Bond Energies In Oxide Systems: Calculated and Experimental Data

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Bond energies in oxide compounds are the main factor determining structure and properties of substances. In some cases bond energies may be used as the energetic parameters in different statistical thermodynamical models. Main goal of the present study is to consider the application of the semiempirical Sanderson's method for calculation of the bond energies in the $BaO-TiO_2-SiO_2$, $CaO-TiO_2-SiO_2$, $Rb_2O-B_2O_3$ and $Cs_2O-B_2O_3$ systems. The accuracy of this calculation was compared with the data obtained by high temperature mass spectrometric method.

The main equations in Sanderson's method used were the following.

$$E=t_cE_c+t_iE_i\ , \qquad [1]$$

where E is bond energy, t_c and t_i are coefficients, E_c and E_i are covalent and ion bond energies. Coefficients t_i, t_c were calculated using partial charges: $t_i=(\delta_A-\delta_B)/2$ and $t_c=1-t_i$. Covalent bond energies were obtained from the equation:

$$E_c= (E_{AA}E_{BB})^{1/2}R_c/R_0, \qquad [2]$$

E_{AA} is nonpolar homonuclear bond energy, R_c is nonpolar covalent radii sum, R_o is bond length.

The bond energies in the components of the gaseous phase were calculated from the equation:

$$E_i=332/R_o \qquad [3]$$

The bond energies in the components of the solid phase were calculated from the Madelung equation:

$$E_i=332Mk/R_0, \qquad [4]$$

M is Madelung constant, k is repulsion coefficient.

Table 1 represents the results of these calculations.

The comparison between the data of bond energies in the systems studied calculated taking into account the second coordination sphere and the experimental values obtained without consideration the second coordination sphere are given in Table 2. There is good agreement between experimental and calculated results in the frame of the accuracy about 15±2%.

The values of bond energies in the gaseous $RbBO_2$ and $CsBO_2$ were also obtained by high temperature mass spectrometric method using the following equations:

$$AE(M^+/MBO_2) \geq IE(M) + D(M–BO_2); \qquad [5]$$

$$D(M–BO_2) \approx AE(M^+/MBO_2) – IE(M); \qquad [6]$$

$$D_{avg}(B\text{-}O) \approx [\Delta_{at}H^0(MBO_2, gas)– D(M–BO_2)]/2, \qquad [7]$$

where AE_i is appearance energy of ion, IE_i is the ionization energy of atom, $D_{i\text{-}i}$ is bond dissociation energy, $\Delta_{at}H^0(MBO_2)$ is the atomization enthalpy of compound. Results are presented in Table 3 and compared with the calculated values of average B–O bond energies.

Table 1. Results of the bond energies calculation in the $BaO-TiO_2-SiO_2$, $CaO-TiO_2-SiO_2$, $Rb_2O-B_2O_3$ and $Cs_2O-B_2O_3$ systems. in gaseous and solid phases at the temperature 0 K.

System	Bond	Bond energy, KJ/mol	
		Gaseous	Solid
$BaO-TiO_2-SiO_2$	Ba-O[-Ti]	382.0	512.7
	Ba-O[-Ba]	348.5	467.7
	Ti-O[-Ba]	331.8	450.6
	Ti-O[-Ti]	364.7	497.6
	Ba-O[-Si]	437.6	585.4
	Si-O[-Ba]	270.3	334.7
	Si-O[-Si]	407.9	421.0
$CaO-TiO_2-SiO_2$	Ca-O[-Ti]	377.1	500.1
	Ca-O[-Ca]	322.2	486.8
	Ca-O[-Si]	441.1	585.1
	Si-O[-Ca]	287.9	358.2
	Ti-O[-Si]	418.5	574.3
	Si-O[-Ti]	294.1	366.7
$Rb_2O-B_2O_3$	Rb-O[-Rb]	387.9	527.6
	Rb-O[-B]	768.7	988.6
	B-O[-Rb]	275.6	339.6
	B-O[-B]	392.0	488.3
$Cs_2O-B_2O_3$	B-O[-Cs]	268.4	330.1
	Cs-O[-B]	820.0	954.7
	Cs-O[-Cs]	372.9	498.4

Table 2. Comparison between the calculated values of bond energies in silicon, boron, calcium, titanium, rubidium and cesium oxides in gaseous phase and reference data.

Bond	Oxide	Bond energy, KJ/mol	
		Calculation	Reference data
Si–O	SiO_2	408.0	315.9±10.5
Ca–O	CaO	322.2	209.2±42.8
B–O	B_2O_3	392.0	449.1±19.2
Ti–O	TiO_2	364.7	314.8±8.4
Rb–O	Rb_2O	388.0	232.2±83.5
Cs–O	Cs_2O	372.9	272.3±29.5

Table 3. Comparison of values of bond energies in the gaseous $RbBO_2$ and $CsBO_2$ calculated by the Sanderson method and obtained by high temperature mass spectrometry

Compound	Parameter	Energies, KJ/mol	
		Experiment	Calculation
$RbBO_2$	$D(Rb\text{-}BO_2)$	540	768
	$D_{avg}(B–O)$	641	349
$CsBO_2$	$D(Cs\text{-}BO_2)$	501	820
	$D_{avg}(B–O)$	693	345

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