

APPARATUS FACTORS IN VARIATIONS OF MEASURED TEMPERATURES IN DTA

PAUL D. GARN*

Mineralogy-Petrography Institute, University of Köln, Federal Republic of Germany

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The ability of an apparatus to reproduce faithfully all the thermal effects which may take place in a sample diminishes with separation of the ΔT thermocouple from the sample. If the temperature is recorded from a separate thermocouple and that thermocouple is not closely coupled to the sample, a drastically unreal view of the sample temperature may result for materials which supercool greatly. These conclusions are based on the data reported from the ICTA test program.

The report by McAdie et al. [1] on the Second International Test Program contains some interesting data which deserve some additional interpretation. The Committee on Standardization had confined its report [2] to the general relationships clearly discernible from the data. The more detailed report [1] drew additional conclusions concerning the influence of a number of parameters upon the ONSET and PEAK temperatures on both heating and cooling, but did not explain the reasons for the observed behaviors. The purpose of this paper is to explain some of the variations in behavior between different apparatuses.

The present author took part in the preparation of both reports in his capacity of Vice Chairman of the Committee on Standardization but this discussion is not an action of that Committee. For this reason no data are included which have not appeared in a printed report or in the scientific literature. Because the U. S. National Bureau of Standards Special Publication 260–40 is not widely circulated, extensive quotations are made herein. The author is grateful to the U. S. Government Printing Office for permission to republish them.

The data from 34 laboratories had been obtained on 35 instruments, four of which had been built in the user's laboratory. The greatest number of anyone *model* of commercial apparatus was four. There were three of another and two each of three other models. The data, then, were from a fair variety of instruments; nevertheless, the general similarities of the sample holders assemblies enabled classifications and comparisons. The comparisons have been by a single parameter at a time, so a pair of instruments having many features in common might, in some comparisons, be in two separate classifications, each joined with instruments which may have *only* that feature in common. Consequently, there are not enough

* Permanent Address: The University of Akron, Akron Ohio 44 325, U. S. A.

data in many groups to justify firm conclusions *on the basis of these data alone*. From extensive related study by the present author, the additional conclusions given below are offered. Not all the conclusions reached by McAdie et al. are discussed here — only those on which further dissertation was judged to be needed — and warranted by the evidence.

McAdie *et al.* [1] calculated the values shown in Table 1. From these data they concluded:

1. The average standard deviation on *heating* for all compounds was $\pm 6^\circ\text{C}$ for the ONSET temperature, and $\pm 7^\circ\text{C}$ for the PEAK temperature.

Table 1

Mean temperatures with standard deviations, ranges of reported data, and number of data points for the standard reference materials

Compound	T_{eq}^a	Heating			Cooling		
		<i>N</i>	Onset	Peak	<i>N</i>	Onset	Peak
KNO ₃	127.7	63	128 \pm 5 (112–149)	135 \pm 6 (126–160)	31	22 \pm 4 (112–128)	119 \pm 4 (110–126)
In	157	59/60	154 \pm 6 (140–162)	159 \pm 6 (140–171)	29/27	154 \pm 4 (146–163)	150 \pm 4 (139–155)
Sn	231.9	57/59	230 \pm 5 (217–240)	237 \pm 6 (226–256)	22/18	203 \pm 16 (168–222)	203 \pm 17 (176–231)
KClO ₄	299.5	67/66	299 \pm 6 (280–310)	309 \pm 8 (296–330)	31	287 \pm 4 (278–296)	283 \pm 5 (274–295)
Ag ₂ SO ₄	430 ^b	64	424 \pm 7 (300–439)	433 \pm 7 (405–452)	30/27	399 \pm 14 (337–413)	399 \pm 15 (336–419)
SiO ₂	573	66	571 \pm 5 (552–581)	574 \pm 5 (560–588)	34/36	572 \pm 3 (565–577)	569 \pm 4 (559–575)
K ₂ SO ₄	583	67	582 \pm 7 (560–598)	588 \pm 6 (575–608)	30/31	582 \pm 4 (572–587)	577 \pm 8 (551–587)
K ₂ CrO ₄	665	63	665 \pm 7 (640–678)	673 \pm 6 (656–692)	31	667 \pm 5 (652–675)	661 \pm 8 (630–671)
BaCO ₃	810	71	808 \pm 8 (783–834)	819 \pm 8 (700–841)	29	767 \pm 13 (742–790)	752 \pm 16 (714–779)
SrCO ₃	925	67/66	927 \pm 7 (905–948)	938 \pm 9 (910–961)	31/30	904 \pm 15 (875–944)	897 \pm 13 (868–920)

^a See reference [4].

^b See reference [5].

2. The average standard deviation on *cooling* for all compounds was $\pm 8^\circ\text{C}$ for the ONSET temperature and $\pm 10^\circ\text{C}$ for the PEAK temperature.

The principal reason for the somewhat greater deviations for the cooling data is the variation in the point of measurement. Nearly all the materials transform without measurable superheating, but several do supercool substantially. Tin,

silver sulfate, barium carbonate and strontium carbonate supercool so badly that the good reproducibility of the cooling peaks of the other materials is hidden. As Table 1 indicates, the onset and peaks of the other materials are *more* reproducible than on heating.

The reason for the higher reproducibility is the nearer approach to temperature homogeneity within the sample holder assembly on cooling. The temperature distribution is distinctly different from the heating case because the entire assembly is the heat source, generating a heat flow by decreasing its temperature. This heat is radiated or conducted in all directions. On heating, however, this same radiation or conduction proceeds *except* for that part of the solid angle which the heater occupies. Note that during cooling *less* heat may be dissipated to the heater than to the rest of the surroundings. Nevertheless, the non-uniformity of the temperature distribution is distinctly less than in heating. The effect may vary substantially from one type of sample holder to another.

Now consider the heating process. There is at least some tendency toward temperature uniformity in the sample holder assembly in steady state heating, so all samples reach the reaction temperature at nearly the same indicated temperature. From this point on, the responses differ. The closer the measuring thermocouple to the sample itself, the less the indicated temperature interval of the reaction because the sample itself is influencing the temperature of the thermocouple. This is expanded upon later.

Now consider the cooling. Again, the process will begin at nearly the same indicated temperatures. The exothermic process arrests the cooling and hence the indicated temperature if there is much contact at all between the sample and the thermocouple. Because of supercooling, the sample actually reheats, and this is detected in some arrangements. This is indicated by the identity of the *average* ONSET and PEAK temperatures for both tin and silver sulfate. Radiation becomes so important at high temperatures that a lesser separation of the thermocouple from the sample is enough to cause the *measured* reheating to disappear. Now the statistics become dominated by the well separated thermocouple. Whether in the reference or somewhere else in the furnace, these are not affected at all by the reheating. They continue to register lower and lower temperatures, diminishing the average temperature and increasing the standard deviation of the whole set.

These conclusions are supported very clearly by Table 2, where the *interval* (defined *ad hoc* as the difference between the ONSET and PEAK temperatures) is tabulated for various locations of the temperature measuring thermocouple. The 00 location is typical of a sample block and deep cups with a recessed well. The 03 location is typical of shallow cups set on a thermocouple. Remembering that there are variations of sample holder type within these classes, the data still show that the central location 00 has the least change in the measured temperature on heating, but the greatest sensitivity to the supercooling. The sensitivity to supercooling implies clearly that the position provides the greatest sensitivity to the actual temperature of the sample. The 03 position is clearly the next best. The others, in effect, simply follow the temperature program.

Table 2

Interval of reaction by compound and location of temperature-measuring thermocouple

	Heating (PEAK minus ONSET)					
	00	03	10	21	30+	X
KNO ₃	5°C	8°C	10°C	5°C	7°C	3°C
In	3	4	7	5	4	—
Sn	3	7	10	7	5	—
KClO ₄	4	9	15	7	8	1
Ag ₂ SO ₄	6	9	12	6	8	5
SiO ₂	2	4	3	3	2	3
K ₂ SO ₄	4	6	11	4	5	3
K ₂ CrO ₄	4	8	16	6	6	3
BaCO ₃	8	9	12	11	12	6
SrCO ₃	14	9	16	11	10	—

	Cooling (ONSET minus PEAK)					
	00	03*	10+	21	30*	X
KNO ₃	2°C	0°C	4°C	3°C	4°C	0°C
In	4	1	4	4	—	—
Sn	-16	-7	1	4	—	—
KClO ₄	1	0	7	5	7	0
Ag ₂ SO ₄	-9	-6	3	5	2	7
SiO ₂	2	11	4	3	2	1
K ₂ SO ₄	2	20	7	5	4	0
K ₂ CrO ₄	3	23	7	6	4	1
BaCO ₃	14	27	10	18	—	-2
SrCO ₃	-13	14	9	9	—	—

00 In the sample, axially

03 In contact with the sample, axially

10 In the reference, axially

21 Location geometrically equivalent to sample and reference, non-axially

30 Location geometrically midway between sample and reference, axially

Data from a thermocouple location used by only one observer are not included. The data are calculated from the mean values without regard for the uncertainty as measured by the standard deviation.

* One observer

+ Two observers (three for a few data points)

X Identified in text later

Concerning the spread of data:

3. The spread of temperatures reported for a given transition on *heating* varied from 22 to 51°C for the ONSET temperature and from 23 to 51°C for the PEAK

temperatures. In both cases there was a tendency toward larger spread at higher transition temperatures.

4. The spread of temperatures reported for a given transition on *cooling* varied from 16 to 76°C for the ONSET temperature and from 16 to 83°C for the PEAK temperature. The freezing point of Sn and the $S_{II} \rightarrow S_I$ transitions in Ag_2SO_4 , $BaCO_3$, and $SrCO_3$ exhibited particularly wide spreads in both ONSET and PEAK temperatures on cooling.

The substantial spread arises from a number of factors, of course, but it is important to note that some observers' data were consistently lower and others consistently higher than the means, as seen in Figure 1. With the variety of sample holders and thermocouple locations such a spread should be surprising, but not very.

The melting metals show the lowest spread. This is in part because some of the observers did not report because their apparatus would not contain liquids; that is, sample holders tended to be more alike. In general, Table 1 shows that the range for phase transitions, except for $BaCO_3$ and $SrCO_3$, is in the vicinity of 30–35°C, already high enough. The highs and lows may and usually do have good agreement between their data, just as do those whose data fall near the mean. To illustrate, the present author's interval data on some of these compounds from the First International Test Program [3] are given in the last column of Table 1. The sample holder assembly was a block with an axial thermocouple, Type 00 in Table 2. The data are rounded to the nearest full degree. The data follow the same trends as do the total set.

The increasing spread of data with increasing temperatures may also be related to the different levels of sample-thermocouple interaction. The increase of the spread, though, is by no means proportional to the increasing temperature. The increasing importance of radiation helps to equalize temperatures within the sample holder assembly.

The spread of data for the cooling transitions of some materials has already been discussed, but it should be noted that, even with large supercooling, the transition *interval* may be small, because of the operational definition of the ONSET. The interval may approach zero because the release of energy brings the sample to the PEAK temperature so rapidly that the measured ONSET is virtually coincident with the PEAK. The data for $BaCO_3$ in the last column of Table 2 illustrates this. The supercooling is great but irreproducible. The irreproducibility is undoubtedly related to the magnitude; that is, a material well below its transition point, yet at a temperature allowing rapid motion, can be expected to be especially sensitive to nucleation. In the seven runs, positive intervals as high as 9° and negative intervals as high as -23°C were found [3].

Concerning agreement with accepted thermodynamic equilibrium values:

5. With the exception of Ag_2SO_4 , the mean ONSET temperatures on *heating* averaged -1°C of the accepted equilibrium transition temperature [4]. For Ag_2SO_4 an equilibrium temperature of 430 ± 3 degrees [5] appears to be more reliable than the 412 degree value cited [4].

6. With the exception of Ag_2SO_4 , the mean deviation of the ONSET temperature on *heating* from the accepted equilibrium transition temperature [4] was -1°C . Accepting that an equilibrium transition temperature for Ag_2SO_4 of $430 \pm 3^\circ\text{C}$ is more reliable than the 412°C cited by NBS [4], the mean deviation of the ONSET temperature from the equilibrium transition temperature was -1.5°C with a spread of -6 to $+3^\circ\text{C}$. The mean deviation of PEAK temperatures on *heating* was $+6^\circ\text{C}$ with a spread of $+1$ to $+9^\circ\text{C}$ from the equilibrium transition temperature.

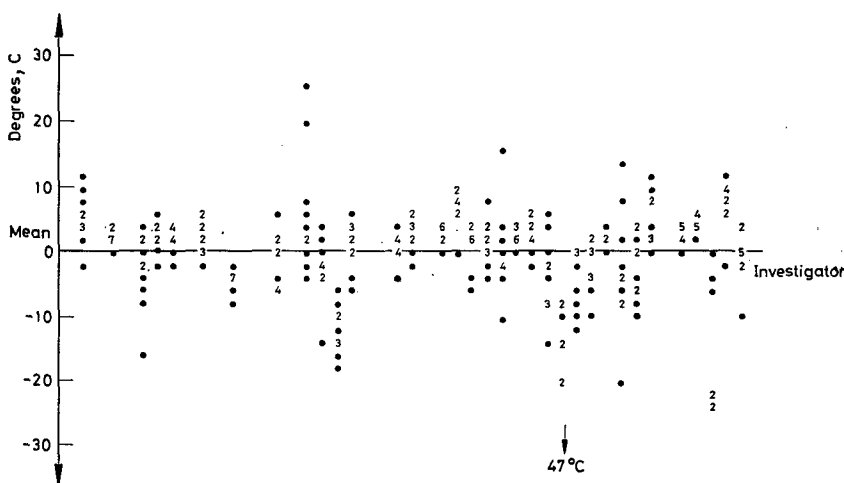


Fig. 1. Deviations from the mean values by individual investigators. Each vertical array of points represents the several deviations of a single investigator's means for a compound from the mean of all the data for that compound. From McAdie et al.

The good agreement of the DTA and thermodynamic values is partly fortuitous, as can be readily deduced from Table 1. Reasonably good agreement is to be expected because the same things are being measured. The agreement should not lead any individual worker to dispute reported thermodynamic values on the basis of DTA data without thorough analysis of his instrument's characteristics and unless he can demonstrate very good agreement for other known values. Yet a preponderance of evidence, as with silver sulfate, should lead to reconsideration of the "accepted" value.

The data quite naturally have some dissymmetry. This is inevitable because real differences in conditions caused the changes as compared to statistical error. A measure of the dissymmetry can be obtained from the spread shown in Table 1, where, in general, the lowest temperature is half again as far from the mean as the high temperature. A greater number of data points in the higher regions has brought the mean upward. From the other point of view, the greater amount of

close-lying data yielding higher temperatures has been influenced by some outlying lower temperatures. There are over half again as many data points above the mean in Figure 1 as below.

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The variations in the ONSET and PEAK temperatures found in the ICTA's Second International Test Program are related to the degree of separation of the measuring thermocouple from the sample. The cooling mode yields data at least equal in precision to the heating mode except for materials which supercool greatly.

References

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RÉSUMÉ — L'aptitude d'un appareil ATD à reproduire fidèlement tous les effets thermiques pouvant survenir dans un échantillon, diminue si on sépare le thermocouple ΔT de l'échantillon. Si l'enregistrement de la température s'effectue à l'aide d'un thermocouple séparé, qui ne soit pas en contact direct avec l'échantillon, on peut obtenir des données complètement erronées de la température de ce dernier dans le cas des substances qui ont une forte tendance à la surfusion. Ces conclusions résultent des données obtenues dans le cadre du programme-test de l'ICTA.

ZUSAMMENFASSUNG — Die Eignung eines Apparates zur getreuen Wiedergabe aller thermischen Vorgänge die in einer Probe stattfinden können, nimmt mit Separation des ΔT Thermoelementenpaars aus der Probe ab. Wenn die Temperatur durch ein gesondertes Thermoelementenpaar registriert wird und dies nicht eng mit der Probe verbunden ist, kann eine sehr ungenaue Information über die Proben temperatur bei stark superfrierenden Stoffen erhalten werden. Diese Ergebnisse wurden auf der Grundlage von bei dem ICTA-Kontrollprogramm erhaltenen Daten zusammengestellt.

Резюме — Показано, что способность аппаратуры к точному воспроизводству всех термических эффектов, имеющих место в образце, уменьшается с разделением ΔT термопары от образца. Если регистрируется температура совершенно отдельной термопары и термопары, которая не была тесно соединена с образцом, то это приводит к очень ненадежному определению истинной температуры образца, особенно, в случае сильно переохлажденных. Эти выводы сделаны исходя из данных, опубликованных по программе ICTA.