

SCANNING CALORIMETRY WITH ADIABATIC OR CONTROLLED DIABATIC SURROUNDINGS

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ABSTRACT

Controlled diabatic (non-adiabatic) scanning calorimetry as a counterpart to the adiabatic method is described in this article. It is shown that two main advantages result from this technique: a) cooling experiments without lack of accuracy in comparison to heating runs can be performed and b) accurate and most reliable c_p -values result from this method because influences of changing calorimetric surroundings are compensated by a selfcontrolling system. Examples of c_p -curves are given in order to elucidate the adiabatic and diabatic method as well.

INTRODUCTION

Adiabatic calorimetry is the most widely used method for measuring specific heats as well as transition and reaction enthalpies of solids at high temperatures (ref. 1). In this paper at first the method of adiabatic scanning will be dealt with and then a dilated method working under non-adiabatic conditions is stressed.

Fig. 1 shows the principal scheme of an adiabatic scanning-calorimeter. The temperature of the probe T_M increases continuously caused by a well defined rate of induced electrical energy L . The temperature of the shield T_U must be controlled to strictly follow T_M (adiabatic condition[†]). Three cases are important:

- a. the applied voltage to the heater of the probe is constant, which means approximately constant power (if the resistance of the heater is only slightly temperature dependent)

[†])this is a simplified definition. Really one has to say that the heat flux between probe and shield should be negligible and this has to be true at any point of the surrounding wall.

- b. the heater is supplied with exactly controlled electric power
- c. mostly used: T_M is regulated to follow a temperature program, e.g.

$$T_M = T_0 + \alpha \cdot t$$

- a. is the easiest to handle method for the scanning experiment but only c. will be stressed in the forthcoming paragraphs. It mostly is applied with the aid of computers and gives the best defined thermal reproducibility for different runs.

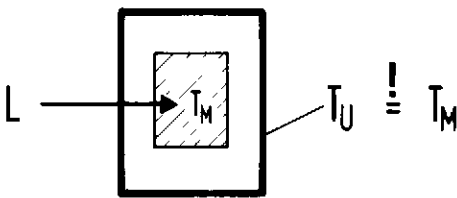


Fig. 1. Principal scheme of an adiabatic scanning calorimeter

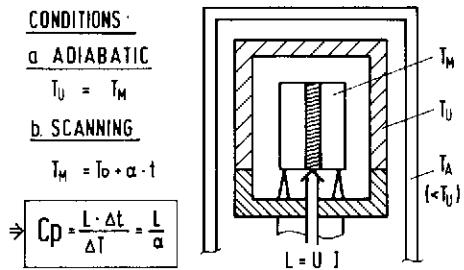


Fig. 2. Principal setup of the adiabatic scanning calorimeter

ADIABATIC SCANNING METHOD

Experimental

Fig. 2 shows the principal setup of the adiabatic calorimeter with measuring sample including the inner heating element, surrounded by the adiabatic shield (divided in an upper and a lower part). The adiabatic shield is regulated to the probe's temperature as close as possible. The outer shield is held at a definite temperature difference to the adiabatic shield in order to be able to maintain its proper temperature regulation. The quantity to be measured is the needed energy to induce a definite temperature increase to the probe.

Several sources of error are inherent in the adiabatic method. Besides of uncertainties of the measuring device an imperfect adiabatic condition can give rise to severe errors predominantly at high temperatures (> 800 °C). They are produced mainly: a. by little displacements caused by different expansion of the component's materials, b. by different altering of thermocouple characteristics and c. by a change of emissivity of the calorimeter walls in the hot zone. Therefore the adiabatic condition often has

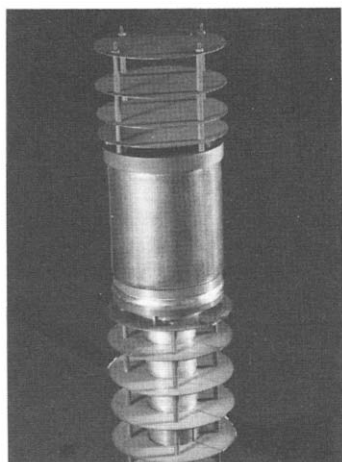


Fig. 3. Calorimetric head with radiation shields, outer thermostat is discarded



Fig. 4. Upper part of adiabatic shield is partly elevated. Matchbox for comparison



Fig. 5. Upper part of adiabatic shield is put aside, inner vessel with graphite container for the probe can be seen

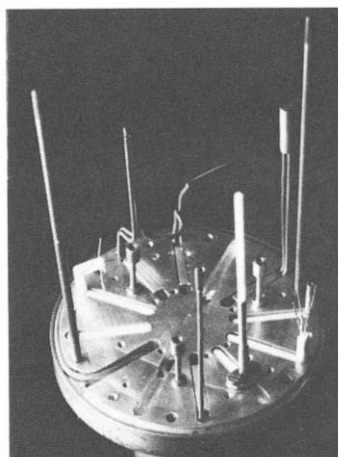


Fig. 6. Demounted lower part of adiabatic shield

by all means to be readjusted. In this case the drift of the inner vessel should be observed with no power fed to the heater while the other components should be regulated under normal experimental conditions to a defined temperature. The drift is then minimized, usually by a small induced offset in a differential thermocouple circuit. This procedure should be repeated several times at various temperatures within the measuring range. Besides of it's labouriousness this procedure is unsatisfying because often the first run above 800 °C will change appreciably the adiabatic condition.

In spite of this, most of c_p -measurements were performed under these conditions up to now. In the next paragraph some examples will be given in order to elucidate the usefulness of the adiabatic method.

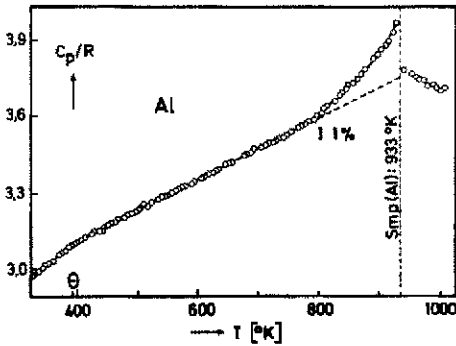


Fig. 7. Specific heat of aluminium

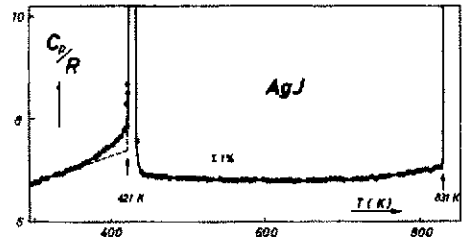


Fig. 9. Specific heat of silver iodide

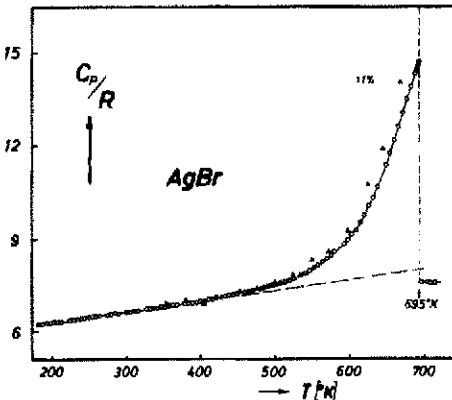


Fig. 8. Specific heat of silver bromide

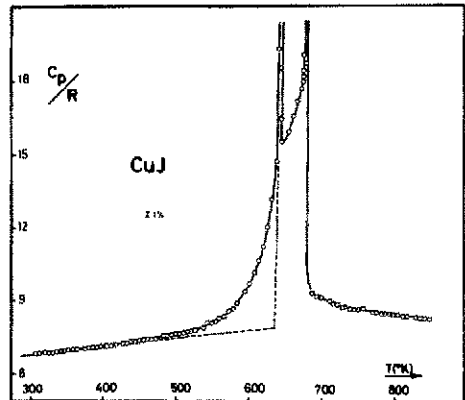


Fig. 10. Specific heat of cuprous iodide (CuI)

Results

Fig. 3, 4, 5 and 6 show photographs of the head of the calorimeter (ref. 2) which was used for most of the measurements.

The scanning method is most useful if the temperature dependence of c_p over wide temperature regions must be observed. As an example the c_p anomaly due to thermal disorder of a crystal lattice will be stressed. In this case the normal lattice specific heat has to be observed at low temperatures, whereas the deviation from this curve has to be followed precisely at high temperatures. The effect is low for fcc metals, (see Fig. 7, and ref. 3) but it can become pronounced with some ionic crystals, e.g. AgBr, where the specific heat due to FRENKEL disorder of the cations is half that of the lattice part near the melting point, fig. 8 (ref. 4). Near lattice transitions an increasing thermal disorder is the normal case (see fig. 10, and ref. 4, e.g. CuJ). The missing of the c_p -anomaly near the melting point often indicates a highly disordered sublattice e.g. the cations of silver iodide, fig. 9, (ref. 5).

A continuous transition to high disorder of the anions is found for many compounds with the fluorite structure (ref. 6). Fig. 11 shows c_p of SrCl_2 with a typical SCHOTTKY-anomaly caused by the continuous transition of ordered Cl^- -ions at tetrahedral sites to disordered octahedral ones. Fig. 12 gives an expression of the extra enthalpy for this process with a value near that for melting. From this the concept of a molten sublattice becomes understandable.

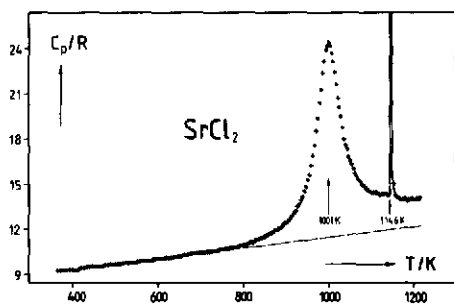


Fig. 11. Specific heat of strontium chloride

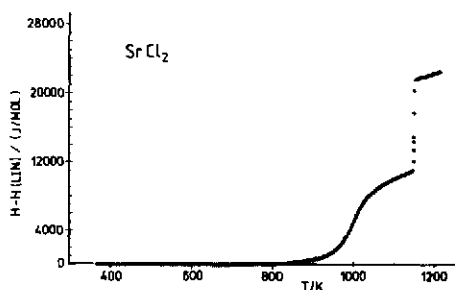


Fig. 12. Enthalpy of strontium chloride

Further applications of scanning calorimetry are concerned with the elucidation of complicated regions of phase diagrams. An example is the system

AgJ/CuJ with a lack of information in the equimolar region (fig. 13). A scanning experiment with an equimolar AgJ/CuJ mixed crystal was sufficient to detect a transition of low enthalpy which clearly indicates the boundaries of the expected two phase region (ref. 7). The complete phase diagram deduced from further runs with AgJ/CuJ mixed crystals at different compositions is

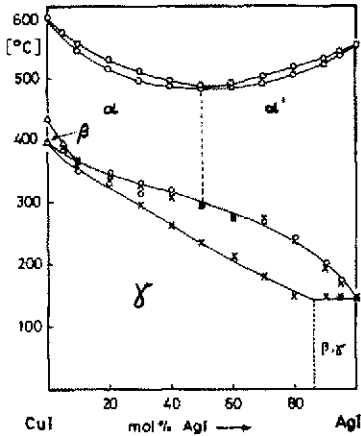


Fig. 13. Phase diagram of AgJ/CuJ mixed crystals (after Quercigh, ref. 7)

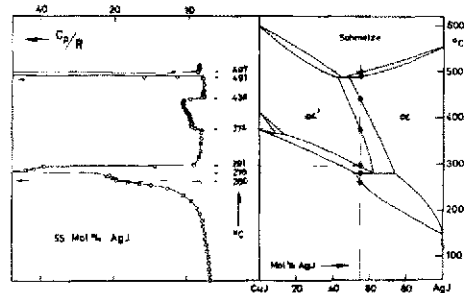


Fig. 14. Phase diagram of AgJ/CuJ (ref. 8)

shown in fig. 14. A second example of this type is given by the system AgBr/CuBr. Jost and v. Salmuth (ref. 8), and Teltow (ref. 9), made interesting proposals to the phase diagram, shown in fig. 15. The physical explanation to the diagram at the right side was of principal importance. At first sight the two different structures of the pure components (AgBr has NaCl-type, CuBr ZnS-type structure) should exclude complete miscibility of the components as shown in fig. 15, right side, near 300 °C. But there was another argument (ref. 10) which favours the miscibility of these crystals: Both anion lattices have cubic face centered structure with almost the same lattice parameter at 300 °C. The cations are disordered according to the FRENKEL model. By this disordered sites of AgBr (tetrahedral) were normal ones of CuBr and vice versa, disordered sites of CuBr (octahedral) correspond the normal AgBr sites. Thus it seems possible to explain a continuous transition of two different crystal structures by a continuously increasing disorder of the lattices' components.

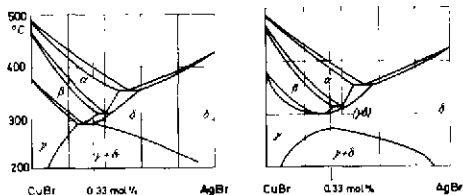


Fig. 15. Phase diagram of AgBr/CuBr (after Jost and v. Salmuth, ref. 8)

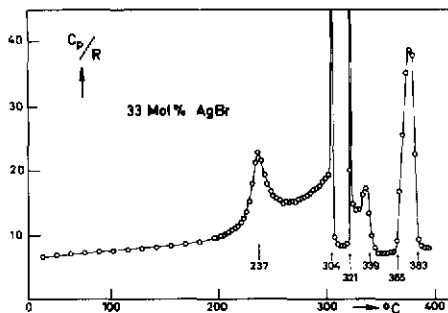


Fig. 16. Specific heat of a mixed crystal 33AgBr/67CuBr

This exciting picture unfortunately was disturbed by only one scanning calorimetric experiment (ref. 11) with a mixed crystal of composition 33AgBr/67CuBr as shown in fig. 16. At 304 °C there is a sharp and significant narrow transition which clearly indicates a miscibility gap by an eutectic line at that temperature. Fig. 17 shows the c_p -curve combined with the phase diagram. The c_p -values elucidate almost all of the details of the phase diagram which then closely agrees with that given by TELTOW (ref. 9). By this example the strength of the scanning principle for measuring c_p values with an adiabatic setup is shown most impressively.

At last a set of scanning c_p -T-curves are given for cerium dioxide with different Ce/O ratios according to the formula CeO_y with $y = 2 - x$, where x is the oxygen deficiency (fig. 18-23). The diversity of lines and shapes may be explained by special arrangements of oxygen vacancies, which give stable configurations to the lattice at distinct Ce/O ratios. The complicated phase diagram shown in fig. 24 was constructed with the aid of several scanning c_p -measurements (ref. 12).

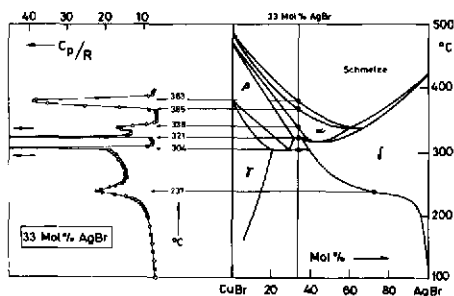


Fig. 17. Phase diagram of AgBr/CuBr mixed crystals (c_p curve from fig. 16)

Nearly stoichiometric CeO_y does not show any phase transitions whereas already $\text{CeO}_{1,967}$ is exhibiting a distinct one combined with a 'shoulder' (two phase region, see fig. 24). At higher oxygen deficiencies a still more complicated behavior is observed. The distinct lines belong to peritectic or eutectic lines in the phase diagram (fig. 24), occurring more and more in the region between $y = 1,80$ and $y = 1,85$. At $y < 1,79$ the c_p -curves become a more easier shape again, corresponding to a less complicated picture of the phase diagram in this composition region.

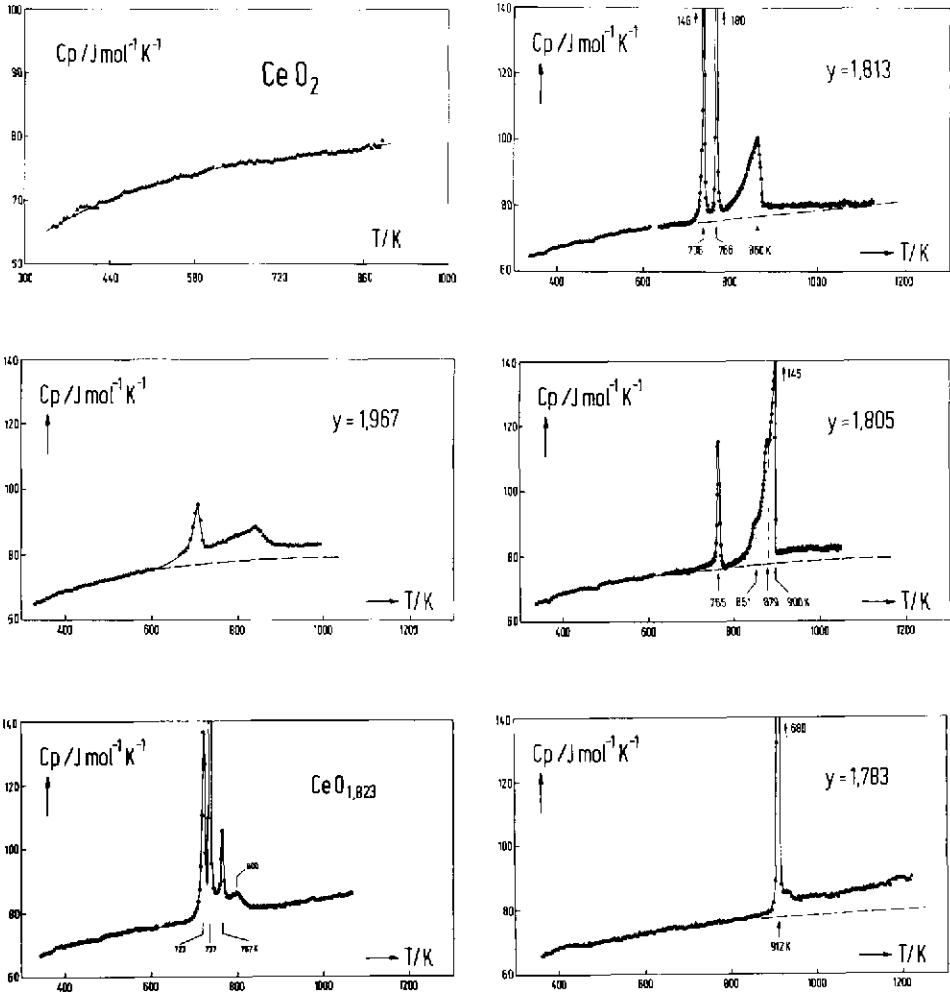


Fig. 18 - 23. Specific heat of nonstoichiometric ceria (CeO_y), with $y \approx 2; 1,967; 1,823; 1,813; 1,805$ and $1,783$

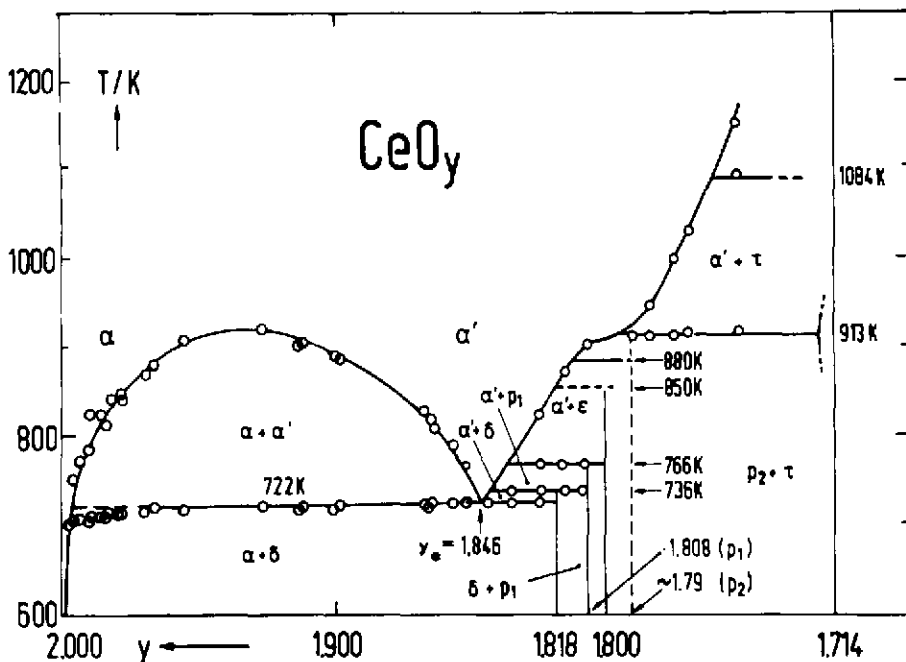


Fig. 24. Phase diagram of nonstoichiometric ceria, CeO_y

CONTROLLED DIABATIC MEASUREMENTS WITH A SCANNING CALORIMETER

Introduction

In spite of the strength of the adiabatic method as shown in the last paragraph there exist quite a lot of disadvantages with it, as already mentioned at the beginning. A principal further handicap is the impossibility of performing experiments at decreasing temperature because one cannot draw heat from the probe under adiabatic conditions. This is true especially to high temperatures where suited Peltier elements do not exist. Therefore only a non-adiabatic (diabatic) method can be used with the surrounding temperature less than that of the probe. The normal procedure is quite laborious, because three runs are necessary at a time: a. one with the empty vessel, b. one with a standard probe and c. a third one with the measuring probe in the vessel. All runs have to be made strictly under the same experimental conditions with all its already mentioned uncertainties.

Diabatic method: Controlled heat loss between probe and surrounding shield.

General Considerations. The method is based on a permanent controlled heat loss of predetermined and precisely known value. How to ensure this is described in the next section. Two facts are of predominant significance: a. The influence of the surroundings are eliminated, e.g. altering of thermocouples or of the emissivity of the surrounding walls are compensated. b. Runs with decreasing temperature are possible because the heat input to the probe can now be varied and regulated according to the scanning temperature program ($T = T_0 + \alpha \cdot t$).

Principle of measurement

The shield which surrounds the measuring probe is held at a constant temperature while the heater inside the probe is fed with constant power of precisely known value L_0 (e.g. $L_0 = 1,00000 \pm 0,00003 \text{ J s}^{-1}$). After sufficient time has elapsed the stationary state is reached and a definite temperature difference ΔT will maintain between probe and surrounding shield. The quantity ΔT is determined by the constant power (which may be called 'heat loss rate' for brevity) and by the shield's temperature. This calibration process for determining ΔT is to be inserted at constant temperature intervals (e.g. every 20 K) into a scanning run. A set of pairs of T and corresponding ΔT values is obtained. They describe a monotonic decreasing curve with increasing temperature and can be approached sufficiently accurate by a five parameter polynomial.

If the scanning experiment is performed by strictly correlating ΔT with the corresponding actual temperature, the desired heat loss is maintained at any time⁺⁾ . If the 'heat loss rate' (which corresponds to the electrical power fed to the probe in the case of constant temperature) is L_0 and the temperature scanning rate is α (see above), then the following situation is given

1. $\alpha > 0$: $L > L_0$ (heating)
2. $\alpha = 0$: $L = L_0$ (ΔT adjusting)
3. $\alpha < 0$: $L < L_0$ (cooling)

L is the actually required power in order to maintain the scanning temperature program ($T = T_0 + \alpha \cdot t$). In a cooling experiment L_0 should not fall short of a

⁺⁾ some limitations to this statement must be made: a. the scanning temperature rate should not be too high, perhaps less than $1\text{K} \cdot \text{min}^{-1}$, b. the stationary condition must be sufficiently approached, which means a sufficient long duration of a foreperiod to the new scanning interval, c. because there are principally adherend temperature gradients inside the probe and the probe's container, great care is to be taken with the setting of the thermocouple inside it. Further details to this point are beyond the scope of this article.

minimum value in order to compensate for the required heat loss rate of the probe (and probe's container) which is determined by the scanning rate α ⁺). The heat capacity is calculated according to the simple relation

$$C_p = (L - L_0) / \alpha$$

To obtain the heat capacity of the probe without it's container, a separate experiment is performed with the empty container⁺⁺) (with L^* instead of L)

$$C_p^* = (L^* - L_0) / \alpha$$

The specific heat of the probe (n moles) is then calculated to

$$c_p = (C_p - C_p^*) / n = (L - L^*) / (\alpha \cdot n)$$

L_0 is lacking in this formula which is to be expected. Nevertheless there should be a convenient choice of L_0 , as already mentioned.

Determination of ΔT

The most important quantity for the diabatic scanning experiment is the precise knowledge of the temperature difference ΔT between probe and surrounding shield. It corresponds to the constant heat loss rate L_0 of the probe. At constant shield temperature T_U the probe is fed with constant electrical power. After sufficient time the probe will exhibit a stationary temperature T_M , from which $\Delta T = T_M - T_U$ is deduced. In a current measurement this procedure is inserted after the scanning temperature has overcome a certain interval, e. g. 20 K. As the controlling computer has the polynomial for ΔT as function of T in his memory (resulting from former runs), every new determination of ΔT only performs a correction and actualisation of this polynomial. But this correction is most important. It takes into consideration all changes of heat transfer parameters inside the calorimetric head, particularly if they are due to long time effects.

In practice the computer evaluates ΔT from the polynomial at a smallest possible measuring cycle, e. g. of 3 s duration. By this ΔT is held to the

⁺) There may be situations where L_0 must be changed during the experiment, e.g. at occurring phase transitions. This can be done without effort by the computer program.

⁺⁺) it is sufficient to perform this measurement only one time if the container's material and it's mass is always the same and if the inner thermocouple is situated at the same place (see below).

correct value almost continuously. Empirically the mismatch of ΔT calculated from the polynomial after a 20 K scanning interval compared with a new value measured in an adjacent constant temperature period is less than 10 mK. In this case an influence to the measured c_p values is not yet observed.

Exceptions may appear when a sporadic process inside the calorimeter head (e.g. displacements of components due to the changing temperature) modify the heat transfer characteristics. But already the next ΔT adjustment will compensate for these effects and give correct ΔT alignment in the adjacent scanning period. As a consequence of this behavior one can expect to measure accurate c_p -values at most time and to recognize clearly faulty values according to sporadic changes in the calorimetric setup. The accuracy with a stable measuring device is determined alone by the given constant power L_0 . It is set without effort to a predetermined value by modern digital meters to within $\pm 1 \cdot 10^{-4}$, which is entirely sufficient for precise calorimetry. L_0 shall not fall short of a minimum value with cooling runs as mentioned before. In a scanning experiment with increasing temperature, L_0 should be chosen at a low level, near adiabatical conditions. But in order to make use of the advantage of the described diabatic method, L_0 must have a certain value to compensate an erroneous heat flux causing the calorimeter drift.

Computer aided control and measurement

A complete measuring sequence ('period') is divided into 1200 'cycles' of 3 seconds. In a cycle all shield temperatures were measured, followed by PID-routines for controlling these temperatures in the next cycle. ΔT is calculated each cycle, too, giving new set-point adjustments for the shields. The heat capacity of the probe (with probe vessel) is calculated every 80th cycle. After 800 cycles scanning is interrupted and a constant temperature interval is inserted. Now L_0 and ΔT will be readjusted (duration approximately 600 cycles) and then a foreperiod of 80 cycles will finish the sequence. A time of approximately one hour will then have elapsed and the achieved temperature difference will be exactly 20 K.

Besides measuring temperatures, heater voltages and currents there are numerous other regulating and controlling routines which have to be worked through in the computer's program cycle. The incoming information is given from a digital voltmeter (6 1/2 digits) with a low voltage scanner, while the output voltages are fed to the electronic power devices by 12- or 16-bit-DAC'S. The computer program has a lot of controlling routines, which decide whether a quantity is out of limiting margins, or whether a single

measured value is out of expected limits and has to be discarded (or put to memory for later printing out). It should be mentioned, that the powerness of a computer (even of low cost versions like a COMMODORE CBM 32 K) gives the chance to get much insight into the measuring device, its sources of error or jet to the physical processes in the area to be observed, like the calorimetric head in our case.

First results from diabatic scanning runs

To elucidate the usefulness of the described method a first experiment was done on aluminium oxide (sapphire). In fig. 25 a scanning experiment with decreasing temperature is shown and compared with the well known data from NBS (ref. 13). There are deviations less than 1 % in the range from 500-1040 °C. They increase somewhat more pronounced for low temperatures. This may be interpreted with precipitation of impurities at low temperatures⁺⁾ .

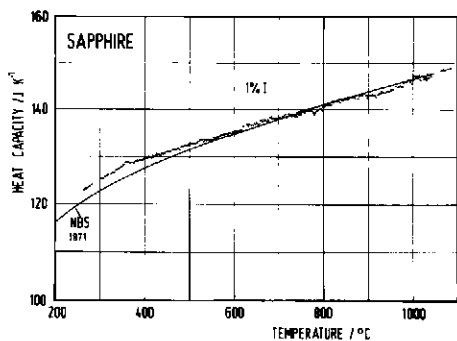


Fig. 25. Heat capacity of a sapphire probe from a diabatic scanning run with decreasing temperature

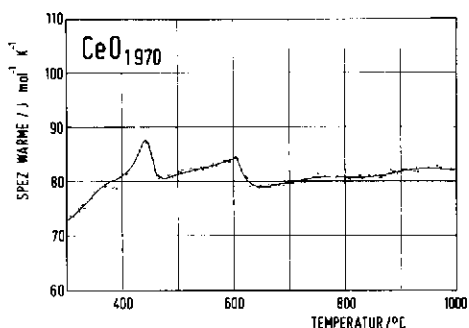
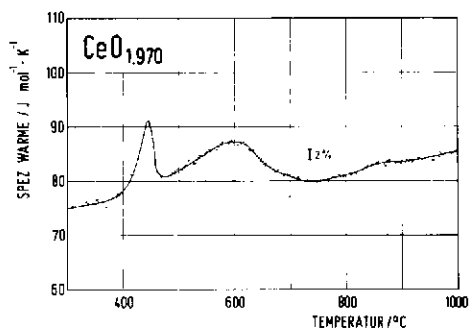


Fig. 26. Specific heat of $\text{CeO}_{1,970}$ from diabatic scanning experiments.
a. with increasing and b. with decreasing temperature

⁺⁾ the sapphire single crystals were from BIEG, D7807 ELZACH/SCHWW., F.R.G. An analysis is not available to us up to now.

Further intensive investigations on CeO_y with the diabatic method have begun now. Fig. 26a is showing the result on $\text{CeO}_{1,970}$ with increasing, and fig. 26b on the same material with decreasing scanning. There are distinct differences for both runs to be recognized. They may be interpreted with an incomplete segregation and ordering of oxygen vacancies which are known from many other experiments. But a first (experimental) conclusion should be, that there evidently equilibrium is not established, if the probe's temperature goes down beyond approximately 600 °C. From this fact other more refined measurement has to be started.

CONCLUSIONS

The last section should give a first impression of the powerness of the controlled diabatic measuring. It is seen that besides advantages already mentioned there is an important information from the diabatic scanning about the probe's internal equilibrium. The importance of this information is clear especially to solid state reactions, e.g. transformation, precipitation and decomposition or ordering and nucleation processes.

On the other hand it should be clear that the wellknown adiabatic method has the advantage of reduced equipment and easer handling. But both methods do not exclude each other. A stage by stage refined measuring can be developed from the adiabatic to the diabatic method. This is possible since a change in the equipment relates mostly to the outer electronic part and to the computer program. The substancial 'hardware' of the calorimeter remains almost unchanged. This fact is understood impressively if one has a glance to Moser's calorimeter (ref. 14), which was used for his famous calorimetric measurements at the Physikalisch-Technische Reichsanstalt, Berlin, almost 50 years ago.

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