Table V. Application of the Cross-Square Rule

Salt Pair	$D'_{0.5}$ 12° C.	$D'_{0.5}$ 25° C.	$D'_{0.5}$ 38° C.
Li_2SO_4-LiCl	0.225	0.206	0.196
Na_2SO_4-NaCl	0.280	0.265	0.261
Li_2SO_4-Na_2SO_4	−0.054	−0.039	−0.023
LiCl-NaCl	−0.079	−0.060	−0.044
$\Sigma\square$ =	0.372	0.372	0.390
Li_2SO_4-NaCl	0.386	0.373	0.363
Na_2SO_4-LiCl	0.002	0.017	0.038
ΣX =	0.388	0.390	0.401

NOMENCLATURE

a,b,c = constants in the equation $\phi'_t - \phi'_0$ or $\Phi'_t - \Phi'_0 = at + bt^2 + ct^3$ representing the equivalent volume or mean equivalent volume as a function of the temperature at constant ionic strength
α,β,γ = constants in the equation $d_t - d_0 = \alpha t + \beta t^2 + \gamma t^3$ representing the density of a solution as a function of temperature
d_0 = density (g./ml.) of a solution at 0° C.
d_1 = density (g./ml.) of water at a given temperature
d_2 = density (g./ml.) of a solution containing a single electrolyte
d_3 = density (g./ml.) of a solution containing two electrolytes
d_t = density (g./ml.) of a solution at temperature t
D' = volume change in ml. per equivalent observed on mixing two solutions at constant ionic strength
$D'_{0.5}$ = volume change in ml. per equivalent observed on mixing two solutions to give an equivalent fraction of 0.5
E_2 = weight equivalent fraction of salt 2
E_3 = weight equivalent fraction of salt 3
m = molality (moles solute per 1000 grams of water)
M = molecular weight of a solute
μ = ionic strength of a solution in moles per 1000 grams of water
p,p' = numerical factor to convert molality to equivalents per 1000 grams of water. $p = 1$ for NaCl and LiCl, p 2 for Na_2SO_4 and Li_2SO_4
ϕ'_2 = apparent equivalent volume (ml. per equiv.) of salt 2 in a solution containing only salt 2 and water
ϕ'_3 = apparent equivalent volume (ml. per equiv.) of salt 3 in a solution containing only salt 3 and water
Φ' = mean apparent equivalent volume (ml. per equivalent) of the solutes present in a solution
t = temperature in degrees centigrade

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Melting Point of 98.9 to 99.6% Pure Boron

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The melting points of four grades of boron varying in their respective purities from 98.9 to 99.6% were determined to be in the range of 3733° to 3766° F. (2056° to 2074° C.), respectively. The values were obtained by using four methods of experimental approach, and comparison of the values for each approach is presented. An endothermic action on heating boron was noted at about 3625° F., and supercooling of liquid boron as much as 200° F. below its melting point was encountered.

PUBLISHED values for the melting point of boron differ appreciably, ranging from 3550° to 4170° F. (1950° to 2300° C.) (*1, 2, 4, 6-8*). During the course of related work with boron, for which a more accurate value of its melting point was needed, melting points were determined in the present investigation for four grades of boron ranging in purity from 98.9 to 99.6% of boron. The results are reported to provide additional and more statistical information concerning the melting point of this material.

GRADES OF BORON INVESTIGATED

Sources and Analyses. Four grades of boron powder from four vendor sources were employed in this investigation. The sources are identified and reported purity of respective grades are given in Table I. All powders except that of Callery Chemical Co. were within the sieve-size range of from 100- to 20-mesh and were free flowing. The Callery powder was of extremely small size (1 micron), fluffy, and difficult to work with until prepressed pellets were formed in a boron nitride die to achieve adequate weight loading of crucibles. All analyses for impurities other than for carbon were made spectrographically. Carbon was determined by the Pregyl method (*9*).

Effect of Remelt on Specimen Purity. In the course of preliminary work to determine a satisfactory material for the containment of boron, boron nitride was most successful. Although this crucible material seemed from outward appearances to be completely compatible with a boron melt, its compatibility was quantitatively investigated to determine whether specimen melts were significantly affected in composition. Crucibles were machined from BN stock supplied by the Carborundum Co. with reported impurities of 0.10% alkaline earth oxides, 0.2% alumina-silica, and 0.01% carbon. Prior to use, the crucibles were subjected to 2800° F. for 30 minutes at 10^{-3} torr pressure followed by 15 minutes' exposure to 3150° F. in argon at atmospheric pressure. This procedure removed the boric oxide binder used in preparing the crucible stock and precluded its subsequent reappearance at high temperature as a white vapor hindrance to optical temperature measurement.

The results of melting a single specimen of Callery boron three times are shown in Table II, in which the composition

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Table I. Typical Analyses of Grades of Boron Investigated

Source[a] Reported	U	Ca	EP	Co-Al	Co-A2
Purity, %	98.4	99.0	99.99	99.0	99.0
Element	Impurity Analyses[b], %				
Fe	0.16	ND[c]	0.028	0.16	0.096
Si	0.04	0.005	0.09	0.058	0.032
C	0.51	0.42	0.28+	0.74	0.27
Mn	0.10	ND	ND	ND	ND
Mg	0.004	0.003	0.003	0.002	0.004
Al	0.12	ND	ND	ND	ND
Ca	0.03	ND	ND	ND	0.008
Cu	0.004	ND	0.002	0.005	ND
Ni	0.03	ND	ND	0.12	0.094
Cr	0.09	ND	ND	ND	ND
Impurity total	1.008	0.428	0.403	1.085	0.504
Analyzed purity	98.99	99.57	99.60–	98.92	99.50

[a] U = U. S. Borax and Chemical Corp., Anaheim, Calif. Ca = Callery Chemical Co., Callery, Pa. EP = Eagle-Picher Corp., Miami, Ohio. Co-Al & Co-A2 = Cooper Metallurgical Corp., Cleveland, Ohio. [b] Analyses made on receipt of material. [c] ND = not detected.

of the specimen before and after the experiment may be compared. With the exception of silicon and calcium, which showed no change, repeated melting indicated a general purification of the specimen.

APPARATUS AND PROCEDURES

Furnace. The design of apparatus employed in determining melting point data is illustrated in Figure 1. It consists of melt crucible and pedestal, induction heater, radiant heat shielding, and an atmosphere container (not shown). The crucible, crucible lid, pedestal, and the two innermost insulating shields were machined from hot-pressed boron nitride and pretreated, as noted above, prior to use in the apparatus. The crucible had a wall thickness of nominally 0.055 ± 0.0003 inch and an internal diameter of 0.50 inch; the depth of the crucible was about 1.40 inches. When partly filled with boron powder, the ratio of the distance between the lid and the top of the powder to the diameter of sight hole in the lid (L/d) was never less than 6. Heating of the specimen was accomplished by conduction through the thin crucible wall of heat radiated from the induction-heated tantalum sleeve susceptor encircling the crucible. Specimen heating was controlled by a rheostat-operated 100-kw., General Electric, 10-kc. generator unit, which energized the seven-turn, water cooled coil. In early work, the furnace assembly (Figure 1) was enclosed in an open-top borosilicate glass bell jar; a water cooled steel enclosure with a Vycor top viewing window recessed in the lid subsequently replaced the bell jar.

Temperature Measurement. METHOD. All temperature measurements were made with a Model No. 95 Microptical Pyrometer (Pyrometer Instrument Co., Bergenfield, N. J.) accurate within 0.5% at 3800° F. and calibrated against a NBS tungsten lamp by the Aerojet Measurement Standards Laboratory. The sight path from the specimen passed through the hole in the crucible lid and the 1-inch diameter opening in the top of the bell jar (or a Vycor window in the lid of the steel enclosure) to a back surface reflection mirror and thence to the pyrometer. Calibration curves for the mirror and for the mirror-Vycor window system of the steel enclosure were prepared for the temperature range 1850° to 4000° F. by sighting onto a notched tungsten filament lamp energized from a constant voltage (accuracy ±0.01%) source. Observed temperatures were then corrected to provide an apparent true temperature.

Table II. Chemical Analyses of Boron[a] before and after Melting in BN Crucibles

Element	Impurity Analysis, % Before melting	Impurity Analysis, % After 3 melts
Si	0.042	0.043
Al	0.051	0.038
Cu	0.003	0.002
C	0.520	0.340
Fe	0.160	0.072
Mg	0.003	0.001
Ca	0.007	0.007
Totals	0.786	0.503

[a] Callery Chemical Co., Lot No. 2782-23-2.

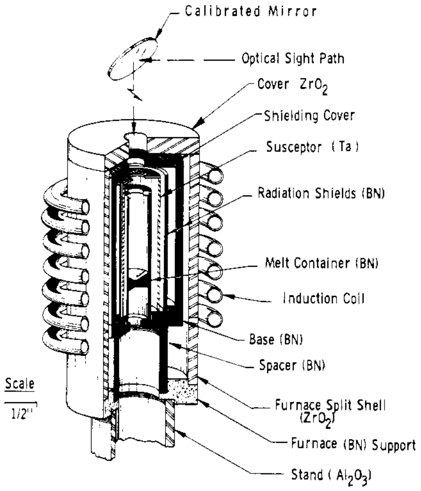

Figure 1. Induction-heated melting furnace

OBSERVER, WINDOW CLOUDING, AND NONBLACKBODY ERROR. Pyrometer temperature values were cross-checked routinely by one observer and then the other reading the pyrometer. No systematic observer error in temperature readings was noted—i.e., neither observer was consistently higher or lower than the other, nor did the source temperature appear to affect the amount of the apparent difference. The differences between observers were normally less than 5° F.

A typical correction encountered in optical measurements from furnaces within an enclosed system is that necessitated from the absorption of radiation by deposited vapor on system windows. The need of such a correction in this work was effectively circumvented with both the glass and steel enclosed systems by employing the following procedures: Furnace hardware was thermally treated prior to use to remove all volatile foreign constituents; the sight path passed through an open-top (1-inch diameter opening) bell jar in the glass enclosed system; and a continuous argon purge throughout heating and cooling cycles was used to sweep any other vapor products from both the glass and steel enclosed systems. In the latter system, argon was introduced through the lid and removed from the bottom of the enclosure, a direction counter to the thermal buoyancy of vapor; with this procedure, the pretest clarity of the sight path window was shown during calibration test of the enclosure not to change significantly—i.e., respective pre- and post-test readings taken through the window onto a calibrated lamp filament temperature of 3700° F. differed, if at all, only by an amount apparently within the operators's ability to read the same temperature within ±5° F.

DeVos (*3*) describes the conditions and gives the equations for nonuniform absorption and emission in a blackbody-type cavity. He shows that for a hole in a long cylinder (the normal viewing conditions in this program), at depth-to-diameter ratios of six, an emissivity value of 0.988 can be expected; at a ratio of 10, emissivity value of 0.997 to 0.998 can be expected even if the radiation is only partially diffuse. The practical maximum emissivity is 0.999, which occurs at length-to-diameter (L/D) ratios of 15 or more for both partially and totally diffuse radiation.

Because some temperature error normally would be expected owing to departure from blackbody conditions, several experiments were designed to estimate such error and to establish that blackbody conditions were closely approached with the standard crucible setup. The experiment best illustrating that essentially blackbody conditions existed in the standard crucible setup was that in which a thin-walled (15 mils), hollow boron nitride stem (I.D. = 30 mils; L/D = 14) was positioned in the center of the crucible. When the crucible was about half filled with the powder specimen around the stem, the distance lid-to-powder surface divided by the diameter of the crucible lid sight hole gave an L/D = 5. Thus, observation of the end of the deep stem cavity and that of the powder "surface" permitted simultaneous measurement and comparison of the two temperatures observed at the two respective ratios (L/D). At temperatures up to 2800° F., a difference of about 10° F. was noted between the observed "surface" temperature of the powder (viewed between surface grains as outlined by a brighter subsurface intensity) surrounding the stem and the temperature with the stem cavity. Above 2800° F. there was no measurable difference (within observer error limits). This is particularly significant in view of the fact that the distance between the lid and the powder surface was less in this instance than that to be used with the standard melt crucible (L/D = 6.5). Therefore, since essentially blackbody conditions existed on the surface of the powder in the described experiment, they were assumed to be present in the standard melt crucible where a powder-fill height of one half or less of the crucible depth was employed.

Experimental Technique. Four approaches to establish the melting point were employed and are described below.

Powdered Specimens. Powdered boron as received from vendors ranged in sizes from 20- to 100-mesh, and 1 micron maximum particle dimensions. With the exception of the latter size, as-received powders were placed in a crucible and temperatures at liquefaction were determined when change of state was evidenced. Prepressed pellets of the 1 micron size powder were necessary merely to permit a significant quantity of this material to be placed in a crucible.

Solid Specimens. Solid ingots formed by melting powder were frequently remelted as a single ingot or in a broken up form of relatively large pieces. Melting points were easier to determine than for powder, particularly when the solids had sharp corners or edges. The temperature at which these outlines became rounded were relatively easy to discern against the background of more near blackbody radiation emanating from the interparticle pores in the immediate subsurface zone.

Disappearing Hole. This is a conventional approach whereby the melting point is assigned as that temperature at which a hole in a solid specimen of material collapses when the change in state to liquid occurs. Solid button specimens having a central hole 0.060 inch in diameter by 0.375 inch (minimum) long were prepared by melting boron powder around a thin-walled (0.015 inch), hollow boron nitride stem. During this specimen preparation, melting temperatures of the powder were measured by sighting into the center of the stem. Following removal of the stem, the boron button was placed in a standard melt crucible for test.

Piston Movement. In the course of related work, a miniature extrusion assembly (Figure 2) was constructed of boron nitride as a method to determine the viscosity of molten boron. Movement of the weighted piston occurred initially upon consolidation of the charge in the crucible and finally upon melting and extrusion of the specimen. Temperatures at the instant of final movement were recorded as auxiliary melting point data. Temperatures were measured using the cavity provided in the section of the piston protruding into the specimen.

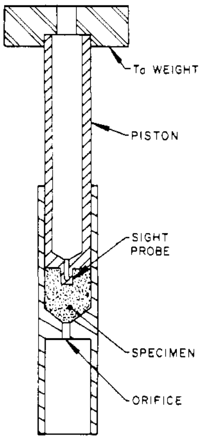

Figure 2. Piston extrusion assembly

Test Procedure. The atmosphere chamber was sealed and the assembly was evacuated to 10^{-3} torr, then backfilled to 700 torr with high-purity argon (−80° F. dewpoint). This cycle was repeated three times followed by purging for 5 minutes with argon at a rate of 10 cubic feet per hour. A steady argon flow of 5 cubic feet per hour was then provided during the test and during furnace cooling.

Specimen heating was controlled by a rheostat-operated 100-kw., General Electric, 10-kc. induction unit. Approximately 30 minutes were required to reach the melting temperature. It proved practical to set the power level to produce a temperature just below the boron melting point and to allow the temperature to rise slowly to or through the melting point with little or no additional power increase. Excepting the piston method, the surface of the boron powder was examined for evidence of melting, which was shown by experience to be manifested by the appearance and coalescence of cool areas that appear as dark spots on the surface. The onset of melting could be visually identified.

DISCUSSION OF RESULTS

A total of 165 melting point determinations are reported. These data are summarized in Table III for each of the several grades of boron investigated and for the method by which the data were produced. These values represent the arithmetic mean of melting temperatures in any given category and have an estimated accuracy of ±0.5%; in terms of precision, each tolerance shown is the mean square error obtained by the equation:

$$E = \left[\frac{\Sigma d^2}{N}\right]^{1/2}$$

where E represents the mean square error, d is the deviation of an observed temperature from the mean temperature, and N denotes the number of observations.

Melting Point Values. The earliest work of the program was done with boron (U.S. Borax Co.) in a standard crucible. Because of the uncertainty existing at that time as to the melting temperature to be expected, a series of crucible powder charges were individually subjected to temperatures progressively lower than an arbitrarily selected 4000° F. The appearance of these specimens (Figure 3) forecasted a melting point value for this grade of boron bracketed between 3714° and 3737° F.

The summary of data for all grades (Table III) indicates that the melting point of boron within the nominal purity

Table III. Summary of Melting Point Data for Several Purities of Boron

Grade and Specimen, Form/Method	Belljar Assembly		Steel Assembly	
	Obsd. M.P., E[a] ° F.	No. tests	Obsd. M.P., E[a] ° F.	No. tests
U. S. Borax, 98.99%				
Powder, as received	3737 ± 40	12	3733 ± 31	21
Preformed ingot	3748 ± 31	5	3729 ± 42	15
Disappearing hole	3717 ± 30	6	...	...
Piston, powder	3731 ± 33	11	...	...
Piston, ingot	3741 ± 24	18	...	...
Assembly mean	3735 ± 32	...	3731 ± 36	...
Mean	3733° ± 34° F., 88 tests			
Cooper Met. Associates-Grade A, 98.9 to 99.5% B				
Powder, as received	...	...	3753 ± 30	23
Preformed ingot	...	...	3759 ± 24	22
Mean			3756 ± 27	...
Eagle Picher, 99.60% B				
Powder, as received	3779 ± 26	3	...	...
Piston, powder	3769 ± 20	3	...	...
Piston, ingot	3753 ± 25	14	...	...
Disappearing hole	3765 ± 19	4	...	...
Mean	3766 ± 22	...		
Callery Chemical, 99.57% B				
Powder, prepressed	3750	1	...	...
Piston, ingot	3758 ± 6	7	...	...
Mean	3757 ± 6	...		

[a] Mean square error.

range of 99 to 99.6% varies from about 3733° to 3765° F. (2056° to 2074° C.), respectively. The data imply that pure boron would exhibit a slightly higher melting value than has been determined here. The three most pure grades show melting temperatures considered to be in good agreement with one another and with their respective purities. The small difference of 23° F. between the U.S. Borax and the Cooper boron, the latter of which does not appear to reflect its 98.9% purity in a lower melting temperature as much as does the former, is attributed to the greater number and identity of elemental impurities inherent in the U.S. Borax material.

Thermal Arrests. In a number of instances prior to melting, when comparatively slower heating rates than usual existed, a sudden lowering of specimen temperature during constant power input was observed between 3625° and 3650° F.; the drop in temperature amounted from 25° to 75° F. Reasonable certainty exists that this occurrence was not attributable to the induction heating procedure employed. It was observed more frequently with ingot rather than powder specimens and was noted with boron of both the lowest and the highest purities. A suggested explanation of this thermal reaction is that a new, though thermally unstable, phase of boron may occur in this region of temperature. According to Hoard (*5*), the highest form currently known to exist above 2730° F. is β-rhombohedral boron.

Supercooling of Melts. The earliest experiments in melting boron were performed by furnace quenching the samples after melting had been achieved. In later work, the procedure employed a very slow and controlled cooling rate to minimize damage to furnace components. In the latter work, the samples did not solidify until a temperature of about 3555° ± 15° F. was reached. Typical liquid surface motion could be seen until the temperature fell below 3600° F.; below this temperature range, the surface exhibited some slight motion, but appeared sluggish in character. As soon as the state change to solid was complete, sample temperatures fell very abruptly. These data indicate supercooling of boron in the liquid state was achieved through nearly 200° F. below its melting point temperature before solidification occurred.

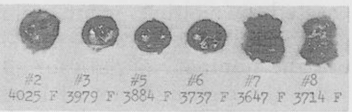

Figure 3. Boron ingot appearance at various temperatures

CONCLUSIONS

The melting point of boron within the nominal purity range of 99 to 99.6% boron varies from 3733° to 3766° F. (2056° to 2074° ± 19° C.), respectively.

Thermal arrest was noted on heating boron in the range of 3625° to 3650° F. (1996° to 2010° C.).

Boron may be supercooled as a liquid by as much as 200° F. below its melting temperature.

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