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

Part II. Remarks to the calculation of the radii and anionic potentials of the complex oxyanions

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1. INTRODUCTION

The complex anionic potential according to *Szádeczky-Kardoss* (1954) is the quotient of the charge and the radius of the complex anion and may be considered as a value characteristic of the complex anion as a whole.

Now the question may arise what distance, given in Å units, may be considered as the radius of the triangular or tetrahedral oxyanions. Namely, the complex anionic radii computed by *Fersman* and used by *Saukov* (1953) and by *Szádeczky-Kardoss* (1954) are computed rather by simple addition of the ionic radii of central cation and oxygen. The ionic distance within the complex anion may be changed depending on the polarizing force of the central cation and the contrapolarizing effect of the neighbouring cation as well as on its coordination number. This possible change of the ionic distances is not taken into consideration calculating the complex anionic radii on the basis of simple ionic model.

Considering the different complex oxyanions as elements of crystal lattices of different solid compounds of anisodesmic and mesodesmic structure, it has been pointed out by the author *(Grasselly,* 1958, 1959a) that the radius of the complex anions due to the factors above-mentioned may be changed from compound to compound also in the case of the same complex anion and therefore the anionic potentials are to be considered as variable values.

In connection with the calculation of the radius as well as the potential of the complex anions a further question may also arise the satisfactorily solution of which, in our opinion, implies the possibility of the further refinement of the calculation method of the complex anionic potential.

The problem and the way of the solution which seems to be practicable at least as approximation, may be discussed as follows.

2. THE MEANING OF THE ANIONIC POTENTIAL
FROM ELECTROSTATIC VIEWPOINT

The ionic potential of the cations from the electrostatic viewpoint is considered by *Mason* (1952) as a measure of the charge density on the surface of the cation. Similarly *Goldschmidt* (1954) in his book considers the quotient charge/radius, that is the ionic potential, as a measure of the field strength at the surface of the polarizing ion. It is to be noted, however, that the z/r is not the quite correct expression for the charge density at the surface of the cation as it would be correctly given by the expression $\dfrac{z \cdot e}{4 \pi r^2}$. The increase of the numerical value of the ionic potentials, however, goes together with the increase of the values computed from the correct expression of the charge density if for example the charge increases at constant radius, though the rate of the increase of the values of these two kinds differs.

Apart from these necessary remarks, howewer, the ionic potentials may be considered at least as a qualitative measure of the charge density on the surface of the cation. Under constant charge the larger is the radius the lower will be the ionic potential that essentially means the decrease of the charge density at the surface.

Analogously the anionic potential of the simple anions — considering them also as spheres apart from the possible deformation — introduced by *Szádeczky-Kardos* (1954) may be considered as a qualitative measure of the density of the negative charge at the surface of the anion.

3. THE CALCULATION METHOD PROPOSED FOR THE DETERMINATION
OF THE RADIUS OF NON-SPHERICAL COMPLEX OXYANIONS

As it has been already mentioned, *Szádeczky-Kardoss* has computed the complex anionic potentials in the same manner as the potential of the cations, i. e., as the quotient of the charge and „radius". In practice it is customary to speak about radii of complex anions and to calculate with these values too and this consideration implies that these complex anions are considered to be spherical. Now the question arises, whether the nonspherical tetrahedral or triangular oxyanions may be considered as rigid spheres and hence it may be calculated with their „radius", or not?

On the one hand, it is a fact that these, essentially nonspherical, complex ions may be considered only in that case as rigid spheres when in the lattice the rotation of these complex ions may occur, consequently showing in statistical average a spherical symmetry. The fact of the rotation of complex ions in crystals especially at higher temperatures is pointed out by several authors. For example, in the lattice of NH_4NO_3 (structure type: CsCl) stable over 125° C both the NH_4^+ and the NO_3^- groups rotate. The radius of the rotation sphere corresponding to the NH_4^+ group is 1,46 Å, whereas that of corresponding to the NO_3^- group is 2,35

On the other hand, *Goldschmidt* (1954) dealing with the ionization potential as a measure of polarizing force of ions mentions that the non-

spherical complex ions as the triangular ions BO_3^{3-}, CO_3^{2-}, NO_3^{1-} or the tetrahedral ions like SiO_4^{4-}, PO_4^{3-}, SO_4^{2-}, ClO_4^{1-} can be considered to be rigid spheres, with a fair degree of approximation if their internal bonds give them a fair degree of rigidity, that is, these internal bonds within these complex anions are strong in comparison with the electrical forces exerted by neighbouring cations.

The radius of the complex anion equals $2a - r_c$, where a is the ionic distance measured roentgenographically and r_c is the radius of the central cation. The distance, considered as the radius of the complex anion, essentially is the radius of the sphere circumscribed around the tetrahedron.

Still an other question is, whether the complex anion would be rightly represented by the sphere of radius $2a - r_c$ and thus would be accurately characterized by the complex anionic potential calculated with this value or it would be better to substitute hypothetically the complex anion with an other sphere, the radius of which differs from that mentioned above.

Should the *Mason*'s opinion be applied to the complex anions too, i. e., the complex anionic potential would be considered as a qualitative measure of the density of the negative charge at the surface of the complex anions considered as spheres, it seems to be expedient to calculate with such a radius, to substitute the complex anion with such a sphere, the surface of which is close to the effective surface of the complex anion. On the other hand, also the importance of volume relationship in the lattice of crystals is well known.

Therefore, it seems to be expedient to substitute hypothetically the complex anion with such a sphere, the volume and surface of which mostly approach that of the complex anion.

This consideration can be presented by showing the possibilities of the calculation-method of the anionic potential of SO_4^{2-} anion.
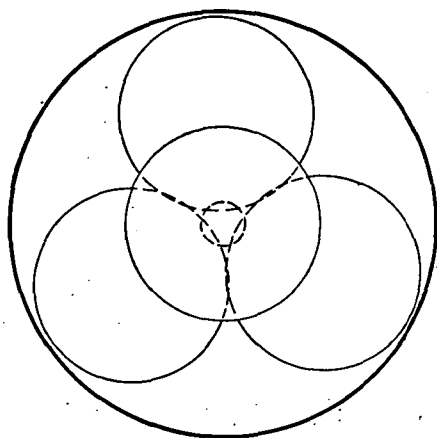

Fig. 1

a) In the lattice of anhydrite, according to *Wooster* (1936), the distance of S—O is 1,55 Å and that of O—O is 2,50 Å. In general the radius of the complex ion $SO_4{}^{2-}$ equals r $= 2 \times 1,55 - 0,28 = 2,82$ Å. Calculating the complex anionic potential too, it will be 0,70. In *Mason*'s opinion this value can be considered as a measure of the density of negative charge at the surface of the sphere to be circumscribed around the tetrahedron and having a radius of 2,82 Å. In Fig. 1, the full line circle represents this sphere. It is observable that this sphere includes to a significant extent such a space too actually not engaged by the SO_4 tetrahedron.

b) Fig. 2 demonstrates within the SO_4 tetrahedron, the tetrahedron whose edge equals with the distance of O—O measured roentgenographically, that is with 2,5 Å. In the Fig. 2, the circle drawn with full line represents the sphere having the same volume as the tetrahedron of edge 2,5 Å. The radius of the sphere is 0,76 Å and the complex anionic potential calculated from this value is 2,6. It is obvious that the complex anion can not be symbolized by this sphere and the radius of this sphere can not accepted as the radius of the complex anion.
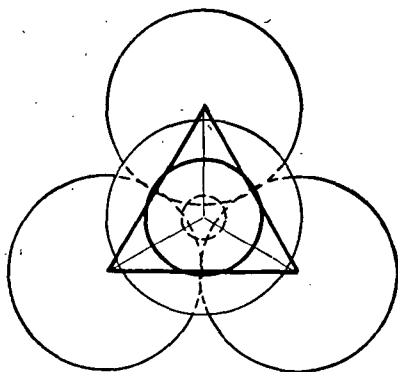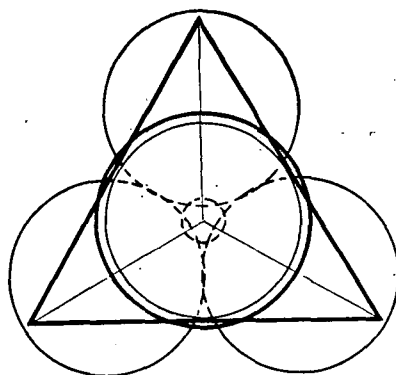

Fig. 2   Fig. 3

c) Fig. 3 shows the tetrahedron wherein the distance between its centre and corner is 2,82 Å that is it equals with the radius of the SO_4 complex anion. The centre of the tetrahedron coincides with that of the central cation. The radius of the sphere having the same volume as this tetrahedron is 1,40 Å and the computed anionic potential from this value is 1,42. As it can be seen in Fig. 3, also this sphere is of less volume and surface than the SO_4 tetrahedron, therefore, tending to calculate the complex anionic potential, the SO_4 anion presumably can not be substituted by the sphere obtained in such manner.

d) So far it was examined how the spheres deduced in different way from data obtained from roentgenographic measurements can be related to the SO_4 complex anion regarding to their volume. Moreover, sketches of b) and c) demonstrate that the $SO_4{}^{2-}$ complex anion can not be substituted by spheres obtained in the manner given under b) and c).

Intending to find the sphere probably most corresponding in its volume to that of the SO_4^{2-} complex ion, firstly the oxygen ions are to be drawn representing by circles, taking as distance between their centre the O—O distance roentgenographically determined. Then tangents will be drawn to these circles on the three sides adn the triangle so obtained is to be considered as a plate of the tetrahedron, the volume of which had to be calculated. Finally, the radius of the sphere identical in its volume to that of the tetrahedron constructed is to be calculated. The O—O distance in the present example is 2,5 Å. The radius of the sphere adequate in volume with the tetrahedron constructed as mentioned above is 2,12 Å and the complex anionic potential is 0,94.

In Table 1 are comprised the data referring to the surface, volume and radius relations of the spheres and tetrahedra, respectively, deduced in the manner given under a), b), c) and d).
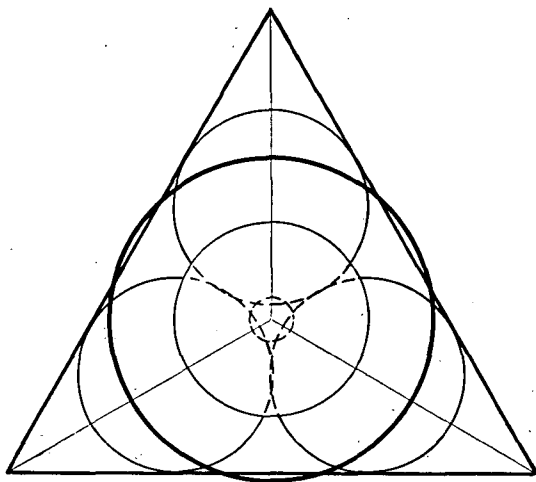

Fig. 4

To illustrate which of the different spheres characterized by the data given in Table 1 corresponds mostly to the SO_4^{2-} complex ion as to its volume and surface, let us make the following calculation of approximative character. The radius of the oxygen ions in SO_4 from the roentgenographic data may be taken as 1,27 Å, since the S—O distance is 1,55 Å and the Ahrens's radius of the S^{6+} ion corrected for four-coordination number is 0,28 Å. On this basis the volume of each oxygen ion considered as spheres, with radius 1,27 Å, amounts to 8,5 $Å^3$ and that of the four oxygen ions is 34 $Å^3$. The surface of the single oxygen ions, at the same radius value, will be 20 $Å^2$ and that of the four oxygen ions 80 $Å^2$, respectively.

As it can be seen the volume and surface values calculated for the SO_4^{2-} anion are close to that of the tetrahedron and of the sphere with equal volume, respectively, constructed in the manner, given under d),

especially taking into consideration that owing to the tetrahedral arrangement of the oxygen ions only a part of the whole surface of the oxygen ions can be effective from viewpoint of the bonding.

Consequently, owing to this conformity, it seems to be very presumable that the SO_4^{2-} ion is hypothetically to be substituted in the lattice by a sphere, the radius of which is determined in the way given under d) and that the complex anionic potential calculated with this radius would be presumably more characteristic of the anion than the anionic potential calculated in the so far manner, i. e., taking as radius of the complex anion that of the sphere to be circumscribed round the tetrahedral anion.

Table 1.

		a	b	c	d
Volume of the tetrahedron and the sphere	Å³	93,87	1,84	11,50	40,40
Surface of the tetrahedron	Å²	148,83	10,82	36,65	84,86
Surface of the sphere	Å²	99,89	7,16	24,62	56,42
Radius of the sphere	Å	2,82	0,76	1.40	2,12
Complex anionic potential		0,70	2,63	1,42	0,94

Table 2.

Anion	O—O distance Å	Compound	Radius	Anionic potential	References
BO_3^{3-}	2,35	$Na_3B_3O_3$	1,96	1,53	Ssu-Mien Fang (1938)
CO_3^{2-}	2,13	$BaCO_3$	1,81	1,10	Colby, La Coste (1935)
NO_3^{1-}	2,10	KNO_3	1,76	0.56	Edwards (1931)
SiO_4^{4-}	2,56	$BaTiSi_3O_9$	2,12	1,88	Zachariasen (1930)
	2,61	$CaMgSi_2O_6$	2,19	1,82	Bragg (1930)
	2,68	$KAlSi_3O_8$	2,24	1,78	Structure Rep. vol. 9.
AsO_4^{3-}	2,60	Ag_3AsO_4	2,20	1,36	Structure Rep. vol. 11.
	2,76	$NaAlFAsO_4$	2,30	1,30	Kokkoros (1939)
	2,85	$BiAsO_4$	2,32	1,29	Structure Rep. vol. 11.
SO_4^{2-}	2,50	$CaSO_4$	2,12	0,94	Wooster (1936)
CrO_4^{2-}	2,61	Na_2CrO_4	2,16	0,92	Miller (1936)
ClO_4^{1-}	2,51	$NaClO_4$	2,09	0,47	Braekken, Harang (1930)
JO_4^{1-}	2,67	$NaJO_4$	2,22	0,45	Hazlewood (1938)

Table 2 includes some of complex anionic radius values determined in the way given in this paper as well as the O—O distances on the basis of which the construction of the hypothetically spherical ion has taken place, the radius of which is considered as the radius of the complex anion. Similarly the new complex anionic potentials are denoted.

4. CONNECTION BETWEEN THE THERMOCHEMICAL RADII OF COMPLEX ANIONS AND THE RADII DETERMINED IN THE WAY PROPOSED IN THIS PAPER

The probability of the correctness of our assumption relating to the computation method of anionic radii proposed in this paper seems to be supported when comparing these values with the thermochemical radii computed by *Kapustinski*. The term of thermochemical radius is introduced by *Kapustinski* and in his opinion it means the radius of a hypothetically spherical ion which isoenergetically substitutes a given ion in the crystal lattice. As it can be seen this definition and our view, discussed above, expresses almost the same.

Table 3.

Anion	Radius used in general computed from equation: $R = 2a - r_c$ R	Thermochemical radius R'	Radius computed by the author R''	Ratio $R'' : R'$
BO_3^{3-}	2,50	1,91	1,96	1,02
CO_3^{2-}	2,40	1,85	1,81	0,97
NO_3^{1-}	2,34	1,89	1,76	0,93
AsO_4^{3-}	2,93	2,48	2,27	0,91
JO_4^{1-}	2,88	2,49	2,22	0,89
SiO_4^{4-}	2,90	2,40	2,18	0,90
CrO_4^{2-}	2,74	2,40	2,16	0,90
SO_4^{2-}	2,76	2,30	2,12	0,92
ClO_4^{1-}	2,91	2,36	2,09	0,88

In Table 3 the thermochemical radii and the radii graphically determined by the author on the basis of roentgenometric data are compared. The thermochemical radii used are taken from *Jazimirski*'s work (1956) dealing with the thermochemistry of complex compounds.

As it can be seen in Table 3, the radius values of the triangular complex oxyanions computed by the author are nearly the same as the correspondig thermochemical radii and in the case of the tetrahedral oxyanions our radius values are more close to the thermochemical radii than the radii used in general calculated on the basis of roentgenographic data from the equation: $R = 2a - r_c$.

The thermochemical radii can be computed according to *Kapustinski* as follows. Knowing the heats of formation of the ingredient ions in gaseous state of a given compound as well as the heat of formation of the crystallized compound, from these data, firstly the lattice energy of the compound is to be computed according to the following equation:

$$U_k = -\Delta H^\circ_{ka} + \Delta H^\circ_k + \Delta H^\circ_a$$

where U_k means the lattice energy, $-\Delta H^\circ_{ka}$, $-\Delta H^\circ_k$ and $-\Delta H^\circ_a$ are the heats of formation of the crystallized complex compound and that

of the cation and the anion, respectively. Then the value U_k obtained is to be substituted into the *Kapustinski*'s equation:

$$U_k = \frac{\Sigma_n \cdot z_1 \cdot z_2}{r_1 + r_2} (1 - \frac{0{,}345}{r_1 + r_2}),$$

where Σ_n means the number of the ingredient ions in the molecule, z_1 and z_2 the charges and r_1, r_2 the radii of the ions, respectively. Knowing the radius of the cation, the radius of the complex anion can be determined.

As it may be seen the computation method proposed by the author based only on roentgenometric data (on the O—O distances within the complex anions) gives nearly the same radius values for complex oxyanions as the method above-mentioned based on thermochemical data in the case of the triangular oxyanions and the new radius values in the case of tetrahedral oxyanions are very close to their thermochemical radii and the quotient of these two values are nearly constant, $0{,}9 \pm 0{,}02$.

In our opinion, during the thorough investigations in progress concerning the connections afore-said, this conformity may offer partly the possibility of a calculation into the opposite direction, i. e., of the calculation of some thermochemical data from these radius values determined graphically from roentgenometric data and partly the possibility of the further refinement of the complex anionic potential calculations and finally it will be also possible to find connections between the complex anionic potentials and thermochemical data.

SUMMARY

The radius of the complex anions in general as a rule is calculated on the basis of roentgenographically measured data (central cation — oxygen distance) from the following equation: $R = 2a - r_c$, where a means the distance measured and r_c the radius of the central cation. This is essentially the radius of the sphere to be circumscribed round the tetrahedral anion. The complex anionic potential is given by the quotient of its charge and radius and may be considered as a qualitative measure of the charge density at the surface of the anion, however, from crystallochemical viewpoint, from the viewpoint of diadochy, substitution of complex anions also the volume relations are essential, therefore, a non-spherical complex anion is probably hypothetically to be substituted in the crystal lattice with such a sphere, the surface and volume of which are closest to that of the complex anion.

It is proposed a graphic method based on roentgenographically measured O—O distance within the complex anion to construct the sphere whereby the anion is to be substituted in the lattice, the radius of which sphere may be considered as the effective radius of the complex anion. These graphically determined „effective" anionic radii agree well with the thermochemical radii of anions introduced by Kapustinski and calculated from thermochemical data, from heats of formation and lattice energy.

REFERENCES

Braekken, H. and Harang, L. (1930): Die kubische Hochtemperaturstruktur einiger Perchlorate. Z. f. Krist., **75,** 538—549.

Bragg, W. L. (1930): The Structure of Silicates. Z. f. Krist., **74,** 237.

Colby, M. Y. and La Coste, L. J. B. (1935): The Crystal Structure of Witherite. Z. f. Krist., **90,** 1.

Edwards, D. A. (1931): A Determination of the Complete Crystal Structure of the Potassium Nitrate. Z. f. Krist., **80,** 154—163.

Fang, Ssu-Mien (1938): The Crystal Structure of Sodium Metaborate. Z. f. Krist. **99,** 1.

Goldschmidt, V. M. (1954): Geochemistry. Oxford, Clarendon Press.

Grasselly, Gy. (1958): Die Veränderlichkeit der Komplex-Anionenpotentiale in anisodesmischen und mesodesmischen Strukturen. Acta Geol. Acad. Sci. Hung., **5,** 293—311.

Grasselly, Gy. (1959): The role and significance of the complex anionic potentials in the geochemistry. Part I. The variability of the complex anionic potentials. Acta Miner. Petr. Univ. Szegediensis, Tom. XII. 3—29.

Hazlewood, E. A. (1938): Determination of the Oxygen Parameters for $NaJO_4$. Z. f. Krist., **98,** 339—446.

Jazimirski, K. B. (1956): Thermochemie von Komplex Verbindungen. Akademie Verlag, Berlin.

Kokkoros, P. (1938): Über die Struktur des Durangit $NaAlF(AsO_4)$. Z. f. Krist., **99,** 38.

Mason, Brian (1952): Principles of Geochemistry. John Wiley, New York.

Miller, J. J. (1936): The Crystal Structure of Anhydrous Sodium Chromate. Z. f. Krist., **94,** 131.

Saukov, A. A. (1953): Geochemie. VEB Verlag Technik, Berlin.

Structure Reports, International Union of Crystallography, vol. **9, 11.**

Szádeczky-Kardoss, E. (1954): Vorläufiges über Anionenpotentiale und Verbindungspotentiale. Acta Geol. Acad. Sci. Hung., **2,** 285—298.

Wooster, W. A. (1936): On the Crystal Structure of Gypsum. Z. f. Krist., **94,** 375.

Zachariasen, W. H. (1930): The Crystal Structure of Benitoite. Z. f. Krist. **74,** 139.