetic sapphire) and a sample is accompanied by the corresponding deflections from the base line. Taking into account the correction due to blank deflection amplitude, the amplitude to mass ratio yields the value of the specific heat $C_p$ of the sample directly.

$$C_p\,(\text{sample}) = \frac{\text{A (sample)}}{\text{A (sapphire)}} \cdot \frac{\text{M (sapphire)}}{\text{M (sample)}} \cdot C_p\,(\text{sapphire}) \qquad (1)$$

Equation (1) is based upon the proportionality between the amplitude and mass values and includes no other parameters, either internal or external. However, as it has been pointed out [1–3] that in DTA analysis peak area is not a linear function of mass, it can be expected that (1) is not generally valid. With our measurements, the specific heat could not be determined by means of Eq. (1) with an error of less than 10% when working with the generally proposed "reasonable" limit of 40 mg.

In this paper, the effects of different parameters on the determination of $C_p$ by DSC are examined in a similar way as was done by Berg and Egunov [4] for the heat of phase transitions in DTA.

## Experimental

A Perkin–Elmer DSC-1B was used for $C_p$ determination. An aluminium sample pan of 5.7 mm diameter and average weight 26 mg was put into the holder, and heated uniformly from the lower side. The temperature of the holder was measured with a platinum resistance thermometer. The sample was put into the sample pan, which was closed; it was always subjected to the same pressure. By this means, the change of the sample mass is reflected only in the change of the height of the closed, pressed down sample pan. This fact is of special importance, because it was thus achieved that the area of the sample pan heating surface always remained constant. The samples were synthetic zeolites NaA and AgA. The zeolite AgA with 90% $Ag^+$ relative to $Na^+$ was produced on an ion-exchange column, by standard means. The 2–3 μm fraction of the particles was rinsed with deionized water (13 MΩ'/cm) to neutral reaction, and then dried at 80°C. The powder so prepared contained considerable amounts of water (20%) in the cavities of the zeolite, which can influence the results considerably. Water is eliminated in DSC by heating up to 773°K. The zeolite was put for 15 minutes in the flow of dry nitrogen at this temperature. In this way, nearly all the water was eliminated. The results of the DSC effluent analyses agreed with the results of the thermogravimetric results with a spiral vacuum micro balance (in both cases the samples contained 22.92% water). The pure zeolite material was then cooled down to 300°K without the samples coming into contact with the ambient atmosphere. After a certain stabilization (20 min waiting) the specific heats were determined at 310°K. For determination of the sample mass Cahn's electro balance, model GRAM, was used, its maximum relative error in the measurement range being 0.025%.

## Results and discussion

The influence of the parameters of Eq. (1) on the precision of the results was examined. A series of experimental measurements on one sample showed that the reproducibility of the amplitude with the DSC-1B instrument is very good, the error of the amplitude determination not exceeding 0.1%. Since the sample mass and specific heat of the standard (sapphire) were determined with considerably higher precision than the amplitude value, Eq. (1), if correct, should give a precision of ~0.1%. This is a full order of magnitude lower than the experimental errors got by simply applying Eq. (1).

The influence of the geometrical shape factor, not appearing in Eq. (1), was investigated. However, it appeared that the dimensions of the sample pan and the holder were so well chosen that the error due to the geometrical factor lies within the general error of 0.1% in determinations of amplitude height.

The basic implication of Eq. (1), direct proportion between the amplitude height and the sample mass, was checked. The results are presented in Fig. 1, where it can be seen that linear proportionality exists only up to 22 mg of zeolite. From the value ~31 mg, there is a region of limited proportionality; the dependence of the amplitude on mass is given by a curve. Finally, from 30 mg on, the validity of Eq. (1) is lost completely. This result is qualitatively similar to that found by Berg and Egunov [4] for the heat of transformation. Quantitatively, there is a considerable difference as regards the order of magnitude, their region of linear proportionality for determination of the transformation heats by DTA

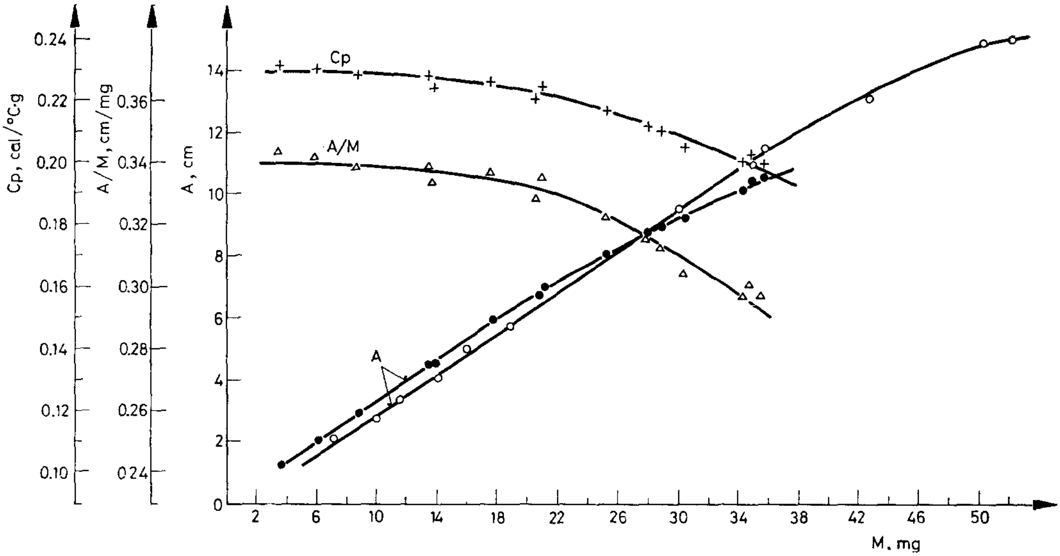

Fig. 1. The dependence of the parameters of Eq. (1) on the sample mass. Amplitude dependence on the mass of the sample: curve *A*: full circles, NaA zeolite; open circles, AgA zeolite; curve *A*/*M*: Specific amplitude vs. mass; curve $C_p$: Specific heat vs. mass

Table 1

Dependence of the specific heat on mass

| No. | *M* g.$10^3$ | *A* cm | *A*/*M* cm.mg$^{-1}$ | $C_p$ cal.°C$^{-1}$.g$^{-1}$ | $\Delta C_p$ $C_p - \overline{C}_p$ | $\Delta C_p$ % |
|---|---|---|---|---|---|---|
| 1 | 2.93 | 1.0 | 0.341 | 0.230 | +0.003 | 1.3 |
| 2 | 3.73 | 1.3 | 0.343 | 0.231 | +0.004 | 1.8 |
| 3 | 6.15 | 2.1 | 0.341 | 0.230 | +0.003 | 1.3 |
| 4 | 8.85 | 2.95 | 0.338 | 0.228 | +0.001 | 0.4 |
| 5 | 13.60 | 4.6 | 0.338 | 0.228 | +0.001 | 0.4 |
| 6 | 13.82 | 4.6 | 0.333 | 0.224 | −0.003 | 1.3 |
| 7 | 17.87 | 6.0 | 0.336 | 0.226 | −0.001 | 0.4 |
| 8 | 20.74 | 6.8 | 0.328 | 0.221 | −0.006 | 2.6 |
| 9 | 21.19 | 7.1 | 0.335 | 0.225 | −0.002 | 0.9 |
| 10 | 25.34 | 8.15 | 0.322 | 0.217 | −0.010 | 4.4 |
| 11 | 27.96 | 8.8 | 0.315 | 0.212 | −0.015 | 6.6 |
| 12 | 28.87 | 9.0 | 0.312 | 0.210 | −0.017 | 7.4 |
| 13 | 30.54 | 9.3 | 0.304 | 0.205 | −0.022 | 9.7 |
| 14 | 34.35 | 10.2 | 0.297 | 0.200 | −0.024 | 10.6 |
| 15 | 34.84 | 10.5 | 0.301 | 0.203 | −0.024 | 10.6 |
| 16 | 35.74 | 10.6 | 0.297 | 0.200 | −0.027 | 11.9 |

$\overline{C}_p$ found as mean value, by averaging the first nine values.

going up to 150 and 350 mg. It is probable that the width of the proportional region characterizes each thermal method and instrument for physico-chemically identical samples. The error of the individual measurements in curve $A/M$ is about 1.5%, while the difference from the mean value is ~0.8% within the interval from 3 to 22 mg of zeolite. Curve $A/M$ allows the measurement of the heat capacity with the desired precision for the given sample.

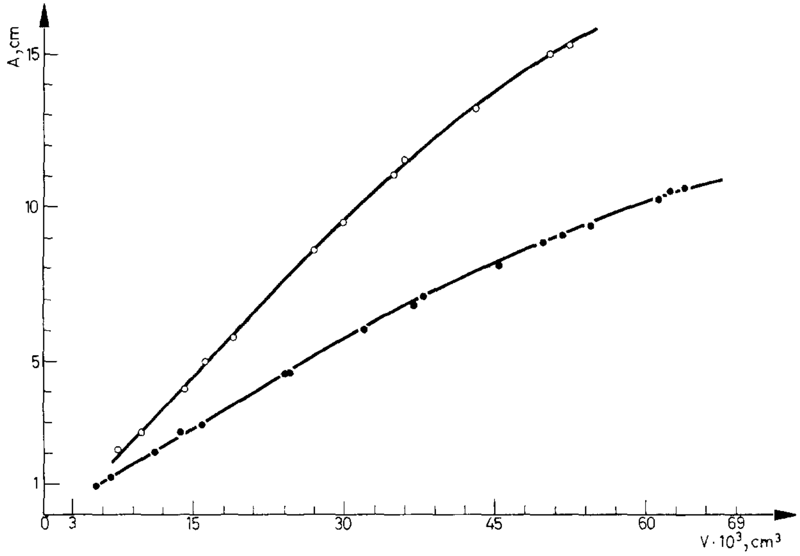

Fig. 2. Amplitude dependence on the volume of the sample (full circles: NaA zeolite, open circles: AgA zeolite)

For curve $C_p$ the error of the mean value in the proportional region is about 1.4%, as seen from Table 1.

Out of the proportional region, the error begins to increase rapidly, and for the sample of mass 36.0 mg is 14%. It is obvious that the error would be even higher for higher masses. The value of the specific heat of the NaA zeolite determined by this means is $C_p = 0.227 \pm 0.003$ cal.°C$^{-1}$.g$^{-1}$.

The question arises whether it is necessary to determine the proportional region again quantitatively with a given DSC instrument for any sample of different physico-chemical nature, or whether a once determined mass region, as for instance Fig. 1, remains valid.

For this purpose, a sample of another zeolite was examined, where the sodium was replaced by silver. Quantitatively, quite the same results were found. From the proportional region (for reasons of legibility only the amplitude on mass dependence is exchanged by the volume dependence as presented in Fig. 2), it is obvious that there is no change in the proportional region for zeolites.

This result yields the possibility of knowing in advance the width of the proportional region for substances of similar heat permeabilities and for a given instrument, even without volume measurements, the latter often being connected with considerable errors and experimental difficulties.

The volume equality due to the same bulk density (same pressure, same powder fraction) shows that the proportional region width ratio is directly proportional to the specific weight ratio of the examined samples. Thus, it is enough to determine the proportional region once for a given instrument and a given sample, because the width of the proportional region for the same bulk density (the same fraction) of the new sample will be approximately proportional to the ratio of the specific weights of the new and the "old" sample.

In the above considerations, the nature of the samples observed was very similar. Accordingly, some very important factors affecting thermophysical properties [5, 6], e.g. heat conductivity, were not examined. Future investigations will probably show the influence of the heat conductivity on the proportional region, and indicate that the above conclusions can be given only for substances with close heat permeabilities.

## References

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Résumé — On discute l'influence de quelques paramètres expérimentaux sur la détermination quantitative des chaleurs spécifiques par analyse calorimétrique différentielle (DSC). On propose des conditions qui permettent d'effectuer la mesure des chaleurs spécifiques avec une erreur relative maximale de 1.5%. On détermine les chaleurs spécifiques de la zéolite NaA ($C_p = 0.227 \pm 0.003$ cal/°C.g) et de la zéolite AgA ($C_p = 0.205 \pm 0.003$ cal/°C.g).

Zusammenfassung — Der Einfluß einiger Versuchsparameter auf die quantitative Bestimmung spezifischer Wärmen mittels der DSC-Methode wurde erörtert. Bedingungen werden vorgeschlagen, welche die Messung der spezifischen Wärme mit einem maximalen relativen Fehler von 1.5% gestatten. Die spezifischen Wärmen von NaA-Zeolit, $C_p = 0.227 \pm 0.003$ cal/°C.g und AgA-Zeolit, $C_p = 0.205 \pm 0.003$ cal/°C.g wurden bestimmt.

Резюме — Обсуждено влияние некоторых экспериментальных параметров на количественное определение теплоемкости методом ДСК. Предложены условия, дающие возможность измерять теплоемкость с относительной ошибкой не более 1,5%. Определены теплоемкости цеолита NaA, $C_p = 0{,}227 \pm 0{,}003$ кал/г·град., и цеолита AgA, $C_p = 0{,}205 \pm 0{,}003$ кал/г град.