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MELTING TEMPERATURES OF REFRACTORY OXIDES : PART I

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Abstract

The values of melting points of selected refractory oxides were critically
assessed and the following recommended values are given (in $^\circ$C): SiO_2 1726 ± 10;
TiO_2 1892 ± 30; ZrO_2 2710 ± 25; Al_2O_3 2054 ± 6; Sc_2O_3 2485 ± 20; Y_2O_3 2439 ± 12;
MgO 2826 ± 30. No values for the melting points of BeO and CaO could be
recommended.

Melting temperatures /"melting points"/ of oxides represent basic refe-
rence points in phase diagrams used in high temperature chemistry, metallurgy,
ceramics etc. Many stable oxides are used as refractory materials, i.e. mate-
rials able to withstand temperatures above 1500°C without chemical change and
physical destruction; in this case the melting point is an important charac-
teristic indicating the maximum temperature of use.

A great number of values for melting points can be found in the litera-
re for refractory compounds but wide variation in reported values is quite
usual; general consensus does not exist. For this reason a Collaborative Stu-
dy Group was formed in 1976 within the Commission on High Temperatures and
Refractory Materials of IUPAC. Its members /C.B.Alcock, A.M.Anthony, J.P.Cou-
tures, J.Hlaváč, W.S.Horton, T.Sata/ were charged to make a critical assess-
ment of published melting point values for oxides and to suggest, if possible,
recommended or "best" values according to the present state of knowledge,
with estimated limits of uncertainty so wide that further determinations will
probably fall within these limits.

Fortunately an excellent basis for this work was available – a detailed
compilation of melting points of the metal oxides by Schneider /1,2/ which
presented all published data up to 1963, with descriptions of experimental
conditions and critical remarks on possible sources of error. The problems of
sample purity, furnace type, environments and temperature measurement were
also discussed. Original melting point values were corrected to IPTS 1948.

This paper will not repeat data and considerations from Schneider's study;
the interested reader is referred to that source. The following comment was
made by Schneider in the conclusion of his monograph: "No attempt will be ma-
de for the present to select one value over another as being absolutely cor-
rect. It is quite difficult to ascertain completely the validity of published
data without additional experimental work". Nevertheless there are some va-
lues of melting points in the monograph marked with an asterisk which are con-
sidered, by that authour, to be the best values among those listed.

Since the publication of this monograph new measurements of melting points
have been performed and published. Some form of critical assessment is still
lacking and seems to be useful also because data on melting points are often
spread in less known or interdisciplinary literature. This is the reason why
even recent articles and handbooks sometimes quote values which do not cor-
respond to the present state of knowledge.

In this article new data published since 1963 will be presented and discussed with reference to earlier data compiled by Schneider. It was also necessary to correct all data to the International Practical Temperature Scale 1968 /3/. Therefore only those earlier values were taken into consideration where corrections to IPTS were possible. It will be apparent from the following that the averages of earlier values in many cases do not differ much from more recent results but the latter show a lower scatter due to the fact that increasingly more attention has been paid by the experimenters to, for example, the temperature scales and standards, purity of the samples, and environmental effects. A similar experience was made in the context of the collaborative melting point determinations of Al_2O_3 and Y_2O_3 /see later/. If it was considered very difficult to prefer or recommend a certain value in 1963, this seems more feasible at present. However, the assessment cannot result from a simple statistical operation; more weight must be given to more recent values obtained under better defined experimental conditions.

The values which have been preferred in previously published surveys were also taken into consideration since they were prepared by experienced authors. The following generally recognized monographs were examined in addition to the primary literature:
E.M.Levin, C.R.Robbins and H.F.McMurdie: Phase Diagrams for Ceramists. Am.Ceram.Soc. 1964, Supplements 1969 and 1975;
A.Muan and E.F.Osborn: Phase Equilibria among Oxides in Steelmaking. Addison Wesley and Pergamon Press, 1965;
O.Kubaschewski, E.L.Evans and C.B.Alcock: Metallurgical Thermochemistry. Pergamon Press, 1967;
N.A.Toropov et al.: Diagramy sostoyania silikatnych sistem. /Phase Diagrams of Silicate Systems/ Vol.2., Nauka, Leningrad 1970;
I.Barin and O.Knacke: Thermochemical Properties of Inorganic Substances. Springer Verlag 1973, Supplement 1977.
JANAF Thermochemical Tables

In the following individual selected oxides will be discussed and new results /since 1963/ will be presented. The estimated uncertainty of the recommended value gives a range within which the "true" value is expected to lie. In many cases it is considerably larger than the accuracy given in the original paper where it usually means repeatability.

Silicon oxide SiO_2

Seven values for melting points for SiO_2 are quoted in Schneider's monograph, ranging between 1691 - 1850 /IPTS 1948/, with a preferred value 1723 ± 5°C. Measurements were carried out mostly in air, in one case in nitrogen, under reduced pressure and in undefined atmosphere.

Only one more recent value was found in the literature: 1734°C /see table 1/ in an article dealing with crystallization and melting kinetics of cristobalite /4/.

The average of all eight values /IPTS 1968/: 1733°C
The average excluding extremes   : 1719°C
The most frequently quoted value in
recent literature   : 1726 ± 5°C
                    Recommended value: 1726 ± 10°C

A wide consensus exists among the authors of compilations: the value by Greig /5/ - 1723 ± 5°C, i.e. 1726°C after correction to IPTS 1968 is preferred by Levin, Sosman, Kubaschewski, Toropov, JANAF, although sometimes the original uncorrected value 1713°C /IPTS 1927/ is still quoted. However, the accuracy given by Greig is too high in comparison with the differences among various authors. Therefore a wider range of uncertainty is given for the recommended value. In this case four values of eight fall outside but three of them originate from earlier literature /1913 - 1921/.

It is impossible to assess from published data the effect of the atmosphere but it does not seem to be significant. The recommended melting temperature is believed to characterize stoichiometric SiO_2 in the stable form of cristobalite.

Table 1. Melting temperatures of oxides /published since 1963/

Oxide	Melting temp. °C/IPTS 1968/	Purity of the sample	Environment	Furnace, container	Reference
SiO_2	1734	187 ppm impur.	dried Ar	ceramic tube, Pt foil	Wagstaff /4/
TiO_2	1870 ± 10 / 1900 ± 10 / 1912 ± 10	99.9 %	Ar / 75Ar-25O_2 / O_2	solar furnace,self-container	Coutures /7/
ZrO_2	2727 ± 20	99.9 %	air	solar furnace,self-container	Noguchi and Kozuka/22/
	2717	99.98 %	air	"	Foex /16/
	2704	99.9 %	air	" " "	Noguchi et al. /23/
	2746 ± 6	99.9 %		solar furnace	Yamada and Noguchi/24/
	2685 ± 15	>99.8 %		inductive,W-container sealed	Latta et al. /9/
	2710 ± 15	100 ppm impur.	vacuum	electron bombardment, W-cell /?/	Ackermann et al. /10/
Sc_2O_3	> 2409	99.9 %	air	induction,Ir-crucible	Schneider and Waring /25/
	2407	99.9 %	air	solar furnace,self-container	Noguchi and Mizuno/26/
	2480 ± 10	99.9 %	air	" " "	Coutures et al. /27/
	2489 ± 12	> 99.9 %	neutral or vacuum	tungsten	Shpilrain et al. /28/
BeO	2475 ± 20	not stated	argon	graphite tube,Ta-tube,Mo-wire	Engsberg and Zehms/29/
	2552 ± 9	99.9 %	-	vacuum furnace,W-capsules	Kandyba et al. /30/
	2560 ± 10	not stated	argon	graphite resistance tube	Riley /11/
	2430 ± 10	> 99.8 %	-	induction,W-capsules	Latta et al. /9/
MgO	2795 ± 20	not stated	pure Ar /?/	graphite resistance tube	Riley /11/
	2823 ± 40	99.5 %	$CO+CO_2+N_2$	inductive, MgO	Pánek /14/
CaO	2590	99 %	air	solar furnace,self-container	Noguchi et al. /21/
	2900 - 2950	99.99 %	air	solar furnace,self-container	Foex /15-19/
	2617 ± 30	spec.pure	$CO+CO_2+N_2$	inductive, CaO	Pánek /14/

Titanium oxide TiO_2

There are as many as eleven original papers cited in Schneider's monograph with values for melting points ranging between 1716 - 1870°C, measured in vacuum or /mostly/ oxidizing atmospheres. The lowest value was found in vacuum - 1716°C. All other values lie within the range 1820 - 1850°C in air, and 1840 - 1870°C in an oxidizing atmosphere with p_{O_2} = 4 x 10⁴ - 1 x 10⁵ Pa. The average for air is 1843°C ± 15°C /corrected to IPTS 1968/; all eight values except one fall into this range - five of them even within the range of ± 5°C which is an extraordinary agreement.

Recommended value: 1843 ± 15°C /air/

However, TiO_2 melted in air is not stoichiometric; the ratio O:Ti is lowered to 1.985, reaching 1.999 in pure oxygen/Coutures /7//. Only two experiments were performed in oxygen:

Brauer and Littke /8/ - 1873 ± 15°C
Coutures /7/   - 1912 ± 10°C

The difference between melting points in air and oxygen seems to be relatively high when one considers the slight deviation in stoichiometry. New measurements are desirable.

Zirconium oxide ZrO_2

The values for melting points published before 1963 /see Schneider's monograph/ which permitted the temperature conversion to IPTS 1948 ranged between 2519 and 2850°C /eight values/. The atmosphere was air, inert gas or hydrogen. Six more determinations were published since 1963 /see table 1/.

The average of eight values up to 1963 /IPTS 1968/: 2680°C
The average excluding extremes   : 2676°C
The average of six values since 1963   : 2715°C

The most frequently quoted values in secondary literature range between 2680 and 2710°C but recent measurements shift the melting temperature to the higher limit of this range.

According to Latta et al./9/ an oxygen deficiency may be presumed in the sample corresponding to the formula $ZrO_{1.998}$. At this composition the liquidus temperature estimated is within 1 - 2°C of the congruent melting point. Ackermann et al./10/ report that the oxide of composition $ZrO_{1.95}$ formed a liquid phase at 2685 ± 15°C. A short extrapolation of the phase boundary yields a m.p. of 2710 ± 15°C for stoichiometric ZrO_2.

Recommended value: 2710 ± 35°C

Aluminium oxide Al_2O_3

A cooperative determination of the melting point of alumina was conducted by a Task Force sponsored by the Commission on High Temperatures and Refractory Materials of IUPAC between 1965 and 1969, under the coordination of Schneider. Nine scientific groups representing seven countries contributed experimental data. All work was performed utilizing a common supply of Al_2O_3 of nominal 99.9 % purity. Experimental techniques varied depending upon the individual investigators; the atmosphere was air, argon or vacuum. The value for the alumina melting point as recommended by the Task Force is 2054 ± 6°C /IPTS 1968/. Furthermore it was recommended to include the alumina melting point as a secondary reference point on the IPTS /see J.Pure Appl.Chem. 21, 117 - 122, 1970/.

Recommended value: 2054 ± 6°C

Scandium oxide Sc_2O_3

The results of four experimental studies are shown in the table 1. The range is 2407 - 2489°C. Because of very good agreement of the two recent measurements the conclusion is:

Recommended value: 2485 ± 20°C

Yttrium oxide Y_2O_3

A similar cooperative determination as mentioned for Al_2O_3 was performed

later, under the coordination of Foex, for yttria of high purity. Ten labora-
tories participated in the investigation. The measurements were carried out
mostly in air or under vacuum, in one case in He and O_2. The atmosphere did
not affect the melting point because yttria is practically stable at the re-
levant temperature under oxidizing or inert conditions.
It was concluded also that yttria would make a useful secondary temperature
standard although the value of $2439 \pm 12^{\circ}C$ obtained by averaging the results
of ten laboratories needs to be more precise for this purpose /see M.Foex in
High Temperatures-High Pressures $\underline{9}$, 269 - 282, 1977/.

<center>Recommended value: $2439 \pm 12^{\circ}C$</center>

Beryllium oxide BeO

Six earlier values reported in Schneider's monograph /where corrections
to IPTS 1948 were possible/ range between 2410 and $2573^{\circ}C$. The determinations
were performed in an oxidizing or inert atmosphere. Possible sources of error
are also noted by Schneider. Two additional values of earlier origin are in-
cluded in table 1; in both cases the measurement of melting temperature was
only a supplementary part of the study. The most recent values by Riley /11/
$-2560^{\circ}C$ and by Latta et al./9/ $-2430^{\circ}C$ reflect the existing discrepancy in
melting point data for BeO: the reported values can be roughly divided into
two groups about the mentioned values.

This discrepancy cannot be explained by the fact that reported values
might refer to α-BeO in some cases and to β-BeO in others /the transformation
occurs at $2050 \pm 50^{\circ}C$/. As stated in the JANAF 1974 review: "α-BeO should
melt ∿ $40^{\circ}C$ below β-BeO. Enthalpy data of Kandyba et al. suggest that their
sample may have remained as α-BeO, yet they reported $T_m = 2547^{\circ}C$. In contrast
$T_m = 2430^{\circ}C$ was found for β-BeO by Latta et al.; their thermal analysis show-
ed both T_t and T_m."

The JANAF Tables /Dec.31, 1974/ suggest - as a result of the critical
assessment - two values for the melting point of BeO: $2507 \pm 100^{\circ}C$ for the
α-polymorph and $2548 \pm 100^{\circ}C$ for the β-polymorph. The first value was adopted
as a compromise from published data and the value for β-BeO was obtained from
thermodynamic calculation.

However, the published information indicates that the polymorphic trans-
formation at $2050^{\circ}C$ is reversible and rapid /see for example, Smith and Cline
in J.Nucl.Mat. $\underline{6}$, 265, 1962/. Furthermore no apparent dependence of the melt-
ing temperature on the environment was observed; BeO is quite resistant to
reduction. The reason for the large scatter in the experimental data cannot
be deduced from published information.

A value cannot be recommended for the melting temperature of BeO; instead
one can only say that it probably lies between 2420 and $2580^{\circ}C$. This range
includes all experimental values published so far except one /Ruff and Lau-
schke, 1916 - $2410^{\circ}C$/.

Magnesium oxide MgO

Three original papers cited in Schneider's monograph result in values for
the melting point ranging between 2150 and $2852^{\circ}C$; the value preferred by
Schneider is from Kanolt /12/ $2852^{\circ}C$. The most recent value quoted there is
by McNally et al./13/ - $2825 \pm 20^{\circ}C$ /all IPTS 1948/.

Another measurement was published later by Riley /11/ - $2790^{\circ}C$. A new
measurement was carried out within the scope of this study by Pánek /14/ with
the resulting value $2823 \pm 40^{\circ}C$ /IPTS 1968/. The average of the four values
/after correction to IPTS 1968/ gives:

<center>Recommended value: $2826 \pm 30^{\circ}C$</center>

Calcium oxide CaO

Four original melting point measurements are cited in Schneider's mono-
graph, ranging from 2565 to $2630^{\circ}C$ /corrected to IPTS 1948/; the preferred
value is $2614^{\circ}C$ /12/.

According to more recent measurements carried out by Foex and coworkers
/15 - 19/ the melting point of CaO is 2900 - $2950^{\circ}C$, i.e. $300^{\circ}C$ higher than
the value reported earlier. The reasons for this surprising discrepancy as
suggested by Foex may be:

a/ formation of tungstates by reaction with tungsten supports in earlier measurements; b/ absorption by vaporized compounds influencing the pyrometric measurement.
Both sources of error were believed to have been eliminated in measurements performed by Foex and the following values were reported: 2900, 2910 and 2950°C. The value given in JANAF Tables 1974 is 2927°C with 50°C as arbitrary uncertainty.

A new measurement was carried out by Pánek /14/ within the scope of this study /see table 1/. A pellet of CaO was placed into the furnace near to a pellet of MgO so that their behaviour could be compared. In all ten experiments performed CaO melted at a lower temperature than MgO. In separate experiments the following melting temperatures were found: 2617 ± 30°C for CaO and 2823 ± 40°C for MgO. Because the value for MgO corresponds very well to other measurements /see preceding paragraph/ it is believed that the value for CaO is also correct. Moreover it is in very good agreement with the other group of values reported earlier. Excluding extremes we have: 2619 /12/, 2625 /20/, 2590 /21/ and 2617 /14/. From these data a melting point value can be deduced as 2613 ± 25°C.

The recent results given above show a wide discrepancy, and therefore new measurements are desirable.

CONCLUSION

As a result of the first part of the collaborative study following values of melting temperatures for selected oxides are recommended /in°C/:

SiO_2 – 1726 ± 10 Al_2O_3 – 2054 ± 6   BeO – /*
TiO_2 – 1843 ± 15 /air/* Sc_2O_3 – 2485 ± 20   MgO – 2826 ± 30
ZrO_2 – 2710 ± 35 Y_2O_3 – 2439 ± 12   CaO – /*

The values for Al_2O_3 and Y_2O_3 were established in an international experimental cooperative programme and have received general acceptance. The values for SiO_2, TiO_2, ZrO_2, Sc_2O_3 and MgO were deduced from published data which do not exhibit extraordinary discrepacies. The scatter of data for BeO is at present too large and new measurements are desirable. The existing discrepancy for the melting point of CaO also does not allow recommendation of any final value until new measurements have been made.

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/*see text

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ERRATA

Volume, Issue and Year	Page no. and location	Correction
49, 5 (1977)	671-673	In the "Recommended Reference Materials for the Realization of Physicochemical Properties – Section: Absorbance and Wavelength" infrared absorption bands were suggested as reference for wavenumber calibration. More recent revised data have been published by IUPAC in a book entitled <u>Tables of Wavenumbers for the Calibration of Infrared Spectrometers</u> compiled by A.R.H. COLE (Pergamon Press, Oxford, 1977). Wavenumbers appearing in sections II/8, II/9, II/10 and II/11 of Recommendations on Reference Materials should be replaced by the values published by COLE.
54, 1 (1982)	208, Abstract, line 2	<u>for</u> 'dexcy' <u>read</u> 'deoxy'
	209, column 2, 3rd name	<u>for</u> 1,1,2,2-Tetrahydro <u>read</u> 1,1,2,2-Tetradehydro
	210, column 1, 4th name	<u>for</u> 6,7,7,8-Tetrahydro <u>read</u> 6,7,7,8-Tetradehydro
	214, column 2, structure for Cladinose	<u>for</u> (structure) <u>read</u> (structure)
54, 3 (1982)	681, Abstract, line 3	<u>for</u> TiO_2 1892 ± 30 <u>read</u> TiO_2 1843 ± 15 (in air)
		<u>for</u> ZnO_2 2710 ± 25 <u>read</u> ZnO_2 2710 ± 35
54, 8 (1982)	1455, Table 1 (i) column $-\Delta H_h^o$ for Hg^{2+}	<u>for</u> 1940 <u>read</u> 1845
	(ii) footnote a to Table 1	<u>add</u> ΔH_h^o of Hg^{2+} has been misprinted in Ref. 19
	1457, Table 2 column 1, last item	<u>for</u> BP_4^- <u>read</u> BPh_4^-
	1459, Table 3 column 1, 12th item	<u>for</u> $Hg(\ell)/Hg^{2+}$ <u>read</u> $Hg(\ell)/Hg_2^{2+}$
54, 10 (1982)	1859, Eq.(14)	correct version is as follows:

$$M^{\diagup O}{}_{\diagdown OR} \; + \; {}_{\diagup}^{}C = C_{\diagdown}^{} \; \rightleftharpoons \; M^{\diagup O}{}_{\diagdown OR} \atop {}_{\diagup}^{}C \overset{\bullet}{=} C_{\diagdown}^{} \; \rightarrow \; M^{\cdot O}{}_{\diagdown O}^{\diagup R} \atop {}_{\diagup}^{}C - C_{\diagdown}^{} \; \rightarrow \; M\text{-}OR \; + \; {}_{\diagup}^{}C - C_{\diagdown}^{} \atop O \qquad (14)$$

$\underset{\sim}{4'}$