



# RESEARCH MEMORANDUM

A REVIEW OF THE PHYSICAL AND THERMODYNAMIC PROPERTIES  
OF BORIC OXIDE

By Paul C. Setze

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RESEARCH MEMORANDUM

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PROPERTIES OF BORIC OXIDE

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SUMMARY

A review of the current literature on the thermodynamic and physical properties of boric oxide ( $B_2O_3$ ) was made. What were considered to be the most accurate data available on each of the following properties are presented in tabular and graphical form: specific heat, sensible enthalpy, total enthalpy, entropy, latent heat of vaporization, and vapor pressure for the crystal, liquid, and vapor states. Also given are data on specific gravity, surface tension, viscosity, and electrical resistivity. In addition, basic molecular and structural data are presented.

A discussion of each property is included, and reasons are stated for choosing one set of data in preference to another.

INTRODUCTION

In 1951 reference 1 was published giving tabulated data on the thermodynamic properties of a number of chemical elements and compounds. Among these compounds was boric oxide. Since that time new data on the properties of boric oxide have become available. This report reviews the published literature, presents what are believed to be the most accurate data now available on both the thermodynamic and physical properties of boric oxide, and extends the data where possible. This review is especially important in the light of some unreported experimental observations which make the extrapolation of existing data questionable. These cases will be discussed.

A search of the literature was made, and the data are presented in both graphical and tabular form. Each property

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is briefly discussed and the reasons for choosing one set of data in preference to another indicated.

A list of the symbols used in this report is given in appendix A.

### THERMODYNAMIC PROPERTIES

An extensive review of the literature on the thermodynamic properties of boric oxide is presented in reference 1, which provides tabulated data on specific heat, sensible enthalpy, total enthalpy, entropy, and equilibrium constants for the crystalline, liquid, and gaseous states. These data are being extensively used at the present time. However, more recent data on the vapor pressure, specific heat, enthalpy, and entropy of boric oxide make it desirable to recalculate the data of reference 1. This recalculation has been done, and a summary of the revised thermodynamic data is given in figure 1 and table I. A discussion of each of the separate thermodynamic properties follows.

#### Specific Heat

The specific heat data for boric oxide crystal, glass, and liquid are taken from a private communication received from the National Bureau of Standards. These values are based on experimental data which have a good order of accuracy. The glass and liquid data have been faired to a smooth curve in the range 900° to 1800° K and extrapolated to 2500° K. New values of the vapor specific heat were calculated using the method presented in reference 2. This method assumes the molecule to be a rigid harmonic oscillator, and the thermodynamic functions are calculated using the fundamental frequencies of oscillation given in reference 2. The equation used in calculating the specific heat is

$$C_p^0 = 7.94872 + \sum C(v_i) \quad (1)$$

where  $\sum C(v_i)$  is the sum of the vibrational contributions of a rigid harmonic oscillator, with frequencies  $v_i$ , to specific heat. This term was evaluated at each temperature from the tables of reference 3. The frequencies of the  $B_2O_3$  molecule as calculated in reference 2 are presented in table II.

### Sensible Enthalpy

The sensible enthalpies of the crystal, glass, and liquid were supplied by the National Bureau of Standards.

The sensible enthalpy of the vapor was calculated using the following equation, which was taken from reference 2:

$$H_T^O - H_O^O = T \left[ 7.94872 + \sum H(v_i) \right] \quad (2)$$

where  $\sum H(v_i)$  is the vibrational contribution to sensible enthalpy calculated from reference 3.

### Total Enthalpy

The values for total enthalpy for the crystal, liquid, and vapor states were calculated using the sensible enthalpies from the preceding section and values of the standard-state total enthalpy at 0° K chosen to be consistent with the tables of reference 1 and the vapor pressure data of reference 4.

### Entropy

The crystal, glass, and liquid entropies are taken from the National Bureau of Standards data.

The vapor entropy was calculated using the following equation (ref. 2):

$$S_T^O = - 2.3472 + 6.863476 \log M + 18.302602 \log T + \\ 2.287825 \log(I_x I_y I_z \times 10^{117}) - 4.57565 \log \sigma + \sum S(v_i) \quad (3)$$

### Latent Heat of Vaporization

The value for the latent heat of vaporization of boric oxide from the liquid was computed by taking the difference between the total enthalpy of the vapor and the total enthalpy of the liquid.

### Vapor Pressure

Speiser, Naiditch, and Johnston (ref. 4) give experimentally determined values for the vapor pressure of boric oxide. Soulen, Sthapitanonda, and Margrave (ref. 5) verified these data within the accuracy of the method used, and Soulen indicated in reference 6 that extrapolation of the data of reference 4 was feasible.

The enthalpies for the liquid and vapor show that the latent heat of vaporization  $\Delta H_v$  varies with temperature. The data presented in reference 4 do not take this change into account. Therefore, a new vapor-pressure - temperature relation was calculated from the following expression:

$$\begin{aligned} -RT \ln p_v &= \Delta F_T^{\circ} \\ &= (H_T^{\circ} - TS_T^{\circ})_v - (H_T^{\circ} - TS_T^{\circ})_l \end{aligned} \quad (4)$$

With a value for the vapor pressure at 1500° K (about the midpoint of the experimental data) from reference 4 a value of  $(H_{1500}^{\circ})_v$  was calculated from equation (4). This calculation fixed the value of  $(H_O^{\circ})_v$  and, therefore, the remaining values of  $(H_T^{\circ})_v$ . From these values, the vapor pressure was calculated from equation (4).

The results of this calculation (shown in fig. 1(e)) agree with the results given in reference 4 to within the experimental error.

#### Heat of Formation

The heats of formation of boric oxide vapor and crystal at 298.16° and 0° K are calculated in appendix B.

#### Miscellaneous Thermodynamic Functions

The infrared and diffraction studies by Soulen (ref. 6) indicate that the structure of the  $B_2O_3$  molecule is a symmetrical bipyramid as illustrated in figure 2. In this structure the three oxygen atoms form an equilateral triangle with one boron atom above and one below the plane of the triangle. Each boron atom is bonded to each of the oxygen atoms. Doubt exists as to the exact interatomic distances. Inasmuch as no recent accurate determinations have been made, the distances used in the calculations of reference 2 will be assumed to be correct until more data are available. These data are presented in table II.

#### PHYSICAL PROPERTIES

The physical properties of boric oxide are fairly well defined up to temperatures approaching 1800° K. Above this temperature materials problems make experimental determinations of physical properties very difficult if not impossible. Consequently, if data are needed at temperatures greater than 1800° K, extrapolation of the existing data is necessary, a procedure which leads to uncertainties in the value of the property.

The physical properties of boric oxide are presented in table III and figure 3. A discussion of each of the separate physical properties follows.

#### Specific Gravity

Reference 7 gives a plot of the coefficient of thermal expansion for  $B_2O_3$  against temperature. Reference 8 gives a value of 1.85 for the

specific gravity of boric oxide at  $298.16^{\circ}$  K. Using the coefficient of expansion  $\alpha$  and the specific gravity at  $298.16^{\circ}$  K gives the following expression:

$$\ln \frac{\rho_{298.16}}{\rho_T} = \int_{298.16}^T \alpha \, dT \quad (6)$$

where

$$\alpha = c_1 + c_2 T + c_3 T^2 \quad (7)$$

The values of  $c_1$ ,  $c_2$ , and  $c_3$  were computed using the thermal expansion data of reference 7.

Substitution of equation (7) into equation (6) and integration gives

$$\ln \frac{1.85}{\rho} = 15.90558 \times 10^{-4} T - 1.095738 \times 10^{-6} T^2 + 2.59248 \times 10^{-10} T^3 - 3.837 \times 10^{-1} \quad (8)$$

as an expression for the specific gravity of  $B_2O_3$  as a function of temperature.

The data of reference 7 ( $\alpha$  plotted against temperature) are given to about  $1600^{\circ}$  K; therefore extrapolation for equation (8) above this temperature would be beyond the range of the data. These data are plotted in figure 3(a).

#### Surface Tension

References 9 and 10 report consistent experimental determinations of the surface tension of boric oxide. The data of reference 9 were run up to  $1700^{\circ}$  K and give quite reproducible results. The equation that fits these data is

$$\beta = 37.9 + 0.0354 T \quad (9)$$

where  $T$  is in  $^{\circ}$ K. The values calculated from this equation are plotted in figure 3(b).

From the experimental data it can be seen that the surface tension of boric oxide increases with temperature. This is not an uncommon occurrence when considering glasses. However, at some point the surface tension must begin to decrease with increasing temperature because at the critical temperature the liquid and vapor phases become indistinguishable and the surface tension approaches zero.

According to Freundlich (ref. 11) a positive temperature coefficient of surface tension can be explained by picturing a molecular species (different from the main body of the liquid) on the surface of the liquid that tends to lower the surface tension. As the temperature increases this species becomes more soluble in the body of the liquid, resulting in a net increase in surface tension. Because of this property, extrapolation of the surface tension data above 1700° K would present a great uncertainty.

### Viscosity

References 12 through 14 give values of the viscosity of liquid boric oxide over a temperature range from 773° to 1373° K. The data are shown in figure 3(c). In general, all the data agree fairly well, but toward the lower temperatures some discrepancy exists. To arrive at some mean values for the viscosity, a curve was drawn through all the data. The values taken from this curve are presented in table III.

### Electrical Resistivity

The electrical resistivity of boric oxide was taken from reference 15 and is presented in table III and figure 3(d). Also shown in the figure is a curve of some previously unpublished NACA data.

### Miscellaneous Physical Properties

Solubility and index of refraction data were taken from reference 16 and are presented in the following table:

Colorless glass or colorless white crystal	
Index of refraction . . . . .	1.464
Solubility, g/100 ml H <sub>2</sub> O at	
273.16° K . . . . .	1.1
373.16° K . . . . .	15.7
Soluble in acids and alcohols	

### CONCLUDING REMARKS

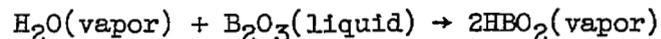
This report presents what are believed to be the most accurate data available on the properties of boric oxide. Whereas there may be some question as to the exactness of the data recommended, it is felt to be consistent.

The largest voids in the data exist when dealing with the species present in a vapor phase in equilibrium with  $B_2O_3$  liquid. Experimental observations have been made that show increases in  $B_2O_3$  vaporization rates due to water vapor in the surrounding atmosphere.

In a system containing  $B_2O_3$  and elemental boron in the liquid state,  $B_2O_3$  appears to be the predominant vapor species.

Dr. John L. Margrave and his coworkers at the University of Wisconsin are presently involved in the most complete study of these phenomena. Their work is reported in references 5, 6, and 17.

In reference 17 the data indicate that the presence of small quantities of water vapor in the inert gas passing over liquid  $B_2O_3$  greatly increased the vaporization rate of the oxide. The following reaction has been proposed to explain this phenomena:



At about  $1300^\circ$  K with a water vapor partial pressure of 4 millimeters in nitrogen the  $B_2O_3$  vaporization rate is increased about tenfold.

Lewis Flight Propulsion Laboratory  
National Advisory Committee for Aeronautics  
Cleveland, Ohio, November 8, 1956

## APPENDIX A

## SYMBOLS

$C_p^{\circ}$	standard-state specific heat at constant pressure, cal/(mole)( $^{\circ}$ K)
$C(\nu)$	vibrational specific heat function
$c_1, c_2, \dots, c_3$	constants in power series
$F_T^{\circ}$	standard-state free energy, kcal/mole
$H_T^{\circ}$	standard-state total enthalpy, kcal/mole
$H_T^{\circ} - H_0^{\circ}$	sensible enthalpy, kcal/mole
$H(\nu)$	vibrational enthalpy function
$\Delta H_f$	heat of formation, kcal/mole
$\Delta H_v$	latent heat of vaporization, kcal/mole
$I_x, I_y, I_z$	moments of inertia with respect to the x-, y-, and z-axes, (g)(cm <sup>2</sup> )
$M$	molecular weight, g/mole
$p$	pressure, atm
$R$	universal gas constant, 1.98718 cal/(mole)( $^{\circ}$ K)
$S_T^{\circ}$	standard-state entropy, cal/(mole)( $^{\circ}$ K)
$S(\nu)$	vibrational entropy function
$T$	absolute temperature, $^{\circ}$ K
$\alpha$	volume coefficient of expansion, $^{\circ}$ K <sup>-1</sup>
$\beta$	surface tension, dynes/cm

$\rho$  specific gravity

$\sigma$  symmetry number

Subscripts:

$l$  liquid

$0$   $0^\circ$  K

$T$  temperature

$v$  vapor

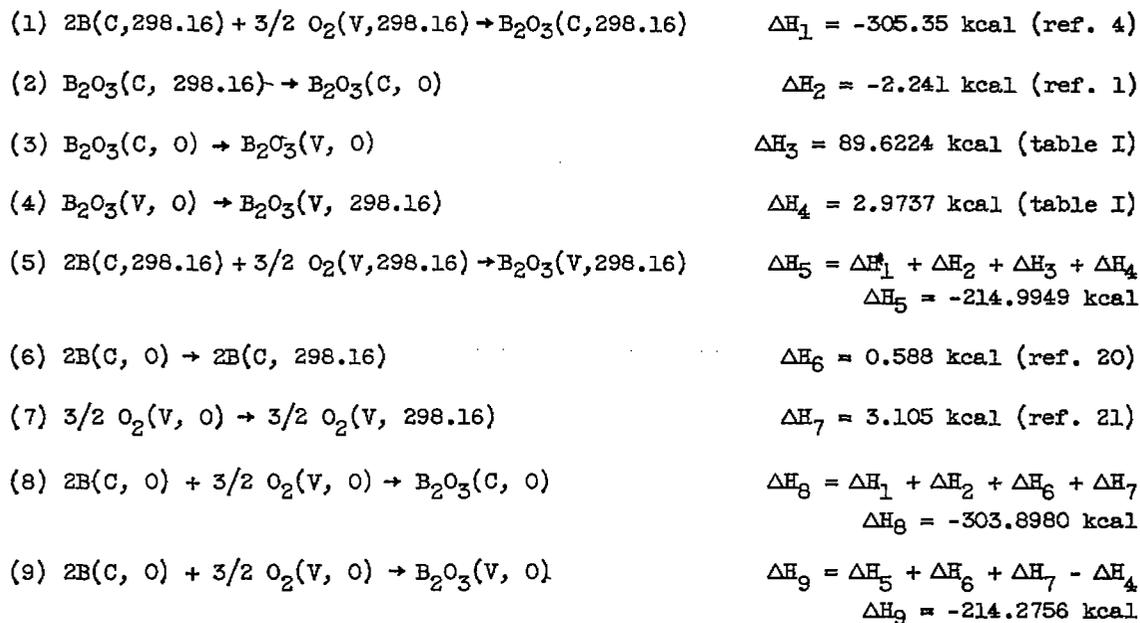
Superscript:

$o$  standard state (1 atm pressure)

## APPENDIX B

## CALCULATION OF THE HEAT OF FORMATION OF BORIC OXIDE

The heat of formation of  $B_2O_3$  was calculated by the following procedure:



Therefore,

$$\Delta H_f(B_2O_3, \text{ vapor}, 0^\circ \text{ K}) = -214.2756 \text{ kcal/mole}$$

$$\Delta H_f(B_2O_3, \text{ vapor}, 298.16^\circ \text{ K}) = -214.9949 \text{ kcal/mole}$$

$$\Delta H_f(B_2O_3, \text{ crystal}, 0^\circ \text{ K}) = -303.898 \text{ kcal/mole}$$

$$\Delta H_f(B_2O_3, \text{ crystal}, 298.16^\circ \text{ K}) = -305.35 \text{ kcal/mole}$$

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TABLE I. - RECOMMENDED THERMODYNAMIC PROPERTIES OF BORIC OXIDE

Temperature, °K	Crystal				Glass and liquid <sup>a</sup>				Vapor				Latent heat of vaporization, AH <sub>v</sub> , kcal/mole	Vapor pressure, P <sub>v</sub> , atm (e)
	Specific heat, C <sub>p</sub> , cal/(°K)(mole)	Sensible enthalpy, H <sub>f</sub> - H <sub>f</sub> <sup>0</sup> , kcal/mole	Total enthalpy, H <sub>f</sub> , kcal/mole	Total entropy, S <sub>f</sub> , cal/(°K)(mole)	Specific heat, C <sub>p</sub> , cal/(°K)(mole)	Sensible enthalpy, H <sub>f</sub> - H <sub>f</sub> <sup>0</sup> , kcal/mole (b)	Total enthalpy, H <sub>f</sub> , kcal/mole (b)	Total entropy, S <sub>f</sub> , cal/(°K)(mole)	Specific heat, C <sub>p</sub> , cal/(°K)(mole)	Sensible enthalpy, H <sub>f</sub> - H <sub>f</sub> <sup>0</sup> , kcal/mole	Total enthalpy, H <sub>f</sub> , kcal/mole	Total entropy, S <sub>f</sub> , cal/(°K)(mole)		
0		0	48.6838						0	139.297				
288.16	15.04	2.2251	50.9070	12.905	14.8	6.586	55.270	19.03	13.0703	2.9737	142.271	60.8804		
300	15.12	2.2509	50.9348	12.998	14.7	6.612	55.296	19.14	13.1080	2.9978	142.295	61.0609		
400	18.6	3.356	52.640	17.68	17.9	8.226	56.980	23.76	13.1838	4.4223	143.709	65.1156		
500	21.0	5.910	54.894	22.14	20.9	10.180	58.964	28.00	17.1316	6.0301	145.327	68.7179		
600	23.2	8.058	56.742	26.14	30.8	12.774	61.458	32.70	16.7700	7.8281	147.125	71.9914		
700	26.4	10.898	59.282	30.05	31.0	15.848	64.532	37.42	20.0754	9.7750	149.070	74.9889		
725					31.5	16.564	65.248	38.30						
800	30.2	11.272	59.958	30.98	31.8	18.932	67.876	41.63	21.0987	11.8338	151.151	77.7370	83.456	
900					31.4	22.149	70.835	46.34	21.8616	13.9847	153.282	80.2896	82.449	
1000					30.9	25.264	73.948	48.82	22.6183	16.2062	155.505	82.6097	81.583	4.12x10 <sup>-11</sup>
1100					30.5	28.334	77.018	51.54	23.4216	18.4636	157.781	84.7789	80.783	1.65x10 <sup>-8</sup>
1200					30.2	31.369	80.033	54.18	23.4086	20.8083	160.102	86.7898	80.049	2.85x10 <sup>-6</sup>
1300					30.1	34.384	83.068	56.69	23.7504	25.1828	162.460	88.6886	79.392	4.65x10 <sup>-7</sup>
1400					30.0	37.383	86.073	58.82	23.9942	26.5494	164.047	90.4882	78.774	4.13x10 <sup>-6</sup>
1500					30.1	40.394	88.078	60.88	24.2127	27.9802	167.237	92.1163	78.178	2.718x10 <sup>-5</sup>
1600					30.4	43.419	82.103	62.84	24.3833	30.3808	169.688	93.6869	77.585	1.39x10 <sup>-4</sup>
1700					30.7	46.474	85.158	64.69	24.5494	32.6383	172.135	95.1708	76.977	5.83x10 <sup>-4</sup>
1800					31.0	49.559	88.243	66.36	24.6904	35.2989	174.697	96.5778	76.354	2.16x10 <sup>-3</sup>
1900					31.2	52.669	101.553	68.04	24.7927	37.7737	177.071	97.9182	75.718	6.80x10 <sup>-3</sup>
2000					31.4	55.799	104.463	69.64	24.8695	40.2879	178.535	99.1894	75.072	1.80x10 <sup>-2</sup>
2100					31.5	58.944	107.628	71.17	24.9737	42.7512	182.048	100.4058	74.420	4.41x10 <sup>-2</sup>
2200					31.8	62.099	110.783	72.64	25.0472	45.2823	184.549	101.5693	73.768	9.87x10 <sup>-2</sup>
2300					31.6	65.269	113.933	74.08	25.1118	47.7803	187.067	102.6848	73.104	2.05x10 <sup>-1</sup>
2400					31.9	68.454	117.138	75.41	25.1888	50.2746	189.671	103.7542	72.435	5.87x10 <sup>-1</sup>
2500					32.0	71.649	120.333	76.71	25.2184	52.7939	192.091	104.7828	71.758	7.28x10 <sup>-1</sup>
2600									25.2644	55.3161	194.615	105.7728		1.30
2700									25.3047	57.8466	197.144	106.7269		2.31
2800									25.3410	60.3754	199.670	107.6478		4.03
2900									25.3756	62.9148	202.212	108.5378		7.00
3000									25.4031	65.4526	204.751	109.3984		11.9
3100									25.4295	67.9885	207.292	110.2318		
3200									25.4548	70.5395	209.837	111.0388		
3300									25.4786	73.0861	212.385	111.8232		
3400									25.4989	75.6347	214.932	112.5840		
3500									25.5155	78.1833	217.482	113.3254		
3600									25.5327	80.7378	220.035	114.0424		
3700									25.5465	83.2918	222.599	114.7422		
3800									25.5631	85.8462	225.143	115.4238		
3900									25.5766	88.4044	227.701	116.0880		
4000									25.5892	90.9627	230.260	116.7357		
4100									25.6008	93.5223	232.819	117.3677		
4200									25.6118	96.0829	235.380	117.9847		
4300									25.6217	98.6446	237.942	118.5873		
4400									25.6312	101.2072	240.504	119.1766		
4500									25.6400	103.7707	243.068	119.7527		
4600									25.6482	106.3352	245.632	120.3184		
4700									25.6559	108.9004	248.197	120.8681		
4800									25.6632	111.4662	250.763	121.4083		
4900									25.6700	114.0330	253.330	121.9375		
5000									25.6764	116.6004	255.897	122.4604		
5100									25.6825	119.1683	258.466	122.9681		
5200									25.6882	121.7367	261.034	123.4638		
5300									25.6936	124.3059	263.603	123.9528		
5400									25.6987	126.8756	266.173	124.4332		
5500									25.7035	129.4457	268.743	124.9048		
5600									25.7081	132.0162	271.313	125.3680		
5700									25.7124	134.5872	273.884	125.8230		
5800									25.7165	137.1587	276.458	126.2702		
5900									25.7204	139.7307	279.028	126.7089		
6000									25.7241	142.3028	281.600	127.1423		

<sup>a</sup>Glass below 725° K; liquid above 725° K.  
<sup>b</sup>Relative to boric oxide crystal at 0° K.  
<sup>c</sup>Extrapolated from 2500° to 3000° K.

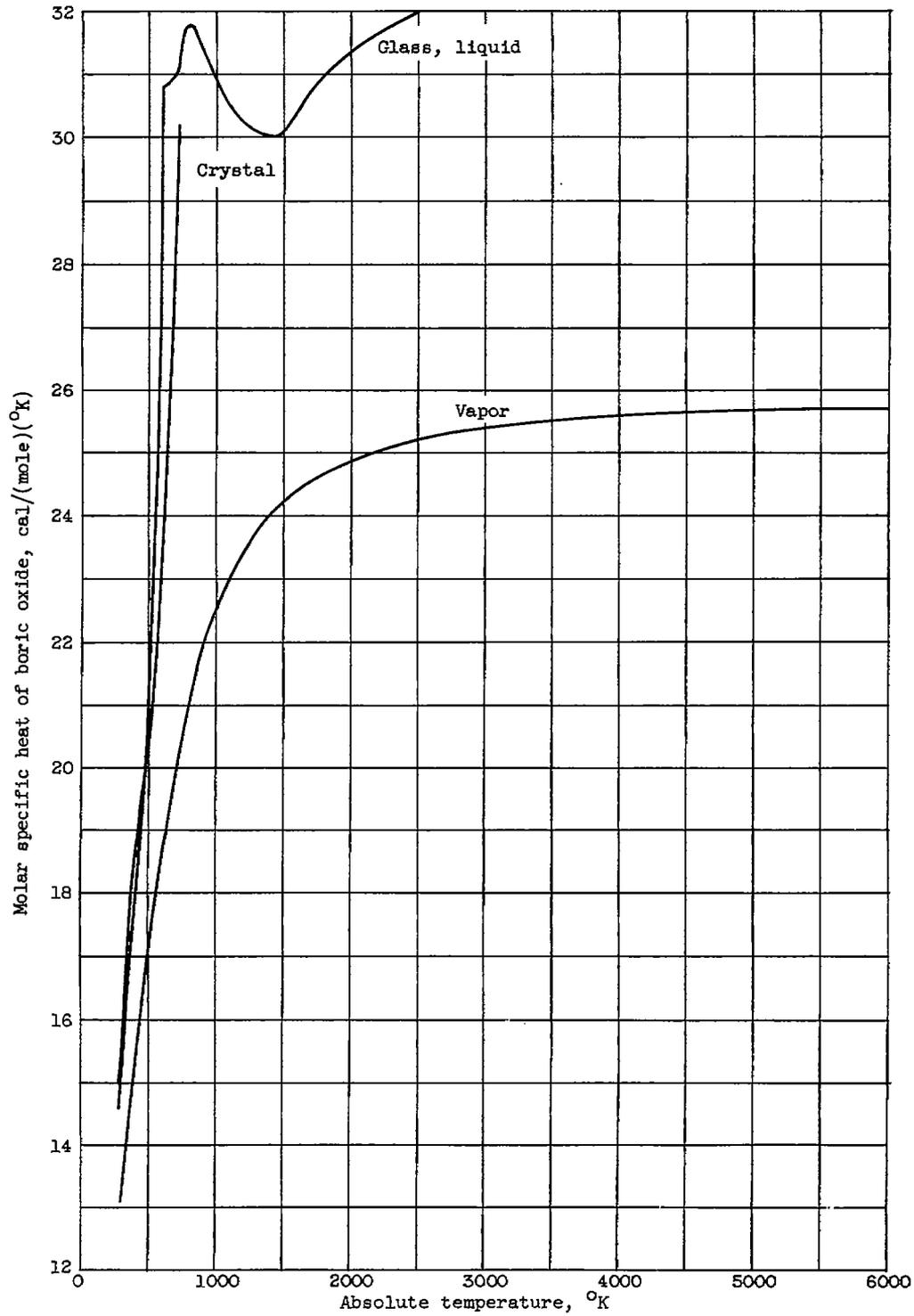
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TABLE II. - RECOMMENDED BASIC DATA ON THE BORIC OXIDE MOLECULE

		Ref.
Formula . . . . .	$B_2O_3$	23
Molecular weight . . . . .	69.64	23
Interatomic distances, A:		2
B-B . . . . .	1.72	
B-O . . . . .	1.36	
O-O . . . . .	1.825	
Electronegativity:		2
B . . . . .	1.90	
O . . . . .	3.45	
Symmetry number . . . . .	6	2
Force constant, dynes/cm:		2
B-O . . . . .	$6.809 \times 10^{-3}$	
O-O . . . . .	$1.240 \times 10^{-5}$	
Moment of inertia, $g/cm^2$ :		2
$I_x$ . . . . .	$88.463 \times 10^{-40}$	
$I_y, I_z$ . . . . .	$70.805 \times 10^{-40}$	
Calculated fundamental frequencies, $cm^{-1}$ :		2
$\nu_1$ . . . . .	1363.6	
$\nu_{2,3}$ . . . . .	1240.8	
$\nu_4$ . . . . .	1525.1	
$\nu_5$ . . . . .	466.3	
$\nu_{6,7}$ . . . . .	1371.0	
$\nu_{8,9}$ . . . . .	382.7	

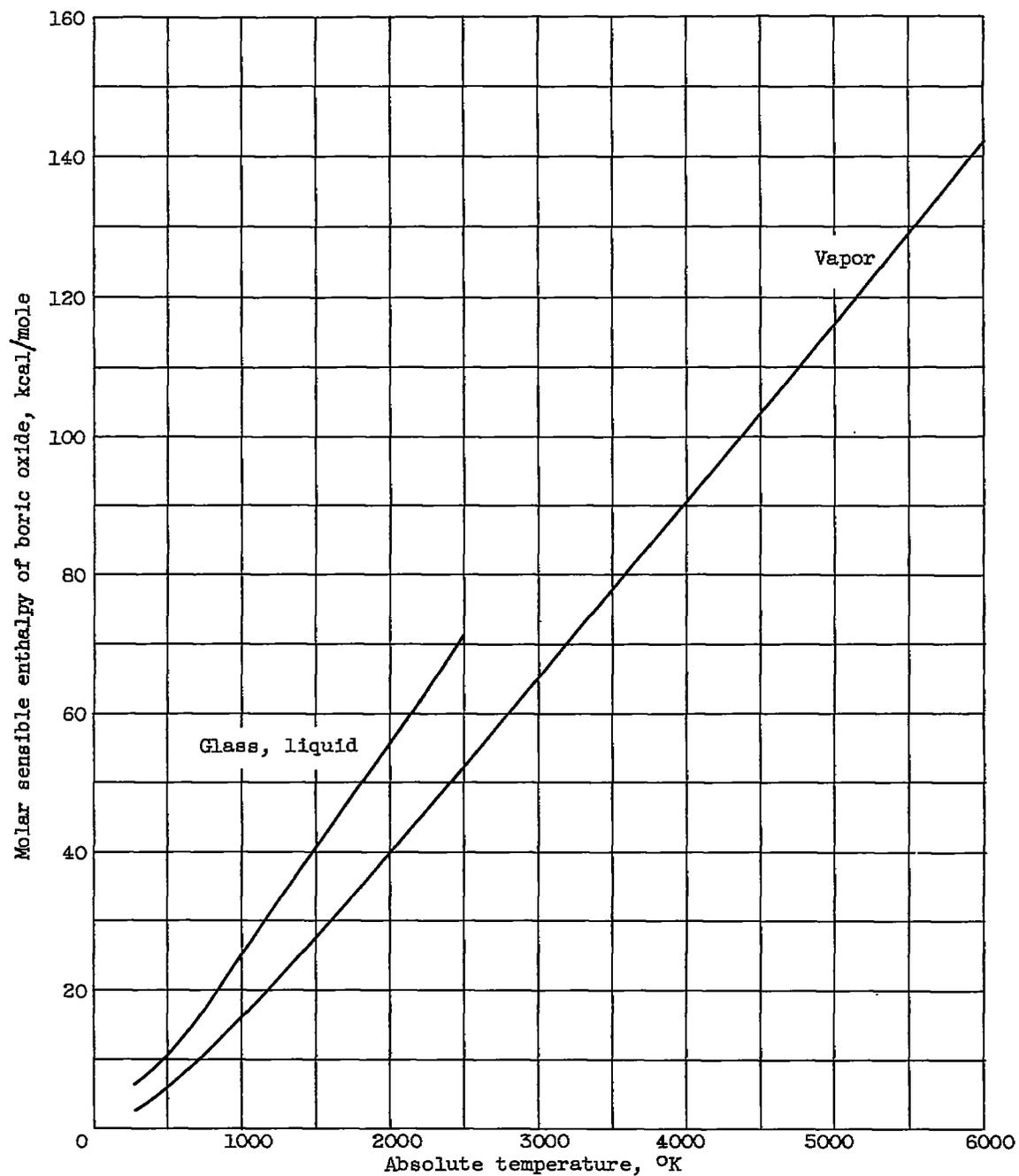
TABLE III. - RECOMMENDED PHYSICAL PROPERTIES  
OF BORIC OXIDE

Temperature, °K	Specific gravity	Surface tension, dynes/cm	Viscosity, poises	Electrical resistivity, ohm/cm
298.16	1.85	48.5	-----	-----
400	1.69	52.1	-----	-----
500	1.56	55.6	-----	-----
600	1.47	59.1	-----	-----
700	1.59	62.7	$>1 \times 10^4$	-----
750	-----	-----	-----	$4.5 \times 10^5$
800	1.34	66.2	$7.0 \times 10^3$	$1.5 \times 10^5$
900	1.30	69.8	$1.6 \times 10^3$	$4.8 \times 10^4$
1000	1.28	73.3	$5.0 \times 10^2$	$2.2 \times 10^4$
1100	1.26	76.8	$2.0 \times 10^2$	-----
1200	1.25	80.4	$9.7 \times 10^1$	-----
1300	1.24	83.9	$5.4 \times 10^1$	-----
1400	1.23	87.5	$3.3 \times 10^1$	-----
1500	1.226	91.0	$2.2 \times 10^1$	-----
1600	1.218	94.5	$1.6 \times 10^1$	-----
1700	1.208	98.1	-----	-----
1800	1.191	101.6	-----	-----
1900	-----	105.2	-----	-----
2000	-----	106.7	-----	-----



(a) Specific heat.

Figure 1. - Recommended thermodynamic properties of boric oxide.



(b) Sensible enthalpy. To convert to total enthalpy, add 48.6839 kilocalories per mole to the glass or liquid sensible enthalpy and 139.297 kilocalories per mole to the vapor sensible enthalpy.

Figure 1. - Continued. Recommended thermodynamic properties of boric oxide.

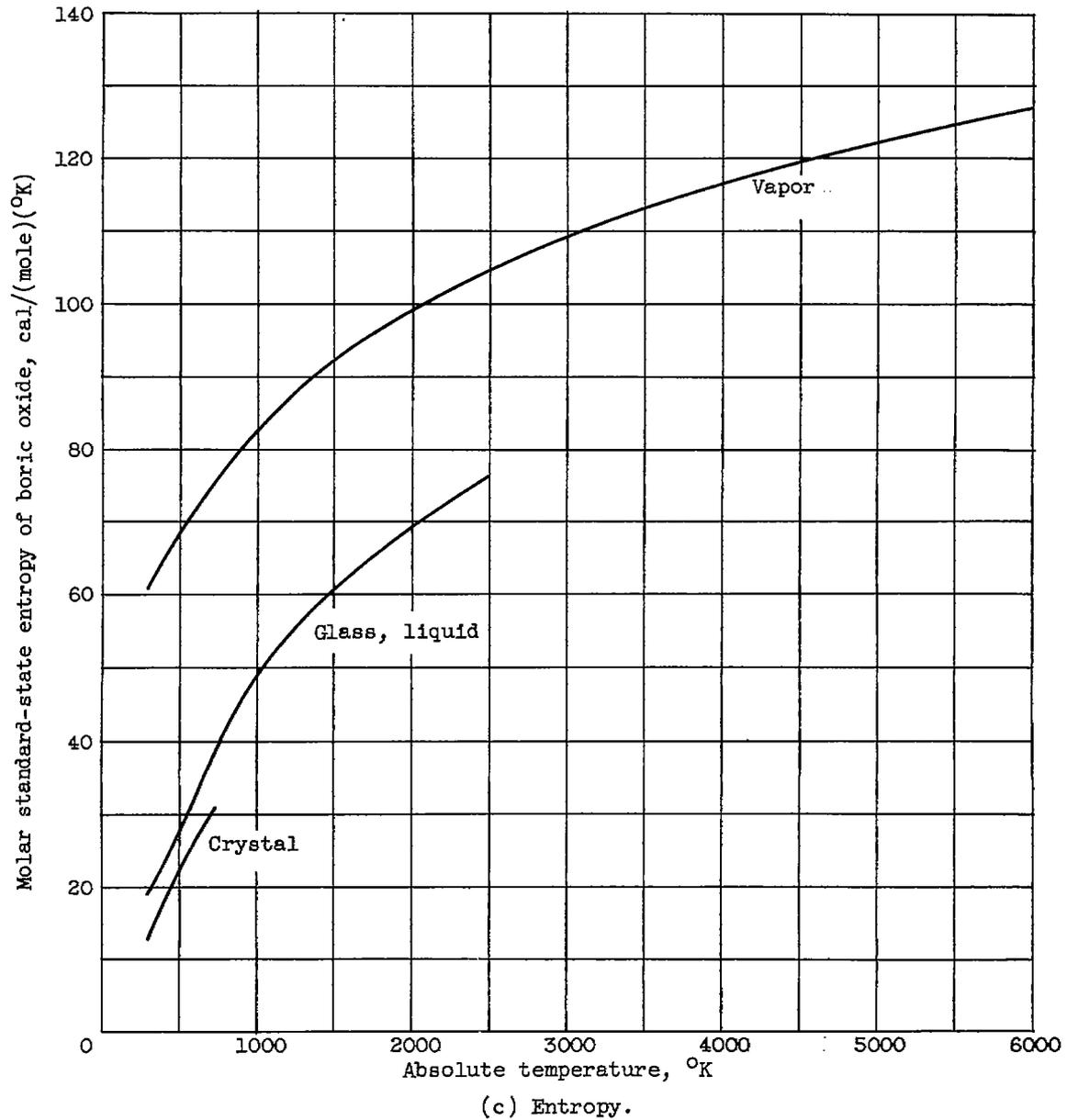
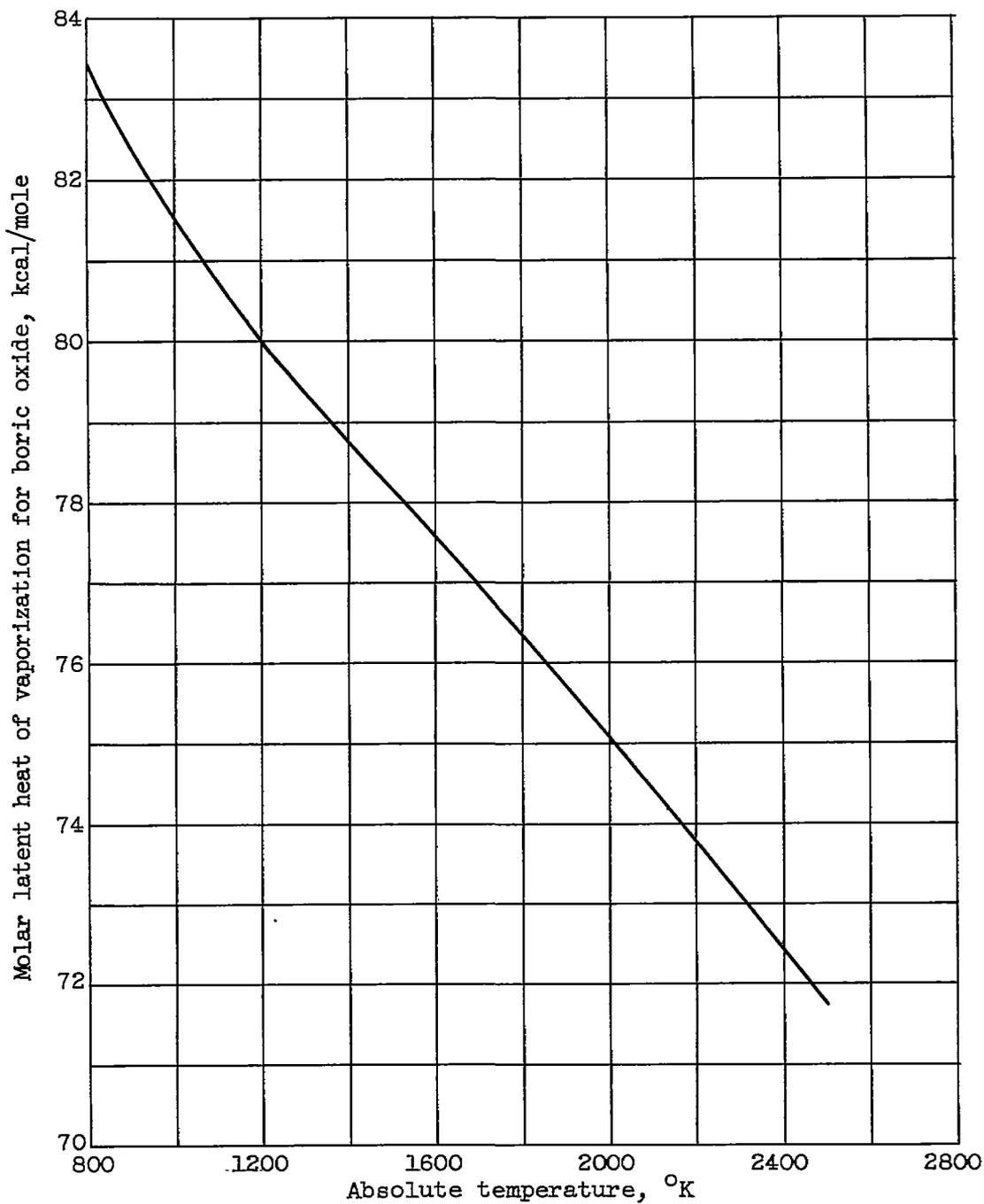


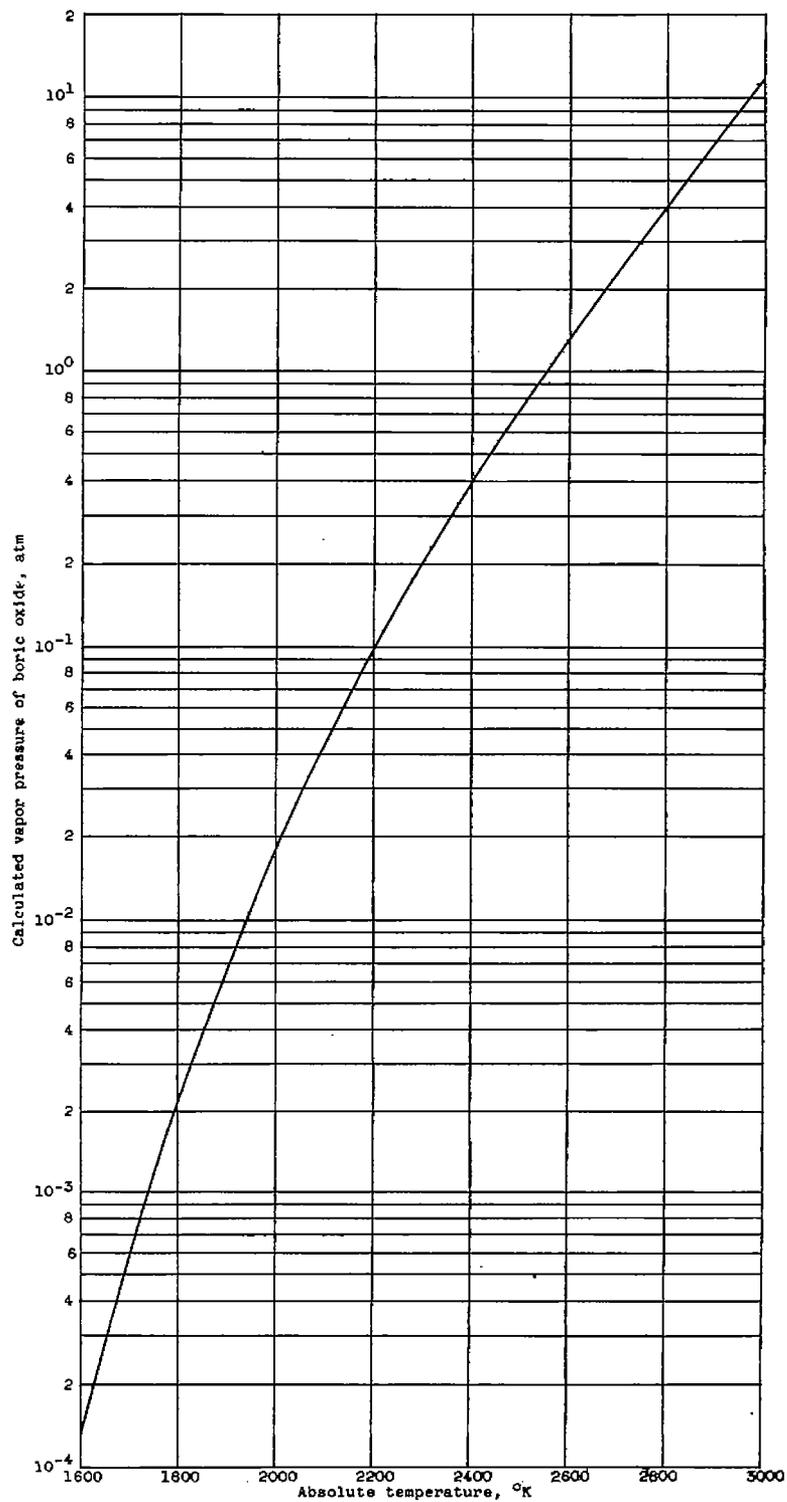
Figure 1. - Continued. Recommended thermodynamic properties of boric oxide.

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(d) Latent heat of vaporization.

Figure 1. - Continued. Recommended thermodynamic properties of boric oxide.



(e) Calculated vapor pressure.

Figure 1. - Concluded. Recommended thermodynamic properties of boric oxide.

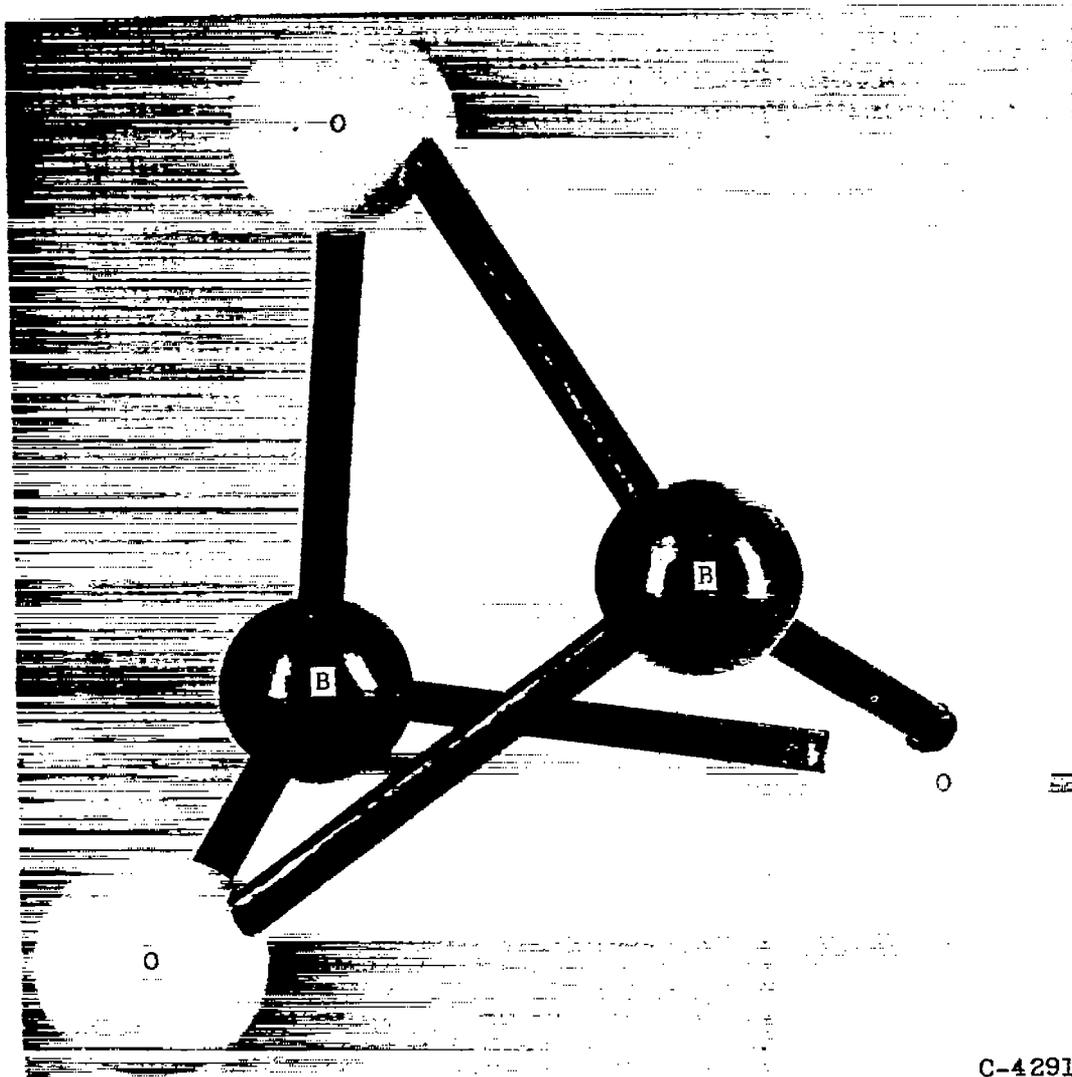
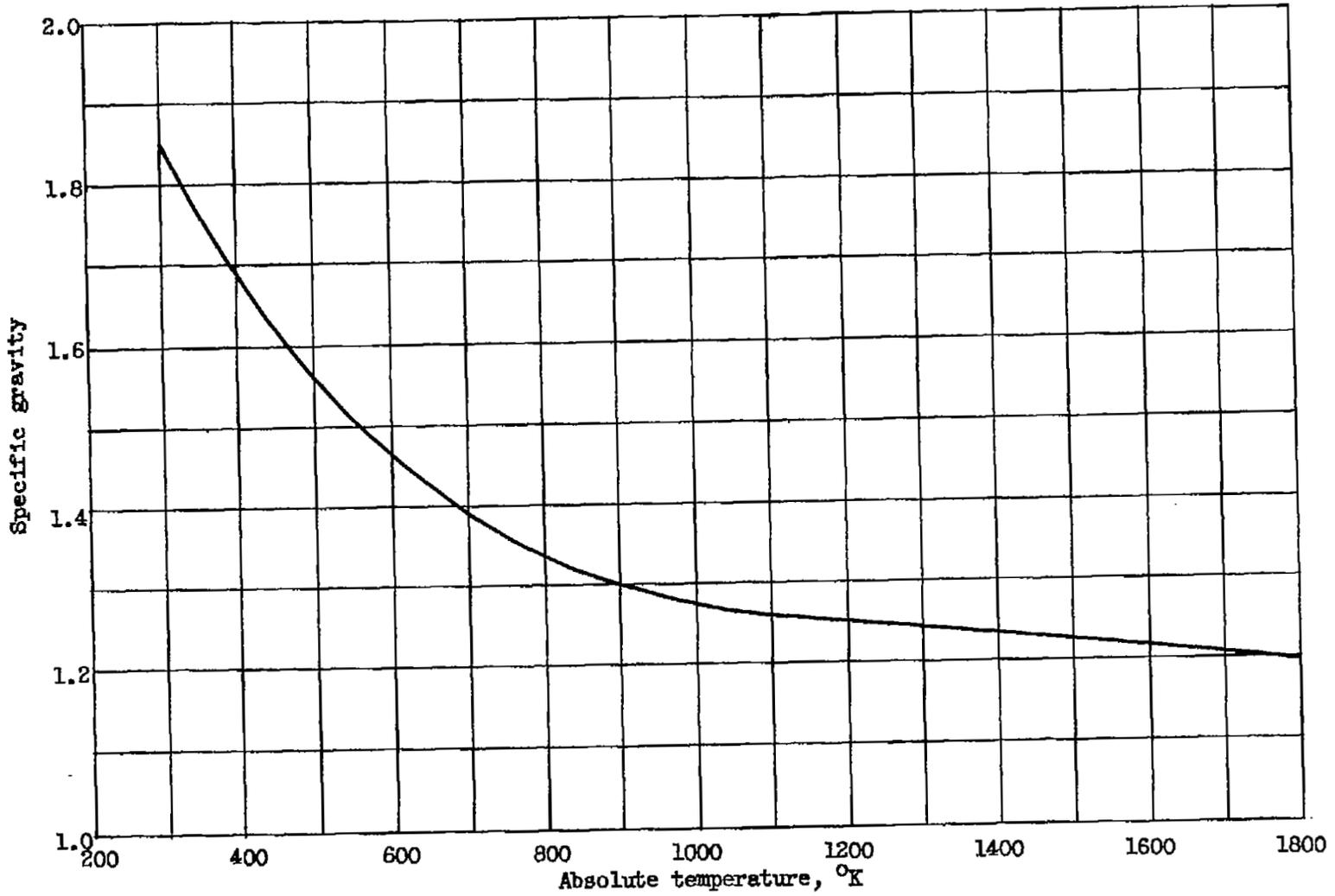


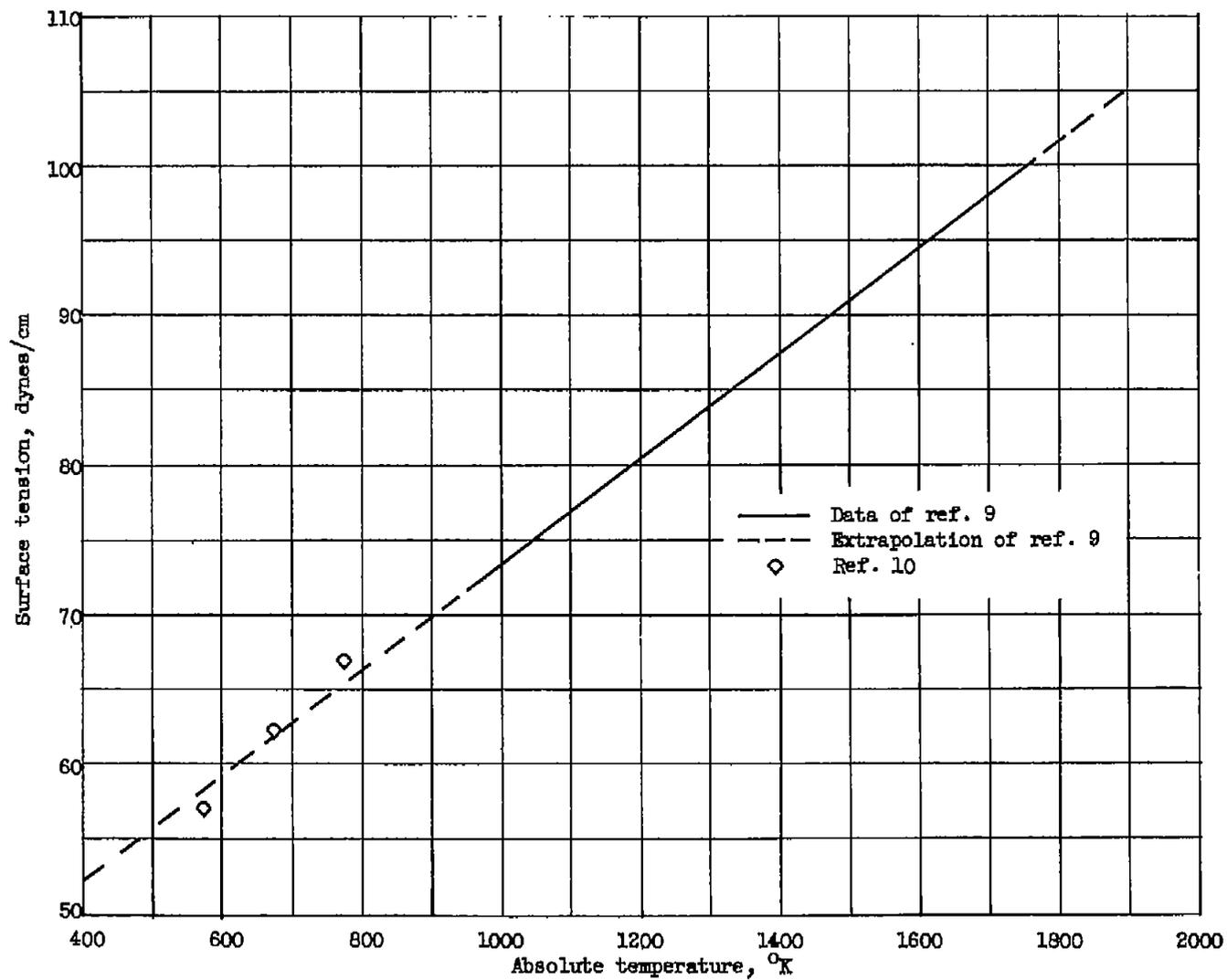
Figure 2. - Model of boric oxide molecule.

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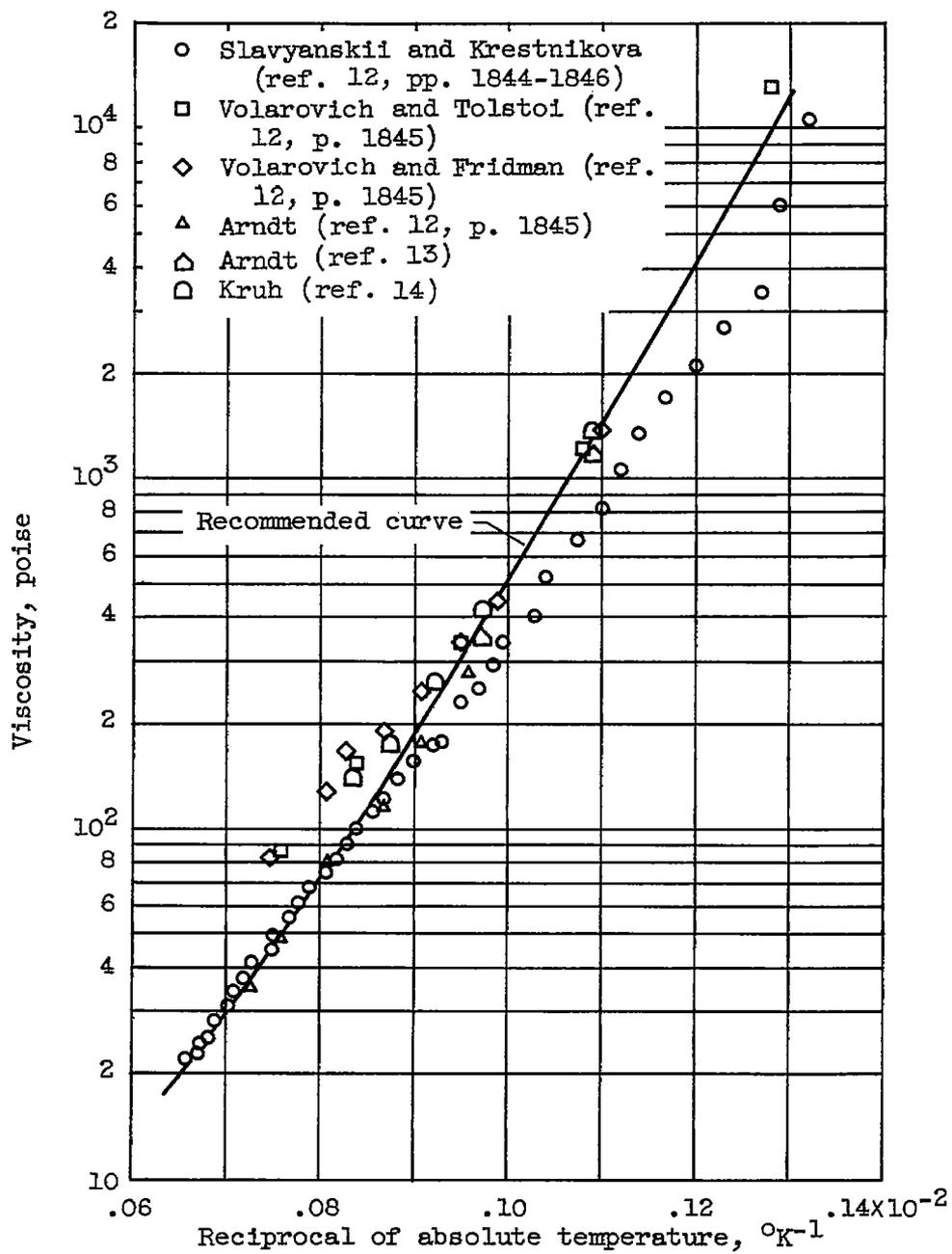
(a) Specific gravity.

Figure 3. - Recommended physical properties of boric oxide.



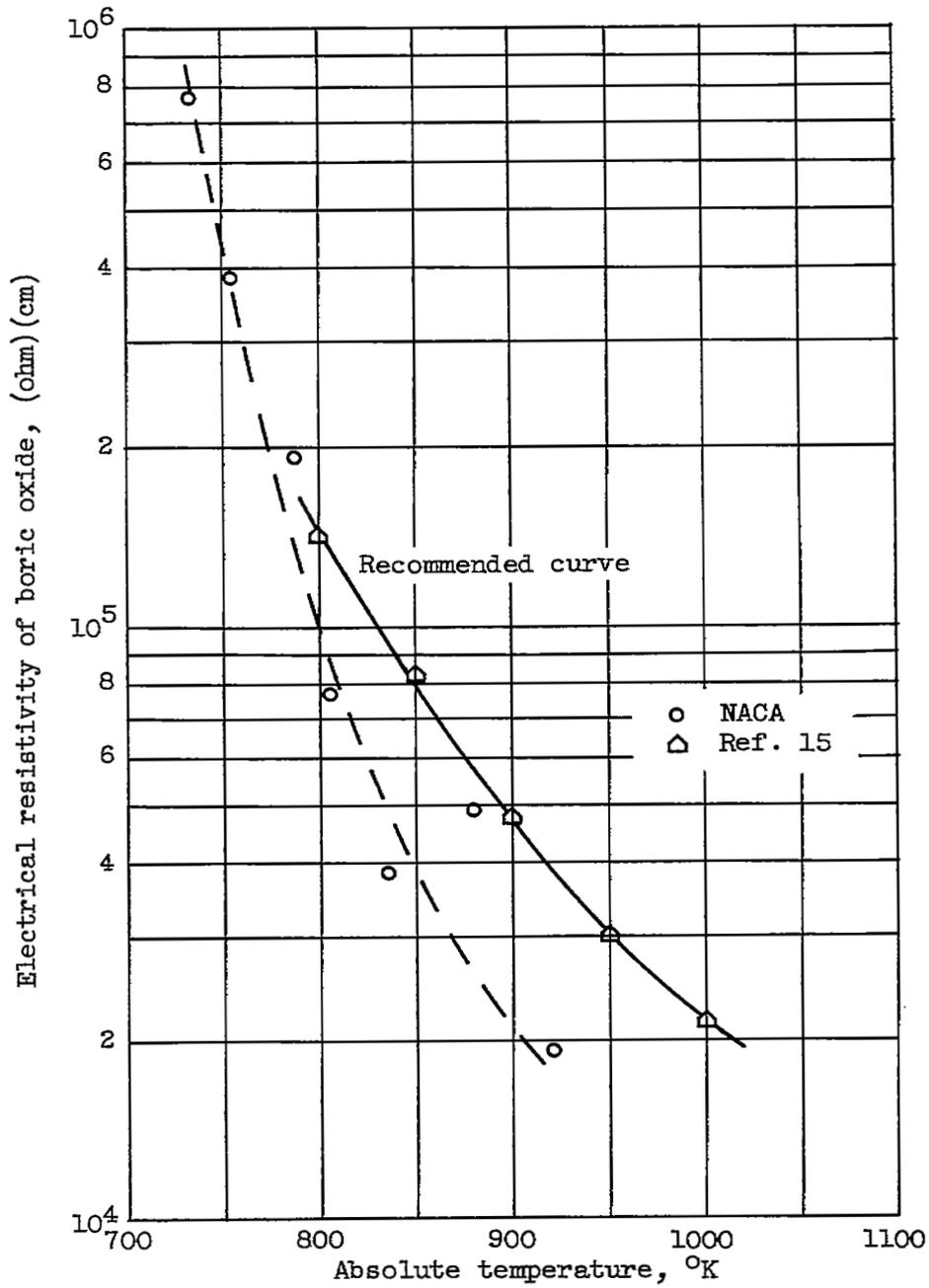
(b) Surface tension.

Figure 3. - Continued. Recommended physical properties of boric oxide.



(c) Viscosity of liquid.

Figure 3. - Continued. Recommended physical properties of boric oxide.



(d) Electrical resistivity.

Figure 3. - Concluded. Recommended physical properties of boric oxide.

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