# CORRELATION BETWEEN ELECTROSTATIC ENERGIES AND ENERGY CONSTANTS OF SOME COMPLEX OXYANIONS

by

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## INTRODUCTION

The author in some of his work dealing with the geochemical role and significance of the complex anionic potentials [GRASSELLY, 1959 a, b, 1960] pointed to that the relative stability relations of the complex anions may be characterized by their electrostatic energy as well by the energy constant ($\varepsilon_M$ in kcal) [HUGGINS and SUN, 1946]. The increase of the relative stability of the complex anions is indicated by the increase of the electrostatic energy values computed or by that of the energy constants calculated from thermochemical data experimentally obtained.

In the first step to simplify the problem, the electrostatic energies of the complex anions were calculated on the basis of simple ionic model taking the sum of ionic radii as the shortest distance between cation and anion. Thus, the radius of the $O^{2-}$ anion was taken as 1,32 Å according to GOLDSCHMIDT in the $MgO_4^{6-}$ „complex anion" just as in the $ClO_4^{1-}$ anion only to mention the members of lowest and highest stability, respectively, of the series.

It is clear that this aspect holds good only in first approximation considering the complex anions as ideal formations independent of the crystal lattice, however, the existence of oxygen ions of same character and size in the $MgO_4^{6-}$ complex — which in the lattice of spinel can not be considered as a real complex anion according to MACHATSCHKI [1931] — as well as in the $SiO_4^{4-}$ or in the $ClO_4^{1-}$ complex anion can not be supposed. Still less may be supposed as the bonding character within the complex anions starting from the $MgO_4^{6-}$ toward the $ClO_4^{1-}$ becomes more and more covalent as shown in Table I in the case of some tetrahedral oxyanions.

The increasing covalent character in the series of the complex anions is due to the increasing polarizing force of the central cation. Correspondingly the deformation of the anion increases — in the present that of the oxygen — thus it is not suitable to consider the oxygen ion in each member of the complex anion series with the same character and radius.

Comparing the electrostatic energies calculated from ionic model and the energy constants given by HUGGINS and SUN it seems, however, to be possible to demon-

strate, at least qualitatively, the change in the character of the oxygen and that of the bonding through the series of oxyanions arranged according to their increasing relative stability.

Table I

| Complex anion | Difference of electronegativity values of cation and anion | Polarity according to PAULING |
|---|---|---|
| $MgO_4^{6-}$ | 2,3 | 73,35% |
| $AlO_4^{5-}$ | 2,0 | 63,21% |
| $SiO_4^{4-}$ | 1,7 | 51,44% |
| $PO_4^{3-}$ | 1,4 | 38,74% |
| $SO_4^{2-}$ | 1,0 | 22,12% |
| $ClO_4^{1-}$ | 0,5 | 6,05% |

# CONSIDERATIONS ABOUT THE POLARIZATION OF THE OXYGEN IN SILICATES OF DIFFERENT STRUCTURE TYPE

The polarization of the oxygen anion may change even in the same complex anion for example in the silicate anion too as shown by RAMBERG [1952, 1954]. In his assumption the stability of silicates is closely related to the degree of polarization of the oxygen, the more polarized it is the more stable the silicate. RAMBERG pointed out that by increasing number of shared oxygen atoms, i..e. by increasing degree of linkage ,,...the nonbridging oxygen atoms which surround Fe, Mg, Ca, etc. in olivine and pyroxene have a greater percentage of double-bond character toward the silicon in metasilicates than in orthosilicates.'' RAMBERG refers to that the electronegativity value of the oxygen increases stepwise from the nesosilicates toward the tectosilicates and due to this fact in the corresponding compounds the bonding character between oxygen of the silicate anion and the neighbouring cations becomes more ionic.

RAMBERG's above-mentioned statements are supported by the examinations of HUGGINS and SUN [1946] and KELLER [1954], respectively, pointing out the change of the energy constant of $Si^{4+}$ ($\varepsilon_{Si}$) in silicates of different structure-type. Similar change may be supposed in the case of the $PO_4^{3-}$ anion too and presumably the value of energy constant of the central cation of each complex anion ready for polymerization changes.

RAMBERG's and KELLER's assumptions concerning the probable change in the electronegativity and polarization of oxygen atoms and the values of energy constants of central cation of oxyanions, respectively, form the starting point of the following consideration.

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As it was mentioned the relative stability of tetrahedral oxyanions could be characterized by the electrostatic energy values calculated in first approximation on the basis of ionic model. The values were calculated from the following equation:

$$U_p = - \frac{4(z_c \cdot z_a - s_p \cdot z_a^2)}{(r_c + r_a)},$$

where $z_c$ and $z_a$ mean the charges of the cation and anion, respectively, $r_c$ and $r_a$ are the radii of the cation and anion, whereas $s_p$ is the screening factor taking into consideration the type of arrangement of the simple anions and 4 is the co-ordination number being tetrahedral oxyanions in question. The numerical value of $s_p$ is 0,92 at the tetrahedral co-ordination. The higher the numerical value of the electrostatic energy expressed in arbitrary units the more stable the oxyanion. The electrostatic energy values were calculated from ionic model only the attractive and repulsive Coulomb-forces, respectively, supposed to be prevalent between opposite and identical charged ions, respectively.

On the other hand, to characterize the relative stability series of the oxyanions the energy constants $\varepsilon_M$ computed by HUGGINS and SUN were also used. Although they refer essentially to the central cation, it seemed, however, still possible to take these values as a measure of the relative stability of the different tetrahedral oxyanions.

Each energy constant „...is a measure of the decrease in energy when one g-atom of the ion $M$ and the equivalent number of oxygen ions ($O^{2-}$) are transferred from the gaseous state to an average simple or complex oxide in the solid state in which each $M$ has as near neighbours only oxygens and each oxygen has as near neighbours only more electropositive atoms." These energy constants depend primarily upon the charge of ions, the interatomic distance between cation and anion, on the co-ordination number — among other factors — as has been stated by HUGGINS and SUN. The higher the numerical value of the energy constant the greater the energy released.

The mentioned authors have pointed out that the attraction between cation and surrounding oxygen contributes most of the ionic energy of formation of a solid compound and though this attractive energy changes from compound to compound, however, not too considerably. According to HUGGINS and SUN the energy of formation ($E_i$) may be additively computed from the energy contributions originated from the attraction between the positive components and their opposite charged neighbours. So

$$E_i = \sum_M m_M \cdot \varepsilon_M$$

where $m_M$ is the relative number of the metal atoms, $\varepsilon_M$ is the energy constant characteristic of the element $M$ deduced from experimentally determined $E_i$ values.

In the author's former papers the correlation between the two values mentioned above and the complex anionic potentials introduced by SZÁDECZKY-KARDOSS [1954] were discussed, the aim of the present paper is to compare the electrostatic energies and the energy constants of the oxyanions.

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In the values of the electrostatic energy the conditions really prevalent in the crystal lattice concerning especially the bonding character and its change, respectively, are not expressed, as, using simple ionic model, merely the Coulomb-force have been taken into consideration.

On the contrary, the energy constants computed from thermochemical data, i. e. from energy of formations experimentally obtained, probably better approach and represent the circumstances in fact existing in the lattice. The change of these energy constants presumably expresses implicitly the change of the polarizing force of the central cation and as a result, the increasing deformation of the anion, the rate of polarization of the anion and thus the change of the bonding character within the oxyanion too. It is to mention, however, that these energy constants

<div align="center">Table II</div>

| Complex anion | $r_c$ | $r_c + r_o$ | $U_p$ | $\varepsilon_M$ kcal. | $U'_p$ | $r'_o$ | $x_M$ electro-negativity of the central cation |
|---|---|---|---|---|---|---|---|
| | | calculated from ionic model | | | given from the diagram of *Fig. 1.* | | |
| $MgO_4^{6-}$ | 0,62Å | 1,94Å | 0,65 | 912 | | | 1,2 |
| $BeO_4^{6-}$ | 0,33 | 1,65 | 0,77 | 1141 | | | 1,5 |
| $GaO_4^{5-}$ | 0,58 | 1,90 | 4,88 | 1827 | the same as $U_p$ | 1,32 Å | 1,6 |
| $AlO_4^{5-}$ | 0,48 | 1,80 | 5,15 | 1878 | | | 1,5 |
| $BO_4^{5-}$ | 0,22 | 1,54 | 6,02 | 2047 | | | 2,0 |
| $ZrO_4^{4-}$ | 0,74 | 2,06 | 8,38 | 2637 | 9,40 | 1,09 | 1,4 |
| $SnO_4^{4-}$ | 0,67 | 1,99 | 8,68 | 2769 | 10,0 | 1,05 | 1,8 |
| $TiO_4^{4-}$ | 0,64 | 1,96 | 8,81 | 2882 | 10,75 | 0,96 | 1,6 |
| $GeO_4^{4-}$ | 0,50 | 1,82 | 9,49 | 3055 | 11,65 | 0,98 | 1,7 |
| $SiO_4^{4-}$ | 0,39 | 1,71 | 10,10 | 3129 | 12,10 | 1,03 | 1,8 |
| $SbO_4^{3-}$ | 0,58 | 1,90 | 13,30 | 4250 | 18,10 | 0,81 | 2,1 |
| $AsO_4^{3-}$ | 0,43 | 1,75 | 14,44 | 4507 | 19,55 | 0,86 | 2,2 |
| $PO_4^{3-}$ | 0,33 | 1,65 | 15,32 | 4737 | 20,85 | 0,88 | 2,1 |
| $TeO_4^{2-}$ | 0,53 | 1,85 | 17,98 | 6167 | 28,50 | 0,63 | 2,1 |
| $SeO_4^{2-}$ | 0,39 | 1,71 | 19,46 | 6886 | 32,35 | 0,63 | 2,4 |
| $SO_4^{2-}$ | 0,28 | 1,60 | 20,80 | 7195 | 34,05 | 0,69 | 2,5 |
| $ClO_4^{1-}$ | 0,25 | 1,57 | 26,29 | 9948 | 49,00 | 0,59 | 3,0 |

The $r_c$ values are the cation radii given by AHRENS and the $r_o$ is 1,32 Å according to GOLDSCHMIDT
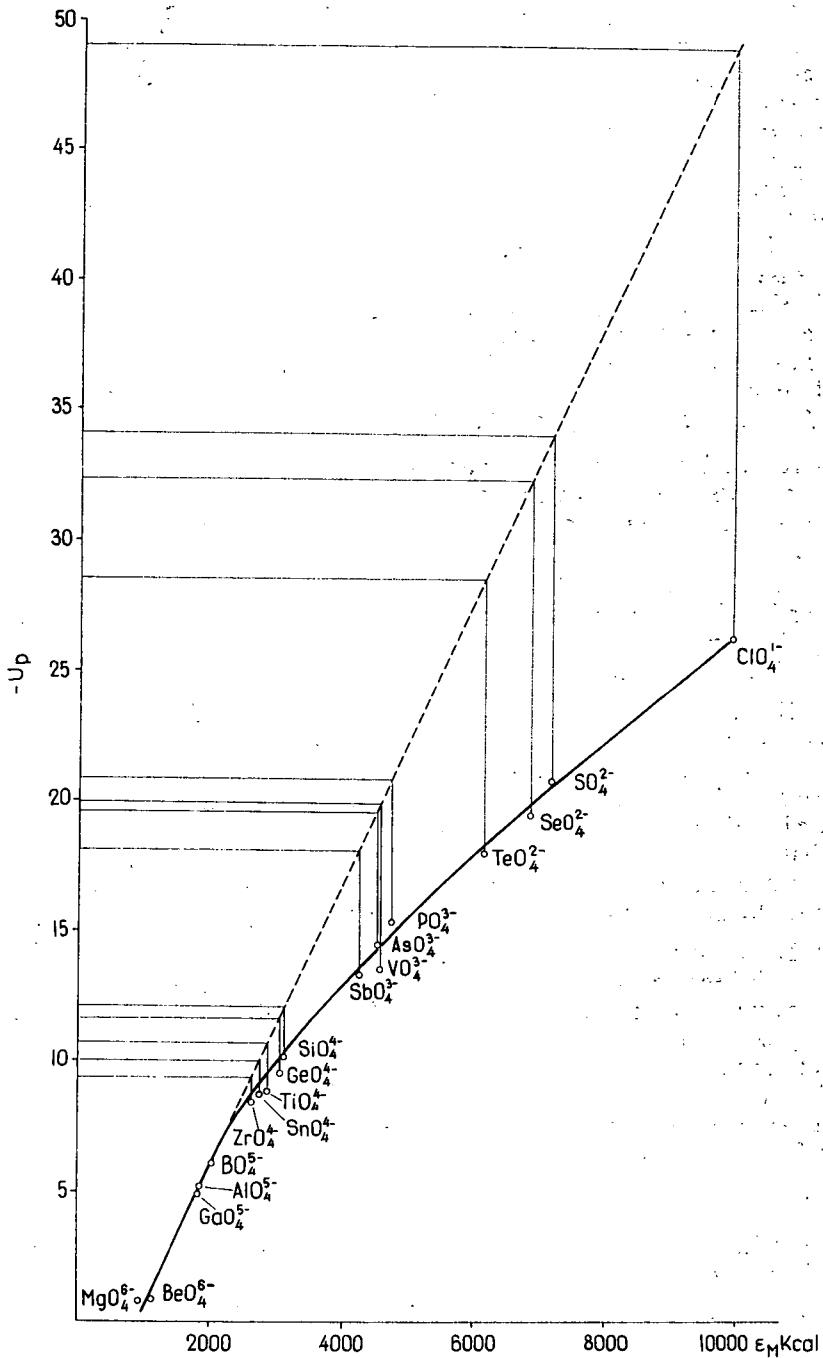
*Fig. 1.* Correlation of electrostatic energy values and energy contants of tetrahedral oxyanions.

are of adequate precision only for an approximation as they are only average values and „....they do not give accurate energies of formation by simple additivity..." as it has been pointed out by the authors.

At any rate, one of our starting points is the obvious fact that the electrostatic energy computed simply from ionic model can not characterize the oxyanions in the solid crystal lattice all the less the more covalent bonding character prevails within the complex anion, i. e. the greater is the deviation from the pure ionic model.

On the other hand — and this may be our second starting point — the energy constants implicitely express the increasing polarization of the oxygen as well as the increase of the covalent bonding character in this series.

The electrostatic energies and energy constants concerning tetrahedral oxyanions are comprised in Table II. *Fig. 1* shows the electrostatic energy values plotted against the corresponding energy constants.

Plotting the electrostatic energy values against the corresponding energy constants *(Fig. 1)* the following may be established.

*a)* As the increasing electrostatic energies and energy constants, respectively, served as a measure for the increasing stability of the complex anions, they are arranged in the diagram from left to right upwards corresponding to their increasing stability.

*b)* Considering the series as a whole, the increase of the electronegativity of the central cation goes nearly together with the increase of the stability as shown also by the data of Table II. This also denotes the gradual decrease of the ionic bonding character in the series.

*c)* The correlation between the values of electrostatic energies $U_p$ and the energy constants $\varepsilon_M$ in the field of anions of lower stability seems to be approximately linear apart from scattering of the points due to inaccurate data.

The linearity may be interpreted that the bonding in these complexes are still dominantly of ionic character thus the $U_p$ values computed from ionic model are suitable to characterize the relationship within the complex anions in solid lattices just as the energy constants calculated from experimental data taking therefore generally better into account the actual relationship of the oxyanions.

*d)* The deviation from the linearity begins about at the $ZrO_4^{4-}$ and toward the $ClO_4^{1-}$ it becomes more and more pregnant. Should the energy constants considered suitable to characterize with a good approximation the relation within the complex anions, the greater the deviation from the linearity, due to increasing covalent bonding character, the less are able the electrostatic energy values computed from ionic model to characterize the actual situation. The rate of the deviation may be taken as a qualitative measure of the deviation of the real state of complex anions from the ionic model.

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The following considerations may be further added to the establishments drawn from *Fig.* 1.

1. *Correction of the electrostatic energies computed*

Calculating the electrostatic energies the covalent bonding character, the deformation of the oxygen atom depending upon — among others — the polarizing force of the central cation were not taken into consideration. Should it have been

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done by some appropriate way (as for example is given in RAMBERG's work referred), the electrostatic energy would have a greater numerical value denoting the increase of the stability, the increase of the covalent character. In this case the correlation of electrostatic energies and energy constants — apart from some scattering — would be probably linear within the whole series.

It seems that from the correlation plotted — without calculations — at least with approximate accuracy such electrostatic energy values could be obtained in which also the increasing covalent bonding character would implicitly expressed and so they can characterize the complex anions as elements of solid crystal lattices too.

Let us lengthen the lower linear part of the diagram of *Fig.* 1 and draw vertical lines from the points corresponding to the different oxyanions till to the intersection of this lengthened straight line and then project these points of intersection to the $U_p$ axis. The values ($U'_p$) obtained in this manner are greater than the calculated $U_p$ values as shown in Table II and these $U'_p$ values may be considered as the more probable values for electrostatic energies of oxyanions.

2. *The transition from ionic oxygen radius to covalent oxygen radius in the series of* $MgO_4^{6-}-AlO_4^{5-}-SiO_4^{4-}-PO_4^{3-}-SO_4^{2-}-ClO_4^{1-}$ *anions.*

From the afore-mentioned correlation may be possible to draw some conclusions concerning the radius of the oxygen in the different oxyanions. It may not be supposed the existence of oxygen atoms of the same size and character in the $MgO_4^{6-}$ complex and in the $SO_4^{2-}$ or in the $ClO_4^{1-}$ anion. The polarity of these anions see in Table I. Should the PAULING's electronegativity values and their differences, respectively, well characterize the ionic percentage of the bonding, in the $MgO_4^{6-}$ complex we can reckon with the real oxygen ion and with its ionic radius, however, in the case of $SO_4^{2-}$ or even in the $ClO_4^{1-}$ anion — in the bonding of the latter already 94% covalent character prevails — we should rather suppose oxygen atom and calculate with the corresponding radius value. It seems that from the rate of deviation from the linearity conclusions may be drawn concerning the rate of the change of the oxygen radius.

In the series of $MgO_4^{6-}-AlO_4^{5-}-SiO_4^{4-}-PO_4^{3-}-SO_4^{2-}-ClO_4^{1-}$ in first rough approximation the charge of cation and anion, the tetrahedral co-ordination and presumably the radius of the central cation may be considered as unvariable and as the lone variable the radius of the oxygen can be taken.

Substituting the $U'_p$ values for the equation of the electrostatic energy and taken as unknown in the equation only the radius of the oxygen, the latter may be calculated (Table II).

As in the sequence of oxyanions $SiO_4^{4-} \rightarrow ClO_4^{1-}$ the bonding character between the central cation and the oxygen becomes more and more covalent, the radius of the oxygen also approaches the covalent oxygen radius. It may be said that the oxygen radii computed in the way outlined above may be considered as transitional oxygen radii corresponding to the ratio of ionic — covalent character prevalent in the given complex anion if the oxygen would be hypothetically taken as spherosymmetrical.

The fact that by increasing covalent bonding character the features of the oxygen atom become dominant instead of that of the oxygen ion, may be demonstrated also by the change of the size of the oxygen. Plotting the oxygen radius

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obtained for the complex anions mentioned against the corresponding differences of electronegativity values of central cation and oxygen, the correlation shown by *Fig.* 2 can be seen.
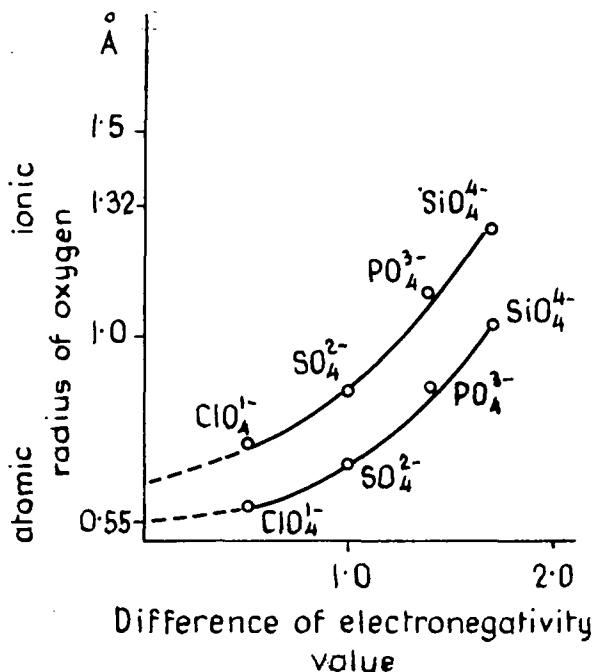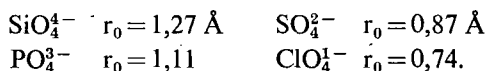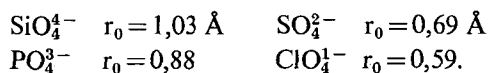


*Fig.* 2. Correlation of electronegativity differences of cation and anion and the radius of oxygen graphically determined and computed from the diagram of *Fig. 1.*

*Fig.* 2 shows two curves. The curve 1 is obtained taking into consideration as transitional oxygen radii the following values in the different complex anions:

$$SiO_4^{4-} \quad r_0 = 1,27 \text{ Å} \qquad SO_4^{2-} \quad r_0 = 0,87 \text{ Å}$$
$$PO_4^{3-} \quad r_0 = 1,11 \qquad\qquad ClO_4^{-} \quad r_0 = 0,74.$$

These values are obtained if at the plotting of the diagram of *Fig* 1 the calculation of the electrostatic energies is carried out using the cation radii of AHRENS and the oxygen anion radius of PAULING (1,40 Å). The curve 2 is obtained on using the cation radii of AHRENS and the oxygen anion radius of GOLDSCHMIDT (1,32 Å) at the calculation the $U_p$ values. In this latter case the transitional oxygen radii computed from the $U'_p$ values are as follows:

$$SiO_4^{4-} \quad r_0 = 1,03 \text{ Å} \qquad SO_4^{2-} \quad r_0 = 0,69 \text{ Å}$$
$$PO_4^{3-} \quad r_0 = 0,88 \qquad\qquad ClO_4^{-} \quad r_0 = 0,59.$$

As the difference of the electronegativity values decreases the bonding within the complex anion becomes more covalent. Extrapolating the curve 1 the radius of the oxygen will be about 0,64 Å which is very close to the single-bond atomic

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oxygen radius (according to PAULING 0,66 Å), whereas the extrapolation of the curve 2 results in an oxygen radius of 0,55—0,56 Å, nearly the oxygen atomic radius of double—bond character (according to PAULING 0,55 Å).
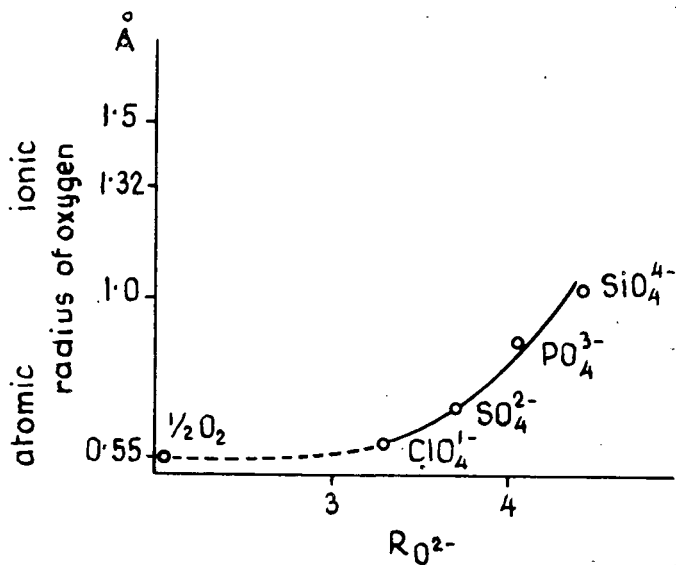


*Fig. 3.* Correlation of oxygen radius computed and the refraction of oxygen.
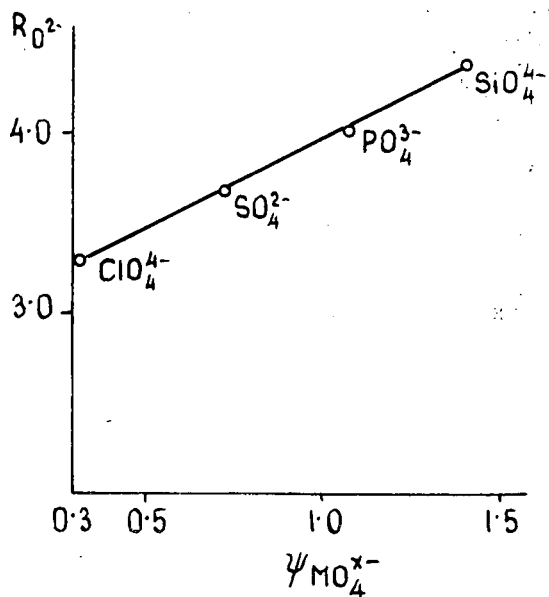


*Fig. 4.* Correlation of complex anionic potential and the refraction of oxygen.

Similar picture can be obtained plotting the oxygen radius values computed against the refraction values of oxygen ($R_0{}^{2-}$) as seen in *Fig.* 3. It was shown by Fajans that the greater the polarizing force of the central cation the greater extent will be deformed the electron shell of the anion, the lower will be the anion refraction. For example the refraction values in some oxyanions are as follows:

| Complex anion: | $SiO_4^{4-}$ | $PO_4^{3-}$ | $SO_4^{2-}$ | $ClO_4^{1-}$ |
|---|---|---|---|---|
| $R_0{}^{2-}$ | 4,42 | 4,05 | 3,70 | 3,30 |

whereas the refraction of the non-polar bound oxygen is 2,02. As it is seen by extrapolating the curve, the oxygen radius of double-bond character is approached again.

Finally is worth to mention the correlation of the oxygen refractions and the complex anionic potentials of the corresponding complex anions as shown in *Fig* 4. The correlation is linear between these two values in this series of anions. This may be considered as a further verification that the complex anionic potentials introduced by Szádeczky-Kardoss are able to geochemical characterization of complex anions in the most different aspects and on the other hand, this correlation shows that the geochemical potential concept furnishes wide usable connections between geochemical and crystallo-chemical problems.

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