THE ROLE AND SIGNIFICANCE OF THE COMPLEX ANIONIC POTENTIALS IN THE GEOCHEMISTRY

Part I. The variability of the complex anionic potentials*

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1. INTRODUCTION

The Cartledge's ionic potential is the quotient of the charge and the radius of the cation, that is

$$\psi = \frac{z}{r}.$$

Szádeczky-Kardoss (1954) has pointed out that analogously may be calculated also the ionic potential of the simple and complex anions, respectively, and the values obtained would be just as charactereistic of the anions as the cationic potentials characterize the cations. Correspondingly, the complex anionic potential is the quotient of the charge and radius of the complex anion.

Szádeczky-Kardoss (1954), introducing the concept of the complex anionic potential, has used the Fersman's complex anionic radii used also by *Saukow* (1953). These radii, however, are rather computed on the basis of additivity of the Goldschmidt's ionic radii and not determined on the basis of the measured actual ionic distances within the complex anion.

Taking into consideration the complex anions as the building elements of crystal lattices it is well known that the bonding within the complex anions, that is, between the central cation and oxygen, is not dominantly ionic but to some extent covalent. Therefore, the distance central cation-oxygen can not be given additively from the radii of the cation and oxygen, thus nor can the complex anionic potential be computed on the basis of simple additivity of radii.

In the sets of BO_3^{3-} — CO_3^{2-} — NO_3^{1-} ions or SiO_4^{4-} — PO_4^{3-} —

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SO_4^{2-} — ClO_4^{1-} ions the ionic character of the A—O bonds becomes gradually less and correspondingly more considerable the covalent character with increasing charge and decreasing radius of the central cation that is with its increasing cationic potential and with decreasing difference between the electronegativity values of the central cation and the oxygen anion. Due to the increasing polarizing effect of the central cation the deformation of the oxygen ion becomes stronger.

These changes, however, naturally can not be expressed by the complex anionic potential calculated on the basis of simple additivity of the ionic radii.

2. THE CHANGE OF THE IONIC DISTANCES WITHIN THE COMPLEX ANIONS. THE COMPUTATION OF THE COMPLEX ANIONIC POTENTIAL

Considering the polarization of the complex anions in crystals beside the polarizing power of the central cation must be taken into consideration also the contrapolarizing effect of the neighbouring cations connected to the oxygen of the complex anion. The contrapolarization may result the increase of the ionic distance within the complex, moreover in some cases may hinder the formation of complex anions. Thus the P—O distance in PO_4^{3-} in average is 1,56 Å. In the PO_4^{3-} anion according to Pauling the resonance of single and double covalent as well as ionic bonds can be supposed. In the lattice of Ag_3PO_4 the covalent character of the Ag—O bonds due to the contrapolarizing effect of Ag, however, hinders the formation of the P—O double covalent bonds within the complex and consequently the P—O distance in the Ag_3PO_4 increases to 1,61 Å and in the lattice of YPO_4 becomes 1,71 Å owing to the increased polarizing power of the neighbouring cation. This latter distance is almost equal to the sum of ionic radii (1,73 Å). It has been mentioned that neighbouring cations of strong contrapolarizing power may hinder the formation of complex anions. Thus, e. g., in the lattice of Li_2MoO_4 the real MoO_4^{2-} complex anion exists, whereas in the lattice of Ag_2MoO_4 the strong contrapolarizing effect of Ag makes impossible the formation of the MoO_4^{2-} complex anion and this compound means transition to the simple coordination structure of spinel-type (*Hiller*, 1952).

The character of the bonding and the variation of the ionic distances within the complexes in crystals depends on the contrapolarizing effect and coordination number of the neighbouring cations as well as on the polarizing power of the central cation and on other factors.

As the same complex anion in its different compounds may be connected with various cations of different coordination number and contrapolarizing power, the ionic distances in complex anion — also in the case of the same complex — may change from compound to compound and hence may also change the value of the complex anionic potential.

Thus the radius of the complex anion must be calculated on the basis of ionic distances measured roentgenographically and therewith the effect of the factors above-mentioned to the change of ionic distances implied is also taken into consideration.

The necessity of the refinement of this kind of the computations has been shown also by *Szádeczky-Kardoss* (1954): „Bei der Berechnung von Tabelle III wurden übrigens die allgemeine gebräuchliche Ionenradien angewandt. Diese Zahlen können und müssen aber später verfeinert werden, u. zw. mit den von dem kovalenten bzw. heteropolaren Verbindungstyp, ferner mit den von der Koordinationszahl usw. abhängenden tatsächlichen Ionenabmessungen . . .”.

Similarly refer *Leutwein* and *Doerffel* (1956) that Fersman's computation-method regarding to the radii of complex anions as well as to the complex anionic radii used by *Saukow* (1953) cannot give accurate results since the change of ionic distances within the complexes due to the factors above-mentioned is not taken into consideration by this method and is not expressed by the values obtained.

The authors mentioned above and also others state that accurate radius values may only be obtained on determining the ionic distances from X-ray measurements or from molrefractions and computing the radius of the complex anions on the basis of these data. In this case the radius,

$$r = 2a - r_c,$$

where r is the radius of the complex anion, a the ionic distance measured and r_c the radius of the central cation.

Bearing in mind the actual ionic distances, the potential of complex anions in crystals may be calculated from the following equation:

$$\psi_{\text{complex}} = \frac{z_c - n \cdot z_a}{2a - r_c},$$

where z_c and z_a mean the charges of the cation and anion, respectively n is the number of anions in the complex around the central cation of radius r_c.

The central cation in general is of small size and highly charged, that is, less polarizable, its radius can be considered as constant in various compounds of the same complex anion. The values given for the cationic radii in the different tables generally regard to 6-coordinated cations. Therefore if tetrahedral oxyanions are in question at the calculation of the potential and radius of the complex anions, the radius of the central cation must be corrected to 4-coordination. Calculating, however, the complex anionic potential of the single tetrahedral oxyanions and using for the central cation the radius values valid for 6-coordination number, the error will not be essential. Thus, e. g., in the following set, the number after the complex anion means the anionic potential computed with the radius value corrected for 4-coordination number and the value in parenthesis means the potential calculated with the radius valid for 6-coordination:

MgO_4^{6-} 1,75 (1,73); TiO_4^{4-} 1,16 (1,14); AlO_4^{5-} 1,52 (1,51); SiO_4^{4-} 1,25 (1,24); PO_4^{3-} 0,95 (0,95); CrO_4^{2-} 0,60 (0,60).

Intending, however, to calculate the compound potentials according to *Szádeczky-Kardoss* (1954), beside the potential of the complex anions also the potential of the neighbouring cations must be taken into calculation, the coordination number of the cations can not be neglected any more as it could yield essential differences in the numerical value of the compound-potential. This is one of the ways of the further refinement of the calculation-method of the compound potentials. It is well known that the change of the coordination number results in the change of the cationic radius and consequently will change also the cationic potential. For example, the cationic potential of the 4-coordinate Ca^{2+} ion is 2,15, that of the 6-coordinated 2,02 and that of the 9-coordinated is 1,90.

The complex anionic potentials calculated on the basis of the actual ionic distances found in the various crystals are rather characteristic of the complex anions than the potential values deduced on the basis of the additivity of the ionic radii. But this calculation too, is to some extent of approximative character since at the calculations the complex anions are considered as rigid spheres and the possible deformation of the tetrahedral oxyanions — resulting the variation of the central cation-oxygen distances in all the four directions — at the most in that manner is taken into account that it is calculated with the mean value of the central cation-oxygen distances of four kinds.

Thus, the polarization revealed in the shortening of the ionic distances not only must but also can be taken into consideration calculating the potential of complex anions existing in different compounds as elements of the lattice in all cases, when the ionic distances are given from X-ray measurements.

In geochemical relations, however, not alone the comparison of the complex anions as elements of crystals is needed on the basis of their complex anionic potential but efforts are made to study the behaviour of the complexes also in the magma, wherein complex anions preformed already exist.

It can be assumed, that the polarization in the case of these independent oxyanions in melts is stronger than in solid crystals due to the onesided polarizing effect of the central cation.

Now the question arises, what degree of polarization must be supposed and with what ionic distances must be calculated the radius of the complex anions and further their potential values?

It would be possible to calculate the radius and the potential on the basis of ionic distances valid in the lattices of the different compounds of the given complex anion. These distances, however, according to the data given in Tables 1—7 change from compound to compound, thus, e. g., the P—O distance in PO_4^{3-} anion varies between 1,44—1,71 Å the S—O distance in SO_4^{2-} anion between 1,44—1,60 Å, the Si—O distance in the SiO_4^{4-} anion changes beween 1,54—1,77 Å in their different compounds.

Calculation with the average of these ionic distances in the case of independent oxyanions existing in melts would mean the account the polarization to some extent. But to apply the ionic distances measured in solid crystals to independent complex anions in melts would mean also some arbitrariness since the formation and the change of ionic distances within the complex anions in lattices is resulted not alone by the polarizing power of the central cation but also by the contrapolarizing effect of the neighbouring cations and this latter effect depends upon the size, charge and coordination number of the cation. In the melts, however, the complex anions exist as independent units and are not yet joined with cations.

Thus would complex anions in melts as independent units be in question the complex anionic potential may be calculated on the basis of ionic model although the polarization, the covalent character of the bonds is not expressed by the potential values computed in this manner. It is obvious that these complex anionic potentials in their numerical values do not correspond the values that would be obtained having data relating to ionic distances measured within the different complex anions in melts. Failing these data, however, instead of doubtful assumptions the ionic model can serve at least as uniform basis of comparison.

The complex anionic potential on the basis of ionic model:

$$\psi_{\text{complex}} = \frac{z_c - n \cdot z_a}{2r_a + r_c},$$

where r_a and r_c mean radii of the anion and the cation, respectively, z_a and z_c mean their charges and n is the number of anions around the central cation.

Though the application of ionic model at the calculation of complex anionic potential in the case of independent complex anions in melts

Table 1.

The variability of the radius and anionic potential of some complex anions.

Complex anion	Values[1] according to Szádeczky—Kardoss		Values[2] calculated on the basis of additivity of ionic radii		New values[2] calculated taking into account the actual ionic distances						Number of the compounds examined
					r			ψ			
	r	ψ	r	ψ	min.	max.	av.	min.	max.	av.	
AlO_4^{5-}	3,15	1,59	3,28	1,52	2,82	3,08	2,92	1,62	1,77	1,71	10
SiO_4^{4-}	2,90	1,38	3,20	1,25	2,82[3]	3,15[3]	2,94[3]	1,24[3]	1,41[3]	1,35[3]	13[3]
BO_3^{3-}	2,68	1,12	3,01	0,99	2,29	2,67	2,50	1,12	1,31	1,19	11
AsO_4^{3-}	2,95	1,02	3,23	0,92	2,83	3,07	2,93	0,97	1,06	1,02	13
PO_4^{3-}	3,00	1,00	3,13	0,95	2,55	3,09	2,79	0,97	1,17	1,07	15
CO_3^{2-}	2,57	0,77	2,95	0,67	2,31	2,19	2,40	0,80	0,86	0,82	8
SO_4^{2-}	2,95	0,68	3,08	0,64	2,60	2,92	2,76	0,68	0,77	0,72	16
CrO_4^{2-}	3,00	0,67	3,29	0,60	2,71	2,85	2,74	0,70	0,73	0,72	6
NO_3^{1-}	2,57	0,39	2,92	0,34	2,30	2,38	2,34	0,42	0,43	0,42	4

[1] On the basis of Goldschmidt's cationic radii and Fersman's anionic radii

[2] On the basis of Ahrens's cationic radii and Pauling's oxygen ionic radius

[3] The values are related to the nesosilicates

is obviously but necessary solution, some problems may be approximately explained and interpreted also on this basis as the stability relations of the tetrahedral complex anions, the periodicity of the anionic potentials, the connection between the electrostatic energy and the anionic potential of the tetrahedral complex oxyanions.

The differences among values calculated on the basis of ionic model and of the average of actual ionic distances measured in lattices of different compounds of anisodesmic (and mesodesmic) structures are given in Table 1.

In the Table 1 are also denoted the minimal, maximal radius and potential values of the complex anions calculated on the basis of ionic distances measured in different lattices.

3. THE VARIATION OF SOME COMPLEX ANIONIC POTENTIALS IN ANISODESMIC STRUCTURES

The complex anionic potential values of some complex anions characteristic of anisodesmic structures are summarized in Tables 2—7 on the basis of X-ray measurements found in the literature. As in many cases the tetrahedron is distorted, computing the anionic radii and the anionic potentials the mean value of the ionic distances determined, was taken into consideration. In the Tables are denoted also the ionic distances, the anionic radii and potential values, respectively, calculated from simple ionic model.

For the cationic radii the Ahrens's values corrected to 4-coordination and for the radius of oxygen anion the Pauling's value of 1,40 Å were used.

Table 2.

The complex anionic potential of the CO_3^{2-} ion in some compounds

Ionic distance: *1,55* Å
Radius: *2,95* Å
Anionic potential: *0,67*
(All the three values are calculated from ionic model.)

Compound	C—O distance	r_{CO_3}	ψ_{CO_3}	References
$PbCO_3$ Cerussite	1,23	2,31	0,86	Landolt - Börnstein (1955)
(Ce,La...)FCO_3 Bastnäsite	1,25	2,35	0,84	Oftedal (1930)
$Na_2CO_3 . NaHCO_3 . 2H_2O$	1,25	2,35	0,84	Structure Rep. vol. 12.
$PbCl_2CO_3$ Phosgenite	1,25	2,35	0,84	Structure Rep. vol. 10.
$CaCO_3$ Calcite	1,29	2,43	0.82	Landolt—Börnstein (1955)
$CaCO_3$ Aragonite	1,30	2,45	0,81	Landolt - Börnstein (1955)
$Ca_2Na_2(CO_3)_3$ Shortite	1,31	2,47	0,80	Structure Rep. vol. 12.
$KAgCO_3$	1,32	2,49	0,80	Structure Rep. vol. 9.
Average	1,28	2,40	0,82	

Table 3.

The complex anionic potential of the NO_3^{1-} ion in some compounds

Ionic distance: *1,55* Å
Radius: *2,95* Å
Anionic potential *0,67*
(All the three values are calculated from ionic model.)

Compound	N—O distance	r_{NO_3}	ψ_{NO_3}	References
$TlNO_3$	1,21	2,30	0,43	Structure Rep. vol. 9.
$Pb(NO_3)_2$	1,22	2,32	0,43	Landolt—Börnstein (1955)
$NaNO_3$	1,25	2,38	0,42	Leutwein and Doerffel (1956)
$LiNO_3$	1,25	2,38	0,42	Pauling and Huggins (1934)
Average	1,24	2,34	0,42	

Table 4.

The complex anionic potential of the PO_4^{3-} ion in some compounds

Ionic distance: *1,73* Å
Radius: *3,13* Å
Anionic potential: *0,95*
(All the three values are calculated from ionic model.)

Compound	P—O distance	r_{PO_4}	ψ_{PO_4}	References
BPO_4	1,44	2,55	1,17	Heritsch (1940)
$Al(PO_3)_3$	1,51	2,69	1,11	Pauling and Sherman (1937)
$(Ce,La,Pr)PO_4$ Monazite	1,52	2,71	1,10	Structure Rep. vol. 9.
$Li(Fe_{1-x},Mn_x)PO_4$ Triphylite	1,53	2,73	1,09	Structure Rep. vol. 13.
$AlPO_4$	1,54	2,75	1,09	Wyckoff (1951)
$Zr_2P_2O_7$	1,54	2,75	1,09	Heritsch (1940)
$Ba_3(PO_4)_2$	1,56	2,79	1,07	Wyckoff (1951)
$Sr_3(PO_4)_2$	1,56	2,79	1,07	Wyckoff (1951)
KH_2PO_4	1,56	2,79	1,07	Landolt—Börnstein (1955)
$NH_4H_2PO_4$	1,58	2,83	1,06	Wyckoff (1951)
Ag_3PO_4	1,61	2,89	1,03	Structure Rep. vol. 9., 11.
$Cu_2(OH)PO_4$ Libethenite	1,61	2,89	1,03	Heritsch (1940) Wyckoff (1951)
$Fe_3(PO_4)_2 . 8H_2O$ Vivianite	1,62	2,91	1,03	Structure Rep. vol. 13.
$NaMnPO_4$ Natrophilite	1,62	2,91	1,03	Structure Rep. vol. 9.
YPO_4 Xenotime	1,71	3,09	0,97	Hiller (1952)
Average	1,56	2,79	1,07	

Table 5.

The complex anionic potential of the SO_4^{2-} ion in some compounds

Ionic distance: 1,68 Å
Radius: 3,08 Å
Anionic potential: 0,64
(All three values are calculated from ionic model.)

Compound	S—O distance	r_{SO_4}	ψ_{SO_4}	References
$K_2Pb(SO_4)_2$ Palmierite	1,44	2,60	0,77	Structure Rep. vol. 11., 13.
$Th(OH)_2SO_4$	1,47	2,66	0,75	Structure Rep. vol. 13.
Ag_2SO_4	1,48	2,68	0,74	Zachariasen (1932)
Na_2SO_4	1,49	2,70	0,74	Structure Rep. vol. 9.
$CaSO_4 . 2\ H_2O$ Gypsum	1,49	2,70	0,74	Wooster (1936)
K_2SO_4	1,50	2,72	0,73	Landolt Börnstein (1955)
$Li_2SO_4 . H_2O$	1,50	2,72	0,75	Ziegler (1934)
$BeSO_4 . H_2O$	1,50	2,72	0,75	Beevers, Lipton (1932)
$KAl(SO_4)_2 . 12\ H_2O$	1,52	2,75	0,72	Landolt—Börnstein (1955)
$NiSO_4 . 7\ H_2O$	1,52	2,76	0,72	Beevers, Schwartz (1935)
$SrAl_3(SO_4)(PO_4\ (OH)_6$ Svanbergite	1,54	2,80	0,71	Structure Rep. vol. 11.
$CaAl_3(PO_4)(SO_4)(OH)_6$ Woodhouseite	1,54	2,80	0,71	Structure Rep. vol. 11.
$NaKSO_4$ Aphthitalite	1,60	2,92	0,68	Structure Rep. vol. 9.
$(NH_4)_2Mg(SO_4)_2 . 6\ H_2O$	1,60	2,92	0,68	Landolt Börnstein (1955)
$Na_8Al_6Si_6O_{24} . SO_4$ Nosean	1,60	2,92	0,68	Barth (1933)
$CaSO_4$ Anhydrite	1,60	2,92	0,68	Wyckoff (1951)
Average	1,52	2,76	0,72	

Table 6.

The complex anionic potential of the CrO_4^{2-} ion in some compounds

Ionic distance: 1,89 Å
Rádius: 3,29 Å
Anionic potential: 0,60
(All the three values are calculated from ionic model.)

Compound	Cr—O distance	r_{CrO_4}	ψ_{CrO_4}	References
Na_2CrO_4	1,60	2,71	0,73	Miller (1936)
K_2CrO_4	1,60	2,71	0,73	Zachariasen and Ziegler(1931)
Rb_2CrO_4	1,60	2,71	0,73	Smith and Colby (1941)
Cs_2CrO_4	1,60	2,71	0,73	Miller (1938)
$CaCrO_4$	1,64	2,79	0,71	Clouse (1933)
$CuCrO_4$	1,67	2,85	0,70	Structure Rep. vol. 9.
Average	1,61	2,74	0,72	

Table 7.

The complex anionic potential of the AsO_4^{3-} ion in some compounds

Ionic distance: 1,83 Å
Radius: 3,23 Å
Anionic potential: 0,92
(All the three values are calculated from ionic model)

Compound	As—O distance	r_{AsO_4}	ψ_{AsO_4}	References
$BiAsO_4$	1,63	2,83	1,06	Structure Rep. vol. 11.
$Cu_2(OH)AsO_4$ Olivenite	1,63	2,83	1,06	Heritsch (1938)
$Fe_3(AsO_4)_2 . 8\ H_2O$ Symplesite	1,64	2,85	1,05	Structure Rep. vol. 13.
$BAsO_4$	1,66	2,89	1,03	Wyckoff (1951)
$AlAsO_4$	1,66	2,89	1,03	Wyckoff (1951)
$Ca_2Na(Mg,Mn)_2(AsO_4)_3$ Berzeliite	1,68	2,93	1,02	Bubeck. Machatschki (1935)
$NaAlFAsO_4$ Durangite	1,68	2,93	1,02	Kokkoros (1938)
$FeAsO_4 . 2\ H_2O$ Scorodite	1,69	2,95	1,01	Structure Rep. vol. 11.
$Zn(ZnOH)AsO_4$ Adamite	1,70	2,97	1,01	Heritsch (1938)
$Fe_4(OH)_2(AsO_4)_3K . 6—7\ H_2O$ Pharmacosiderite	1,71	2,99	1,00	Structure Rep. vol. 11.
$YAsO_4$	1,73	3,03	0,99	Heritsch (1938)
KH_2AsO_4	1,74	3,05	0,98	Wyckoff (1951)
Ag_3AsO_4	1,75	3,07	0,97	Structure Rep. vol. 9., 11.
Average	1,68	2,93	1,02	

As it may be seen from Table 1 there is sometimes a significant difference among the minimal, maximal and average values of the radii and potentials of the complex anions computed from measured ionic distances and the corresponding values calculated on the basis of ionic model. Thus, e. g., the average value of the radius of PO_4^{3-} anion is 10,8 per cent lower than that of computed from ionic model. Correspondingly the average complex anionic potential is 11,2 per cent higher than that of calculated on the basis of ionic model. Even the minimal and maximal potential values reckoned from actual ionic distances show a fluctuation of about ± 9 per cent relating to the average value.

These data included in the Tables seem to be enough to verify that the radius and consequently the potential of the same complex anion can change from compound to compound. Thus, computing the complex anionic potentials — especially intending to calculate the compound-potential of the given compound too — seems to be expedient to reckon on the basis of the actual ionic distances determined in the complex anion. It is obvious that the *Szádeczky-Kardoss's* compound-potential values — which are essentially composed of the potential values of the ingredient elements of the compounds and can be considered as the arithmetical mean of these potential values — will be the more characteristic of each compound the more the relations valid in the lattice of the compound in question are taken into account.

4. THE VARIABILITY OF THE ANIONIC POTENTIAL OF SiO_4^{4-} ANION IN MESODESMIC SILICATES

A. The change of the properties of the tetrahedral SiO_4^{4-} anion in the various types of silicates due to their polymerization

Silicates are characterized partly by the presence of SiO_4 tetrahedra partly by the degree of polymerization. From the nesosilicates toward the tectosilicates by increasing polymerization increases the number of shared oxygens per silicon tetrahedron. While the nesosilicates are characterized by discrete SiO_4 tetrahedra not linked directly together, in the lattice of tectosilicates the polymerization reaches the highest degree.

The SiO_4 anion possesses presumably other properties in such a lattice wherein only discrete SiO_4 groups exist connected only with cations like in the nesosilicates and in those structures wherein all of the oxygens are common with two tetrahedra like in the tectosilicates to mention merely the two extreme types.

Should the anionic potentials correctly characterized the properties of complex anions — as shown by *Szádeczky-Kardoss*'s so far results (1954, 1955a, 1955b, 1958) — the change of the properties of the SiO_4 tetrahedra, effected by the gradual polymerization, had to be expressed by the change of the numerical value of the complex anionic potential.

Schaefer, Matossi and *Wirtz* (1934) as well as *Matossi* and *Krüger* (1936) studying the infrared reflection spectra of silicates of different structural types stated as follows: „Zwischen 8 und 12 μ tritt bei allen Silikaten eine Reflexionsbande auf, die wir der dreifachen kurzwelligen aktiven Eigenschwingung des SiO_4-Tetraeders zuschreiben; die Aufspaltung dieser Bande wechselt sehr von Silikat zu Silikat. Im Einklang mit der Feststellung in I erkennt man, dass mit steigender Verknüpfung der SiO_4-Tetraeder eine Tendenz zur Verschiebung nach kürzeren Wellen besteht, die zwar manchmal, besonders bei Übergangsstrukturen verwischt wird, bei einer Auswahl typischer Vertreter der einzelnen Strukturen aber deutlich zum Ausdruck kommt."

Fig. 1 showing the shift of the reflection bands characteristic of SiO_4 tetrahedron toward the shorter wawe lengths by increasing grade of polymerization from the nesosilicates to the tectosilicates is drawn on the basis of the data of the papers mentioned above. In Fig. 1 the thicker lines mean the relatively strong maxima and the thin lines the less strong ones.

Keller, Spotts and *Biggs* (1952) dealt with the infrared absorption spectra of some common carbonates, sulphates, phosphates and silicates. On the influences of the cation and the anion on the spectra they state as follows: „Just as the crystal architecture is dominated by the larger oxygen-containing anions, so are the absorption spectra dominated by the bonds between the oxygen and the element which characterizes the anion. The cations exert only a secondary influence. From another viewpoint, the infrared absorption spectra owe their origin to the covalent bonding which is accentuated in the anions." Of their discussion of silicate spectra from our point of view the following statements are of importance: „The position of the strongest absorption band by the silicate radical shifts slightly but regularly toward longer wave lengths from tectosilicates to nesosilicates, the cyclosilicates excepted because they vary within themselves. As the number of shared oxygens per silicon tetrahedron decreases, and as the number of aluminum and other non-silicon atoms injected into the silica assemblage increases, the position of the strong absorption bands shifts toward longer wave lengths."

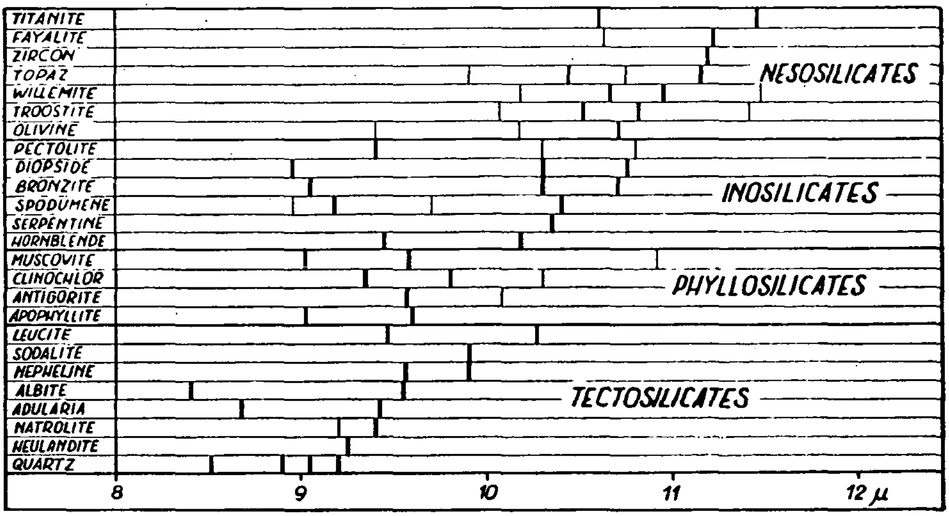


Fig. 1. The shift of the reflection bands in the infrared reflection spectra of the silicates depending upon the degree of silification.

The change of the properties of the SiO_4 group influenced by the type of linkage is also pointed out by *Huggins* and *Sun* (1946) establishing the change of energy constant of Si^{4+} ion depending on the structure type. Thus the values of the r_{Si} in the different structures are the following: nesosilicates — 3142 kg. cal.; sorosilicates — 3137 kg. cal.; inosilicates — 3131 kg. cal.; phyllosilicates — 3123 kg. cal.; tectosilicates (SiO_2) — 3110 kg. cal.

Ramberg (1952, 1954) has pointed out that the degree of polarization of oxygen ions varies depending on the polymerization. The more polarized is the oxygen the more stable are the silicates.

The change of the properties of the SiO_4 group owing to the linkage of the SiO_4 tetrahedra is both theoretically and experimentally proved.

The anionic potential of SiO_4^{4-} anion till now both in nesosilicates and in tectosilicates amounted to 1,38. Therefore, it seems to be obvious that this constant value can not characterize the SiO_4^{4-} anion existing in the different silicates of different structure types. Hence, it had to be found the possibility to express the variable properties of SiO_4 anion by the complex anionic potential.

The study of the variability of the anionic potential of SiO_4^{4-} anion in the different silicates is more essential than that of in the case of complex anions characteristic of anisodesmic structures, owing to the geochemical and petrographical importance of silicates.

It has been shown that the complex anionic potentials are variable and that this variability is the result of the change of the character of the bonding in the anion. This change is expressed by the shortening or lengthening of the ionic distances in the anion.

In the value of the anionic potential of SiO_4^{4-} in the silicates of different structure types may also be stated a fluctuation caused by the same factor. As it can be seen in Table 8 the Si—O distance varies between 1,61—1,81 Å in the nesosilicates, correspondingly does the anionic potential between 1,42—1,24 too. The value computed on the basis of Fersman's anionic radius is 1,38.

In our opinion, however, in the case of silicates as well as borates, beside the change of this kind of the anionic potential, is rather important an other change depending firstly on the structural pecularities of the silicates and borates. This change of the complex anionic potential both in its numerical value and in geochemical significance means a much greater change than the one depending mainly upon the change of the ionic distances.

Let us focus our consideration partly the SiO_4 tetrahedron present with variable properties in all structure types of silicates, partly the change of its properties depending on the degree of linkage of the tetrahedra, that is on the degree of silification.

Therefore, computing the anionic potential values characteristic of the SiO_4 tetrahedra in the different structure types, the degree of the silification had to be taken into consideration by regarding the number of the shared oxygens per silicon tetrahedron.

The potential values new computed are designated as ψ/SiO_4 potentials to express in this way too that the values refer always to the single SiO_4 groups existing in the various structures.

B. The calculation of the ψ/SiO_4 potentials

The average Si—O distance taking into consideration the silicates of different types according to the data of Table 8 is 1,62 Å. The complex anionic radius computed from this distance is 2,84 Å and the anionic potential is 1,40. Attempting only to illustrate the principle of the method applied for calculations in further discussions, in the case of all structural types this mean value will be used as starting value. In the case of calculations relating to given silicates naturally the calculations must be made on the basis of ionic distances valid in the given silicates including in this manner also the change of the potential value caused by the change of the ionic distances. Thus by computing the ψ/SiO_4 potentials in Table 8 the effects on the change of complex anionic potential caused by both the ionic distances and the grade of polymerization in the given silicates were taken into calculation.

a) Nesosilicates

As in the lattice of nesosilicates independent separate SiO_4 tetrahedra exist, not linked directly together only by cations, the complex anionic potential is 1,40. As it has been mentioned, in the nesosilicates the change of the anionic potential depends mainly on the change of the ionic distances (*Fig. 2.*)

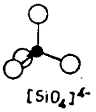


Fig. 2.

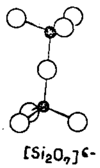


Fig. 3.

Table 8.

The change of the Si—O distance as well as that of the radius and anionic potential of the SiO_4^{4-} anion in some silicates.

Silicate	Si—O distance	r_{SiO_4}	ψ_{SiO_4}	ψ/SiO_4	References
Nesosilicates		Complex anion: SiO_4^{4-}			
Andalusite Al_2OSiO_4	1,61	2,82	1,41	1,41	Landolt—Börnstein (1955)
Disthene Al_2OSiO_4	1,62	2,84	1,40	1,40	Landolt—Börnstein (1955)
Titanite $CaTiOSiO_4$	1,62	2,84	1,40	1,40	Landolt—Börnstein (1955) Wyckoff 1951)
Zircon $ZrSiO_4$	1,62	2,84	1,40	1,40	Landolt—Börnstein (1955)
Willemite Zn_2SiO_4	1,62	2,84	1,40	1,40	Bragg and Zachariasen (1930)
Phenacite Be_2SiO_4	1,62	2,84	1,40	1,40	Bragg and Zachariasen (1930)
Uvarovite $Ca_3Cr_2(SiO_4)_3$	1,66	2,93	1,36	1,36	Menzer (1929)
Andradite $Ca_3Fe_2(SiO_4)_3$	1,67	2,95	1,35	1,35	Menzer (1929)
Eucryptite $LiAlSiO_4$	1,69	2,98	1,34	1,34	Structure Rep. vol. 11.
Pyrope $Mg_3Al_2(SiO_4)_3$	1,72	3,05	1,31	1,31	Menzer (1929)
Almandite $Fe_3Al_2(SiO_4)_3$	1,72	3,05	1,31	1,31	Menzer (1929)
Spessartite $Mn_3Al_2(SiO_4)_3$	1,74	3,09	1,29	1,29	Menzer (1929)
Grossularite $Ca_3Al_2(SiO_4)_3$	1,77	3,15	1,27	1,27	Menzer (1929)
Olivine $(Mg,Fe,Mn)_2SiO_4$	1,81	3,22	1,24	1,24	Landolt—Börnstein (1955)

Silicate	Si—O distance	r_{SiO_4}	ψ_{SiO_4}	ψ/SiO_4	References
Sorosilicates	Complex anion: $Si_2O_7^{6-}$				
Thortveitite $Sc_2Si_2O_7$	1,60	2,80	2,50	1,25	Landolt—Börnstein (1955)
Hemimorphite $Zn_4(OH)_2Si_2O_7.H_2O$	1,63	2,86	2,44	1,22	Ito (1933)
Lawsonite $CaAl_2(OH)_2Si_2O_7.H_2O$	1,65	2,90	2,41	1,20	Structure Rep. vol 11.
Lievrite $CaFe_2^{II}Fe^{III}(OH)OSi_2O_7$	1,74	3,09	2,26	1,13	Structure Rep. vol. 11.
Cyclosilicates	Complex anions: $Si_3O_9^{6-}$ and $Si_6O_{18}^{12-}$				
Beryl $Be_3Al_2Si_6O_{18}$	1,58	2,76	6,51	1,08	Bragg (1930) Structure Rep. vol. 13.
Benitoite $BaTiSi_3O_9$	1,62	2,84	3,16	1,05	Zachariasen (1930)
Inosilicates	Complex anions: $Si_2O_6^{4-}$ and $Si_4O_{11}^{6-}$				
Enstatite $Mg_2Si_2O_6$	1,58	2,76	2,16	1,08	Warren and Modell (1930)
Spodumene $LiAlSi_2O_6$	1,60	2,80	2,15	1,07	Structure Rep. vol. 9. and 13.
Ramsayite $Na_2Ti_2O_3Si_2O_6$	1,62	2,84	2,12	1,06	Warren and Biscoe (1931)
Hypersthene $(Fe,Mg)_2Si_2O_6$	1,62	2,84	2,12	1,06	Landolt—Börnstein (1955)
Diopside $CaMgSi_2O_6$	1,65	2,90	2,07	1,03	Warren and Bragg (1929), Bragg (1930), Landolt—Börnstein (1955)
Anthophyllite $(Mg,Fe)_7(Si_4O_{11})_2(OH)_2$	1,62	2,84	3,87	0,96	Structure Rep. vol. 13.
Phyllosilicates	Complex anion: $Si_4O_{10}^{4-}$				
Muscovite* $KAl_2(OH,F)_2(AlSi_3O_{10})$	1.60	2,80	3,70	0,92	Landolt—Börnstein (1955)
Pyrophyllite $Al_2(OH)_2Si_4O_{10}$	1,57	2,74	3,65	0,91	Landolt Börnstein (1955)
Gillespite $BaFeSi_4O_{10}$	1,59	2,78	3,60	0,90	Structure Rep. vol. 9.
Antigorite $Mg_6(OH)_8Si_4O_{10}$	1,67	2,94	3,40	0,85	Structure Rep. vol. 13.
Tectosilicates*	Complex anions $AlSi_3O_8^{1-}$ and $Al_2Si_2O_8^{2-}$				
α-Celsian $BaAl_2Si_2O_8$	1,66	2,92	3,06	0,76	Structure Rep. vol. 13.
Orthoclase $KAlSi_3O_8$	1,64	2,88	2,92	0,73	Structure Rep. vol. 13.
Sanidine $KAlSi_3O_8$	1,66	2,93	2,90	0,72	Taylor (1933)
Albite $NaAlSi_3O_8$	1,67	2,94	2,90	0,72	Taylor and Derbyshire (1934)
β-Tridymite	1,54	2,68		0,74	Landolt—Börnstein (1955)
β-Cristobalite	1,57	2,74		0,73	Nieuwenkamp (1935), Bragg (1930), Tertsch (1941)
α-Cristobalite	1,59	2.78		0,71	Tertsch (1941)
α-Quartz	1,60	2,80		0,71	Machatschki 1936, Bragg (1930), Tertsch (1941)
β-Quartz	1,61	2,82		0,71	Tertsch (1941), Pei Hsiu Wei (1933)

* In the case of the muscovite and in that of the tectosilicates, computing the complexanionic potentials as well as the $\psi/(Si,Al)O_4$ values also the Al substitution is taken into consideration.

b) Sorosilicates

In the sorosilicates two SiO_4 tetrahedra are linked together by one shared oxygen to $Si_2O_7^{6-}$ silicate anion. From the potential value of 1,40 the portion for one oxygen is 0,35. Since two tetrahedra are linked from the twofold value of the SiO_4 anionic potential (1,40) is to be subtracted the potential portion for one oxygen. That is $2 \times 1{,}40 - 1 \times \times 0{,}35 = 2{,}45$. The value obtained is the anionic potential of $Si_2O_7^{6-}$ silicate anion. According to the basis started, however, the anionic potential, characteristic of single SiO_4 groups present in all of the different structures, is to be calculated. This value in the sorosilicates is $2{,}45/2 = 1{,}22$. *(Fig. 3)*

c) Cyclosilicates

Three SiO_4 tetrahedra form the ring characteristic of benitoite. The complex anion is $Si_3O_9^{6-}$. Here, therefore, the portion for three oxygens is to be subtracted from the threefold value of SiO_4 anionic potential, that is $3 \times 1{,}40 - 3 \times 0{,}35 = 3{,}15$. This value would be the anionic potential of the $Si_3O_9^{6-}$ anion and the corresponding ψ/SiO_4 is 1,05.

Six tetrahedra form the ring characteristic of the beryl. The complex silicate anion is $Si_6O_{18}^{12-}$. The ratio of $Si : O$ is $1 : 3$. From the sixfold value of the SiO_4 anionic potential the portion of potential value for six oxygens is to be subtracted, that is $6 \times 1{,}40 - 6 \times 0{,}35 = 6{,}30$. The value obtained can be considered as the potential of the $Si_6O_{18}^{12-}$ anion. From this value the potential characteristic of the single SiO_4 tetrahedron in cyclosilicates is 1,05. *(Fig. 4)*

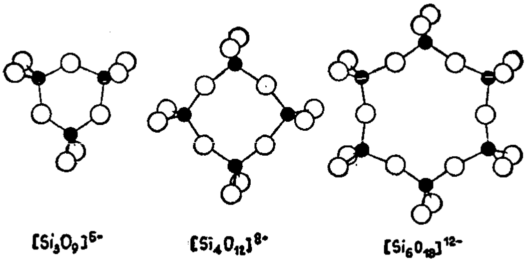


Fig. 4.

d) Inosilicates

In the structure of pyroxenes the SiO_4 tetrahedra form single-chains and the complex anion is $Si_2O_6^{4-}$ anion. Anyhow, even in the case of inosilicates characterized by single or double-chains or in that of the phyllosilicates characterized by sheets of linked SiO_4 tetrahedra, it is arbitrary to some extent, how great portion of these chains, bands or sheets consisting of linked tetrahedra are considered as complex silicate anions characteristic of the single structure types. So in the case of pyroxenes the SiO_3^{2-} or the $Si_2O_6^{4-}$ or in the case of phyllosilicates the $Si_2O_5^{2-}$ or the $Si_4O_{10}^{4-}$ complexes may also be considered as anions characteristic of the given structures although in all structures mentioned the real complex anions are the SiO_4 tetrahedra able to manifold linkage.

Also from this point of view seems to be justified to consider rather the SiO_4 tetrahedron present in all the various structures and its potential calculation, respectively, as the basis of anionic potential computations than the silicate anions being expressed in the chemical formulae and their potential calculations, respectively.

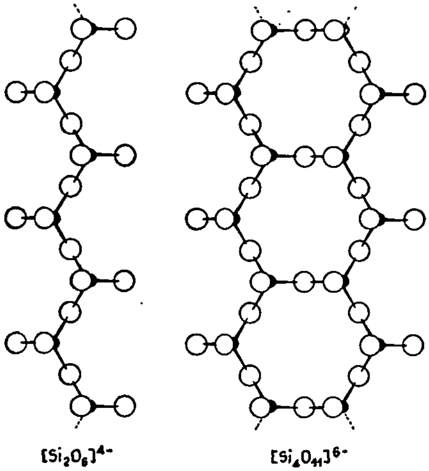


Fig. 5.

The ψ/SiO_4 in the pyroxenes is also 1,05 as the ratio of Si : O is the same as in the case of cyclosilicates that is 1 : 3.

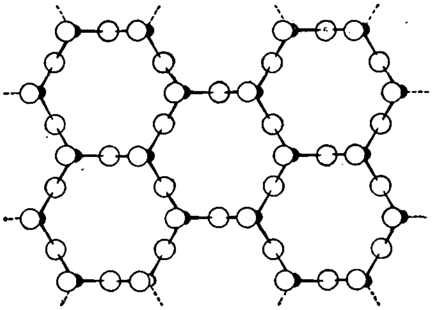
In the structure of amphiboles the characteristic silicate anion formed by linkage of two single chains is $Si_4O_{11}^{6-}$. The anionic potential of this anion would be $4 \times 1{,}40 - 5 \times 0{,}35 = 3{,}85$, whereas the ψ/SiO_4 potential characteristic of amphiboles is 0,96. *(Fig. 5)*

e) *Phyllosilicates*

In the lattice of phyllosilicates the silicon tetrahedra are linked together to sheets and the characteristic complex silicate anion $Si_4O_{10}^{4-}$. Its potential value is $4 \times 1{,}40 - 6 \times 0{,}35 = 3{,}50$ and the ψ/SiO_4 potential is 0,87. *(Fig. 6)*

f) *Tectosilicates*

The SiO_4 tetrahedra form a framework lattice and the Si : O ratio is 1 : 2, that is the characteristic radical would be SiO_2^0 (the structure of the SiO_2 varieties). In the structure of tectosilicates the Si^{4+} ion can be replaced by Al^{3+} ion in different proportions. Such anions are $AlSiO_4^{1-}$, $AlSi_2O_6^{1-}$, $AlSi_3O_8^{1-}$, $Al_2Si_2O_8^{2-}$. The Si + Al : O ratio in these anions is 1 : 2. Consequently in general — for the time being apart from the presence of AlO_4 tetrahedra — merely the Si : O ratio taking into calculation, the potential would be $1 \times 1{,}40 - 2 \times 0{,}35 = 0{,}70$. This value is essentially the potential reckoned for one tetrahedron of the SiO_2^0 complex and may also be considered as the compound-potential of the SiO_2. *Szádeczky-Kardoss* (1954) on the basis of other considerations also assumes that the compound-potential of the quartz would possibly be 0,69.



$[Si_4O_{10}]^{4-}$

Fig. 6.

Calculating the ψ/SiO_4 potentials in the case of tectosilicates, must be taken into consideration the presence of AlO_4 tetrahedra, the type of linkage as well as the ratio of SiO_4 and AlO_4 tetrahedra. The mode of calculations demonstrated on $AlSiO_4^{1-}$ is as follows:

According to the data of Table 9 the average Al—O distance in the AlO_4 tetrahedra is 1,70 Å, the average of the anionic radius is 2,92 Å and consequently the anionic potential is 1,70. (In the potential value of 1,70 the linkage of the AlO_4 tetrahedra is not taken into account.)

The portion for one oxygen from the anionic potential value of AlO_4 tetrahedron is 0,42, whereas that of in the SiO_4 tetrahedron is 0,35. If the ratio of the SiO_4 and AlO_4 tetrahedra in the structure is 1 : 1, the anionic potential of the $AlSiO_4^{1-}$ complex anion may be computed as follows:

$$\psi/AlO_4 = 1 \times 1{,}70 - 2 \times 0{,}42 = 0{,}86$$
$$\psi/SiO_4 = 1 \times 1{,}40 - 2 \times 0{,}35 = 0{,}70.$$

Therefore the potential of the $AlSiO_4^{1-}$ anion is $0{,}86 + 0{,}70 = 1{,}56$ and the $\psi/(Si,Al)O_4$ potential characteristic of one tetrahedron of this structure is 0,78.

Similarly can be calculated the potential value of other complex silicate anions with Al substitution and divided this value by the number of (Si + Al) atoms, the $\psi/(Si,Al)O_4$ potential characteristic of one tetrahedron of the given structure will be obtained.

The data of Tables 8 and 10 clearly show the decreasing tendency of the ψ/SiO_4 potentials relating to the single SiO_4 tetrahedra from the nesosilicates to the tectosilicates. The decrease of the ψ/SiO_4 potentials with increasing polymerization is illustrated in Fig. 7.

Table 9.

The change of the Al—O distance as well as that of the radius and anionic potential of the AlO_4^{5-} anion in some silicates.

Mineral	Al—O distance	r_{AlO_4}	ψ_{AlO_4}	References
α-carnegieite $NaAlSiO_4$	1,65	2,82	1,77	Barth and Posnjak (1935)
Scapolite 3 $NaAlSi_3O_8 . NaCl$	1,65	2,82	1,77	Schiebold and Seumel (1932)
Nosean $Na_8Al_6Si_6O_{24} . SO_4$	1,66	2,84	1,76	Barth (1933)
Sanidine $KAlSi_3O_8$	1,67	2,86	1,74	Taylor (1933)
Albite $NaAlSi_3O_8$	1,67	2,86	1,74	Taylor (1934)
Eucryptite $LiAlSiO_4$	1,69	2,90	1,72	Structure Rep. vol. 12.
Sillimanite Al_2SiO_5	1,70	2,92	1,71	Bragg (1930), Hey and Taylor (1931)
Haüynite $Na_6Ca_2Al_6Si_6O_{24}(SO_4)_2$	1,71	2,94	1,70	Bubeck and Machatschki 1935
Sodalite $Na_8Al_6Si_6O_{24} . Cl_2$	1,74	3.00	1,66	Barth (1933)
Zunyite $Al_{13}Si_5O_{20}(OH,F)_{18}Cl$	1,74	3,00	1,66	Pauling (1933)
Cordierite $Mg_2Al_4Si_5O_{18}$	1,78	3,08	1,62	Structure Rep. vol. 9.
Average	1,70	2,92	1,71	

Table 10.

The variation of the ψ/SiO_4 potential depending on the degree of polymerization.

Si : O ratio	Structure type	Complex anion	$\psi_{complex}$	ψ/SiO_4 calculated on the basis	
				of the average Si—O distances of 1,62 Å	of the actual Si—O distances within the single groups
1 : 4	Nesosilicates	SiO_4^{4-}	1,40	1,40	1,35
1 : 3,5	Sorosilicates	$Si_2O_7^{6-}$	2,44	1,22	1,20
1 : 3	Cyclosilicates	$Si_3O_9^{6-}$	3,15	1,05	1,07
		$Si_6O_{18}^{12-}$	6,30		
1 : 3	Inosilicates Pyroxenes	$Si_2O_6^{4-}$	2,10	1,05	1,05
1 : 2,75	Amphiboles	$Si_4O_{11}^{6-}$	3,85	0,96	0,96
1 : 2,5	Phyllosilicates	$Si_4O_{10}^{4-}$	3,50	0,87	0,89
1 : 2	Tectosilicates and quartz, resp.	$Al_2Si_2O_8^{2-}$	3,20	0,80	0.76
		$AlSi_3O_8^{1-}$	2,96	0,74	0,72
		$Si_4O_8^{0}$	2,80	0,70	0,72

In Fig. 7 the ψ/SiO_4 potentials of various types of silicates represented by the points found on the full line are calculated from the average (1,62 Å) of the Si—O distances measured in the different silicates, whereas the circles, partly close to the line, represents the ψ/SiO_4 potentials computed on the basis of the average of the Si—O distances determined in the single groups of the silicates.

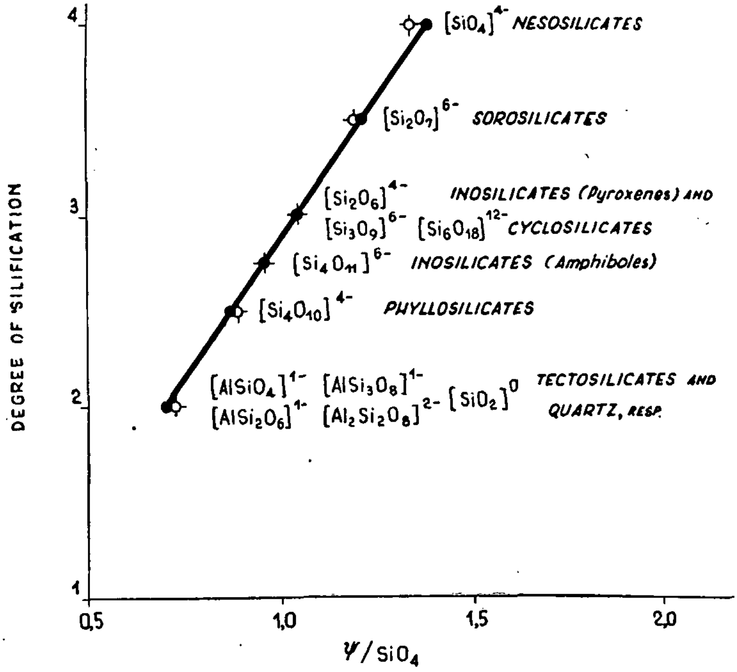


Fig. 7. The change ot the ψ/SiO_4 potentials depending on the degree of the silification

It was assumed also by *Szádeczky-Kardoss* (1954) that in the silicates the potential value presumably decreases by the linkage of the tetrahedra relating to the 1,38 potential value given for the separate SiO_4 anion, as it is shown by his following statements: „Bei weiterer Verknüpfung der SiO_4-Tetraeder setzt sich die Abnahme des Ionenpotentials weiter fort. So ist z. B. das Ionenpotential der durch die Assoziation von zwei SiO_4-Tetraedern zustande gekommenen $(Si_2O_7)^{6-}$-Gruppe offenbar kleiner als 1,38, das von noch grösseren Gruppe allmählich noch kleiner." Thus, in *Szádeczky-Kardoss*'s opinion the decrease of the potential values may be expected in the relation of the different complex silicate anions, that is, in that of $Si_2O_7^{6-}$, $Si_2O_6^{4-}$, $Si_4O_{11}^{6-}$, $Si_4O_{10}^{4-}$ silicate anions.

The correctness of *Szádeczky-Kardoss*'s supposition is proved also by the results of the present work, that is, the complex anionic potential decrease by increasing degree of linkage, this decrease, however, is revealed in the decrease of the ψ/SiO_4 potentials relating to the single SiO_4 tetrahedron.

Summarizing it can be stated that the change of the anionic potential of the SiO_4 depending on the degree of silification corresponds to the conclusions of infrared spectra of silicates and the correctness of the assumption relating to the variability of the SiO_4 anionic potentials expressed in the ψ/SiO_4 potentials seems to be supported by the results of exact physical examinations. The SiO_4^{4-} complex anionic potential became more expressive by introducing of the ψ/SiO_4 values and thereby a greater possibility of their application is obtained in different fields as for example the calculation of the compound-potentials of the silicates, the interpretation of the sequence of magmatic crystallization as well as the examination of the stability relations of the silicates on the basis of the complex anionic and the compound-potentials, respectively.

5. THE VARIABILITY OF THE BO_3^{3-} COMPLEX ANIONIC POTENTIAL AND THE STRUCTURAL PECULIARITIES OF THE BORATES

The connection between the anionic potential of BO_3^{3-} ion and the structures characteristic of borates may be briefly discussed as follows.

In all types of borates the characteristic anion is the BO_3^{3-} anion capable of being linked together in different ways. There are also among the borates that compounds characterized by independent, separate BO_3^{3-} groups and such compounds wherein two BO_3^{3-} groups are linked together to $B_2O_5^{4-}$ anion. The BO_3^{3-} groups can be linked forming rings or chains too.

Bearing in mind the data of Table 11 it can be stated that also the potential of the BO_3^{3-} anion changes — similar to the of the other complex anions — depending upon the change of the ionic distances and on the other hand the ψ/BO_3 value changes by the degree of polymerization of the BO_3 groups. The ψ/BO_3 potential also in the case of borates shows a decreasing tendency by the increasing degree of polymerization as it could be seen in the silicates. It would be worthwhile to know what connection could be established between the change of the anionic potential of BO_3^{3-} depending on the polymerization and the results of the infrared sprectroscopical examinations referring to the borates of different structural types.

It is to be mentioned, although the possibility of the linkage of the complex anions is characteristic firstly of the silicates and borates, sometimes also the linkage of some complex anions in general characteristic of anisodesmic structures can be established. Thus the structures of BPO_4 and $BAsO_4$, respectively, are closely related to that of the α-cristobalite. In the case of $AlPO_4$ having lattice of SiO_2-type all the modifications of SiO_2 were established.

In such cases calculating the potential of the given anion — according to the calculation-method given for the silicates — beside the change of ionic distances, the degree of polymerization must be also taken into consideration.

Table 11.

The change of the complex anionic potential of BO_3^{3-} anion depending on the change of the ionic distance and on the degree of polymerization.

Compound	B—O distance	Complex anion	r_{BO_3}	$\psi_{complex}$	ψ/BO_3	References
$ScBO_3$	1,25	BO_3^{3-}	2,29	1,31	1,31	Leutwein and Doerffel (1956)
Be_2BO_3OH Hambergite	1,35		2,49	1,20	1,20	Zachariasen (1931)
H_3BO_3 Sassolite	1,36		2,51	1,19	1,19	Zachariasen (1934) Landolt—Börnstein (1955)
$Mg_3(BO_3)_2$ Kotoite	1,38		2,55	1,17	1,17	Structure Rep. vol. 11.
$(Mg.Mn^{II})Mn^{III}O_2BO_3$ Pinakiolite	1,40		2,59	1,15	1,15	Structure Rep. vol. 13.
$(Mg,Fe^{II})Fe^{III}O_2BO_3$ Ludwigite	1,40		2,59	1,15	1,15	Structure Rep. vol. 13.
$Mg_3(F,OH)_3BO_3$ Fluoborite	1,44		2,67	1,12	1,12	Structure Rep. vol. 13.
$Ca_2B_2O_5$	1,29	$B_2O_5^{4-}$	2,37	2,10	1,05	Structure Rep. vol. 13.
CaB_2O_4	1,36	$B_2O_4^{2-}$	2,51	1,60	0,80	Zachariasen and Ziegler 1933
$K_3B_3O_6$	1,36	$B_3O_6^{3-}$	2,51	2,38	0,79	Fang (1938)
$Na_3B_3O_6$	1,36		2,51	2,38	0,79	Fang (1938)

6. COMPLEX ANIONS IN GEOMETRICAL AND IN PHYSICAL SENSE IN CRYSTALS

It has been pointed out that owing to the variability of the complex anionic potentials they must be always computed bearing in mind the actual conditions in the lattice in question. The calculation with the actual ionic distances, however, means merely the one part of the circumstances valid in lattice to be taken into consideration. Non the less is essential the establishment — especially from the point of view of the calculation of the compound potential — whether the complex anion expressed in the chemical formula in the lattice of the crystals exists as real complex anion in physical sense or in the lattice rather geometrical groups exist merely, that is, whether the given structure is an anisodesmic or mesodesmic structure with discrete complex anions or simple coordination lattice without formation of radicals.

It is known this question can not be decided but on the basis of the chemical formula.

For example in the lattice of the spinel (Al_2MgO_4) the presence of the loose complex anion MgO_4^{6-} was yet supposed by *Goldschmidt.* Studying, however, the structure of the spinel it has been proved by

Machatschki (1931) that in the lattice MgO_4^{6-} complex anion can not exist, since: „Die geringere Raumbeanspruchung und höhere Wertigkeit des Ions Al^{3+} gegenüber dem Ion Mg^{2+} macht eine kräftige Kontrapolarisation unter Bildung eines neuen Radikals MgO_4 im Gitter ohnehin unwarscheinlich."

Leutwein and *Doerffel* (1956) have computed the Fersman's EK (energy coefficient) values of different complex anions from the following equation:

$$EK = \frac{128 \cdot z^2}{r^{3/2}},$$

where z means the charge and r the radius of the complex anion. Moreover they have computed the EK values of the NbO_3^{1-}, TiO_3^{2-}, JO_3^{1-} „complex anions" expressed in the chemical formulae of the corresponding compounds, that is, in that of the $NaNbO_3$, $CaTiO_3$ and KJO_3. According to these formulae momentarily the presence of the anions mentioned in the lattice may be assumed, this assumption, however, does not correspond to the real conditions in the lattice. Namely, in the lattices of the compounds enumerated, the presence of such complex anions can not be established, since in these lattices such groups which would be distinguished from the other components of the lattice as discrete units owing to the strength and character of the bonding within the groups, do not exist. Each compound mentioned, have perowskite type structure, that is, they have simple coordination structure and not anisodesmic one. In the lattice of perowskite ($CaTiO_3$) the Ti^{4+} ion, in the lattice of $NaNbO_3$ the Nb^{5+} ion and in the lattice of KJO_3 the J^{7+} ion is surrounded by six oxygen ions, that is in the lattices of this type TiO_6, NbO_6, JO_6 octahedral groups exist, which, however, can not be considered as complex anions in physical sense.

As among the compounds of ABO_3-type neither in the structure of ilmenite ($FeTiO_3$) type nor in that of the perowskite ($CaTiO_3$) type BO_3 complex anions do not exist, so, it is not quite correct to mention the compounds of such type as titanates, zincates, zirconates, iodates etc., as it has been emphasized also by *Hiller* (1952).

Similarly the $TlJO_3$ possesses structure of perowskite type that is in its lattice merely JO_6 octahedral groups may be distinguished but not JO_3^{1-} complex anions, while in the lattice of $NaJO_3$ on the basis of investigations of *Náray-Szabó* and *Neugebauer* (1947) the presence of the JO_3^{1-} complex anion can be supposed. The difference between the formal and real complex anion in the two compounds mentioned above is expressed also by the difference between the ionic distances within the complexes, as the J—O distance in the $TlJO_3$ is 2,22 Å whereas that of in the $NaJO_3$ 1,80—1,83 Å.

In the lattice of Li_2WO_4 isomorphous with phenacite the presence of LiO_4 as complex anion similarly can not be assumed. *Schaefer, Matossi* and *Wirtz* (1934) as well as *Matossi* and *Krüger* (1936) studying the infrared reflection spectra of the silicates and the compounds abovementioned stated: „. . . dass zwar BeO_4-Tetraeder (Phenacit) und

BO_4-Tetraeder (Danburit) als mit den SiO_4-Gruppen gleichberechtigte physikalische Baugruppen in den Silikaten existieren, nicht aber LiO_4-Tetraeder im Wolframat, denen hier nur geometrische Bedeutung zukäme." In the spectra of the corresponding compounds it was possible to point out reflection bands characteristic and attributable to SiO_4-, BeO_4-, BO_4-tetrahedra, respectively, but the band expected for the LiO_4 tetrahedron was missing.

Leutwein and *Doerffel* (1956) in their paper computed also the EK value of the SiO_3^{2-} complex anion supposed in the lattice of $MgSiO_3$. However, such an assumption seems to be more probable that also in the lattice of this compound essentially SiO_4 tetrahedra exist similarly to the lattices of the different silicates and the formula above-mentioned with the apparent SiO_3^{2-} complex anion is obtained only due to the linkage of these tetrahedra. *Schaefer, Matossi* and *Wirtz* (1934) mention the previous examinations of *Schaefer* and *Schubert* intending to establish — in analogy with carbonates — the existence of independent SiO_3^{2-} groups in the lattice of the metasilicates on the basis of their infrared spectra. The existence of the SiO_3 groups was not to be proved by their results. The complicated structure of the silicates at that time was yet not fully known, but in connection with the structure of the quartz, however, was acquainted that the infrared spectra of quartz can not be correlated with the existence of SiO_2 groups. The authors mentioned final. concluded that: „Die scheinbare SiO_3-Gruppe der Metasilikate durch ganz verschiedene Anordnungen von SiO_4-Tetraedern erzeugt werden kann." Similarly stated *Kujumzelis* (1938) examining the correlations between the vibrations of XO_3 ions and their structure by Raman-spectra: „Der Einbau der SiO_4 Tetraeder ins Gitter der Metakieselsäurepolymere geschieht in so verschiedener Weise, dass die SiO_3-Gruppe als einfaches Ion nicht ohne Zweifel betrachtet werden kann." These statements are supported by *Fyfe*'s (1954) examinations relating to the problem of bond type discussing why there is no SiO_3^{2-} group corresponding to the CO_3^{2-} groups, and conversely no CO_4^{4-} group corresponding to SiO_4^{4-}.

What possibilities of error is implied without taking into consideration the peculiarities of the structure in question, without distinguishing between formal, only geometrical groups and the real complex anions, especially tending to compute tha lattice energy or the compound potential?

Calculating the compound potential of the spinel assuming in the lattice the real existence of the apparent MgO_4^{6-} complex anion in the chemical formula, then

$$\psi_{Al_2MgO_4} = \frac{2 \cdot \psi_{Al} + 1 \cdot \psi_{MgO}}{3} = \frac{2 \cdot 5,88 + 1 \cdot 1,75}{3} = 4,5$$

whereas considering the spinel according to *Machatschki* as simple coordination lattice without complex anion as it was considered also by *Szádeczky-Kardoss* at the computation of the compound potential, then

$$\psi_{Al_2MgO_4} = \frac{2 \cdot \psi_{Al} + 1 \cdot \psi_{Mg} + 4 \cdot \psi_{O}}{7} = \frac{2 \cdot 5,88 + 1 \cdot 3,22 + 4 \cdot 1,51}{7} = 3,0$$

It has been previously mentioned that *Leutwein* and *Doerffel* have computed EK values for NbO_3^{1-}, JO_3^{1-}, TiO_3^{2-} complex anions too, although the structures wherein they assumed the presence of the complex anions mentioned, are simple coordination structures without complex anions. It is questionable, whether the EK value calculated for a complex anion, in fact not found in the lattice, may be considered as real and characteristic value and particularly it is doubtful, whether the compound can be characterized accurately by the lattice energy computed from such EK values?

Thus, supposing the existence of the TiO_3^{2-} anion in the perowskite and calculating the lattice energy by addition of the corresponding EK values, it would be obtained

$$U'_{CaTiO_3} = EK_{Ca} + EK_{TiO_3} = 572 \text{ kg. cal./mol.},$$

that is the energy needed to decompose the compound into Ca^{2+} and TiO_3^{2-} ions if in the $CaTiO_3$ would be really exist the TiO_3^{2-} anion. Calculating on this basis the complex anionic potential, it would be 0,62, whereas the compound potential of the $CaTiO_3$ 1,25.

Correct results, however, will be obtained only taking into consideration the real conditions in the lattice, that is, the perowskite must be considered as simple coordination structure without any complex anion with three sorts of ions. Accordingly the lattice energy would be

$$U_{CaTiO_3} = EK_{Ca} + EK_{Ti} + 3\ EK_{O} = 3647 \text{ kg.cal./mol.},$$

and the calculated compound potential 2,53.

These two examples seem to be enough to show how essential is, from the point of view of calculation of both the lattice energy and the compound potential, to take into consideration the really existing conditions in the lattice.

Summarizing the above-mentioned, it can be stated that only after studying the structures of the different compounds and the bonding character within the complex anions, supposed firstly merely on the basis of the chemical formula of the compound can be decided, whether this group can be considered as a real complex anion or it is only a geometrical group without the characteristics of a complex anion.

When the existence of complex anion is proved in the compound, it can be stated also from the structure investigations, whether the complex anion expressed formally in the chemical formula corresponds to the complex anion existing really in the lattice.

The emphasize of these aspects seems to be no less important from the point of view of the computations of lattice energy or compound potential than to take into consideration the change, the variability of the ionic distances and the complex anionic potentials, respectively.

SUMMARY

1. The complex anionic potentials introduced by *Szádeczky-Kardoss* are not constant values nor in the case of the same complex anion. The ionic distances within the same complex anion in the different compounds may be varied depending upon the polarizing force of the central cation and the contrapolarizing effect as well as the coordination number of the neighbouring cations. Since the change of the ionic distances within the complex anion is associated with the change of the radius of the complex anion, consequently, the complex anionic potential may be varied from compound to compound also in the case of the same anion. This possible change depends primarily on the change of the ionic distances in the anisodesmic structures. In the mesodesmic structures like in the silicates and borates beside the change of the anionic potentials due to the change of the ionic distances, yet in consequence of its numerical value as well as of its geochemical significance the variation of the complex anionic potential depending on the degree of polymerization proves to be considerably more significant.

To take into account the variability of the complex anionic potentials is especially essential calculating the compound potentials.

2. The most distinctive feature of the silicates is partly the presence of the SiO_4^{4-} group in all the silicates of different structure types and partly the manifold linkage of these tetrahedral groups. The behaviour and properties of the SiO_4 anion, that is, that of the fundamental structure element of the silicates vary depending upon the degree of polymerization of the SiO_4 tetrahedra as it is proved either by the results of infrared spectroscopical investigations of silicates or by the statements of other examinations based on thermochemical data. The experimental results and the theoretical considerations equally show that the peculiarities of the SiO_4 tetrahedra change depending on the degree of polymerization from the nesosilicates toward the tectosilicates. To characterize these changes the ψ/SiO_4 potentials were introduced as the expression of the variable complex anionic potential relating to the SiO_4 tetrahedron equally present in all silicates with variable properties. These values are characteristic of the single groups of silicates and by these values the influence on the change of the complex anionic potential exerted by both the ionic distances and the degree of polymerization is expressed. The ψ/SiO_4 potentials can be simply calculated taking into account the ionic distances as well as the degree of silification. The ψ/SiO_4 potentials decrease from the nesosilicates toward the tectosilicates.

3. In the mesodesmic borates can be similarly pointed out the change of the complex anionic potential depending partly on the change of ionic distances and partly on the degreee of polymerization of BO_3^{3-} groups. The value of ψ/BO_3 potentials decreases as the degree of polymerization increases.

4. The compound potential can be calculated from the ionic potential of the cations and the anionic potential of the complex anion taking into account also the number of ions in the molecule according to the given formula. The lattice energy may be calculated from the Fersman's EK

values by simply adding these values. It is shown that from the point of view of calculation of both the compound potentials and the lattice energies (from EK values of the cation and complex anion) is essential to decide whether the group — which seems occasionally to be complex anion on the basis of chemical formula of the compound in question — can be considered as real complex anion in physical sense also in the crystal lattice of the compound or it is only a geometrical group without the characteristics of a complex anion.

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