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The Acidic and Basic Properties of Oxides

III. Relative Acid-Bace Strenghts of some Polyacids

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In a previous communication [1] the general traits of the acid-base properties of the oxides were outlined. The acid-base function in systems built up of oxides may, according to Lux, be defined as

$$\text{acid} + O^{2-} \rightleftharpoons \text{base}$$

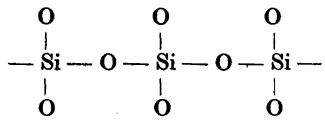
where O^{2-} is an oxygen ion.

The present paper will deal with the acid-base equilibria in systems with polyacids in more detail.

The characteristic feature of the polyacids is the linking of the single groups to large complexes by means of oxygen bridges of the type

$$X - O - X$$

e. g. $[SiO_3^{2-}]_n$ may consist of SiO_4-tetrahedra which are linked together to long chains



or rings where each SiO_4-group has two shared oxygen atoms. $[SiO_{2.5}^-]_n$ forms in a similar way two dimensional nets of SiO_4-tetrahedra, $[BO_2^-]_n$ forms chains or rings of BO_3-groups etc.

These *macromolecular structures* are well known from the lattice investigations of solid compounds. They appear, however, in melts as well, as is indicated for instance by high viscosity and a tendency to form glasses on cooling.

The tendency to form structures with oxygen bridges is especially noticeable in ions of medium ionic potential (*i. e.* charge/radius), as indicated by Zintl and Morawietz [2]. This is illustrated by the crystal structures of the oxides formed by the elements,

Mg, Al, Si, P, S, Cl.

Compare

MgO	SiO_2, (B_2O_3)	SO_3, Cl_2O_7
simple ionic crystal	macromolecular structure	molecular crystal

The transition of a polyacid to its corresponding base consists in a breaking of an oxygen bridge and a simultaneous binding of an oxygen atom.

The acid-base reaction is thus connected with a disintegration of the macromolecular structure. This must presumably take place in steps, as represented schematically by

$$SiO_2 \text{ (space lattice)} \rightarrow SiO_{2.5}^{-} \text{ (nets)} \rightarrow$$
$$SiO_3^{2-} \text{ (chains, rings)} \rightarrow Si_nO_{3n+1}^{(2n+2)-} \text{ (pyro ions etc.)} \rightarrow$$
$$SiO_4^{4-} \text{ (orthosilicate ion)}$$

Hence it seems likely that a correspondingly complicated scheme of reaction has to be applied to explain the acid-base properties of the polyacids.

In the literature only few investigations in this field have been reported, despite the great practical significance in metallurgy and ceramics, glass-technology etc.

Lux and Rogler [3] have investigated acid-base reactions in sodium borate glass by means of the Cr^{VI}/Cr^{III} indicator. These experiments are refered to in a previous communication [1].

There is, however, another type of acid-base reaction, which seems well suited for the study of the acid-base properties of these substances, namely equilibria of the type

$$CO_3^{2-} + \text{acid} \rightleftharpoons CO_2 + \text{base}$$

Several investigations on systems of this kind have already been carried out (*cf.* Niggli [4], Krøger and Fingas [5]). In this connection Niggli's investigations on the systems

$SiO_2 - K_2CO_3 - CO_2$, $SiO_2 - Na_2CO_3 - CO_2$ and
$SiO_2 - Li_2CO_3 - CO_2$,
$TiO_2 - K_2CO_3 - CO_2$ and $TiO_2 - Na_2CO_3 - CO_2$

are of special interest. He investigated homogeneous melts in equilibrium with CO_2 gas at one atmosphere at different temperatures and compositions of the melts. The results thus obtained render possible a discussion of the value of the acid-base constants of the polyacids. The present authors have extended this material by investigating the systems

$B_2O_3 - K_2CO_3 - CO_2$, $B_2O_3 - Na_2CO_3 - CO_2$ and
$B_2O_3 - Li_2CO_3 - CO_2$.

An account will now be given of the experimental methods and the results obtained, after which the experimental material will be discussed.

EXPERIMENTAL

In a platinum crucible alkali carbonate and B_2O_3 or alkali tetraborate were weighed to a total amount of 1—2 g. The mixture was carefully melted over a gas burner, whereby the reaction between carbonate and borate might take place without spraying. The crucible was then placed in the furnace, which consisted of a long, vertical porcelain tube heated by an electric coil. The middle part of the porcelain tube was surrounded by a nickel tube (ca. 25 cm long) in order to equalize the temperature in the reaction zone. A slow stream of CO_2 dried by P_2O_5 was conveyed through the furnace. The crucible was placed in the lower, cold part of the tube and the air replaced by CO_2, whereafter the crucible was raised into the reaction zone, immediately below a Pt-Rh-thermocouple (protected by a pythagoras mantle).

A heating time of about 30 minutes proved to be sufficient to attain equilibrium with the charges used. The equilibrium was then »frozen» by removing the crucible from the reaction zone as quickly as possible. After cooling (in a desiccator) the amount of CO_2 expelled at the equilibrium temperature was determined by weighing the crucible (in a weighing bottle). The greatest source of error in this procedure is the measurement of the temperature in the reaction zone.

The EMF of the thermocouple was measured by compensation to an accuracy of 0.000001 V, which corresponds to 0.1° C. However, this constancy of temperature could not be attained owing to the strong pulsations in the voltage on the heating circuit. Even by using a voltage stabilizer and regulating by hand, an accuracy better than $\pm$ 1° could not be attained.

The experimental results are shown in Table 1, which gives the original composition of the charge and the amount of CO_2 expelled, further the calcu-

Table 1. $M_2CO_3 - B_2O_3$ *at 1000° C.*

M	M_2CO_3	mol · 10^{+2}		O/B	$-\log N_{CO_3^{2-}}$
		B_2O_3	expelled CO_2		
K	0.796	0.0771	0.0818	2.03	0.085
	»	0.223	0.241	2.04	0.256
	0.805	0.227	0.237	2.02	0.256
	»	0.409	0.432	2.03	0.505
	»	0.502	0.530	2.03	0.670
Na		$Na_2B_4O_7$			
	2.003	0.0127	0.0472	2.68	0.011
	1.370	0.0147	0.0505	2.90	0.019
	»	0.0529	0.1615	2.51	0.070
	»	0.1675	0.424	2.38	0.233
	»	0.314	0.734	2.34	0.474
	»	0.465	0.985	2.28	0.749
	1.612	0.0142	0.0495	2.63	0.016
	»	0.0454	0.144	2.55	0.051
	1.560	0.1107	0.330	2.48	0.135
	0.455	0.0668	0.165	2.37	0.284
Li		B_2O_3			
	1.683	»	1.660	2.65	2.735
	2.345	»	2.005	2.93	0.719
	2.97	»	2.10	2.99	0.426
	1.007	0.363	0.945	2.80	1.105
	1.132	»	1.002	2.88	0.816
	1.310	»	1.043	2.97	0.599
	1.460	»	1.052	2.98	0.460
	1.330	0.460	1.235	2.84	1.033

(N is the mole fraction refering to a mixture of the components $BO_{1.5}$,BO_2^-, etc. and CO_3^{2-}.)

lated degree of the reaction between CO_3^{2-} and polyborate (given as average number of oxygen atoms per borate group).

Some orientating experiments regarding the dependence of the equilibrium on dilution were also carried out. In these the carbonate-borate system was diluted with alkali sulphate. These relations will later be subjected to a more thorough investigation, but in view of the subsequent discussion a few results are given i Table 2.

Table 2. Na_2CO_3—B_2O_3 diluted with sulphate at 1000° C.

mol · 10^{+3}				O/B	-log $N_{CO_3^{2-}}$
Na_2CO_3	Na_2SO_4	$Na_2B_4O_7$	expelled CO_2		
6.80	0	0.145	0.46	2.55	0.038
»	1.63	»	0.46	2.55	0.13
»	7.04	»	0.45	2.53	0.34
7.26	0	1.774	4.10	2.33	0.51
»	10.39	»	3.76	2.28	0.78

(N in this case refers to a mixture of the components $BO_{1.5}$, BO_2^-, etc, CO_3^{2-} and SO_4^{2-}).

DISCUSSION

The acid-base reactions of the polyacids may be regarded as consisting of the real acid-base reaction (*e. g.* the transition of an oxygen ion from one degree of polarization to another) and a polymerization reaction.

For instance, in the case of the acid-base transition ortho-metaborate, the following scheme of reaction may be set up,

$$BO_3^{3-} \rightleftharpoons \tfrac{1}{2}\,(BO_{2.5}^{2-})_2 + \tfrac{1}{2}\,O^{2-} \rightleftharpoons$$

acid-base reaction

$$\frac{1}{n}\,(BO_2^-)_n + \tfrac{1}{2}\,O^{2-}$$

polymerization $(BO_2^-)_n$

$$\left\{\begin{array}{l} (BO_2^-)_3 \text{ [ring with 3 links]} \\ \quad \downarrow\uparrow \\ (BO_2^-)_4 \text{ [» » 4 »]} \\ \quad \downarrow\uparrow \\ (BO_2^-)_5 \text{ [» » 5 »]} \\ \quad \text{etc.} \qquad \text{etc.} \end{array}\right.$$

Hence the complete computation of the equilibrium demands a thorough knowledge of the distribution of the polymerization in the system.

At present, however, we know very little about these relations.

Our knowledge regarding the deviations from the laws of ideal mixtures is also very limited at present. (The deviations from ideal mixtures in calcium carbonate-alkali carbonate melts will be treated in a subsequent communication.[7])

At the present stage we shall have to be content with semi-quantitative conclusions, but even these include points of interest for the further treatment of the problems.

When trying to set up convenient schemes of reaction two possibilities are at hand.

The polyacid molecule may be regarded as one reactive unit (as a single molecule); then scheme (I) applies,

$$\text{acid} + n\ CO_3^{2-} = (n + 1)\ \text{base} + CO_2 \qquad \text{(I)}$$

for example

$$S_2O_7^{2-} + CO_3^{2-} = 2\ SO_4^{2-} + CO_2$$

The use of this scheme demands knowledge of the molecular distribution of the polymerization in the melt. It should be noted that the number of homogeneous reactants remains unchanged as the reaction takes place, hence the equilibrium should not be influenced by dilution as long as polymerization does not have to be considered.

As a simpler alternative each single group in the polyacid molecule may be regarded as a reactive unit. If this holds, scheme (II) applies.

$$2\ \text{acid} + CO_2^{2-} = 2\ \text{base} + CO_2 \qquad \text{(II)}$$

for example,

$$2\ BO_{2.0}^{-} + CO_3^{2-} = 2\ BO_{2.5}^{2-} + CO_2$$

In this case the number of reactants is changed, and the equilibrium must accordingly be influenced by dilution.

For the sake of orientation a few experiments were carried out in which the borate carbonate melt was diluted with sulphate. (This is based on the presumption that the equilibrium

$$SO_4^{2-} + CO_2 \rightleftharpoons CO_3^{2-} + SO_3$$

and even

$$2SO_3 \rightleftharpoons 2\ SO_2 + O_2$$

does not cause any perceptible disturbance. This should be true as $(p_{SO_2} + p_{SO_3})/p_{CO_2}$ is estimated to 10^{-9} at 1000° C).

Table 2 gives the results of two experiments, one carried out in a melt of low polymerized borate (corresp. to $BO_{2.55}$) and the other one in a higher polymerized melt (corresp. to $BO_{2.34}$). The effects of dilution observed seem to indicate that in the region of low polymerization, scheme I has to be employd, while in the region of higher polymerization scheme II is well suitable. This

is in qualitative agreement with what we might expect. The question will, however, be more thoroughly dealt with in a later communication.

With these reservations it is reasonable to use the simple scheme II in the computation of the acid base constants. In the case of the borate system we may write,

$$2\ BO_{1.5} + CO_3^{2-} = 2\ BO_2^- + CO_{2\,(g)}$$
$$2\ BO_2^- + CO_3^{2-} = 2\ BO_{2.5}^{2-} + CO_{2\,(g)}$$
$$\left[2\ BO_{2.5}^{2-} + CO_2^{2-} = 2\ BO_3^{3-} + CO_{2\,(g)}\right]$$

The scheme is formally the same as for the stepwise formation of complexes, (*cf.* also Bjerrum [6]) and may therefore be treated in the same way.

By introducing

$$\frac{N_{BO_{1.5}} \cdot N_{CO_3^{2-}}^{\frac{1}{2}}}{N_{BO_2}} = 1/K_I \text{ etc.}$$

(where N is the mole fraction refering to a mixture of the components $BO_{1.5}$, BO_2^- and CO_3^-).

$$\bar{n}' = \frac{n_O}{n_B} = \frac{1}{2} \cdot \frac{K_I N_{CO_3^{2-}}^{\frac{1}{2}} + 2\,K_I K_{II} N_{CO_3^{2-}} + 3\,K_I K_{II} K_{III} N_{CO_3^{2-}}^{\frac{3}{2}}}{1 + K_I\ N_{CO_3^{2-}}^{\frac{1}{2}} \cdot + K_I K_{II} N_{CO_3^{2-}} + K_I K_{II} K_{III} N_{CO^{2-}}^{\frac{3}{2}}}$$

where $\bar{n} = \bar{n}' + 3/2$ is the average number of oxygen atoms per boron atom.

By means of this equation the values of K_I, K_{II} (and K_{III}) which satisfy the experimental values of $\bar{n}$, are readily computed by plotting $\bar{n}$ against $\log N_{CO_3^{2-}}$ and putting $\log K_I \simeq \frac{1}{2} \log N_{CO_3^{2-}\,(n\,=\,1.75)}$ etc. [Fig. 1].

The values thus computed for constants of the borate and silicate systems are given in Table 3. (Later investigations, not yet concluded, seems to indicate that Nigglis data on the silicate systems needs some corrections.)

Table 3. Equilibrium constants in alkalicarbonate-borate and -silicate systems.

System	T° C	log K_I	log K_{II}	log K_{III}
Na_2CO_3—B_2O_3	1,000		0.40	
»	900		0.23	
Li_2CO_3—B_2O_3	1,000		(1.4)	0.63
K_2CO_3—SiO_2	998	(1.7)	0.40	(— 1.1)
»	956		0.30	
»	898		0.18	
Na_2CO_3—SiO_2	956			0.35

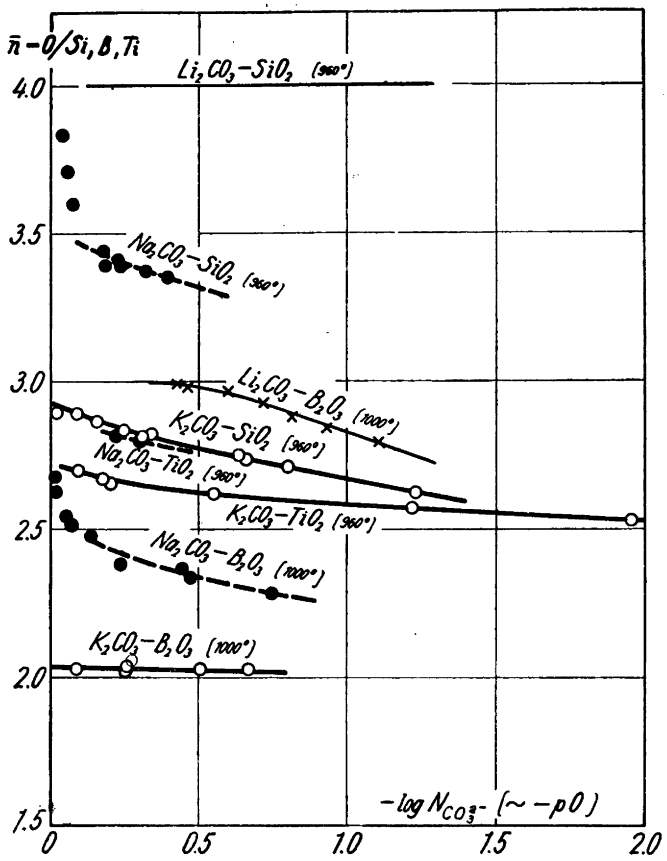


Fig. 1. The average number of O atoms per Si, B or Ti atom as a function of the mole fraction of CO_3^- in the melt. (P_{CO_2} = 1 atm.).

These data illustrate in a striking manner to what extent the values of the constants depend on the cations present. The acid strength of the polyacid decreases strongly in the order,

Li, Na, K

Thus log K_{II} decreases from ca. 1.4 to 0.40 in passing from lithium to sodium borate at 1000° C, and log K_{III} decreases from 0.35 to ca. — 1.1 in passing from sodium to potassium silicate at 956° C.

The temperature variations of the constants permit a computation of the heat of reaction in a homogeneous melts of sodium borate

$$NaBO_2 + \tfrac{1}{2}\,Na_2CO_3 = Na_2BO_{2.5} + CO_{2(g)}$$
$$\Delta H = 12 \text{ kcal}$$

This value may, of course, only be considered as a rough orientation.

SUMMARY

The acid base-equilibria in melts of alkali-carbonate and boron trioxide at 1000° C have been investigated by examining equilibria of the type

$$\text{acid} + CO_3^{2-} \rightleftharpoons \text{base} + CO_2 \quad (1 \text{ atm.})$$

for various compositions of the melt (compare Niggli's studies on the equilibria SiO_2—K_2CO_3, SiO_2—Na_2CO_3 SiO_2—Li_2CO_3, TiO_2—K_2CO_3 and TiO_2—Na_2CO_3). The results show a distinct dependence of the acidity of the polyacids on the cations present and that the acidity decreases in the order

Li, Na, K

The formulation of suitable schemes of reaction for use in the computation of the acid-base constants of the polyacids has been discussed briefly.

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