ACID-BASE PROPERTIES OF MELTS
AND GLASSES OF Na$_2$O.P$_2$O$_5$–x B$_2$O$_3$ SYSTEM

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Boron oxide in the Na$_2$O.P$_2$O$_5$–x B$_2$O$_3$ system behaves as a Lux base. Its addition to Na$_2$O..P$_2$O$_5$ brings about transformation of a Co(II) indicator from octahedral to tetrahedral configuration, increase in the optical basicity $\Lambda_{Pb(II)}$, increase in the relative basicity of the melt as determined by means of a galvanic cell, and depolymerization reactions releasing PO$_4^{3-}$ ions. In the Na$_2$O–B$_2$O$_3$ system free of P$_2$O$_5$, boron oxide behaves as a Lux acid. The amphoteric nature of B$_2$O$_3$ is explained in terms of Lux's acid-base theory extended in analogy with the protolysis theory. The theoretical optical basicity values do not indicate the amphoretic behaviour of B$_2$O$_3$ because in this approach boron oxide is *a priori* regarded as more acidic than Na$_2$O.P$_2$O$_5$.

The degree of acidity or basicity of oxide melts is an important parameter in relation to their structure and chemical and physical properties. Oxides are conventionally classed as acidic or basic with respect to their behaviour in water. About twenty empirical relations have been suggested since 1869 for expressing the basicity of slags and glasses[1], all of them based on the concentration of acidic or basic oxides in the solidified sample. Proceeding from the idea that the O^{2-} ion in oxide melts plays a similar role as the H$^+$ ion in aqueous solutions, Lux[2] defined acids and bases by means of the relation

$$\text{base} = \text{acid} + \text{O}^{2-} . \tag{A}$$

Flood[3] extended this concept also to polyacids, where the acid-base transformation (A) is associated with a breakdown of oxygen bridges:

$$2\,(\text{X—O})^- \;=\; \text{X—O—X} + \text{O}^{2-} , \tag{B}$$
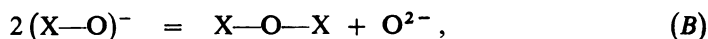
where X = Si, P, B.

In analogy with the pH in aqueous solutions, the pO exponent, *i.e.*, the negative value of the common logarithm of activity of O^{2-} ions, can be used to characterize the acid-base nature of oxide melts; high pO values characterize acid melts, low pO

values, basic melts. The activity of the ions, however, cannot be defined thermodynamically because $a(O^{2-})$, *i.e.*, the absolute basicity of the melt, cannot be directly determined. In work[4,5] pO has been determined as the ratio of $a(O^{2-})$ in the melt under study to the corresponding value in a reference melt, established by measuring the electromotive voltage of concentration galvanic cells with oxygen electrodes. Chemical galvanic cells with so-called indicator cations[6] can also be employed for this purpose.

The acid-base nature of glasses can be evaluated based on the absorption spectra of cobalt(II) or lead(II) indicators. The configuration of Co(II) is transformed from octahedral to tetrahedral as the basicity of the glass is increased[7]. The optical basicity $A_{Pb(II)}$ can be determined[8-10] based on the position of the absorption maxima in the UV spectra of Pb(II). According to[11], the theoretical optical basicity A can be calculated from the electronagetivities regardless of whether the substance forms a glass or not.

The aim of the present work was to evaluate the acid-base nature of boron oxide in $Na_2O.P_2O_5$. Melts and glasses of the $Na_2O.P_2O_5-x\,B_2O_3$ systems with $x = 0-1.5$ were measured by means of chemical galvanic cells and spectroscopic Co(II) and Pb(II) indicators. In practice, $Na_2O.P_2O_5$ is used as a fluxing agent in X-ray fluorescence analysis, and molten sodium phosphates serve as model systems in the study of metallurgical slags[12,13].

EXPERIMENTAL

Chemicals

All the chemicals used were of reagent grade purity. $Na_2B_4O_7$, B_2O_3, and $Na_2O.P_2O_5$ were prepared by fusing $Na_2B_4O_7.10\,H_2O$, H_3BO_3, and $NaH_2PO_4.2\,H_2O$, respectively, in a platinum crucible. The spectroscopic measurements were performed using cobalt oxide and lead nitrate as indicators. After the measurements the samples were analyzed for sodium, total phosphorus, and the indicator ions by atomic absorption spectrometry on a Perkin–Elmer 3030 instrument. Phosphate (PO_4^{3-}) in the presence of polymeric $(PO_3^-)_n$ ions was determined spectrophotometrically in the form of vanadatomolybdatophosphoric acid.

Absorption Spectra of Glasses

The absorption spectra of cobalt(II) and lead(II) in the glass bead samples were measured over the ultraviolet-visible region at 20°C on a Specord UV-VIS instrument (Carl Zeiss, Jena); sample free of indicator served as the reference standard. The indicator was added to the sample in the form of Co_2O_3 or as two or three drops of a 10^{-2}M solution of $Pb(NO_3)_2$, and the whole was fused in a platinum crucible at 900°C for 2 h. The melt was cast in a preheated Pt–Au–Rh mold. The weight of the cold glass beads was 5 g, thickness about 0·25 cm.

Measurement of Electromotive Voltage of Galvanic Cell in Melts

An $\ominus$Ni | NiO in melt | O_2, Pt$\oplus$ galvanic cell was used for the measurements. Nickel oxide was added to the $Na_2O.P_2O_5-x\,B_2O_3$ system in an amount such that the Ni^{2+} ions replaced 1 mol.%

Na^+ ions. The layout of the cell is shown in Fig. 1. The melt was accomodated in a platinum crucible **1**. The oxygen electrode was constituted by a platinum capillary **2**, i.d. 1 mm, through which dry oxygen was passed. The upper end of the capillary was connected to a copper tube serving for the air feed and also for the oxygen feed. The nickel electrode **3** was a wire 1 mm in diameter accomodated in a protective Al_2O_3 tube **4** sealed to a platinum tube **5**. Tubes **4** and **5** were flushed with argon. The temperature was measured with a PtRh 10 thermocouple submerged in the melt. The measurements were performed in an electric resistance furnace and the electromotive voltage was recorded on a Minigor R 501 recorder.

RESULTS AND DISCUSSION

The results obtained by using the Co(II) optical indicator are given in Table I and shown in Fig. 2. Curve **1** has a shape typical of octahedrally bonded Co(II) in glasses[7], whereas curves **2** and **3** have shapes typical of the tetrahedral configuration. The Co(II) configuration transformation is described by the equation[9]

$$Co^{2+}(O_h) + 4\,O^{2-}\ (\text{solvated}) \;\rightleftharpoons\; [CoO_4]^{6-} \quad (T_d\text{-solvated}) \qquad (C)$$
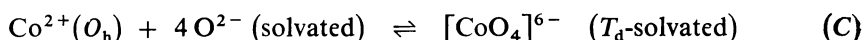
This transformation in the $Na_2O.P_2O_5$ system is promoted by added B_2O_3, which implies that shifting the equilibrium (C) forwards, boron oxide behaves as a base and is an O^{2-} ion donor. In the absence of P_2O_5, however, in the $Na_2O–B_2O_3$ system, B_2O_3 acts as an acidic oxide. The Co(II) configuration is transformed from
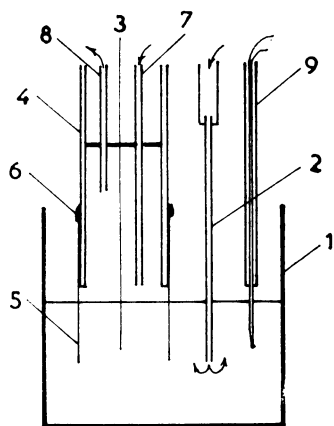

FIG. 1

Layout of the galvanic cell. **1** Pt crucible with melt, **2** Pt capillary, **3** Ni wire, **4** Al_2O_3 tube, **5** Pt tube, **6** ceramic seal, **7** argon inlet, **8** argon outlet, **9** thermocouple
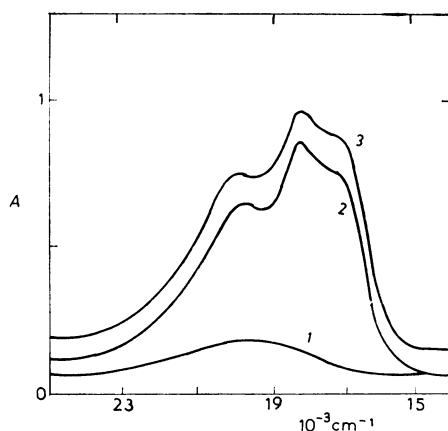
FIG. 2

Absorption spectra of cobalt(II) in the glasses at 20°C. *1* $Na_2O.P_2O_5$, *2* $Na_2O.P_2O_5.$ $.0\cdot5\ B_2O_3$, *3* $Na_2O.P_2O_5.B_2O_3$

tetrahedral to octahedral as the amount of B_2O_3 is increased (Table I), in agreement with the data[7]. It is a drawback of this approach that the changes in the acid-base properties are not indicated continuously. For instance, in the Na_2O–B_2O_3 system the $T_d \rightarrow O_h$ transformation takes place when the amount of the latter reaches the level of $Na_2O.4 B_2O_3$ (ref.[7]).

The use of the Pb(II) optical indicator enabled a continuous scale of the so-called optical basicity to be defined[9]; the optical basicity values are calculated as

$$A_{Pb(II)} = (60\ 700 - v'_{max})/31\ 000 , \tag{1}$$

where v'_{max} is the frequency of the UV maximum in the system under study. The values can be compared with the theoretical optical basicity A_{theor}, calculated as[11]

$$A_{theor} = (z_A r_A/2)(1/\gamma_A) + (z_B r_B/2)(1/\gamma_B) + (z_C r_C/2)(1/\gamma_C) , \tag{2}$$

where z_A, z_B, and z_C are the charge numbers of the ions A, B, and C, respectively, r_A, r_B, and r_C are the ratios of the numbers of the A, B, and C cations, respectively, to the total number of oxygen atoms in the compound, and $\gamma = 1.36(x' - 0.26)$ where x' is the Pauling electronegativity.

The results for the $Na_2O.P_2O_5$–$x B_2O_3$ systems and, for a comparison, for the Na_2O–B_2O_3 systems are given in Table I. The optical basicity values in the Na_2O– –B_2O_3 system agree with the published data[9] as well as with the results obtained by us by using the Co(II) indicator. Both $A_{Pb(II)}$ and A_{theor} decrease with increasing B_2O_3 content. As to the optical basicity in the $Na_2O.P_2O_5$–$x B_2O_3$ systems, no litera-

TABLE I

Symmetry of the cobalt(II) complexes in the glasses at 20°C and the basicity values A

System	Cobalt(II) complexes symmetry	A_{theor}	$A_{Pb(II)}$
$Na_2O.P_2O_5$	O_h	0·53	0·54
$Na_2O.P_2O_5.0·25 B_2O_3$	T_d	0·52	0·55
$Na_2O.P_2O_5.0·5 B_2O_3$	T_d	0·51	0·56
$Na_2O.P_2O_5.B_2O_3$	T_d	0·49	0·58
$Na_2O.P_2O_5.1·5 B_2O_3$	T_d	0·48	0·58
$Na_2O.2 B_2O_3$	T_d	0·53	0·53
$Na_2O.7 B_2O_3$	O_h	0·46	0·45

ture data are available. The $\Lambda_{Pb(II)}$ basicity agrees with the results obtained with the Co(II) indicator only in that the values increase with increasing proportion of B$_2$O$_3$. No conclusions can be drawn from the numerical values of $\Lambda_{Pb(II)}$, the optical basicity concept only being under development[4]. For instance, the acid-base nature of Na$_2$O .P$_2$O$_5$ and Na$_2$O.2 B$_2$O$_3$ is better shown by Co(II) exhibiting the O_h and T_d configurations respectively, than by the $\Lambda_{Pb(II)}$ data which are identical for the two systems. According to the electrochemical data of relative basicity[4], the acidity of Na$_2$O. .P$_2$O$_5$ is 10^7 times higher than that of Na$_2$O.2 B$_2$O$_3$. It should be borne in mind, however, that it cannot be decided whether a relation exists between the optical basicity and the Lux basicity or not[11]. According to Duffy and Ingram[11], the $a(O^{2-})$ and Λ values can be regarded as separated and independent measures of basicity. A relation between them has been found for borate melts in work[14], where the differences between Λ_{theor} and $\Lambda_{Pb(II)}$ are also discussed.

The fact that Λ_{theor} decreases with increasing B$_2$O$_3$ content can be explained in terms of the amphoteric behaviour of a component being not allowed for by the method in question. Even the definition (2) fails to take into account the fact that the acidity or basicity only manifests itself in the interaction with the environment. By the γ_X values the acidity increases in the series Na$_2$O–CaO–Al$_2$O$_3$–SiO$_2$–B$_2$O$_3$– –P$_2$O$_5$. In binary systems such as Na$_2$O–B$_2$O$_3$, CaO–SiO$_2$, or MgO–SiO$_2$, Λ_{theor} decreases monotonically with increasing amount of the more acidic oxide. Similarly, in the Na$_2$O–P$_2$O$_5$–B$_2$O$_3$ ternary system in the Na$_2$O/P$_2$O$_5$ = 1 section, an addition of B$_2$O$_3$ $(\Lambda = 0.42)$ must lower the Λ value of the mixture with $\Lambda_{Na_2O.P_2O_5} = 0.52$. It can be proved that in the Na$_2$O.P$_2$O$_5$–x B$_2$O$_3$ system the Λ_{theor} value is a monotonic function of x over the region of $0.52 - 0.42$.

The acid-base nature of the Na$_2$O.P$_2$O$_5$–x B$_2$O$_3$ melts was evaluated at 945°C by the electromotive voltage measurements. The relative basicity, i.e., the $a_n(O^{2-})$: : $a_1(O^{2-})$ activity ratio, was determined by means of Eqs (3), (4). The activity ratio was calculated from the E_n, $x_n(Ni^{2+})$ values assuming that $\gamma_1 \approx \gamma_n$ (in general, $\gamma_i = \gamma$ for $1 \leq i \leq n$).

$$E_n - E_1 = -(RT/2F)\ln\left[a_n(NiO)/a_1(NiO)\right] \tag{3}$$

$$a_n(NiO) = \gamma_n(Ni^{2+})\, x_n(Ni^{2+})\, a_n(O^{2-}) \tag{4}$$

The relative basicity values, as given in Table II, increase with increasing B$_2$O$_3$ content.

The measurements on the Na$_2$O.P$_2$O$_5$–x B$_2$O$_3$ system by means of the optical indicators and the galvanic cell were supplemented with analysis for PO$_4^{3-}$ ions in solutions obtained by dissolving the rapidly cooled melts. The fraction of PO$_4^{3-}$ from the total phosphorus is plotted against $x(B_2O_3)$ in Fig. 3. The amount of PO$_4^{3-}$

increases with x increasing up to $x = 1$. The addition of B_2O_3 brings about depolymerization of the $(PO_3)_n^{n-}$ chain. According to [15], the chain length in $Na_2O.P_2O_5$ obtained by fusing NaH_2PO_4 is $n = 20-50$. Phosphate ions can form also by hydrolysis,

$$(PO_3)_n^{n-} + H_2O \rightleftharpoons (PO_3)_{n-1}^{-(n-1)} + PO_4^{3-} + 2H^+ \qquad (D)$$
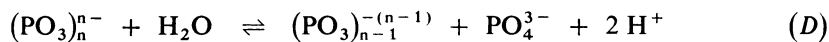
If $Na_2O.P_2O_5-x\,B_2O_3$ is dissolved in neutral medium at $20°C$, as little as $5 . 10^{-6}\%$ PO_4^{3-} is formed per second by hydrolysis. The presence of PO_4^{3-} ions in the solution after the sample dissolution is indicative of the occurrence of this ion in the melt itself[12]. Methods for the determination of the ion distribution have been worked out also for metallurgical slags insoluble in water[13], based on the ion distribution in the soluble polymeric phosphates.

TABLE II

Electromotive voltage values and relative activities at 945°C

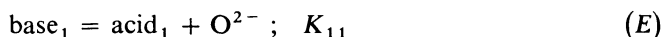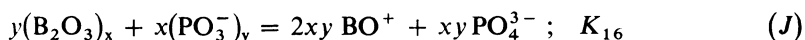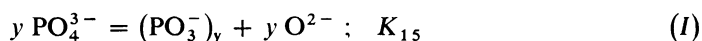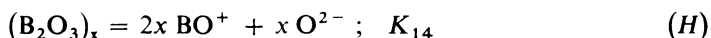| n	System	E V	$x(Ni^{2+})$ %	$\log[a_n(O^{2-})/a_1(O^{2-})]$
1	$Na_2O.P_2O_5$	1·111	1·04	0·000
2	$Na_2O.P_2O_5.0.25\,B_2O_3$	1·047	1·03	0·533
3	$Na_2O.P_2O_5.0.5\,B_2O_3$	1·001	1·05	0·875
4	$Na_2O.P_2O_5.B_2O_3$	0·966	1·01	1·213
5	$Na_2O.P_2O_5.1.5\,B_2O_3$	0·940	1·05	1·411
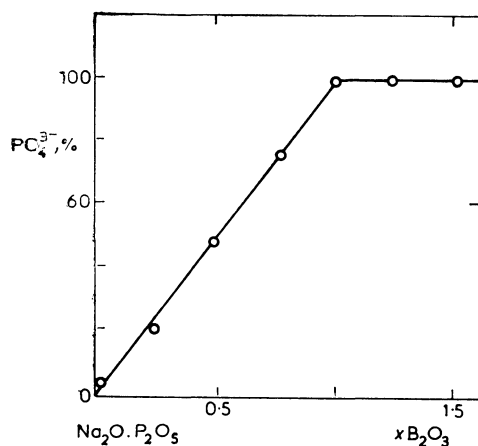
FIG. 3

Dependence of the PO_4^{3-} fraction from total phosphorus on x in the $Na_2O.P_2O_5.x\,B_2O_3$ system

Boron oxide in the Na$_2$O.P$_2$O$_5$-x B$_2$O$_3$ system behaves as a Lux base, its addition to Na$_2$O.P$_2$O$_5$ inducing a) change in the cobalt(II) configuration from octahedral to tetrahedral; b) increase in the optical basicity $\Lambda_{Pb(II)}$; c) increase in the relative basicity of the melt determined as the $a(O^{2-})_{exp}/a(O^{2-})_{ref}$ ratio; and d) depolymerization reaction resulting in the formation of PO$_4^{3-}$ ions. In the absence of P$_2$O$_5$, boron oxide behaves as a Lux acid. The amphoteric nature of B$_2$O$_3$ can be explained in terms of the Lux's definition (A), by extending it is analogy with the protolysis theory and looking upon the reaction between acid and base as the difference between two simple buffer equilibria,

$$base_1 = acid_1 + O^{2-} \; ; \quad K_{11} \tag{E}$$

$$base_2 = acid_2 + O^{2-} \; ; \quad K_{12} \tag{F}$$

$$\overline{base_1 + acid_2 = base_2 + acid_1 \; ; \quad K_{13}} \tag{G}$$
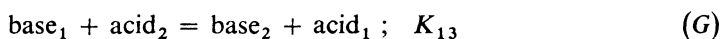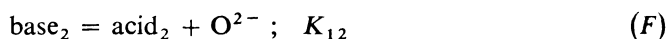
Taking for base$_1$ = B$_2$O$_3$, base$_2$ = PO$_4^{3-}$, acid$_2$ = PO$_3^-$, then in analogy with $(E)-(G)$,

$$(B_2O_3)_x = 2x\, BO^+ + x\, O^{2-} \; ; \quad K_{14} \tag{H}$$

$$y\, PO_4^{3-} = (PO_3^-)_y + y\, O^{2-} \; ; \quad K_{15} \tag{I}$$

$$\overline{y(B_2O_3)_x + x(PO_3^-)_y = 2xy\, BO^+ + xy\, PO_4^{3-} \; ; \quad K_{16}} \tag{J}$$

Reaction (J) takes place provided that $K_{14} > K_{15}$. The PO$_4^{3-}$ content increases linearly with the amount of B$_2$O$_3$ and the reaction is quantitative up to $x = 1$ which gives evidence that the above assumption is satisfied. The BO$^+$ ion can be formed by reaction (J) similarly as SiO^{2+} is formed[16] by reaction of SiO$_2$ with H$_3$PO$_4$.

For more accurate measurements, the classification of oxides as acidic or basic is insufficient even for melts. Also in these systems the acidity or basicity only appears during their interaction with the environment.

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