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Abstract

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Energetics of the Complex Crystal Lattice of Silicates

In recent years a number of studies have appeared, and some of the earlier data on the enthalpies of formation of alkaline-earth metal silicates have been revised (1-6). These experimental data have served as the basis for our calculation of lattice energies and standard enthalpies of formation of anionic radicals of the most important structural types of silicates.

As is known, the structure of silicon-oxygen anions depends on the manner in which the tetrahedra $[SiO_4]$—the elementary structural units of silicates—are joined. The crystal chemistry of silicates includes a great variety of modes of condensation of Si tetrahedra, as well as of simple silicon-oxygen radicals into more complex ones (7). However, in the present work, for the energetic analysis of the crystal lattices of silicates as complex salts, we have limited ourselves to the simplest structural types.

The division of a substance into elementary ions corresponds to the maximum value of the lattice energy U_{p} (total), and into gaseous complex ions to U_{k} (complex). The relationship between them is written as follows:

$$U_{\mathrm{p}} = U_{\mathrm{k}} + U_a', \tag{1}$$

where U_a' is the energy of formation of the anionic radical from elementary gaseous ions. The experimental U_{p} were calculated by us from circular thermodynamic cycles. The initial data are given in Table 1.

Table 1

Cations and oxides	ΔH°_{298}, kcal/mol	Silicates	ΔH°_{298}, kcal/mol	Silicates	ΔH°_{298}, kcal/mol
Mg^{2+}	561	SiO_2	217.75	$Ca_3Si_2O_7$	945
Ca^{2+}	461	Ba_4SiO_6	836	$MgSiO_3$	370.2
Sr^{2+}	421	Ca_3SiO_5	712	$CaSiO_3$	390.7
Ba^{2+}	390	Sr_3SiO_5	702	$SrSiO_3$	390.1

Cations and oxides	ΔH°_{298}, kcal/mol	Silicates	ΔH°_{298}, kcal/mol	Silicates	ΔH°_{298}, kcal/mol
Si^{4+}	2453	Ba_3SiO_5	695	$BaSiO_3$	388.8
MgO	143.8	Mg_2SiO_4	520.5	$Ba_2Si_3O_8$	1001.1
CaO	151.8	γ-Ca_2SiO_4	554	$BaSi_2O_5$	609.8
SrO	141.1	Sr_2SiO_4	550		
BaO	133.1	Ba_2SiO_4	548.4		

The standard heat of formation of the oxygen anion O^{2-} is taken as 225 kcal/mol. U_{k} values were calculated from an equation of the Kapustinskii type (^{8}), with an empirically found constant for each isotypic group of compounds: ortho-, pyro-, and pseudowollastonite metasilicates. By analogy with complex compounds (^{9}), for the calculation of the lattice energies U_{k} of island silicates, their low-symmetry anions were reduced to an isoenergetic spherical symmetry with the corresponding thermochemical radius, or to an equivalent spherical one. For the anion $[SiO_4]^{4-}$, the thermochemical radius 2.40 Å was reliably calculated by Yatsimirskii (^{9}). In metasilicates $Me_3[Si_3O_9]$, the ring radicals $[Si_3O_9]^{6-}$, in a first approximation, may be inscribed in a flattened ellipsoid of revolution. The thermochemical radius of $[Si_3O_9]^{6-}$, 3.13 Å, was calculated by us in several ways from the packing coefficient of pseudowollastonite. In pyrosilicates of the general formula $Me_n[Si_2O_7]$, the thermochemical radius of $[Si_2O_7]^{6-}$, 2.87 Å, was calculated from the packing coefficient in the structure of thortveitite $Sc_2[Si_2O_7]$, and also from the decrease in the volume of silicon-oxygen radicals per one oxygen anion O^{2-} released upon condensation of Si tetrahedra.

Experimental values of U_k are calculated from the transformed equation of the Born-Haber thermodynamic cycle:

$$U_k = m\Delta H^0_k + n\Delta H^0_a - \Delta H^0_{298}, \tag{2}$$

where ΔH^0_k, ΔH^0_a, and ΔH^0_{298} are the standard heats of formation of the cation, anion, and silicate, respectively; m and n are the coefficients of the chemical formula. The standard heats of formation of silicates and gaseous cations were calculated by us in accordance with the latest experimental data (see Table 1). However, the unknown quantity in equation (2) is the heat of formation of the anion ΔH^0_a, which is eliminated if one takes the difference of the experimental values U_p or U_k for two comparable silicates of the same type:

$$\Delta U^{(\mathrm{exp})}_{p(1-11)} = \Delta U^{(\mathrm{exp})}_{k(1-11)} =$$

$$= \Delta\left(\Delta H^0_k\right)_{1-11} + \Delta\left(\Delta H^0_{298}\right)_{11-1} =$$

Figure 1

Figure 1: Figure 1

$$= K \cdot \left(\frac{1}{r_{\mathrm{K_I}} + r_a} - \frac{1}{r_{\mathrm{K_{II}}} + r_a} \right). \tag{3}$$

From relation (3) we determined empirical values of the constants K, or $k' z_1 z_2 \sum n$ (see Table 2), for olivine and pseudowollastonite silicates. The empirically determined constant k' takes into account, in each individual case, the structural features and polarization properties inherent in the given group of compounds of the same type. The values of the radii of alkaline-earth cations were taken from the compilation by N. V. Belov and G. B. Bokii [10]. From the calculated U_k, the heats of formation of gaseous anions were calculated: 1) standard values, ΔH_a^0, by equation (2), and 2) from gaseous ions, U_a', by equation (1); see Table 2.

Fig. 1. Isocomponents of the energy of the crystal lattices of silicates of alkaline-earth metals

The energy of the crystal lattice of complex oxo-orthosilicates $\mathrm{Ba_4[SiO_4]O_2}$ and $\mathrm{Me_3[SiO_4]O}$, where $\mathrm{Me = Ca, Sr, Ba}$, was calculated from the experimental equation:

$$U_k = (2m + n)\Delta H^0_{\mathrm{Me}^{2+}} + m\Delta H^0_{[\mathrm{SiO4}]^{4-}} + n\Delta H^0_{\mathrm{O}^{2-}} - \Delta H^0_{298},$$

the terms of which are the standard heats of formation of the cation and anion with the corresponding coefficients, and of the oxo-orthosilicate. The heats of formation of anionic radicals, referred to one Si tetrahedron, are given in Table 2. The greatest energy of formation, $U_a' = 3045$ kcal/mol, is that of the isolated tetrahedron with four free valence bonds; the smallest is that of pure silica, $U_a' = 2967$ kcal/mol, with four closed vertices. The formation energies U_a' of highly condensed radicals—

Table 2

$[Si_{mO}n]^{(2n-4m)-}$	r_a, Å	k' in the lattice-energy equation	U_a'/n	$\Delta H_a^0/n$	Structural type of silicate
$[SiO_4]^{4-}$	2.40	256	3045	308	Olivine
$[Si_2O_7]^{6-}$	2.87	225	3025	215	Rankinite
$[Si_3O_9]^{6-}$	3.13	253	3008	120	Pseudowollastonite
$[n(SiO_3)]^{2n-}_{\infty}$	–	–	3008	120	Pyroxenoid
$[Si_4O_{11}]^{6-}_{\infty}$	–	–	2997	75	Amphibole

$[Si_{mO}n]^{(2n-4m)-}$	r_a, Å	k' in the lattice-energy equation	U'_a/n	$\Delta H^0_a/n$	Structural type of silicate
$[Si_6O_{16}]^{8-}_{\infty}$	–	–	2994	59	Dibarium trisilicate
$[Si_4O_{10}]^{4-}_{\infty}$	–	–	2985	31	Layer silicate
$\frac{1}{2}Si^{4+}[SiO_4]^{4-}$	–	–	2967	−64	Silica

for silicates of chain, ribbon, and layered structure have been calculated from the additivity of closed $Si—O—Si$ and free $Si—O\ldots(Me)$ bonds in the radical. The decrease in the energy of formation $U'_{a/n}$ of gaseous $[SiO_4]$-radicals with increasing degree of condensation of the Si tetrahedra is consistent with the analogous change in the energy constants E_M of the Si^{4+} cation in different structural types of silicates, according to the data of Huggins and Sun ([11]).

A comparison of the values $\Delta H^0_a/n$ for different structural types shows that the formation of a single tetrahedron is the most endothermic, $\Delta H^0_a = 308$ kcal/mol. As the degree of condensation of the silicon-oxygen radicals increases, the values $\Delta H^0_a/n$ decrease on average by a constant amount $\simeq 93$ kcal/mol as a result of the successive closure of each free valence bond $Si—O\ldots(Me)$ into the bridging $Si—O—Si$ bond. For pure silica with four closed bonds, $\Delta H^0_a/n = -64$ kcal/mol–the heat of formation of gaseous silica.

The method of isoatoms (isocomponents) of enthalpies of formation ([12, 13]) gives a comparative estimate of the energetic strength of compounds of a homologous series. In Fig. 1 are given the isocomponents of the crystal-lattice energy $U_p/\sum n$ and $U_k/\sum n$–the lattice energy per one "averaged" component. As can be seen from the figure, the values $U_k/\sum n$ of silicates decrease as the degree of condensation of Si tetrahedra in the anionic radicals increases. For pure silica, $U_k/\sum n$ is found graphically at the point of convergence of the four curves for the systems $MeO—SiO_2$ and has the value 154 kcal/mol, equal to the heat of sublimation (experimental value 136 ± 8 kcal/mol ([14])). The correspondence between thermal strength and lattice energy is clearly manifested if U_k is referred to the number of structural units actually existing in the melt, i.e., divided by the sum of elementary and complex structural units–$\sum$ e.c.s.u. As an example, Fig. 1 gives the isocomponent of the lattice energy $U_k/\sum$ e.c.s.u. for the system $BaO—SiO_2$. In the region from Ba_2SiO_4 to SiO_2, $U_k/\sum$ e.c.s.u. coincides with $U_k/\sum n$, since in the silicates $Ba_2Si_3O_8$ and $BaSi_2O_5$ the sum of oxide components in each of them is equal to the number of structural units: Ba^{2+} cations and Si tetrahedra. Both the isocomponent of the enthalpies of formation and the isocomponent of the lattice energy $U_k/\sum$ e.c.s.u. in the system $BaO—SiO_2$ have a minimum of energy reserve falling at Ba_2SiO_4, on both sides of which the thermal stability decreases in accordance with the decrease in $U_k/\sum$ e.c.s.u. of the silicates.

$U_p/\sum$ e. ions, where $\sum$ e. ions is the sum of elementary ions, as is seen from the figure, gives a broken curve with which the thermal stability is not connected, since $U_p/\sum$ e. ions does not take into account the actually existing complex units into which the silicate dissociates on melting.

The isocomponent $U_\mathrm{p}/\sum n$ is a dependence close to linear and reflects the additivity of changes in bond energies in the homologous series of silicates.

In conclusion, we note that the study of the complex crystal lattice of alkaline-earth silicates and of its dependence on crystal-chemical parameters makes it possible to extend the regularities obtained to the most diverse groups of silicates and their analogues.

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