

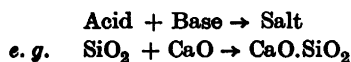
The Acidic and Basic Properties of Oxides

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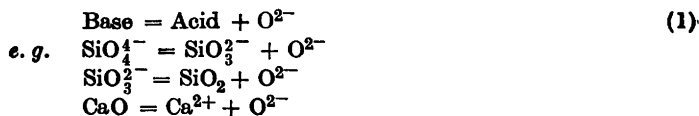
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I. ACID BASE DEFINITIONS

Since the days of Berzelius oxides have been connected with acid base character, *e. g.* CaO, MgO, FeO are commonly known as basic, SiO₂, CO₂ as acidic oxides. The acidic and basic properties of these compounds were characterised by their ability to react mutually forming salts:



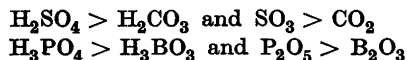
Recently Lux¹ has announced a more precise acid base definition suitable for compounds like these, writing:



In this way there is obtained an analogy to the acid base functions of Brönsted for the protolytic systems.



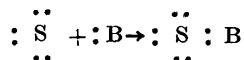
The analogy is not only a formal one. There exists at least a qualitative parallellism between the proton affinity and the tendency to split off an oxygen ion, as will be seen on comparing the acid strength of the compounds:



(A stronger bond between the oxygen and the central atom is usually connected with a weaker binding tendency for a proton to the oxygen atom.)

Other acid-base definitions have also been advanced in order to formulate a wider acid base conception. Especially to be mentioned are the theories of Ussanowich ² and Lewis ³. According to the definition of Ussanowich the red-ox as well as the protolytic reactions are special cases of the general acid base reactions, which also comprise all reactions which involve ion exchanges, dissociations or associations of ions. This concept is so extensive, that according to it there would apparently be few reactions that are not to be considered as acid base reactions.

Lewis connects the acid base reactions with the formation of a coordinative bond:



The difficulties connected with the use of this acid base criterion in inorganic chemistry have become evident as the progress during the later years has led to an understanding of the limited validity of the Lewis-Langmuir octet ⁴. Applied to oxides, the definition would give only one single base, the O²⁻ ion; on the other hand oxides as CaO, Na₂O are not bases, but Na⁺ and Ca²⁺ are acids.

This should be sufficient to demonstrate the advantage of the definition of Lux, where the acid and base formulation is in agreement with the older, well known acid base terminology. In addition to the already mentioned analogy with the Brönsted acid base function, the definition of Lux also has the great advantage that it does not imply any theoretical assumption as to the way in which the oxygen ion is bound to the cation. On the other hand it excludes the possibility to regard the analogous reactions of the sulphide and fluoride ions as acid base reactions. However this limitation of Lux' definition seems to be of less importance than the difficulties one will meet on applying the mentioned extended acid base concepts to oxides.

Using the formulation:



the constant:

$$K = \frac{\alpha_{\text{acid}} \cdot \alpha_{\text{O}^{2-}}}{\alpha_{\text{base}}} \quad (2)$$

will be a measure of the strength of the acid base pair.

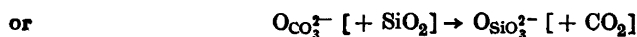
The characteristic point of the protolytic acid base reaction is the proton exchange between an acid and a base molecule. It would be interesting to

consider to what extent we may treat the role of the oxygen ion from the same point of view.

The systems we are considering, are built up of great oxygen ions and relatively small cations. The oxygen ions are, however, always more or less polarized by the adjacent cations. Even in a melt of alkali oxides we have to take into account a polarization of the oxygen ion.

[In this connection it is important to remember that oxides of cations with only weak polarizing character are unstable at room temperatures. The weakly polarized oxygen ions show a marked tendency to combine to O_2^{2-} or even to O_2^- . According to older data Cs_2O_2 is stable up to $1100^\circ C$ in oxygen atmosphere, while K_2O_2 gives off oxygen already at $600^\circ C$.]

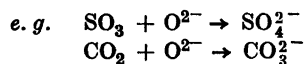
Consequently we have to assume that in a system of oxides or salts of oxy-acids the oxygen ions present are in a more or less polarized state dependent on the adjacent positive ions. The characteristic process of acid base reactions will then be the transfer of an oxygen ion from one state of polarisation to another. For example the reaction between carbonate and silicon dioxide to silicate and carbon dioxide may be written:



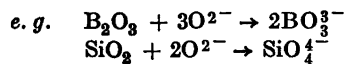
[It should be noticed that the oxygen ions within a silicate group cannot be split off independent of each other. Each group acts as a reactive unity.]

In systems built up of oxygen ions we meet three important types of acid base transitions:

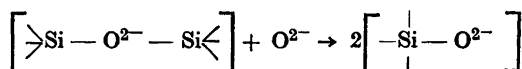
a) Atoms with a high ionisation energy (S, C, etc.) frequently give acid base transitions accompanied by an alteration of their coordination number for oxygen,



b) For atoms with a medium ionisation energy the coordination number may be unchanged,

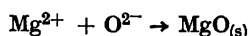


In these cases the acid base transition consists in the breaking of an oxygen bridge between two SiO_4 or BO_3 groups:



The transition of the acid to the corresponding base may therefore be connected with a breaking down of macromolecule structures.

c) For atoms with a low ionisation energy (the typical cation forming ones) the acid base transition may be connected with a formation of an oxide phase:



In general the heterogeneous reactions are of considerable importance in these acid base systems. (Reactions of this kind offer a simple method of studying activity coefficients in melts ⁵.)

II. EXPERIMENTAL METHODS FOR THE INVESTIGATION OF ACID-BASE EQUILIBRIUMS IN SYSTEMS OF OXIDES AND SALTS OF OXY-ACIDS

According to the Lux' acid base definition (1), which has been introduced in the foregoing chapter, the determination of an acid base equilibrium may in the principle be regarded as an examination of oxygen ion activities.

Several experimental methods for examinations of this kind are already proposed. Of these the following may be mentioned:

a. The oxygen electrode

Electrometric determination of oxygen ion activities should be possible by means of an electrode where a reaction like



is potential determining. There are still very few details known about the use of the oxygen electrode for this purpose ^{1, 6, 7, 8} and the results published are not very satisfying.

Experiments carried out at temperatures of about 1000° C show a variation in the potential with the composition of the melt which is difficult to explain theoretically. It is interesting, however, to notice that measurements of potentials with electrodes of C and SiC in slags at 1600° C have given interesting results which indicate the possibility of obtaining well repeatable potentials at these temperatures ⁹.

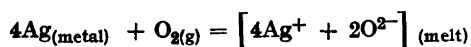
In spite of the difficulties hitherto encountered, there is still reason to believe that this method will find its use in the present problem.

b. Partition of solutes between metal and oxide phases

To illustrate this type of equilibrium we may mention the metallurgically important reaction:

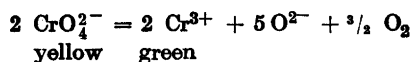


which already has been the object of several examinations. Even the solubility of metals in melts in the presence of oxygen should presumably be useful for this purpose, *e. g.* a reaction like:



c. Indicators

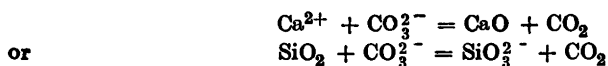
The use of indicators for the purpose of examining the acidity of glasses was proposed more than 10 years ago^{8, 10}. The principle is demonstrated by the function of the chromate indicator:



At a constant oxygen pressure the colour of the melt will be a function of the oxygen ion activity. The colour has to be determined after the melt has been cooled, and therefore indicates a frozen equilibrium. As, however, the equilibrium of the indicator system probably is slowly adjusted, due to the participation of gaseous oxygen in the equilibrium — the cooling of the melt should not be any serious source of errors.

d. Measurements of equilibria involving volatile acids or bases

The hitherto most important equilibria suitable for the examination of acid base properties are the decompositions of carbonates. The relative acidity of acids may be determined by means of reactions like:



by examination of the composition of the melt in equilibrium with CO_2 gas at constant pressure.

In addition to the system $\text{CO}_3^{2-}\text{-CO}_2$, other systems may be usable and of interest in order to extend the pO-range outside the limits of the carbonate system, *e. g.* $\text{SO}_4^{2-}\text{-SO}_3$, in some cases $\text{SO}_3^{2-}\text{-SO}_2$, $\text{OH}^-\text{-H}_2\text{O}$ and the corresponding systems with volatile oxyhalogenides as POCl_3 , VOCl_3 .

REVIEW OF THE PRESENT EXPERIMENTAL MATERIAL

The experimental results hitherto are rather qualitative in nature. It seems justified, however, briefly to consider them as disclosing some general traits of the acid base equilibria in these systems which have no analogies in the protolytic acid base systems. This applies especially to the case of the polyacids.

Before discussing these, however, we shall briefly consider the base scale of some of the common basic oxides.

A qualitative picture of the differences in base strength of a number of basic oxides may be obtained by comparing reversible thermic decomposition reactions as:



Table 1. The standard free energy change by thermal decomposition of carbonates and sulphates.

M	$\Delta F_{\text{carbonate}}$	$\Delta F_{\text{sulphate}}$	Diff.
Ba	52	108	56
Na			57
Li	40	94	54
Ca	31	86	55
Mg	16	61	45
Mn	15	51 (61)	36 (46)
Cd	12	50	38
Pb	10	62	42
Co	9	44	35
Ag	7	58	51
Fe ^{II}	7		
Zn	4	46	42
Ni	— 2	46	48
Cu	— 2	42	44
Fe ^{III}		31	
Be		29	

The picture was strictly correct only if the carbonate and sulphate ions might be considered as quite unpolarized and if effects arising from differences in crystal structure were negligible. We may, however, presume that the base strength is the deciding factor determining the decomposition equilibrium.

In Table 1 values of free energy ΔF_{298} in kcal are compared for a number of reactions of type (1) and (2). We find with only few inversions the same succession in the two sequences, starting with Ba, Sr, Li and Ca, and ending with Zn, Ni and Cu^{II}. The carbonates of the higher alkali metals melt before perceptible decomposition and cannot be directly compared.

It also appears that ions with inert gas structure are exceptionally weak acids (the oxides are strong bases) and that the sequence of the acid strength of these coincides with that of the ionic potentials.

Ions without inert gas structure are distinctly stronger acids (the oxides weaker bases). In this case it is not so easy to point out a simple relation between ionic potential and acidity (*cf.* Mn^{II}, Co^{II}, Fe^{II}, Ni^{II}, Ag etc). Most of the values in the table are taken from Kelleys data ¹¹. The ranges of error are in some cases rather wide, especially in ΔF_2 (*cf.* the two values for Mn). It is therefore uncertain whether the inversions in the sulphate series as compared with the carbonate series are real ones, or if they are merely due to errors in the quoted values of ΔF . The values of the carbonate series are generally more reliable than those of the sulphate series and should therefore at present be regarded as the best measure of the relative acid base strengths of oxides.

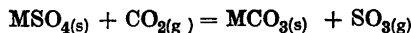
Table 2. The free energy change by thermal decomposition of carbonates at 25, 1000 and 1600°C.

M	$\Delta F_{\text{carbonate}}$ (25° C)	$\Delta F_{\text{carbonate}}$ (1000° C)	$\Delta F_{\text{carbonate}}$ (1600° C)
Ba	52	15	— 4
Li	40	— 1	— 23
Ca	31	— 4	— 24
Mg	16	— 22	— 39
Mn	15	— 24	— 41
Cd	12	— 22	— 37
Pb	10	— 22	— 35
Co	9	— 31	— 54
Ag	7	— 25	— 43
Fe	7	— 33	— 52
Zn	4	— 31	— 45

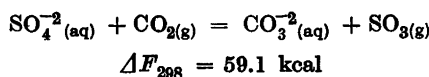
The extrapolation of ΔF to higher temperatures gives an acid-base scale not very different from the one at 298° K. Table 2 represents ΔF at 25°, 1000° and 1600° C for some common oxides.

The difference

$\Delta F_1 - \Delta F_2 = \Delta F'$ represents $\Delta F'_{298}$ for the reaction

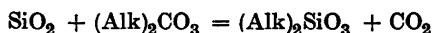


For the stronger bases (BaO etc) $\Delta F'$ is approximately equal to $\Delta F'_{298}$ for the reaction:



$\Delta F'$ shows a slightly decreasing tendency with decreasing base strength of the oxides.

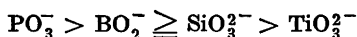
The acidity of more acid oxides may in the principle be measured in relation to the acidity of the carbon dioxide by examining equilibriums like



Niggli¹² has investigated the systems $\text{K}_2\text{CO}_3 - \text{SiO}_2$, $\text{K}_2\text{CO}_3 - \text{TiO}_2$, $\text{Na}_2\text{CO}_3 - \text{SiO}_2$, $\text{Na}_2\text{CO}_3 - \text{TiO}_2$ and $\text{Li}_2\text{CO}_3 - \text{SiO}_2$ by examining the composition of melts in equilibrium with carbon dioxide gas of 1 atm.

Flood, Förland and Roald have investigated carbonate systems including $\text{K}_2\text{CO}_3 - \text{B}_2\text{O}_3$, $\text{Na}_2\text{CO}_3 - \text{B}_2\text{O}_3$ and $\text{Li}_2\text{CO}_3 - \text{B}_2\text{O}_3$. The results of these investigations will be reported in a subsequent communication¹³. In the present paper only a few general traits will be mentioned.

In a melt of K_2CO_3 at temperatures about 1000° C the following sequence of the acid strengths is found



This is in accordance with general metallurgical experience.

If we, however, compare these systems with the corresponding Na_2CO_3 and Li_2CO_3 -systems we observe the interesting effect that the polyacids appear to behave as much stronger acids in the Li than in the Na systems and here again much stronger than in the K systems.

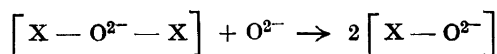
In a melt of K_2CO_3 a relatively small addition of B_2O_3 expels an amount of CO_2 corresponding to the formation of metaborate (BO_2^-). In the corresponding Na system the reaction comes to an end approximately midway

between the meta and ortho compositions (near $\text{BO}_{2.5}^{2-}$), while in Li_2CO_3 all B_2O_3 is converted to orthoborate (BO_3^{2-}).

The corresponding effect is even more pronounced in the silicate systems, somewhat less in the titanate systems.

As we have seen, only a small effect of this kind was demonstrated in connection with the relative acidity of SO_3 and CO_2 .

It is therefore difficult to explain this effect except by assuming that the stability of the oxygen bridges of the polyacid depends upon the cations in such a way that the tendency



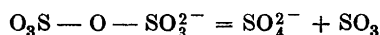
increases in the sequence K^+ , Na^+ , Li^+ .

This opinion is supported by observations from different fields. Lux and Rogler¹⁰ have by means of the chromate indicator examined the acidbase character of different oxides when these are added to a sodiumborate melt. They found that a number of oxides usually regarded as typical basic (among others BaO and Li_2O) at low concentrations behave as strong acids. This they attempted to explain as a special property of the boron atom by assuming that the boron, which normally coordinates 3 oxygen in a planar configuration may under the influence of a polarizing cation be forced to coordinate 4 oxygen in a tetrahedral configuration. Hence, they suppose, the boron trioxide should appear as a substantially stronger acid.

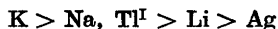
The assumption of 4 coordination in these systems must, however, be regarded as a rather questionable hypothesis. 4 coordination of oxygen to boron in anhydrous compounds is known in borosilicates and borowolframates only. Even by means of Na_2O Zintl and Morawietz¹⁴ was unable to produce stronger basic borate than corresponding to the BO_3^{3-} ion. It has been claimed that 4 coordinated boron exists in acidic sodium borate glasses¹⁵ but other investigations deny this¹⁶. Besides, according to this theory, the 4 coordination structure at the sodium oxide content used by Lux and Rogler should be complete even before the addition of the second oxide.

As we have seen these effects are by no means special for the borate systems. On the contrary they seem to be still more pronounced in the silicate systems.

Effects similar in kind also seem to be determining for the thermic stability of the pyrosulphates. They decompose according to



The essential accordingly is the breaking of an oxygen bridge. Experiments (which will be described in a subsequent paper¹⁷ show a distinctly decreasing stability in the sequence



Hence it may be regarded as a general effect that the stability of the oxygen bridges depends on the cations present. The simplest explanation of this would be that pure geometrical relations are decisive. By breaking down the macrochains and nets connected by the oxygen bridges, a closer packing of the ions may be the result. The tendency of the bridges to break up should then depend on the gain in energy which may be larger the less the cation radius is.

The decomposition of the pyrosulphates, however, clearly demonstrates that the cation radius is not the only determining factor. As a matter of fact Tl-pyrosulphate is less stable than K, and Ag less than Na, despite the fact that the relation between the ionic radii in this case is opposite.

This indicates that a polarizing effect as well has to be taken into account. As is known the polarizing power of ions of the transition elements are stronger than that of the inert gas ions (with equal radius).

Observations from other fields also demonstrate the existence of these effects. The viscosity in acid silicate melts shows a distinct dependence of the cation in such a way that the viscosity decreases in the succession



The simplest explanation of this is that the size of the macromolecules decreases in the same succession.

Effects similar in kind have also been noted by the geochemists. It has been stated as a general rule for the minerals formed by cooling the magma that the larger the cation and the less its charge, the more will its silicate type tend towards a low excess in charge per oxygen atom in the Si-O structure. (Compare also Paulings second rule determining ionic crystal structures.)

The same rule is also demonstrated by number and stability of existing polysilicates. This is evident from Table 3.

Bowen and Morey¹⁸ have characterized the alkalisilicates by stating that the »dissociation of disilicate» ($Si_2O_5^{2-}$) decreases rapidly with increasing atomic weight of the alkali metal. Comparing the silicates of the transition elements with those of the alkali and alkaline earth metals the existence of polarizing

Table 3. *Polysilicates of some common elements.*

System	Compound		Cation radius
Li ₂ O—SiO ₂	Li ₂ SiO ₃		0.60
	Li ₂ Si ₂ O ₅	Diss. before melting	
Na ₂ O—SiO ₂	Na ₂ SiO ₃		0.95
	Na ₂ Si ₂ O ₅	M. p. ca 960° C	
K ₂ O—SiO ₂	K ₂ SiO ₃		1.33
	K ₂ Si ₂ O ₅	» ca 1045° C	
	K ₂ Si ₄ O ₉		
MgO—SiO ₂	MgSiO ₃	Diss. before melting	0.65
CaO—SiO ₂	CaSiO ₃	M. p. 1540° C	0.99
SrO—SiO ₂	SrSiO ₃	» 1580° C	1.13
BaO—SiO ₂	BaSiO ₃	» 1600° C	1.35
	2BaO3SiO ₂		
	BaO2SiO ₃		
FeO—SiO ₂	no metasilicate		0.75
ZnO—SiO ₂	»		0.74
PbO—SiO ₂	PbSiO ₃	» 780° C	1.32

effects is evident besides the purely geometrical one. Fe²⁺, Zn²⁺ and Pb²⁺ behave, when compared with the alkaline earth metals, as if they had a smaller ionic radius than corresponding to the space they actually occupy in the crystals.

The general conclusion from this review of the present experimental material is that the stability of the polybridges depends largely on the cation present in such a way that the stability decreases with increasing ionic potential and increasing polarizing power of the cation.

In molten systems this is manifested as a distinct increase in the acidity of the polyacids, and as a decrease in the viscosity, while in the solid systems the effect is manifested as a decrease in number and stability of the existing polycompounds.

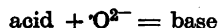
These effects partly correspond to the well known rule that polarizable anions are able to form salts with moderately polarizing cations only (compare the stability of salty hydrides, peroxides, halogenides etc).

The difference is that in the last cases the polarizing power is the deciding factor in determining the stability, while in the case of polybridges, the stability seems to be quite as much determined by purely geometrical relations.

In this last case both effects must be taken into account.

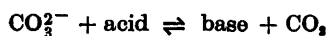
SUMMARY

The acid base properties of the oxides can, according to Lux be formulated in analogy to Brönsted's acid base function by the scheme of reaction

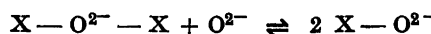


The general types and the characteristic traits of reactions of this kind are discussed, as well as experimental methods for investigating them.

The most important results are so far obtained in equilibria of the type



In the case of polyacids, where the acid base transition consists in a breaking of oxygen bridges, as schematically represented by



it appears that the acid strength is largely dependent on the cations present. The tendency of the reaction to go towards the right is stronger the less the cation, and the stronger its polarizing power.

These phenomena are also displayed by the viscosity of melts, by the thermic stability of pyrobridges and by the stability relations of the solid silicates.

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