Phase Equilibria in the System Niobium Pentoxide-- Boric Acid

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The phase-equilibrium diagram for the system $Nb_2O_5-B_2O_3$ was determined experimentally using the quenching technique and examining the samples by optical microscopy and x-ray powder diffractometry. The system contains one binary compound of approximate composition "$3Nb_2O_5 \cdot B_2O_3$," which melts incongruently at about 1150 °C to $H-Nb_2O_5$ and B_2O_3-rich liquid. A large region of liquid immiscibility extends, at 1352 °C, from 10 mole percent Nb_2O_5 to 65.7 mole percent Nb_2O_5. The theoretically calculated extent of immiscibility is in reasonable agreement with the experimentally determined value.

Key Words: Boric oxide, immiscibility, niobium pentoxide, oxides, phase equilibria.

1. Introduction

Consistent with the objective expressed in the Introduction to the preceding paper on the system $Nb_2O_5-GeO_2$ [1],[1] the systematic study of immiscibility was extended to include the phase relations in the system $Nb_2O_5-B_2O_3$. The Nb^{5+} cation has a high charge and moderate ionic radius, 0.69 Å; and, consequently, a high ionic field strength. Notwithstanding the high field strength, the $Nb_2O_5-GeO_2$ system does not show liquid immiscibility. However, the $Nb_2O_5-SiO_2$ system was found to contain a large region of immiscibility [2]. Based on the observation that no case has been reported in which liquid immiscibility exists for the silicate system but not for the corresponding borate system, immiscibility in the $Nb_2O_5-B_2O_3$ system was to be expected. Furthermore, the system offered a possible opportunity to apply and to extend the principles of immiscibility developed mainly from systems of borates with the oxides of divalent cations.

2. Sample Preparation and Test Methods

Starting materials for the preparation of mixtures consisted of high-purity niobium pentoxide and reagent grade boric acid powder. The Nb_2O_5 contained the following impurities when examined by the general qualitative spectrochemical method: Si—less than 0.1 percent; Fe, Sn, Ti—0.001 to 0.01 percent; Ca, Mg—0.0001 to 0.001 percent; Cu—? The boric acid was of especially high purity, containing only faint traces (0.0001 to 0.001%) of Mg and Si.

Three-gram batches, on an ignited basis, of the starting materials were formulated by mixing or grinding, pressing, and heating for 4 hr, at three successively higher temperatures: 700, 800, and about 900 °C. Phase equilibrium relations were studied by the well-established quenching technique. Samples were heated in sealed Pt tubes for periods of 1 to 336 hr.

Temperatures were measured with a calibrated Pt-90Pt:10 Rh thermocouple. Quenched samples were examined with the binocular and polarizing microscopes and by x-ray powder diffractometry (Ni-filtered CuK_α radiation) using a high-angle Geiger-counter diffractometer. The technique and details of sample preparation, apparatus, and method have been described in previous publications [3] and were the same as for the study of the $Nb_2O_5-GeO_2$ system [1]. The overall maximum uncertainty of the liquidus temperatures reported are estimated to be within ± 10 °C.

It should be noted that the polarizing microscope was of limited value because clear homogeneous glass was not observed, even for the compositions richest in B_2O_3. Quenched liquid devitrified, to lesser or greater extent, and the grains appeared brownish, finely mottled, and very weakly birefringent, when viewed under the microscope.

3. Chemical Analysis

Formulated compositions were analyzed by the Analytical Chemistry Division. For most of the compositions only the Nb_2O_5 content was determined, by titration of an unbuffered solution at pH 4.5 with standard EDTA solution. Percent B_2O_3 was estimated by difference from 100 percent. Analyses of three compositions (formulated at 25, 50, and 66.7 mole percent Nb_2O_5) as well as analysis of the mechanically separated heavy and light devitrified liquids in the immiscibility region were made for both Nb_2O_5 and B_2O_3. B_2O_3 was determined by titration of a neutral solution (pH 7.00) with standard NaOH solution, after the additions of manitol. Nb_2O_5 was determined from the weight of the ignited residue. Analyzed values were used in constructing the phase diagram. Those compositions for which one of the components was determined by difference have an estimated uncertainty of about 2 mole percent. Those for which both components were analyzed have an estimated accuracy of better than 1 mole percent.

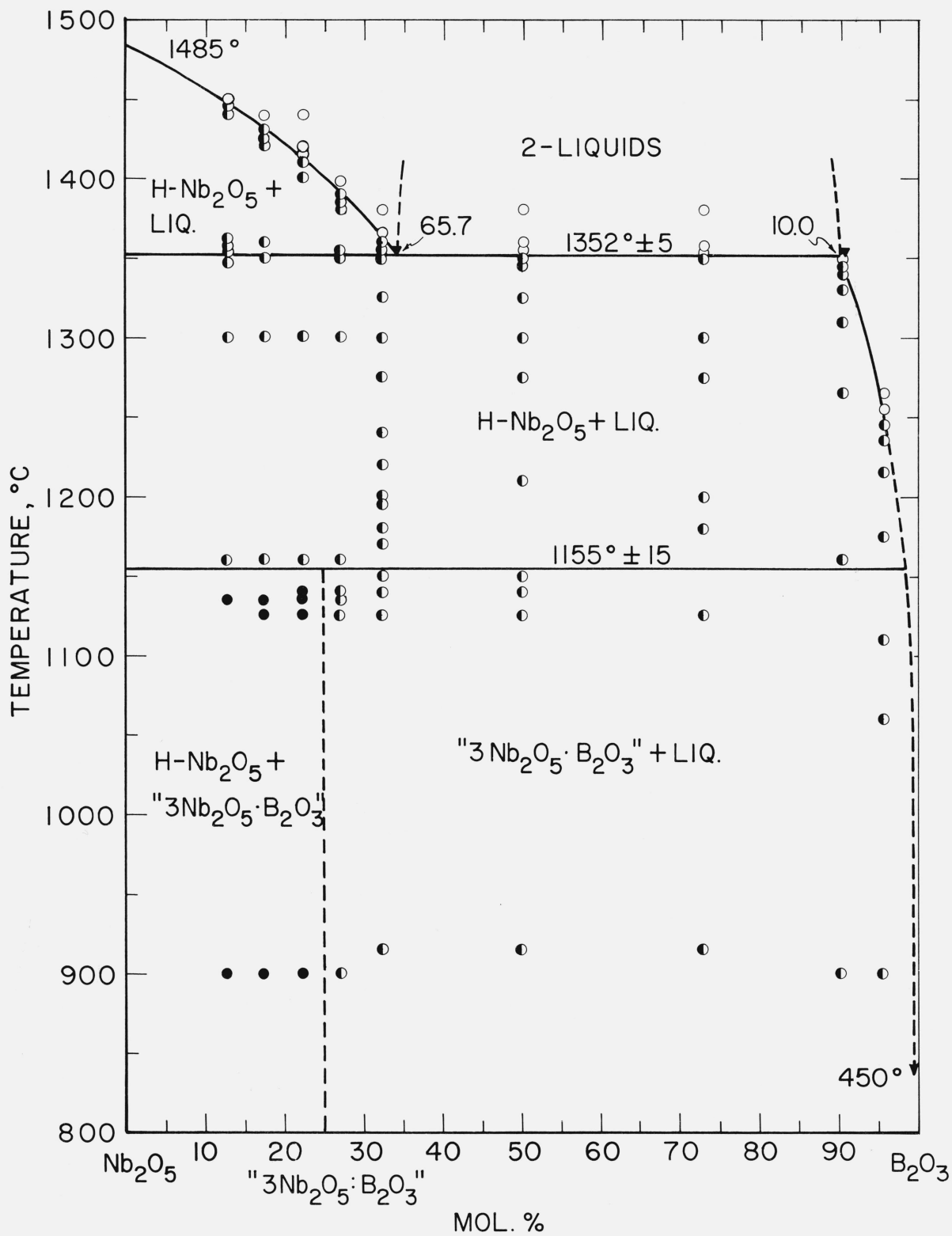[1] Figures in brackets indicate the literature references at the end of this paper.

FIGURE 1. *Phase diagram for the system* $Nb_2O_5-B_2O_3$.
● —No melting; ◖—partial melting; ○—complete melting;
▼—chemically analyzed value of mechanically separated phases in
two liquid regions.

4. Results and Discussion

4.1. Nb₂O₅ and B₂O₃ Components

No quenching experiments were made with the components, as they were the same materials that had been used previously in phase equilibrium studies originating in this laboratory [3, 4]. As regards the Nb₂O₅ component, the same remarks pertain as for the Nb₂O₅−GeO₂ system [1]. For purposes of consistency with previous publications the indicated melting temperature of B₂O₃ is given as 450 °C, although this value may be 5° to 10° low [5].

4.2. Phase Diagram

The phase diagram for the system is shown in figure 1, and table 1 lists the compositions studied, heat treatments, and phases identified. The system is characterised by a large region of liquid immiscibility, extending from about 10 mole percent to 65.7 mole percent Nb₂O₅, and by a binary compound, "3Nb₂O₅ · B₂O₃" melting incongruently at 1150 °C, some 200° below the monotectic.

The two triangles in figure 1 designate the chemically analyzed values for the B₂O₃-rich and the Nb₂O₅-

TABLE 1. *Experimental data for compositions in the binary system* $Nb_2O_5-B_2O_3$

Composition [1]		Heat treatment [2]		Results		Notes
Nb₂O₅	B₂O₃	Temp.	Time	Physical observation	X-ray diffraction analyses [3]	
Mole %	*Mole %*	*°C*	*Hour*			
4.4	95.6	900	3	Considerable melting.	3:1 + glass hump + [H₃BO₃]	
		1061	1	Considerable melting.		
		1109	1.5	Considerable melting.	3:1 + glass hump + [L−Nb₂O₅]	No H−Nb₂O₅ detected.
		1175	1	Considerable melting.	3:1 + glass hump + [L−Nb₂O₅]	
		1216	1	Considerable melting.	[H₃BO₃] + 3:1 + [L−Nb₂O₅] + H−Nb₂O₅	Tube leaked.
		1235	2	Considerable melting.	[L−Nb₂O₅] + 3:1 + [H₃BO₃] + H−Nb₂O₅	
		1246	2	Near complete melting.	3:1 + [H₃BO₃] + [L−Nb₂O₅] + H−Nb₂O₅	
		1256	2	Complete melting.	[L−Nb₂O₅] + [3:1]	
		1265	2	Complete melting.	[L−Nb₂O₅] + [3:1]	
9.7	90.3	900	3	Some melting.	3:1 + glass hump	
		1161	68	Considerable melting.	3:1 + H−Nb₂O₅	Above decomp. 3:1.
		1265	2	Considerable melting.	[L−Nb₂O₅] + 3:1	Very weak x-ray pattern.
		1310	1.5	Considerable melting.	3:1 + [L−Nb₂O₅] + H−Nb₂O₅	
		1331	1.5	Considerable melting.	3:1 + [L−Nb₂O₅] + H−Nb₂O₅	
		1339	1.5	Considerable melting.	3:1 + [L−Nb₂O₅] + [H₃BO₃]	Tube leaked.
		1345	1.5	Near complete melting.	[L−Nb₂O₅] + 3:1 + H−Nb₂O₅	
		1350	1.5	Complete melting.	[L−Nb₂O₅]	One liquid.
27.2	72.8	915	4	Slight melting.	3:1	B₂O₃-rich glass present.
		1180	53.5	Some melting.	3:1 + H−Nb₂O₅	Above decomp. 3:1.
		1200	66.5	Some melting.	3:1 + H−Nb₂O₅	
		1275	15	Some melting.	3:1 + H−Nb₂O₅	
		1300	18	Some melting.	H−Nb₂O₅ + 3:1 + [L−Nb₂O₅]	
		1300	18⎫		3:1 + H−Nb₂O₅	{Shows reversibility:
		1125	117⎭			3:1 ↔ H−Nb₂O₅ + liquid.
		1349	2	Some melting.	H−Nb₂O₅ + [L−Nb₂O₅] + 3:1	Above monotectic.
		1354	1.5	Complete melting.	[L−Nb₂O₅] + [H−Nb₂O₅]	Chem. Analysis of each phase.
		1357	1	Complete melting.		
		1380	2	Complete melting.		
50.2	49.8	915	4	Slight melting.	3:1	
		1140	69	Slight melting.	3:1 + [H₃BO₃]	
		1150	45	Some melting.	3:1	
		1210	40	Some melting.	3:1 + H−Nb₂O₅	Above decomp. 3:1.
		1275	15	Some melting.	H−Nb₂O₅ + 3:1	
		1300	18	Considerable melting.	H−Nb₂O₅ + 3:1	
		1300	18⎫		3:1 + H−Nb₂O₅	{Shows reversibility:
		1125	117⎭			3:1 ↔ H−Nb₂O₅ + liquid.
		1325	1	Considerable melting.	3:1 + H−Nb₂O₅	
		1345	1.25	Considerable melting.	3:1 + H−Nb₂O₅	
		1350	1	Considerable melting.	H−Nb₂O₅ + [L−Nb₂O₅] + 3:1	Decomp. 3:1 sluggish.
		1356	1.5	Complete melting.	[H−Nb₂O₅] + [L−Nb₂O₅]	Above monotectic.
		1360	1.25	Complete melting.		For chem. analysis.
		1380	2	Complete melting.		Above monotectic.
67.8	32.2	915	4	Slight melting.	3:1	B₂O₃-rich glass present.
		1140	69	Slight melting.	3:1	
		1150	45	Slight melting.	3:1	
		1170	20	Melting.	3:1 + H−Nb₂O₅(?)	
		1180	53.5	Melting.	3:1 + H−Nb₂O₅	
		1194	1.75	Melting.	3:1	Decomp. 3:1 sluggish.
		1200	66.5	Melting.	3:1 + H−Nb₂O₅	
		1220	8.5	Melting.	3:1 + H−Nb₂O₅	
		1240	1.5	Melting.	3:1 + H−Nb₂O₅	
		1275	1.5	Melting.	H−Nb₂O₅ + 3:1	
		1300	18	Melting.	H−Nb₂O₅ + 3:1 (?)	
		1300	18⎫		3:1 + H−Nb₂O₅	{Shows reversibility:
		1125	117⎭			3:1 ↔ H−Nb₂O₅ + liquid.
		1325	1		3:1 + H−Nb₂O₅	
		1350	1		H−Nb₂O₅ + [L−Nb₂O₅]	Above monotectic.
		1356	1	Considerable melting.	H−Nb₂O₅	
		1361	1.5	Near complete melting.	H−Nb₂O₅ + [3:1]	
		1367	1	Complete melting.	[L−Nb₂O₅] + [3:1]	One liquid.
		1380	2	Complete melting.	[L−Nb₂O₅] + [3:1]	

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Composition [1]		Heat treatment [2]		Results		Notes
Nb_2O_5	B_2O_3	Temp.	Time	Physical observation	X-ray diffraction analyses [3]	
Mole %	Mole %	°C	Hour			
73.0	27.0	900	3	Opalescent.	3:1	
		1135	336	Opalescent.	3:1	
		1140	69	Opalescent.	3:1	
		1161	68	Opalescent.	$3:1 + H - Nb_2O_5$	Above decomp. 3:1.
		1300	18	Opalescent.	$H - Nb_2O_5 + 3:1$ (?)	
		1300	18⎱		$H - Nb_2O_5 + 3:1$	⎧Shows reversibility:
		1125	117⎰			⎩$3:1 ↔ H - Nb_2O_5 +$ liquid.
		1351	1.5	Slight melting.	$H - Nb_2O_5$	
		1355	1.5	Melting.	$H - Nb_2O_5 + 3:1$	Above monotectic.
		1380	1.5	Considerable melting.	$H - Nb_2O_5 + 3:1$	
		1385	1.5	Near complete melting.	$H - Nb_2O_5 + [L - Nb_2O_5] + 3:1$	
		1390	1.5	Near complete melting.	$[L - Nb_2O_5] + H - Nb_2O_5 + 3:1$	
		1398	1.5	Complete melting.	$[H - Nb_2O_5] + [L - Nb_2O_5] + [3:1]$	All devitrify from liquid.
77.8	22.2	900	3	No melting.	3:1	
		1135	336	No melting.	3:1	
		1140	69	No melting.	3:1	
		1161	68	Slight melting.	$3:1 + H - Nb_2O_5$	Above decomp. 3:1.
		1300	18	Opalescent.	$H - Nb_2O_5 + 3:1$ (?)	
		1300	18⎱		$H - Nb_2O_5 + 3:1$	⎧Shows reversibility:
		1125	117⎰			⎩$3:1 ↔ H - Nb_2O_5 +$ liquid.
		1401	1	Considerable melting.	$H - Nb_2O_5 + [L - Nb_2O_5] + 3:1$	
		1409	2.5	Near complete melting.	$H - Nb_2O_5 + [L - Nb_2O_5] + 3:1$	
		1415	1.5	Complete melting.	$[H - Nb_2O_5] + [L - Nb_2O_5] + [3:1]$	
		1420	1	Complete melting.	$[H - Nb_2O_5] + [L - Nb_2O_5]$	
		1440	1	Complete melting.	$[L - Nb_2O_5] + [H - Nb_2O_5]$	
82.9	17.1	900	3	No melting.	3:1	
		1135	336	No melting.	$3:1 + H - Nb_2O_5$	
		1161	68	Slight melting.	$3:1 + H - Nb_2O_5$	Above decomp. 3:1.
		1300	18	Melting.	$H - Nb_2O_5 + 3:1$ (?)	
		1300⎱	18		$H - Nb_2O_5 + 3:1$	Reversibility sluggish.
		1125⎰	117			
		1349	3	Melting.	$H - Nb_2O_5 + [L - Nb_2O_5]$	Below monotectic.
		1359	3	Considerable melting.	$H - Nb_2O_5 + [L - Nb_2O_5]$	Above monotectic.
		1420	1	Considerable melting.	$H - Nb_2O_5 + [L - Nb_2O_5] + 3:1$	
		1425	1.5	Near complete melting.	$H - Nb_2O_5 + 3:1$ (?)	
		1430	1	At liquidus.	$[H - Nb_2O_5] + [L - Nb_2O_5] + [3:1$ (?)$]$	
		1440	1	Complete melting.	$[H - Nb_2O_5] + [L - Nb_2O_5]$	
87.2	12.8	900	3	No melting.	$3:1 + H - Nb_2O_5$ (?)	
		1135	336	No melting.	$3:1 + H - Nb_2O_5$	
		1161	68	Melting.	$3:1 + H - Nb_2O_5$	Above decomp. 3:1.
		1300	18	Melting.	$H - Nb_2O_5 + 3:1$ (?)	
		1348	2	Melting.	$H - Nb_2O_5$	$N_{g1} < 1.47$, below monotectic.
		1356	2	Moderate melting.	$H - Nb_2O_5$	Above monotectic.
		1358	1.5	Moderate melting.	$H - Nb_2O_5$	
		1362	1.5	Moderate melting.	$H - Nb_2O_5$	
		1440	1	Considerable melting.	$H - Nb_2O_5 + 3:1$ (?)	
		1445	1	Near complete melting.	$H - Nb_2O_5 + [L - Nb_2O_5] + [3:1]$	
		1450	1	Complete melting.	$[L - Nb_2O_5] + [H - Nb_2O_5]$	

[1] Analyzed value for Nb_2O_5; B_2O_3, by difference.
[2] Specimens quenched in sealed Pt tubes.
[3] Phases identified are listed in order of amount present at room temperature. Phases not necessarily present at the elevated temperatures are enclosed in brackets. 3:1 refers to $3Nb_2O_5 \cdot B_2O_3$, the most likely composition of the binary compound.

rich devitrified liquids which were mechanically separated from samples quenched from above the monotectic. When the Pt was removed from the quenched specimens, two distinct layers were clearly visible. The top layer appeared opalescent white and was found to be hard and glassy when ground. An index of refraction of approximately 1.51 ± 0.01 was determined for clear portions of some of the grains. The lower layer appeared crystalline, metallic grey in color. Under the microscope the grains were dark and very weakly birefringent. The x-ray powder patterns showed that the top layer (B_2O_3-rich) contained low-Nb_2O_5 with a trace of high-Nb_2O_5, whereas the lower layer (Nb_2O_5-rich) contained appreciable high-Nb_2O_5, low-Nb_2O_5, and a small amount of "$3Nb_2O_5 \cdot B_2O_3$."

Homogeneous glasses were never obtained for any composition as the liquids devitrified on quenching. X-ray examination showed either low-Nb_2O_5, high-Nb_2O_5, "$3Nb_2O_5 \cdot B_2O_3$", or combinations. The low-Nb_2O_5 phase corresponded to the pseudo-orthorhombic subcell of low-Nb_2O_5 found for some of the quenched liquids in the $Nb_2O_5 - GeO_2$ system. It had the same unit cell dimensions [1]. The metastable low-temperature niobia-type phase of hexagonal symmetry occurring in the GeO_2 system was not found.

4.3. Compound "3Nb₂O₅ · B₂O₃"

The exact composition of this compound could not be determined because of insufficient sensitivity, in this instance, of the microscopic and x-ray methods together with some uncertainty in the chemical analyses. Therefore, the 3:1 ratio of oxides is given as the most probable.

The compound formed readily for all compositions in the system. It melted incongruently at about 1150 °C to liquid and $H-Nb_2O_5$. However, disappearance of the compound above the melting point was extremely sluggish. The compound could be detected in diminishing amounts up to the monotectic and liquidus temperatures (see table 1). Even compositions heated at 1161 °C for 68 hr showed appreciable amounts of the compound, but the appearance of $H-Nb_2O_5$ indicated that the temperature was above the incongruent melting point. X-ray powder diffraction data suitable for identification is given in table 2. The pattern is of low symmetry with regions of closely spaced low-intensity peaks and could not be indexed.

TABLE 2. *X-ray powder diffraction data* (CuK$_\alpha$ *radiation*) *for the compound* "3Nb₂O₅ · B₂O₃"

(Pattern of low symmetry and could not be indexed)

d	I/I_0	d	I/I_0
Å	%	Å	%
*14.4(b)	4	2.434	3
7.16	7	2.389	6
6.93	6	2.369	4
4.774	34	2.337	3
4.741	27	2.302	17
3.770	71	*2.094(b)	3
3.584	90	2.049	26
3.553	100	2.033	27
3.170	12	1.9125	33
2.864	6	*1.7918(b)	5
2.833	10	1.7746	10
2.773	57	1.7697	10
*2.730(b)	7	1.6995	22
2.675	9	1.6874	21
2.576	6	1.6842	23
2.520	7	*1.5838(b)	6
2.506	9	1.5769	16
2.473	4		

*b = broad peak.

4.4. Application to Liquid Immiscibility Theory

The niobium borate and niobium silicate systems both contain large regions of immiscibility, whereas the niobium germanate system shows complete liquid miscibility. Thus, as previously discussed [1], the niobium cation possesses a critical ionic field strength for the formation of two liquids with the glass-forming cations.

With data on immiscibility in the niobium borate and silicate systems, it is possible to test and to extend the principles of immiscibility developed mostly from data on the divalent cations to the cations of high charge. A fundamental consideration in the structural approach is the average number of oxygens associated with a modifier cation, in the modifier-rich liquid. Once this value is known, statement of the nominal composition is a routine calculation. The oxygen-volume method, discussed in previous publications [3, 6] is an attempt to make a reasonable estimate of this number.

TABLE 3. *Calculated composition of modifier-rich liquids, in #0/Nb and in mole percent* Nb₂O₅, *based on the oxygen-volume method [6] and two values both for the niobium separation and the volume of space occupied by* 0^{-2} (V_0).

System	Experimental		Calculated from Nb–Nb separation:					
			of 4.18 Å [2(1.40 + 0.69)], and				of 4.08 Å, and	
			$V_0 = 17$ Å³	$V_0 = 19$ Å³			$V_0 = 19$ Å³	
	Nb₂O₅	#0/Nb	#0/Nb	#0/Nb	Nb₂O₅	#0/Nb	Nb₂O₅	#0/Nb	Nb₂O₅
	Mole %			*Mole %*		*Mole %*		*Mole %*
Nb₂O₅–B₂O₃	65.7	3.28	4.18	4.18	47.2	3.72	55.1	3.45	61.1
Nb₂O₅–SiO₂ [2]	47.5	3.61	4.18	4.18	37.4	3.72	45.0	3.45	51.2

Table 3, column 3 gives the number of oxygens per modifier cation calculated directly from the experimentally determined composition of the modifier-rich liquid. For example, in the $Nb_2O_5-B_2O_3$ system:

$$\#0/Nb = \frac{5 \times 0.657 + 3(1.00 - 0.657)}{2 \times 0.657} = 3.28.$$

Similarly, in the $Nb_2O_5-SiO_2$ system:

$$\#0/Nb = \frac{5 \times 0.475 + 2(1.00 - 0.475)}{2 \times 0.475} = 3.61.$$

As a first approximation the number of oxygens per cation may be considered independent of the glass-forming cation. Using the data in column 3 for one of the systems, it is possible to calculate the composition of the modifier-rich liquid in the other system. The calculation yields 57.5 mole percent Nb₂O₅ in the borate system,[2] using the 3.61 value, and 56.2 mole percent Nb₂O₅ in the silicate system, using the 3.28 value. The calculated value in the borate system is about 8 mole percent low, that in the silicate system about 9 mole percent high. As will be shown later, this seemingly large discrepancy is due to the sensitivity of the calculations in the niobium oxide systems.

Table 3 (columns 4−7) lists the calculated #0/Nb and the corresponding mole percent Nb₂O₅, based on the oxygen-volume method using a $Nb-O-Nb$ bond angle of 180° and Ahrens' ionic radii for Nb⁺⁵ and O^{-2}. In the original papers on immiscibility the value of 17 Å³ was taken as the average volume of space occupied by an oxygen atom in the modifier-rich liquid.

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[2] Nominal oxide formula = $\frac{Nb_2O_5 \cdot (2 \times 3.61 - 5)}{3}$ $B_2O_3 = Nb_2O_5 \cdot 0.74B_2O_3$ (57.5 mole % Nb₂O₅).

An analysis of the experimental data in about 40 borate and silicate systems showing immiscibility [7] gives an empirical value of about 19 $Å^3$. Therefore, in table 3 calculations are given for both oxygen values. It may be seen that for the 19 $Å^3$ value in the silica case agreement is good between the calculated mole percent Nb_2O_5 (45.0) and the experimental one (47.5). In the borate case the calculated value is 11 mole percent low.

For the case of small highly charged modifier cations, such as niobium, the calculations are very sensitive to cationic radius because a small difference in separation has a large effect on the calculated number of oxygen per cation. For example, using a separation of only 0.1 Å less than 4.18, will increase the calculated value by about 6 mole percent (column 9); and the calculated number of oxygens per niobium (column 8) is intermediate between 3.28 and 3.61, the experimentally determined values for the borate and silicate systems, respectively. Gatehouse and Wadsley [8], from a crystal structure determination of high-Nb_2O_5, have concluded that in Nb_2O_5 the average ionic radius of O^{2-} is 1.40 Å and that of Nb^{5+}, 0.59 Å. The latter value is 0.1 Å less than Ahrens' ionic radius.

5. Summary

The phase equilibrium diagram for the system $Nb_2O_5 - B_2O_3$ was constructed from "quenching" data on nine selected compositions. Solidus and liquidus values were determined by examination of the samples with the binocular and polarizing microscopes and x-ray powder diffractometry.

The system was found to contain one binary compound, "$3Nb_2O_5 \cdot B_2O_3$", which melts incongruently at about 1150 °C, some 200 below a monotectic. The liquidus is characterized by a large two-liquid region, at 1352 °C, extending from about 10 mole percent Nb_2O_5 to 65.7 mole percent Nb_2O_5.

Experimental limitations precluded an unequivocal statement of the composition of the "$3Nb_2O_5 \cdot B_2O_3$" compound. Above the incongruent melting point its decomposition to $H - Nb_2O_5$ and B_2O_3-rich liquid is sluggish. X-ray powder data suitable for identification is listed.

In the modifier-rich liquid in the immiscibility region, an average of 3.28 oxygen are associated with each Nb atom, as compared to 3.61 for the corresponding silicate system. Calculation of the composition of the modifier-rich liquid, by the oxygen-volume method, gives acceptable agreement with the experimentally determined value, considering that for cations of large valence the calculation is sensitive to small changes in the parameters.

6. References

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