of a chemical potential with respect to concentration variables. Reliance upon the critical conditions thus obtained for quantitative results requires a greater faith in the complete applicability of the chosen model than is probably justified.

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A Study of Molten Borates with the Cr(VI)–Cr(III) Indicator

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The Cr(VI)–Cr(III) indicator is applied to binary borate melts at 1200°. The concentrations of the two valences, each below 0.1%, are determined by titration. Their ratio, corrected for the oxygen pressure above the melt, is taken as a measure for the availability of oxygen ions for bond formation. The systems of B_2O_3 with Li_2O, BaO and ZnO show minima of this oxygen ion availability which are correlated to anomalies in some physical properties reported for the corresponding glasses. With K_2O and PbO, no minima are observed.

Several physical properties of binary boric oxide–metal oxide glasses indicate that an increase in metal oxide concentration, starting from pure B_2O_3, first tightens the structure of the glass to loosen it up above metal oxide equivalent fractions of about 0.1.[2,3c]: For instance, the "apparent molar refraction" $R_{O^{2-}}$ introduced by Fajans and Kreidl[4] as a measure of the looseness of oxygen bonding shows minima at equivalent fractions of 0.06 to 0.08 in the systems with Na_2O, K_2O and BaO.[3] It seemed worthwhile to see whether the availability of the oxygen ion for bond formation, as measured with an indicator, would exhibit similar features in the molten mixtures at 1200°.

Indicators which have been employed in liquid oxide systems by Weyl,[5a] Dietzel[5b] and Lux[6] are pairs of metal ions like Cr^{6+}–Cr^{3+}. Their equilibrium, at a specified oxygen pressure, is determined by the availability of oxygen ions (the "oxygen ion concentration" in the terminology of Lux and Flood[7]). The range of the indicator can be extended by using different oxygen pressures. The present view of molten oxides[8] does not permit the assignment of definite formulas to the indicator ions. Formally, their equilibrium can be written as

$$\text{Cr(VI) (in melt)} \leftrightarrows \text{Cr(III) (in melt)} + {}^3/_4\text{O}_2 \quad (1)$$

In order to compare the results measured at different oxygen pressures, a quantity K' is defined

$$K' = \frac{c_6}{c_3} \times p_{O_2}{}^{-3/4} \quad (2)$$

c_6, c_3 and p_{O_2} denoting the concentration of hexa- and trivalent chromium found by analysis (in weight %) and the partial pressure of oxygen in atmospheres, respectively. This K' is primarily a function of the pseudo-binary oxide composition. All its factors are measured; thus log K' is the analog of Hammett's H-function[9] in protic solvents. The composition of the pseudo-binary borate systems is expressed in this paper by the equivalent fraction of the metal oxide

$$q_{MeO} = 2n_{MeO} / (6n_{B_2O_3} + 2n_{MeO})$$

Me denoting K_2, Ba, etc., n the oxide mol number.

The indicator equilibrium was to be followed by chemical analysis. Therefore the Cr(VI)–Cr(III) pair was chosen. Its hexa- and trivalent ions are fairly stable in aqueous solution and can be titrated without special precautions; also, one would expect only these two valences under the oxygen pressures applied.[10] As to the second component to be added to boric oxide, all oxides occurring in several valences were ruled out by the analytical method used for the indicator. Evaporation from the melt and narrow homogeneous liquidus ranges[11] were other limitations. To have cations of different charge, size and polarizability, the oxides of Li, K, Ba and Zn were chosen, and PbO which permits investigation over the whole concentration range.

Experimental

The general procedure was as follows: A mixture of boric oxide and the corresponding metal oxide containing about 0.1% Cr was held at 1200° in an oxygen–nitrogen atmosphere of known composition until equilibrium was reached. The sample was then quenched and analyzed for the metal oxide and for hexa- and trivalent chromium. By choosing the proper gas atmosphere, the c_6/c_3 ratio was kept between 0.1 and 10 which is convenient for the analysis.

The reagents were boric acid, the nitrates of lithium, potassium and barium, and zinc and lead(II) oxide, all of analytical grade. Chromium was added as $K_2Cr_2O_7$. These components were premelted under either hydrogen or oxygen, checked for the absence of nitrate and then placed into a small 1-ml. platinum crucible. Two of these were hung together into a vertical ceramic tube of 1¼" i.d.

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[2] B. E. Warren, *J. Am. Ceram. Soc.*, **24**, 256 (1941).

[3] The calculation of R_{O_2} was based on refractive indices and densities from the following sources: For Na: (a) P. Wulff and S. K. Majumdar, *Z. physik. Chem.*, **B31**, 319 (1936); (b) J. M. Stevels, *J. Soc. Glass Tech.*, **30**, 303 (1946). For K: (c) R. L. Green, doctor's thesis M.I.T., Cambridge, Mass., 1940; *J. Am. Ceram. Soc.*, **25**, 83 (1942); for Ba: (d) E. M. Levin and H. F. McMurdie, *ibid.*, **32**, 99 (1949); (e) J. M. Stevels, *J. Soc. Glass Tech.*, **30**, 173 (1946); *cf.* S. P. Varma and W. A. Weyl, *Nature*, **162**, 938 (1948).

[4] (a) K. Fajans and N. J. Kreidl, *J. Am. Ceram. Soc.*, **31**, 105 (1948); (b) F. L. Jones and N. J. Kreidl, *J. Soc. Glass Tech.*, **33**, 239 (1949).

[5] (a) W. Weyl and E. Thümen, *Sprechsaal*, **66**, 197 (1933); (b) W. Stegmaier and A. Dietzel, *Glastech. Ber.*, **18**, 297, 353 (1940).

[6] (a) H. Lux and E. Rogler, *Z. anorg. Chem.*, **250**, 159 (1942); (b) H. Lux, J. Cordon and R. Frey, *ibid.*, **257**, 79 (1948). *Cf.* H. Lux and E. Proeschel, *ibid.*, **257**, 59, 67 (1948).

[7] (a) H. Lux, *Z. Elektrochem.*, **45**, 303 (1939); (b) H. Flood and T. Førland, *Acta Chem. Scand.*, **1**, 592 (1947).

[8] See, for instance, J. O'M. Bockris and J. W. Tomlinson, *Research (London)*, **2**, 362 (1949).

[9] P. L. Hammett and A. J. Deyrup, THIS JOURNAL, **54**, 2721 (1932).

[10] However, for CrF_4 and $CrCl_4$ *cf.* H. v. Wartenberg, *Z. anorg. Chem.*, **247**, 135 (1941); **249**, 100 (1942); **250**, 122 (1942).

[11] (a) F. P. Hall and H. Insley, "Phase Diagrams for Ceramists," *J. Am. Ceram. Soc.*, November, 1947, and December, 1949; (b) M. A. Foex, *Ann. chim.*, **11**, 359 (1939).

which was heated in a SiC rod furnace. The temperature was measured with a calibrated external Pt–Pt/Rh thermocouple; it could be held at 1200° within ±10° for many hours by manually regulating the furnace voltage. The gas mixture inside the tube was made up from oxygen or air and nitrogen; these gases were purified and dried in the usual manner and measured within ±5% in flowmeters similar to those described by Darken and Gurry.[12] The gas flowed upwards in the tube at a velocity of 0.95 cm./sec. at which rate thermal diffusion is negligible.[12]

To reach equilibrium, the majority of the samples were heated for 12 hr., the ones containing much B_2O_3 for 24 hr., and the mixtures rich in K_2O and PbO, having a high vapor pressure, for 2 to 4 hr. For each composition one sample had been reduced to blue color by the premelting under hydrogen; the other one had been over-oxidized under oxygen. If this was not possible, one sample was made to have about $^1/_4$ the volume of the other. Both were heated simultaneously under the corresponding O_2–N_2 mixture. When they gave the same c_6/c_3 ratio within the limits of error, it was concluded that equilibrium had been attained.

For quenching the samples, the crucibles were lowered into the pool of mercury at the bottom of the furnace tube. A slower cooling certainly would not alter the oxygen content of the very viscous liquids, but in some mixtures rich in B_2O_3 and Cr^{III} it resulted in a precipitation of Cr_2O_3 insoluble for analysis.[13]

Analysis.—The finely ground samples of about 0.5 g. were dissolved in boiling 0.5 *N* HCl. Li_2O and K_2O were titrated directly with HCl, whereas the barium borates had to be dissolved in an excess of acid and titrated with NaOH. An antimony electrode as the electrometric indicator gave satisfactory end-points. To dissolve the lead borates, boiling 3 *N* NaOH was employed. ZnO and PbO were determined by the usual gravimetric methods in a separate sample.

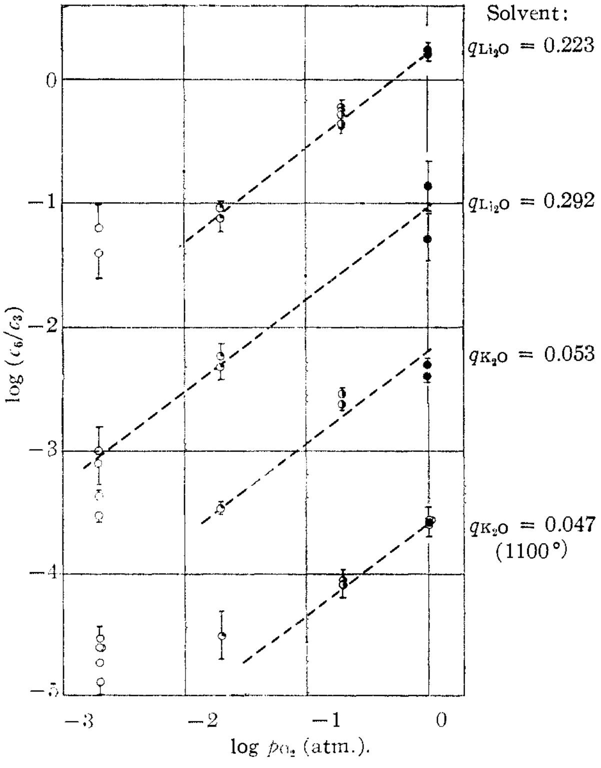

Fig. 1.—Cr(VI)-Cr(III) equilibrium at different oxygen pressures in constant solvent, 1200°, 0.1% Cr. The points for q_{Li_2O} = 0.292, q_{K_2O} = 0.053 and 0.047 have been shifted downwards by 2, 2.6 and 4 units in log (c_6/c_3), respectively. Straight lines drawn with slope 3/4. Further explanations see below Fig. 2.

The hexavalent and the trivalent chromium were fractions of the total amount of 0.1% Cr or less, so that quantities of 20 to 500 μg. Cr of either valence had to be determined. A direct titration seemed to be the most promising method. For the Cr^{III}, the procedure of Hahn[14] was adopted. A suitable fraction of the solution resulting from the acid titration was added to twice the volume of boiling 10 *N* NaOH and titrated with 0.01 *N* cyanoferrate(III) after the addition of a few drops of 0.0005 *N* thallium(I) nitrate to serve as an accelerator. The 10 *N* NaOH had to be "neutralized" previously with a little cyanoferrate(III) up to the end-point potential, which was at ±0 mv. with the platinum and saturated calomel electrodes used. It was found that lead(II) is oxidized quantitatively to Pb(IV) under these conditions. For the lead borates, therefore, a NaOH solution of only 2.5 *N* was employed, which prevented the oxidation of lead and still gave complete Cr(III) oxidation with a satisfactory end-point. The Cr(VI) was titrated with 0.01 *N* iron(II) sulfate in another fraction of the solution.

Probable Errors.—An oxidation of the sample during the grinding is very unlikely. That dissolving under the conditions specified did not alter the respective chromium concentrations was checked with known mixtures. An appreciable error could be due to the fact that some of the samples rich in boric oxide gave whitish opalescent solutions which did not clear up after addition of a strong acid or base. In view of its smallness this residue was not further analyzed. If one assumes that it contained Cr(III), then the trivalent chromium found for these samples would be too low. It is believed that the scatter in the high boric oxide region is due to this phenomenon. The metal oxides titrated are thought to be accurate within ±0.5%. For Cr(III) and Cr(VI) the following error can be estimated: An uncertainty of ±0.05 ml. of titrating agent corresponds to ±9 μg. of Cr, which may be as much as $^1/_4$ of the amount of one valence giving for log (c_6/c_3) an error of ±0.2 in unfavorable cases. In most samples, the sum of c_6 and c_3 was found as 80 to 105% of the original Cr concentration. In the samples containing lead oxide the agreement was within 5%; thus, the presence of higher lead oxides appears improbable.

Results and Discussion

Indicator Equilibrium.—First of all, the behavior of K' at constant solvent composition had to be checked. Table I shows that from 1.0 to 0.1% Cr, and presumably below, K' is independent of the indicator concentration. (0.1% Cr equals about 0.03 gram atom per liter.) Changing the temperature from 1200 to 1100° gave an increase of 0.29 and 0.14 in log K' for a K and a Li borate, respectively.[15]

TABLE I

LOG K' FOR CONSTANT SOLVENT COMPOSITION

(a) Solvent: K_2O–B_2O_3, q_{K_2O} = 0.078, p_{O_2} = 0.2 atm., 1100°. (b) Solvent: Li_2O–B_2O_3, q_{Li_2O} = 0.223, p_{O_2} = 0.2 atm., 1200°. (c) Solvent: K_2O–B_2O_3, q_{K_2O} = 0.060; interpolated from Fig. 2. (d) Solvent: Li_2O–B_2O_3, q_{Li_2O} = 0.223, p_{O_2} = 0.2 atm., 0.1% Cr.

Variation of indicator concentration				Variation of temperature		
(a)		(b)			(c)	(d)
Total Cr % $c_6 + c_3$	log K'	Total Cr % $c_6 + c_3$	log K'	Temp., °C.	log K'	
0.115	1.07	0.102	0.30	1100	0.77	0.40
.121	0.92	.104	.28			.45
.124	0.97	.553	.23	1200	.48	.30
.108	1.13	.559	.16			.28
.552	1.08	1.070	.23			
.550	1.08	1.075	.25			
1.012	1.07					

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[12] L. S. Darken and R. W. Gurry, THIS JOURNAL, **67**, 1398 (1945).

[13] At 1200°, B_2O_3 dissolves 1.72 weight % Cr_2O_3 (11b); the quenched glass holds less than 0.04%.

[14] F. L. Hahn, *Z. angew. Chem.*, **40**, 349 (1927).

[15] This yields some +10 kcal. for the ΔH of reaction (1). According to O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry," Academic Press, Inc., New York, N. Y., 1951, the ΔH_{298} = +2.2 ± 2.3 kcal. for the reaction: $CrO_3(c) = {}^1/_2Cr_2O_3(c) + O_2(g)$.

To show the effect of different oxygen pressures, log (c_6/c_3) was plotted *vs.* log p_{O_2}. It is seen on Fig. 1 that, at least down to $p_{O_2} = 0.02$ atm., the points lie on a straight line with a slope of 3/4. It seems unlikely to the author that the deviation at low oxygen pressures can be explained by experimental error only. The conclusion was drawn that, for constant solvent, K' can be considered as an apparent equilibrium constant representing the indicator reaction as written in eq. (1). This holds for Cr

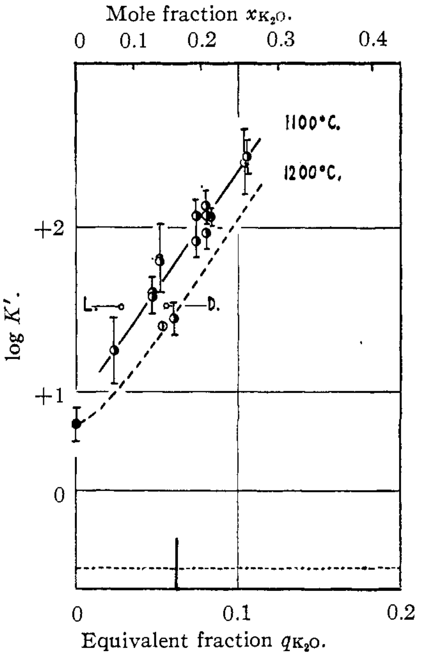

Fig. 2.—Log K' in the system $K_2O–B_2O_3$. "L." and "D." points according to Lux[6] and Dietzel.[5b] Estimated analytical error given with each point. Oxygen pressures: ●, 1; ◑, 0.2; ◔, 0.02; ○, 0.002 atm.; ⦶, mean from experiments at different pressures. Phase diagram[11] information at bottom: Thick vertical lines symbolize crystal phase with m.p., if dotted, incongruent melting. Thin dotted vertical lines: limits of two phase range. Horizontal dotted lines: range in which glassy samples were obtained.

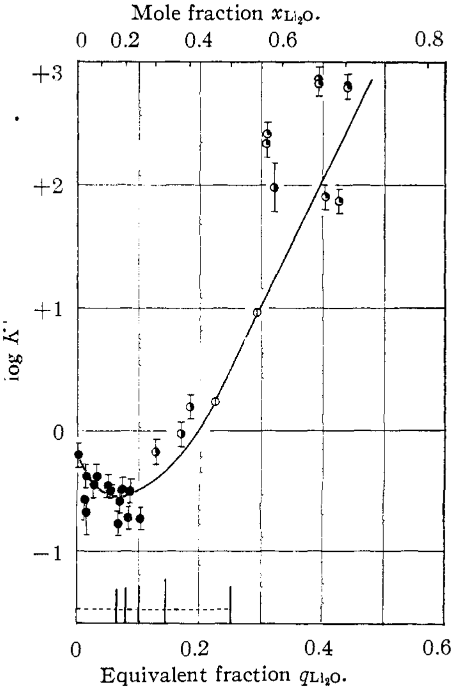

Fig. 3.—Log K' in the system $Li_2O–B_2O_3$; for explanations see below Fig. 2.

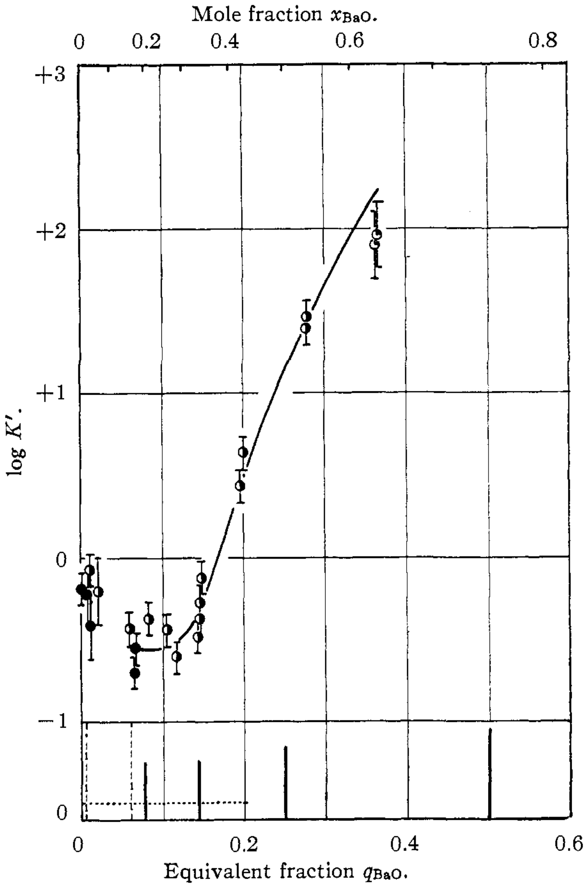

Fig. 4.—Log K' in the system $BaO–B_2O_3$; for explanations see below Fig. 2.

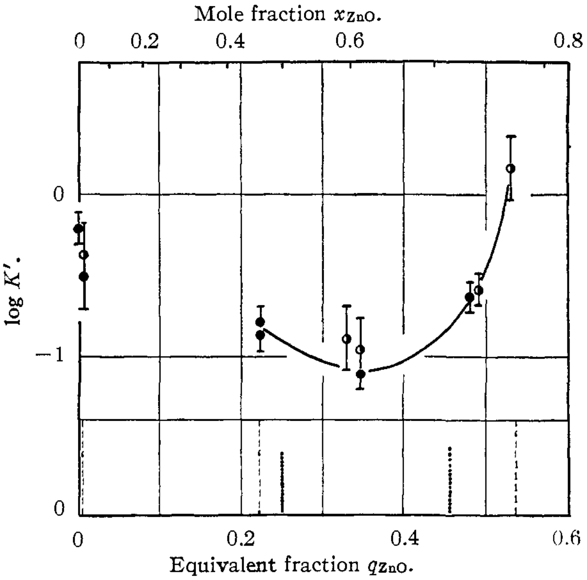

Fig. 5.—Log K' in the system $ZnO–B_2O_3$; for explanations see below Fig. 2.

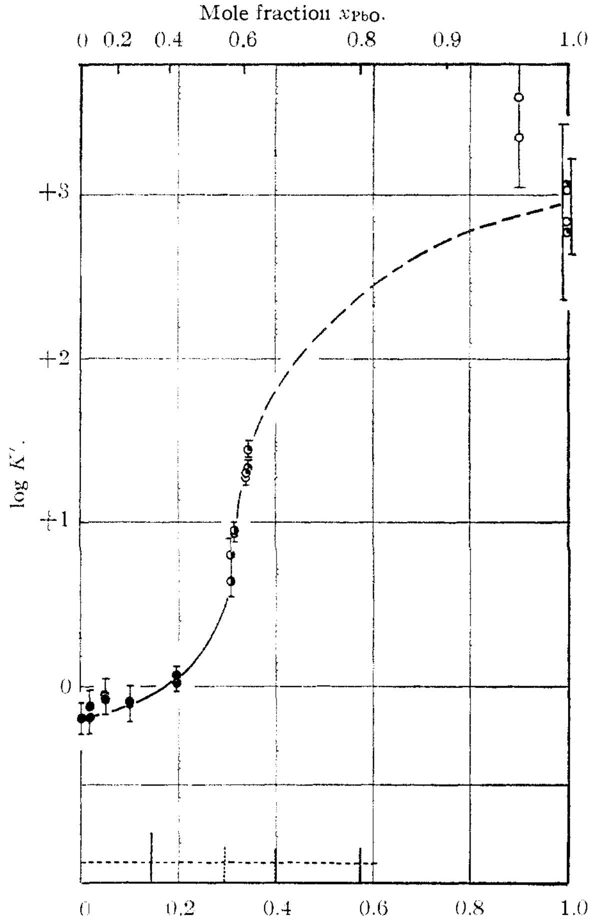

Fig. 6.—Log K' in the system $PbO–B_2O_3$; for explanations see below Fig. 2.

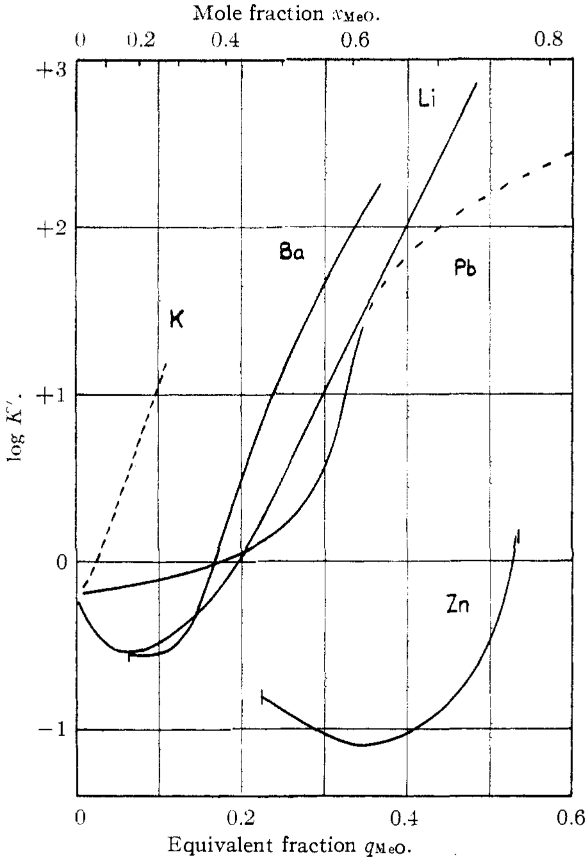

Fig. 7.—Log K' in the 5 pseudo-binary systems investigated.

concentrations below 1% and oxygen pressures between 0.02 and 1 atm., a variation in temperature of ±20° giving no appreciable change. The log K' values reported below were obtained within these limits.

Log K' Values for Pseudo-binary Borate Systems.—The results for the 5 systems investigated are plotted *vs.* composition in Figs. 2–6; the curves which seemed to give the best fit are reproduced together in Fig. 7. For the systems with Li_2O and BaO (Figs. 3 and 4) the curves are quite similar except for the miscibility gap in the latter. A minimum is observed around $q_{MeO} = 0.1$; one may presume that the decrease in oxygen ion availability is caused by the same reasons as the structure tightening of the corresponding glasses.[2] With ZnO, furnishing a cation of high polarizability, the minimum occurs at higher metal oxide concentration with a log K' value much below the one for boric oxide (Fig. 5).

The system $K_2O–B_2O_3$ (Fig. 2) does not reflect the anomalies found in the glass, nor does the system with PbO (Fig. 3).[16] From the fact that in these two systems the melts are relatively volatile and little viscous, one may guess that the log K' minima will disappear also in the other systems if the temperature is increased. In the $PbO–B_2O_3$ liquids up to $q_{PbO} = 0.2$ the oxygen ion availability is almost the same as in pure B_2O_3; indeed, a similarity in the oxygen bonds of Pb, B and Si is suggested by magneto-optical measurements[17] indicating the presence of tetracovalent lead in lead silicate glasses. The steep increase of log K' around $q_{PbO} = 0.3$ is paralleled by an anomaly in the surface tension of these liquids.[18]

At a constant composition of $q_{MeO} = 0.25$ the log K' values are found to decrease in the order K, Ba, Li, Pb, Zn, which is very much the same as in the various "basicity series" reported.[7b] The order is changed, however, at different q_{MeO}.

If another indicator were chosen, one might expect similar log K' values (except for an additional constant), only if the ion pair is of the same charge type. This is suggested by the results of Dietzel[5b] obtained with the $Mn^{6+}–Mn^{3+}$ pair. It would permit extension of the method to mixtures not accessible by the Cr(VI)–Cr(III) indicator.

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(16) For this system, a minimum in the heat of formation of the glasses has been observed at qPbO = 0.2 (calculated per gram atom of oxygen). L. Shartsis and E. S. Newman, *J. Research Natl. Bur. Standards*, **40**, 471 (1948); *J. Am. Ceram. Soc.*, **31**, 213 (1948).

(17) H. Cole, *J. Soc. Glass Tech.*, **34**, 220 (1950).

(18) L. Shartsis, S. Spinner and A. W. Smock, *J. Research Natl. Bur. Standards*, **40**, 61 (1948).