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THE CALORIMETRIC CALIBRATION OF DIFFERENTIAL SCANNING CALORIMETRY CELLS

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ABSTRACT

In this paper it is shown that in many cases enthalpy determinations can be carried out with a precision <1%. The influences of various sample and instrumental properties are described. The enthalpies of 24 compounds with 30 phase changes (polymorphic transitions or melting points) were redetermined. Twelve of the compounds with 15 transitions in the temperature range 0–670°C are selected and recommended for calorimetric DSC calibration. The linearization of the calibration curve as stated by the manufacturer of the instrument employed was fully confirmed.

INTRODUCTION

Calorimetric measurements with DSC cells are becoming increasingly common because of the very simple and fast measuring procedures. The method has been improved considerably by applying on-line micro-computers. In this paper the calorimetric calibration of a heat-flux DSC cell with control and data evaluation by a micro-computer is reported. Investigations appeared necessary because no comprehensive work could be found in this field and no recommendations of the ICTA Standardization Committee are yet available. The authors hope that the results will also be of help to this committee.

Calorimetric measurements with DSC cells are based on the well-known equation

$$\Delta H = \frac{K'}{m} \int_{t_0}^{t_e} \Delta T \, \mathrm{d}t \qquad (1)$$

where ΔH = enthalpy, m = sample mass, t = time, 0 and e = onset and end of peak, respectively, and T = temperature. K' is a temperature-dependent factor (Fig. 1). In the instrument employed in this paper, the K' curve is linearized and set constant electronically. Thus the calibration curve need no

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longer be determined experimentally.

Substituting [1]

$$\Delta\dot{Q} = K'\Delta T \tag{2}$$

gives

$$\Delta H = \frac{1}{m}\int_{t_0}^{t_e}\Delta\dot{Q}\,\mathrm{d}t \tag{3}$$

where $\Delta\dot{Q}$ = heat flux difference*. The instrument records $\Delta\dot{Q}$ as a function of time.

If the left-hand side of eqn (3) is considered as ΔH_{ref} (ref = reference) and the right-hand side ΔH_{m} (m = measured), both sides can be equalized by introducing a proportionality constant, K, to give

$$\Delta H = \frac{K}{m}\int_{t_0}^{t_e}\Delta\dot{Q}\,\mathrm{d}t \tag{4}$$

For calibration

$$K = \frac{\Delta H_{\mathrm{ref}}}{\Delta H_{\mathrm{m}}} \tag{5}$$

must be determined. The calibration can be carried out using defined electrical "ΔH signals" or materials with well-known transition enthalpies. In the present work, the latter possibility is used.

Since K is independent of temperature, theoretically only one calibration run is necessary for the whole temperature range. For several runs, the mean value of K eliminates systematic errors. Its confidence interval reflects the statistical deviations, whether they arise from the instrument, from sample preparation, or from the calibration materials. Accuracy and reproducibility of K are the predominant factors for the quality of the measurements.

In the present work an attempt is made to determine which sources of error are the most relevant and to investigate and characterize them as independently as possible. Fortunately, the instrumental uncertainties of modern apparatus can be kept very small and the errors depend predominantly on the samples. Thus the choice of suitable calibration materials is the most important factor.

The detailed aims of this paper are to (a) determine the bulk error, (b) characterize the influences and sizes of the various single errors, (c) recommend suitable calibration materials, and (d) prove the efficiency of the

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* The heat flow $\dot{Q} = \mathrm{d}Q/\mathrm{d}t$ is usually measured in mW.

** The letter K is used instead of the common C, since C is reserved internationally for heat capacity.

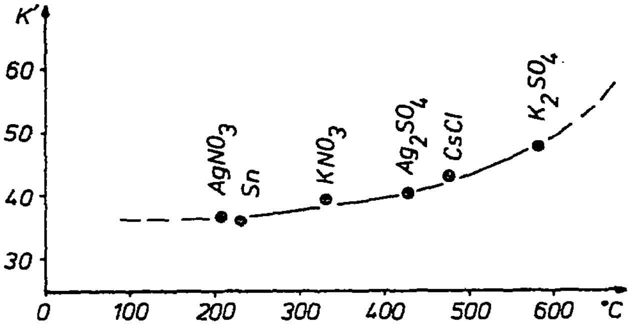

Fig. 1. Temperature dependence of the calibration constant K', recalculated from Eysel [2] with calibration enthalpies measured in the present work.

linearization of K'. Points (a), (b) and (c) are of general interest, point (d) is restricted to the instrument employed.

EXPERIMENTAL

The investigations were carried out on a DuPont Thermal Analyzer 1090, equipped with a micro-computer for experimental control as well as storage and evaluation of data (program INTERACTIVE DSC V 2.0). A DuPont DSC 910 cell was used. Samples were pressed between bottom to bottom aluminum pans. Only for K_2CrO_4 were gold pans employed. In all runs argon was used as purge gas (50 ml min^{-1}). H_2O was investigated in sealed Al pans. If not otherwise stated, sample sizes ranged from 10 to 20 mg and heating rates from 2 to 10°C min^{-1}

Sources of error

Twenty-four compounds with 30 phase changes (melting or polymorphic transitions) were chosen from the literature, for which the ΔH values appeared to be reliable (Table 1). The samples cover the temperature range 0–670°C and a ΔH range of 0.3–40 kJ mole^{-1}. Each sample was investigated several times under varying conditions. Error determinations were carried out with respect to influences of weighing error, sample size, size of enthalpy, heating rate, heat conductivity and quality of background correction.

Two types of mathematical presentation of the errors of measurement are used: (a) in Figs. 3, 7 and 9 the standard deviation, s, and (b) in Table 2 the confidence interval for the mean $\bar{s} = s/\sqrt{n}$ (n = number of measurements).

The heating rate β was changed systematically from 1 to 50°C min^{-1}. The results in Fig. 2 indicate a slight increase of the measured enthalpy. For small

TABLE 1

Enthalpies and transition temperatures from literature and $K = \Delta H_{\mathrm{Ref.}}/\Delta H_{\mathrm{m}}$

Compound	Temp (°C)	Transition [a]	ΔH (kJ mole^{-1})	Ref.	$K \pm s$
H_2O	0	m.p.	6.01	3	1.043±0.036
Benzophenone	48.2	m.p.	17.9	5	0.970±0.032
NH_4NO_3	32	p.t.	1.59	4	0.849±0.031
NH_4NO_3	125	p.t.	4.22	4	0.964±0.037
KNO_3	129.7	p.t.	5.002	6	1.024±0.054
AgI	154	p.t.	6.153	7	0.981±0.010
NH_4Br	179	p.t.	3.683	7	1.070+0.024
In	156.3	m.p.	3.27	3	1.043±0.014
In	156.63	m.p.	3.27	5	1.043±0.014
In	156.4	m.p.	3.27	8	1.043±0.014
In	156.51	m.p.	3.265	9	1.042±0.014
$RbNo_3$	166	p.t.	3.976	7	1.075±0.013
$AgNO_3$	160	p.t.	2.552	4	1.176+0.007
NH_4NO_3	169.6	m.p.	6.4	5	1.061±0.035
NH_4Cl	196	p.t.	4.478	7	1.050±0.027
$AgNO_3$	210	m.p.	11.53	4	0.994±0.014
$RbNO_3$	228	p.t.	2.721	7	0.892±0.007
Sn	231.7	m.p.	7.154	3	1.041±0.012
Sn	231.8	m.p.	7.003	9	1.019±0.012
Sn		m.p.	7.121	10	1.036±0.012
Sn		m.p.	7.086	8	1.031±0.012
Sn		m.p.	7.204	11	1.048±0.012
Bi	271.3	m.p.	10.909	8	1.029±0.023
Bi	271	m.p.	10.496	3	0.990±0.022
Bi	271.3	m.p.	10.867	11	1.025±0.023
Bi	271.3	m.p.	11.243	9	1.035±0.023
$RbNo_3$	278	p.t.	1.465	7	1.188±0.012
$NaNO_3$	306.2	m.p.	15.7	5	1.043±0.016
$NaNO_3$	310	m.p.	15.72	3	1.044±0.016
Cd	320.9	m.p.	6.396	8	1.077±0.037
Cd		m.p.	6.407	10	1.079±0.037
Cd	320.8	m.p.	6.069	3	1.022±0.035
Cd	320.9	m.p.	6.115	11	1.030±0.035
Cd	320.93	m.p.	6.290	9	1.059±0.036
Pb	327.3	m.p.	5.116	3	1.117±0.022
Pb	327.5	m.p.	4.77	5	1.042±0.021
KNO_3	334.4	m.p.	9.944	12	1.076±0.064
$Na_2Cr_2O_7$	355	m.p.	35.364	13	1.036±0.022
$K_2Cr_2O_7$	395	m.p.	40.389	13	1.054±0.015
Zn	419.4	m.p.	6.677	3	0.984±0.012
Zn	419.4	m.p.	7.12	9	1.049±0.013
Ag_2SO_4	412	p.t.	15.66	14	1.030±0.023
Ag_2SO_4	427.2	p.t.	16.10	6	1.059±0.024

TABLE 1 (continued)

Compound	Temp (°C)	Transition [a]	ΔH (kJ mole^{-1})	Ref.	$K \pm s$
Ag_2SO_4	430	p.t.	16.76	5	1.103±0.025
CsCl	445	p.t.	2.889	15	1.042±0.023
CsCl	479	p.t.	2.428	7	1.194±0.027
SiO_2	572.6	p.t.	0.395	6	
SiO_2	575	p.t.	0.360	7	
Li_2SO_4	579	p.t.	28.88	7	1.235±0.009
K_2SO_4	584.5	p.t.	5.638	6	1.024±0.023
K_2SO_4	579	p.t.	8.957	7	1.627±0.037
K_2CrO_4	667.3	p.t.	6.925	6	1.067±0.016

[a] p.t. = Polymorphic transition, m.p. = melting point.

variations of the heating rate, these changes can be neglected, especially up to 10°C min^{-1}.

The influence of the weighing error is often underestimated. This error depends on the sample size as well as the sensitivity, calibration and reproducibility of the balance employed. Since the DSC is often used as a micro-method, very small samples down to a few mg have to be weighed. The relative and absolute weighing errors directly influence the enthalpy results [cf. eqn. (4)]. Figure 3 shows the dependence of the weighing precision on the sample mass for a typical analytical balance and its influence on the bulk error of the enthalpy determination. With this balance only samples > 10 mg should be weighed.

Figures 4–6 show that, apart from the weighing error in very small samples, the enthalpy results do not vary with sample size, at least not up to 50 mg. Also the enthalpy size does not influence the results, as evident from the standard deviations in Fig. 7.

For good results a precise peak integration is necessary which depends predominantly on the background correction. Actually the latter is a major source of error. Figure 8 shows the examples of Li_2SO_4, $RbNO_3$ and quartz. Li_2SO_4 enables an excellent correction since the baseline on both sides of the peak is smooth, parallel and at the same level. Also $RbNO_3$ with different levels allows an acceptable correction since the beginning and end of the peak are well defined. In contrast, quartz does not allow a reasonable background correction, as already shown by Gray [6]. This transition (second order transition of λ-point type) starts very slowly already at 0 K, increases in speed and reaches its highest transition rate at 573°C where it ends spontaneously. Thus a peak onset is not defined and the measurement of the enthalpy does not make sense, as can be seen from the two attempts

TABLE 2

Enthalpies and transition temperatures obtained in the present work

Compound [a]	Temp. (°C)	Transition [b]	ΔH (kJ mole^{-1})	$\bar{s}$ ± (kJ mole^{-1})	$\bar{s}$ ±%	n	Origin and purity of sample/prod. No.	Properties [c]
+ H_2O	0	m.p.	6.03	0.12	2.0	4	Aqua dest.	
− Benzophenone	49	m.p.	19.30	0.44	2.3	3	Merck, 98%	
− NH_4NO_3	54	p.t.	1.96	0.05	2.6	3	DuPont	III
− NH_4NO_3	127	p.t.	4.58	0.12	2.7	3	DuPont	III
KNO_3	130	p.t.	5.11	0.19	3.7	3	Merck, 99%	III
+ AgI	149	p.t.	6.56	0.05	0.7	3	Fluka, puriss	I
NH_4Br	152	p.t.	3.60	0.06	1.6	3	Merck, 1122 suprapur	
+ In	157	m.p.	3.28	0.02	0.6	6	Fluka, 99.999%	
+ $RbNO_3$	166	p.t.	3.87	0.02	0.6	5	EGA-Chemie, 99.99%	
+ $AgNO_3$	168	p.t.	2.27	0.01	0.3	5	Merck, 99.8%	I
NH_4NO_3	170	m.p.	6.31	0.15	2.3	3	DuPont	
NH_4Cl	192	p.t.	4.46	0.08	1.8	3	Merck, 99.8%	
+ $AgNO_3$	211	m.p.	12.13	0.08	0.7	5	Merck, 99.8%	I
+ $RbNO_3$	225	p.t.	3.19	0.01	0.4	5	EGA-Chemie, 99.99%	
+ Sn	232	m.p.	7.19	0.03	0.4	9	Fluka, 99.999%	

+ Bi	272	m.p.	11.09	0.12	1.1	5	Fluka, 99.9995%	
+ $RbNO_3$	285	p.t.	1.29	0.01	0.5	5	EGA-Chemie, 99.99%	
+ $NaNO_3$	306	m.p.	15.75	0.11	0.7	6	Merck, puriss	I
Cd	321	m.p.	6.21	0.11	1.7	5	Fluka, 99.9998%	
+ Pb	327	m.p.	4.79	0.07	1.4	3	Fluka, 99.999%	
KNO_3	334	m.p.	9.67	0.41	4.2	3	Merck, 99%	I
− $Na_2Cr_2O_7$	354	m.p.	35.70	0.75	2.1	2	Hydrate, Merck p.a., 99%	I
− $K_2Cr_2O_7$	394	m.p.	40.07	0.40	1.0	3	Merck 4865, p.a.	I
+ Zn	419	m.p.	7.10	0.04	0.6	5	Fluka, 99.999%	
+ Ag_2SO_4	426	p.t.	15.90	0.16	1.0	6	Merck, 99.5%	I
+ CsCl	476	p.t.	2.90	0.03	1.0	6	Merck, 99.5%	
− SiO_2	573	p.t.	>0.3			3	Merck 7530, Quarz, p.a.	IV
+ Li_2SO_4	576	p.t.	24.46	0.07	0.3	7	Hydrate, Merck 5697, suprapur	II
− K_2SO_4	584	p.t.	5.76	0.09	1.6	3	Merck 5153, p.a.	IV
+ K_2CrO_4	668	p.t.	6.79	0.10	1.5	2	Merck 4952, p.a.	IV

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[a] + = Recommended for calibration; − = not recommended. Compounds without signs may be used, but those with + in the same temperature regions are preferred.

[b] p.t. = Polymorphic transition; m.p. = melting point

[c] I = Danger of decomposition; II = hygroscopic; III = unreproducible phase transition; IV = background correction difficult.

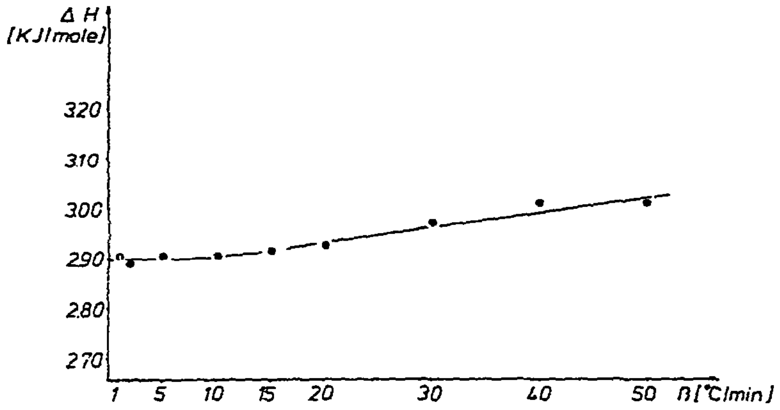

Fig. 2. Dependence of the transition enthalpy of CsCl on heating rate (polymorphic transition at 476°C).

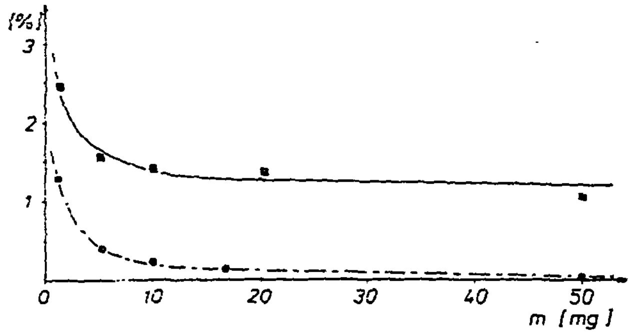

Fig. 3. Dependence of the standard deviations of the enthalpy bulk error (■) on the weighing error (●). Each point is based on five measurements of CsCl.

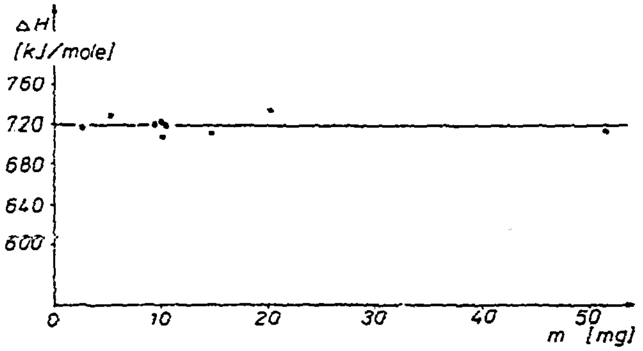

Fig. 4. Dependence of the enthalpy measurement on sample mass for melting of Sn at 232°C. $\Delta H = 7.19$ kJ mole^{-1} $\pm 0.4\%$.

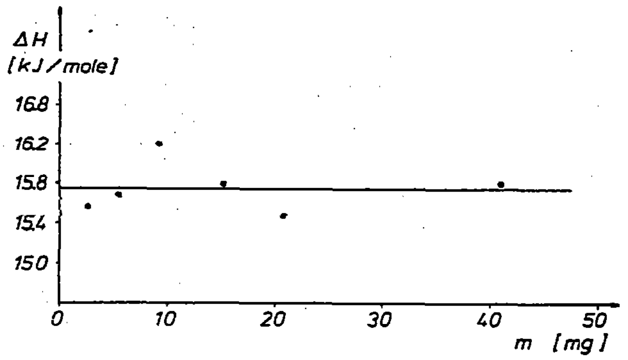

Fig. 5. Dependence of enthalpy measurement on sample mass for melting of $NaNO_3$ at 306°C. $\Delta H = 15.75$ kJ $mole^{-1} \pm 0.7\%$.

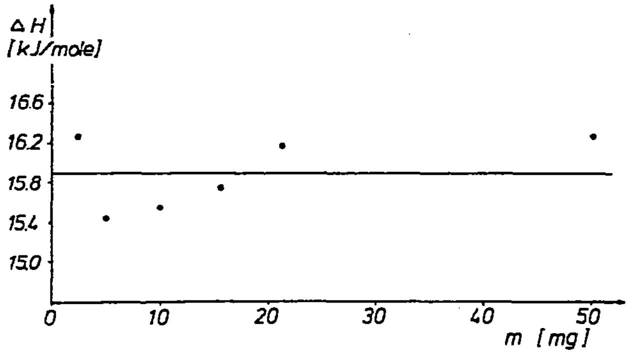

Fig. 6. Dependence of enthalpy measurement on sample mass for polymorphic transition of Ag_2SO_4 at 426°C. $\Delta H = 15.90$ kJ $mole^{-1} \pm 1.0\%$.

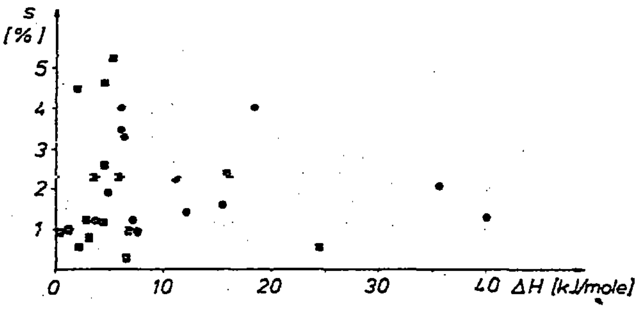

Fig. 7. Dependence of standard deviation on size of ΔH for all phase transitions of Table 2. ● = Melting points; ▨ = polymorphic transitions.

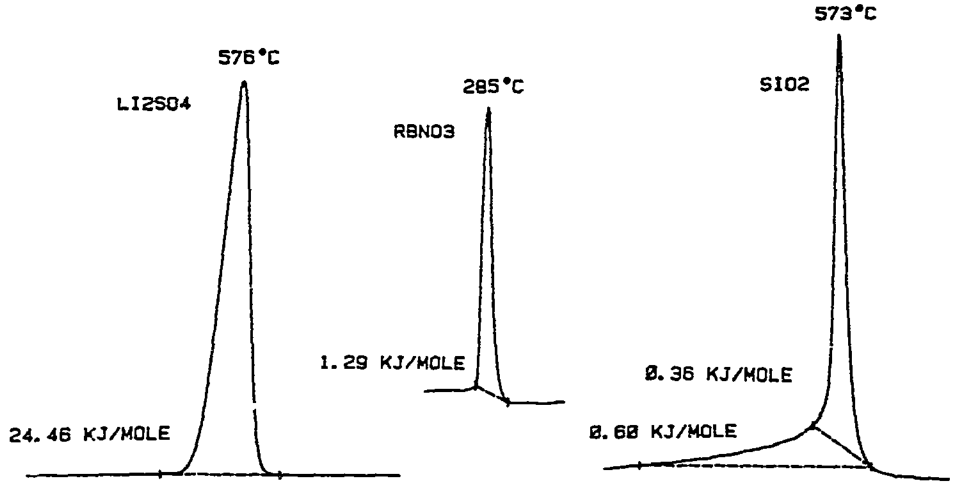

Fig. 8. Background correction for Li_2SO_4, $RbNO_3$ and SiO_2 (quartz).

for baseline correction and enthalpy determination in Fig. 8. All intermediate stages between the cases in Fig. 8 can be found with other materials.

The quality of the peak integration itself is not discussed here. It may be done by hand or fully automated by a micro-computer, as in the present work.

The cell constant K

The transitions in Table 1 were used to determine the calibration constant as $K = \Delta H_{\mathrm{Ref.}}/\Delta H_{\mathrm{m}}$, with $\Delta H_{\mathrm{Ref.}}$ = reference and ΔH_{m} = measured value. For each sample two to nine DSC runs were carried out and for each run a new sample was prepared. The results are presented graphically in Fig. 9. If several $\Delta H_{\mathrm{Ref.}}$ values exist only the most reliable and the worst one are plotted. Figure 9 allows the following conclusions. (a) The majority of the measured K values can be represented very well by a straight line with constant K over the whole temperature range. (b) Transitions marked by open circles are obviously due to wrong enthalpy values in the literature. (c) K is represented on a relative scale (which can be shifted instrumentally). In the present case $K = 1.046 \pm 0.3\%$ was obtained. (d) The fact that metals, oxides and halides all result in the same K value demonstrates that the very different heat conductivities and capacities are without significant influence. This is due to the preparation technique, in which thin sample layers are pressed between aluminum pans, so that most of the heat conduction proceeds reproducibly via the aluminum.

Since all results were obtained recently no discussion about an eventual change of K with time is possible here.

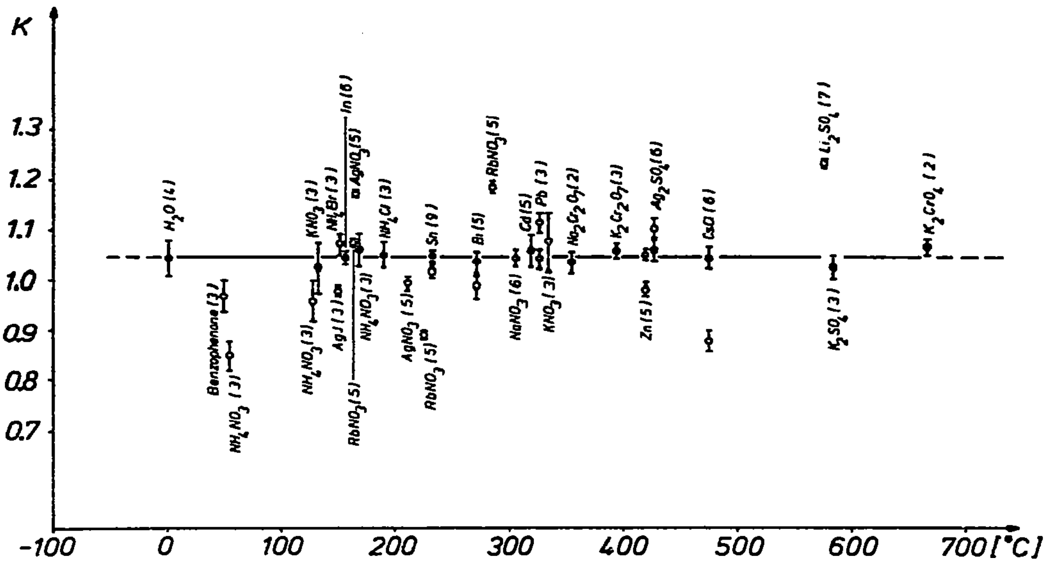

Fig. 9. Calibration constant K as determined from literature enthalpies (Table 1). ●, Considered reliable; ○, rejected because of various reasons. Number of runs in parentheses.

Standards for calibration

The cell constant $K = 1.046 \pm 0.3\%$ was used to redetermine all enthalpies of Table 1. The results are given in Table 2. The transition temperatures were measured at the extrapolated peak onsets. They do not agree in all cases with the literature values in Table 1. The deviations, however, are not discussed here, since temperature measurement and temperature calibration are not the aim of the present work. Table 2 also contains the properties and origins of the samples used. Behind the name of the manufacturer the purity in % or—if not available—other criteria are given (p.a. = pro analysi = analytical grade). In two cases the starting material was a hydrate, which was dehydrated either before or during the DSC run. This is indicated by "Hydrate".

Some points for selection or handling of the samples should be noted. (a) Danger of decomposition before or during the measured transition ($Na_2Cr_2O_7$, $K_2Cr_2O_7$) or due to light or heat (silver salts). In all cases in which vaporization from the melt or decompositions or reactions with the sample pans may be expected, only the first melting run should be used—if at all. This applies for compounds like KNO_3, NH_4NO_3, Ag_2SO_4, etc. The influence of these negative properties usually increases with decreasing heating rate. (b) Irreproducible phase transitions occur because of kinetic or other reasons (e.g., the polymorphic transitions of KNO_3 and NH_4NO_3). (c) Hygroscopicity as for Li_2SO_4 effects weighing. Li_2SO_4 therefore is employed as $Li_2SO_4 \cdot 2\ H_2O$. (d) Correction of background may be difficult or impossible as described in detail for quartz. Quartz, therefore, should be completely avoided. The same difficulties apply to a smaller extent* also to K_2SO_4 and K_2CrO_4. Quartz (573°C) and K_2SO_4 (584°C) therefore are rejected in favour of Li_2SO_4 (576°C). K_2CrO_4 is to be used as long as no better alternatives are available for the upper temperature range.

In Table 2 the errors $\bar{s}$ (in kJ $mole^{-1}$ and %) are based on the number of runs for each compound and range from 0.3% to 4.2%. Their sizes are also a quality criterium. Very small errors were found for $AgNO_3$ (p.t.), $RbNO_3$ (three transitions), Sn (m.p.) and Li_2SO_4 (p.t.). Usually a compound is not recommended for calibration if $\bar{s} > 1\%$. Exceptions are H_2O, Pb and K_2CrO_4. Attempts should be made to replace these by better materials in the future. Perhaps H_2O can be replaced by organics, which may also allow an extension to lower temperatures.

For the measurement of unknown enthalpies the same error criteria and results as discussed for Table 2 can be applied. In cases in which the material investigated does not exhibit unusually bad properties (as difficult background correction, sluggish transition, decomposition, etc.) and with suitable experimental preparation (good balance, DSC-calibration, mean of several DSC-runs with newly prepared samples, etc.) an error $\bar{s} < 1\%$ is easily obtainable.

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* Both transformations probably consist of a large part of a first and a smaller part of a second order transition.

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