

Kinetics and mechanism of free-surface vaporization of zinc, cadmium and mercury oxides analyzed by the third-law method

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Abstract

On the basis of critical comparison of experimental and theoretical values of the E parameter and investigation of the retardation effect of oxygen on the evaporation rate of ZnO, CdO and HgO, it was concluded that the dissociative evaporation of ZnO and HgO proceeds with releasing of atomic oxygen (O) as a primary product of decomposition. By contrast, the mechanism of dissociative evaporation of CdO corresponds to the equilibrium reaction with releasing of molecular oxygen (O₂) as a primary product of decomposition. As was shown, this difference in mechanisms is not related with interatomic O–O distances in these oxides. From the analysis of crystal structure for 12 different oxides, which evaporate with releasing of atomic oxygen, and for 13 compounds, which evaporate with releasing of molecular oxygen, it was revealed that the first mechanism is observed for all oxides with the cubic crystal structure. It was proposed that a decisive role in this difference belongs to a local symmetry in the position of O atoms.

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1. Introduction

Kinetics and thermodynamics of vaporization of ZnO, CdO and HgO has been discussed recently in two fundamental books [1,2]. Nevertheless, many questions remain to be answered. These three oxides for IIB Group of metals evaporate with formation of only gaseous products and, at first sight, the interpretation of the mechanism of their vaporization creates no problems. However, in fact, this is not the case. In spite of rather high number of works devoted to the investigation of evaporation kinetics of these oxides, the E parameters of the Arrhenius equation reported in [3–20] vary in the range of factor 2.4 for ZnO and 1.5 for HgO (Table 1). In contrast to the reversible dissociation of solid CdO up to Cd atoms and molecular oxygen (O₂), the decomposition of ZnO and HgO yields atomic oxygen (O). This was proved more than 40 years ago by Harano [4] by col-

oration in MoO₃ (from pale yellow to blue) in the process of ZnO, HgO, CuO and PtO₂ decomposition in vacuum. The reason of this difference remains an enigma.

The purposes of this work included: thermogravimetric determination of the E parameters for ZnO and HgO vaporization by the third-law method; theoretical calculation of the enthalpies for ZnO, CdO and HgO dissociative evaporation; investigation of the retardation effect of oxygen on the evaporation rate of ZnO, CdO and HgO oxides and, what is the most important, analysis of the possible effect of crystal structure of these and some other oxides on the mechanism of their evaporation (up to molecular or atomic oxygen).

2. Theoretical

2.1. Theoretical values of the E parameter

In the case of a solid compound S decomposed in vacuum into gaseous products A and B, that is



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Table 1
The literature data on evaporation kinetics of ZnO, CdO and HgO

Oxide	Sample	Crystal face	Atmosphere	<i>T</i> (K)	Point number	<i>E</i> (kJ mol ^{−1})	Ref.
ZnO	Powder		Vacuum	1133–1273	24	180 ± 21	[3]
	Crystal	Zn-reach	Vacuum	1389–1531	20	375.4 ± 13	[7]
		O-reach	Vacuum	1423–1555	15	392.7 ± 21	
	Film		Vacuum	1215–1385	6	318.0	[9]
	Crystal	Zn-reach		1236–1361	10	326.7	
	Crystal	O-reach		1238–1341	12	328.4	
	Spinel ^a		Vacuum	1608–1773	6	355.6	[10]
	Pellet			1300–1800		312.0	[11]
	Monolayer			1100–1200	10	428 ± 20	[12]
	Crystal		Vacuum	1400	1	364 ^b	[13]
CdO	Powder		N ₂ (1 atm)	1150–1374	17	240 ± 7	[14]
	Monolayer		Ar (1 atm)	650–800	10	233 ± 20	[12]
HgO	Powder		Air	733–763	4	240.6	[15]
	Powder		Vacuum	652–730		162.3–201.3	[16]
	Powder		Vacuum	701–783	9	216.5 ± 5	[17]
	Powder		Vacuum	643–834	60	195 ± 8	[18]
	Powder		Vacuum	673–773	7	170	[19]
				298		200.8 ^c	[20]

^a (Zn_{0.2}Co_{0.8})O·Al₂O₃.

^b Calculated by the third-law method from the data reported by Galuzzo and Searcy [7].

^c Theoretical value calculated from thermodynamic data.

the *E* parameter for reaction (1) is equal to:

$$E = \frac{\Delta_r H_T^\circ}{\nu} \quad (2)$$

Here, ν is the total number of moles of gaseous products, (*a* + *b*), and $\Delta_r H_T^\circ$ is the change of the enthalpy in reaction (1). The latter value is calculated by the obvious equation:

$$\Delta_r H_T^\circ = \Delta_f H_T^\circ(A) + b\Delta_f H_T^\circ(B) - \Delta_f H_T^\circ(S) \quad (3)$$

The magnitudes of thermodynamic functions (the entropy and enthalpy) for the components of decomposition reactions and for the reactions as a whole (marked by bold) at different temperatures are listed in Tables 2–4. A possible error (S.D.) in these calculations of $\Delta_r H_T^\circ$ values is within 1–2 kJ mol^{−1}.

2.2. The third-law method for the experimental determination of the *E* parameter

The third-law method is based on the direct application of the basic equation of chemical thermodynamics:

$$\Delta_r H_T^\circ = T(\Delta_r S_T^\circ - R \ln K_P) \quad (4)$$

where $\Delta_r S_T^\circ$ is the entropy change and K_P is the equilibrium constant for the reaction (1) in terms of the partial pressures, *P*, of the gaseous products:

$$K_P = P_A^a \times P_B^b \quad (5)$$

(The equilibrium character of decomposition reactions that is at the basis of the physical approach to the interpretation of the kinetics of thermal decomposition of solids has

received recently [13] strong experimental confirmation.) Taking into account Eqs. (2) and (5), Eq. (4) can be reduced to the equation:

$$E = T \left(\frac{\Delta_r S_T^\circ}{\nu} - R \ln P_{eq} \right) \quad (6)$$

In this case, a measurement at only one temperature is sufficient for the determination of *E* but knowledge of absolute values of the entropy of all components in the reaction is necessary for the calculation. Tables 2–4 contain these values for all the oxides under investigation.

Table 2
Thermodynamic functions for ZnO decomposition [21,22]

Function ^a	<i>T</i> (K)	
	1200	1300
<i>S</i> _T [°]		
Zn _g	189.8	191.5
ZnO _s	111.7	116.1
O ₂	249.9	252.8
O	190.5	192.2
Δ _r <i>S</i> _T [°]	268.6 ± 1	267.6 ± 1
Δ _f <i>H</i> _T [°]		
Zn _g	149.3	151.4
ZnO _s	−305.6	−300.1
O ₂	38.4	42.0
O	272.5	274.6
Δ _r <i>H</i> _T [°]	727.4 ± 1	726.1 ± 1

^a All *S*_T[°] values are in J mol^{−1} K^{−1} and all Δ*H*_T[°] values are in kJ mol^{−1}. The uncertainties indicated here and in the text correspond to the S.D.

Table 3
Thermodynamic functions^a for CdO decomposition at 1300 K [21,22]

S_T°	
Cd _g	198.2
CdO _s	131.1
O ₂	252.8
O	192.2
$\Delta_r S_T^\circ$	193.5 ± 1
$\Delta_f H_T^\circ$	
Cd _g	132.6
CdO _s	−204.8
O ₂	42.0
O	274.6
$\Delta_r H_T^\circ$	358.4 ± 2

^a All S_T° values are in J mol^{−1} K^{−1} and all ΔH_T° values are in kJ mol^{−1}. The uncertainties indicated here and in the text correspond to the S.D.

The equivalent pressure of the gaseous product is related to the absolute rate of decomposition in vacuum, J (in kg m^{−2} s^{−1}), by the Hertz–Langmuir equation [23]:

$$P_{\text{eq}} = \frac{(2\pi RT)^{1/2} J}{\gamma(a+b)} \left(\frac{a\sqrt{M_A} + b\sqrt{M_B}}{M_r} \right) \quad (7)$$

Here, M_A , M_B and M_r are the molar masses of the gaseous products A and B and reactant S and $\gamma = 101,325 \text{ Pa atm}^{-1}$ is the conversion factor from pascals to atmospheres used to calculate partial pressures in chemical thermodynamics. The factor $(a + b)$ in denominator and additional factor in brackets are installed in this equation to take into account the fact that the J value actually includes the flows of two gaseous products (A and B) with the different molar masses.

Our analysis of results reported in [2,21] for several tens of substances has shown that the data calculated by the third-law method are in general the order of magnitude more precise than those calculated by the second-law or equivalent Arrhenius-plots method. This conclusion has been sup-

ported by the results of theoretical analysis [13] and by the results of application of the second- and third-law methods to the determination of the E parameter for 22 different decomposition reactions [13,23–25].

As can be seen from a consideration of Eq. (6), the self-cooling effect results in the overestimation of the E values calculated by the third-law method. Therefore, it is preferable to use for the calculation the result(s) of low-temperature measurement when this effect is minimal.

2.3. The retardation effect of excess of gaseous product on the evaporation

As it follows from Eqs. (5) and (7), in case of dissociative evaporation of oxide in accord with the reaction:



at two different external partial pressures of oxygen, $P_1(\text{O}_2)$ and $P_2(\text{O}_2)$, the evaporation rates should be related as

$$\frac{J_1}{J_2} = \left(\frac{P_2(\text{O}_2)}{P_1(\text{O}_2)} \right)^{0.5} \quad (9)$$

In case of dissociative evaporation of oxide in accord with the reaction:



the difference in the partial pressures of O₂ at temperatures lower than 1500 K (when the dissociation degree of O₂ into atomic oxygen is negligible) should have no effect on the evaporation rate, i.e.

$$\frac{J_1}{J_2} = 1 \quad (11)$$

Therefore, a comparison of the evaporation rates of oxide at two different external partial pressures of O₂ can be used as a criterion for choosing the true mechanism of dissociative evaporation.

3. Experimental

The experiments were carried out with a Netzsch STA 429 instrument on the TG and DSC measuring head. The actual measured quantities were the mass change of the sample per time unit, $\Delta m/\Delta t$, and the absolute crucible temperature. An open alumina crucible 5.7 mm inner diameter and 4.0 mm high was used as a sample container. The reacting materials were high purity powders of ZnO, CdO and HgO. A powder sample (20 mg) introduced into a crucible was leveled and pressed manually (about 1 kg mm^{−2}) into a flat pellet. The total (outer) surface area of pellet was calculated taking into account the crucible diameter and the width of pellet (estimated from the sample mass and the apparent density of powder measured separately).

In experiments on determination of the E parameter, the sample chamber was evacuated to a residual pressures about 5×10^{-4} or 5×10^{-8} atm with the use, respectively, of only

Table 4
Thermodynamic functions for HgO decomposition [21,22]

Function ^a	T (K)		
	600	700	800
S_T°			
Hg _g	189.5	192.5	195.5
HgO _s	105.7	114.2	121.0
O ₂	226.3	231.4	235.8
O	176.0	179.2	182.0
$\Delta_r S_T^\circ$	259.8 ± 1	257.5 ± 1	256.5 ± 1
$\Delta_f H_T^\circ$			
Hg _g	67.8	69.8	71.9
HgO _s	−75.5	−69.9	−64.0
O ₂	17.9	21.2	24.5
O	260.0	262.1	264.2
$\Delta_r H_T^\circ$	403.3 ± 1	401.8 ± 1	400.1 ± 1

^a All S_T° values are in J mol^{−1} K^{−1} and all ΔH_T° values are in kJ mol^{−1}. The uncertainties indicated here and in the text correspond to the S.D.

rotation pump or rotation and oil and diffusion pumps. All measurements have been conducted at continuous pumping under isothermal conditions. The heating rate of the sample from the room temperature to intermediate one (20 K lower than the desired temperature) was 20 K min^{-1} and from intermediate to the desired temperature was 2 K min^{-1} . At the beginning of each measuring cycle, the system was heated at the temperature chosen, usually during 10 min, to reach a constant rate of the decomposition. The changes of the mass and surface area of crystals and powders during this period were taken into account. A decrease of the surface area, as was checked experimentally, was proportional to $(1 - \alpha)^{2/3}$ where α is the decomposition degree. (This dependence can be interpreted as a combined result of the reduction of number and size of particles in the process of decomposition.) Temperature was measured with Pt–Pt10%Rh thermocouple placed with its junction immediately below the crucible. Temperature variations in the process of mass and change measurements (usually, during 20–30 min) did not exceed $\pm 0.2 \text{ K}$. A single measurement of the decomposition rate took entirely about 2–3 h.

The absolute value of the decomposition rate for powder samples was estimated using the method proposed in our previous work [24]. It consists in the evaluation of the absolute decomposition rate of a powder sample (reduced to the unit of the outer surface area of a pellet formed by the powder sample in a cylindrical crucible). The value received is lowered by the correction (empirical) factor and then used for the calculation of the E parameter by the third-law method. The value of this factor (2.8 ± 0.4), as was shown in [23,25], does not depend on the temperature, residual pressure of gas in the reactor, grain size and mass of a powder sample.

The experiments on the retardation effect of oxygen on the decomposition of Cd and Hg oxides were carried out under constant volume conditions in two different gases: nitrogen and air at atmospheric pressure. In this case, only relative losses of mass were measured under isothermal conditions. In case of ZnO evaporation, the similar experiments were performed in vacuum, at two different pressures of residual air in the furnace: 5×10^{-4} and 5×10^{-8} atm (or about 10^{-4} and 10^{-8} atm of oxygen).

Table 6

Kinetics of isothermal decomposition of oxides in atmosphere of nitrogen^a and air

Oxide	T (K)	$\Delta m/\Delta t^b$ ($\mu\text{g s}^{-1}$)		Ratio (air/N ₂)	
		Nitrogen	Air	Experiment	Theory
CdO	1302 ± 1	1.3	0.16	0.12	0.022
	1302 ± 1	1.8	0.20	0.11	0.022
	1254 ± 1	0.53	0.053	0.10	0.022
HgO	709 ± 1	1.20	1.14	0.95	1.00
	709 ± 1	1.18	1.17	0.99	1.00

^a Pure nitrogen was introduced after evacuation of the furnace chamber up to $P_{\text{air}} = 5 \times 10^{-4}$ atm or $P_{\text{O}_2} = 1 \times 10^{-4}$ atm.

^b Averaged value for 40 min in all cases.

4. Results and discussion

4.1. Mechanisms of ZnO, CdO and HgO evaporation

The experimental conditions and results of determination of the E parameter for ZnO and HgO in vacuum by the third-law method are presented in Table 5. Table 6 contains the results of comparative experiments on the retardation effect of O₂ on the evaporation rate of CdO and HgO.

The following conclusions can be deduced from the analysis of these data:

- The complete independence of the evaporation rate for ZnO on the residual partial pressure of air in the furnace (ca. 10^{-4} and 10^{-8} atm of O₂) and for HgO in air and nitrogen (0.21 and 10^{-4} atm of O₂) supports the mechanism of evaporation described by reaction (10). In case of reaction (8), the expected difference in the evaporation rates should reach, as it follows from Eq. (9), a factor of 100 and 46 for ZnO and HgO, respectively.
- The strong retardation effect of oxygen on the evaporation rate of CdO (Table 6) proves the mechanism of its evaporation described by reaction (8). Five-fold discrepancy between experimental and theoretical values of the retardation effect can be related with the higher partial pressure of O₂ in nitrogen (as compared with 10^{-4} atm used in calculations) because of desorption of

Table 5

Experimental conditions and results of determination of the E parameter for oxide decomposition in vacuum by the third-law method

Oxide	P_{air} (atm)	T (K)	m_0 (mg)	S_0 (mm ²)	α_m^a	S_m^b (mm ²)	$\Delta m/\Delta t^c$ ($\mu\text{g s}^{-1}$)	J_{corr}^c ($\text{kg m}^{-2} \text{ s}^{-1}$)	P_{eq} (atm)	$\Delta_f S_T^\circ/\nu$ ($\text{J mol}^{-1} \text{ K}^{-1}$)	E (kJ mol ⁻¹)
ZnO	5×10^{-8}	1255.3	20.0	57.30	0.0182	56.60	0.220	1.39×10^{-6}	8.25×10^{-9}	134.1	362.6
	5×10^{-8}	1255.5	20.0	57.30	0.0047	57.12	0.073	4.56×10^{-7}	2.71×10^{-9}	134.1	374.3
	5×10^{-8}	1255.4	20.0	57.30	0.0045	57.13	0.100	6.25×10^{-7}	3.71×10^{-9}	134.1	371.0
	5×10^{-4}	1257.6	20.0	57.30	0.0009	57.27	0.052	3.30×10^{-7}	1.96×10^{-9}	134.1	378.3
	5×10^{-4}	1257.2	20.0	57.30	0.0018	57.23	0.061	3.80×10^{-7}	2.25×10^{-9}	134.1	376.7
HgO	5×10^{-4}	681.0	40.0	56.41	0.0551	53.37	1.82	1.22×10^{-5}	3.01×10^{-8}	129.0	185.9
	5×10^{-4}	711.0	40.0	56.41	0.2119	48.13	6.28	4.66×10^{-5}	1.18×10^{-7}	128.7	185.8

^a The decomposition degree by the time of measurement.

^b The surface area by the time of measurement calculated by the equation $S_m = S_0(1 - \alpha_m)^{2/3}$.

^c $J_{\text{corr}} = (\Delta m/\Delta t)/(2.8 S_m)$.

Table 7

The ultimate theoretical and experimental values of the E parameter

Decomposition reaction	T (K)	E (kJ mol ⁻¹)		Refs.
		Theory	Experiment	
ZnO (s) → Zn (g) + O	1256	363 ± 1	373 ± 6	This work
CdO (s) → Cd (g) + 0.5O ₂	1300	239 ± 1	240 ± 7	[14]
HgO (s) → Hg (g) + O	700	201 ± 1	186 ± 1	This work

oxygen from the furnace wall in the process of 40 min heating in N₂ atmosphere under constant volume conditions.

- (iii) As can be seen from Table 7, the averaged values of the E parameter for ZnO and HgO found in this work and the E parameter for CdO measured by Gilbert and Kitchener [14] are in good agreement with the theoretical values of $\Delta_r H_T^\circ/\nu$ listed in Tables 2 and 4 for reaction (10) in cases of ZnO and HgO and for reaction (8) in case of CdO. A small underestimation (8%) of the E parameter in case of HgO evaporation can be explained by interference from the secondary decomposition reaction of lower oxide:



which, in its turn, forms at low temperatures (<500 K) as a result of oxidation of free atoms of Hg by atomic oxygen in the interface between the two solid phases (HgO/Hg₂O). The interference of Hg₂O formation and

its successive decomposition was discussed in detail by L'vov in [20] with illustration of this peculiarity by the corresponding Arrhenius plot (taken from the literature).

- (iv) Our experimental results for ZnO and HgO (Table 7) are in agreement with the literature data listed in Table 1. If to omit the extreme results reported in [3,12] and in [15,19], the averaged values (344 ± 30 kJ mol⁻¹ ($n = 7$) for ZnO and 189 ± 22 kJ mol⁻¹ ($n = 5$) for HgO) become rather close to our data. The value of $E = 364$ kJ mol⁻¹ for ZnO, which was calculated in [13] by the third-law method from the data reported by Galuzzo and Searcy [7], practically coincides with the theoretically predicted value (363 ± 1 kJ mol⁻¹).

The above results make it possible to conclude that the mechanism of dissociative evaporation of ZnO and HgO corresponds to reaction (10) and atomic oxygen (O) is the primary product of their decomposition. By contrast, the mechanism of dissociative evaporation of CdO corresponds

Table 8

Crystal structure and evaporation mechanism for some oxides and sulfates

Oxide	Singony ^a	Space group	Minimum O–O distance (Å)	Primary product	Refs.
Li ₂ O	I	225	2.31	O ₂	[12]
Cu ₂ O	I	224	3.68, 4.25	O ₂	[28]
Ag ₂ O	I	224	4.09, 4.72	O ₂	[4,29]
MgO	I	225	2.98	O ₂	[12]
CaO	I	225	3.39	O ₂	[12]
SrO	I	225	3.63	O ₂	[12]
CdO	I	225	3.34	O ₂	[12,14]
MnO	I	225	3.14	O ₂	[12]
FeO	I	225	3.06	O ₂	[28]
CoO	I	225	3.01	O ₂	[28]
NiO	I	225	2.95	O ₂	[28]
PbO	II	129	1.98	O ₂	[12]
CaO ₂	II	139	4.62	O	[30]
SrO ₂	II	139	3.55	O	[30]
BaO ₂	II	139	5.12	O	[30]
GeO ₂	II	136	2.86	O	[31]
SnO ₂	II	136	3.19	O	[31]
Pb ₃ O ₄	II	135	3.28	O	[31]
SiO ₂	III	182	2.91	O	[31]
PtO ₂	IIIa	164	2.74	O	[4]
ZnO	III	186	2.60	O	[4,31]
HgO	IV	62	3.50	O	[4,20]
MgSO ₄	IV	63	2.47	O	[23]
BaSO ₄	IV	62	2.44	O	[23]
CuO	V	15	2.62	O	[4]

^a I: cubic, II: tetragonal, III: hexagonal, IIIa: trigonal, IV: rhombic and V: monoclinic.

to equilibrium reaction (8) and the molecular oxygen (O_2) is the primary product of its decomposition.

4.2. Effect of crystal structure on the evaporation mechanism

It seems, the most important problem now is to explain this difference in mechanisms of evaporation. Our first attempt was to relate this difference with O–O distances in corresponding crystals. To estimate these values, we used the PowderCell Program developed by Kraus and Nolze [26] and Tables [27]. The minimum O–O distances found with the help of this program for ZnO, CdO and HgO were as follows: 2.60, 3.34 and 3.50 Å. In all cases, these values are much higher than the internuclear distance in O_2 molecule (1.21 Å). However, this is not retarding the release of O_2 molecules in the process of CdO evaporation. It means that some other factors are responsible for the difference in mechanisms.

To investigate the situation in more detail, we collected all available data on the evaporation mechanisms of 23 different oxides (and two sulfates) and correlated them with their crystal structure (Table 8). When all these compounds were arranged into two groups differed in the releasing mechanism of oxygen, some remarkable differences in their crystal structure have been appeared. As can be seen from these data, all oxides, which evaporate with the release of molecular oxygen, except for PbO, are of the cubic singony (I).

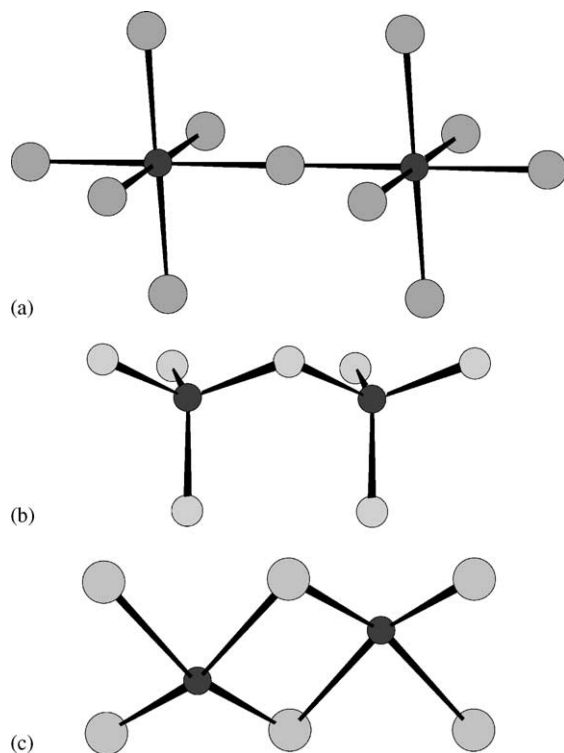


Fig. 1. Fragments of crystal structure for (a) CdO, (b) ZnO and (c) HgO. Large and small circles represent, respectively, atoms of metals and oxygen.

For all other compounds of different (from cubic) singony (II, III, IIIa, IV or V), the release of oxygen occurs in the form of free O atoms. As for PbO, the release of molecular oxygen can be related with the anomalously small O–O distance (1.98 Å) in comparison with that for other oxides.

We are not ready now to propose any quantitative explanation of this phenomenon. The only obvious conclusion consists in correlation of these differences with the structure symmetry. It can be proposed that a decisive role here belongs to a local symmetry in the position of O atoms. Fragments of structure, presented in Fig. 1, illustrate the differences in symmetry of O atoms in crystal structure of Cd, Zn and Hg oxides. For those oxides, where this symmetry is highest and environment is close to isotropic, there is the molecular mechanism of dissociation. Oxygen atoms, which are in low – should be low – symmetrical positions, release their sites without recombination. It is probable that there are some differences in electronic structure of these atoms responsible for the mechanism of recombination. To conclude, this interesting problem calls for further experimental and theoretical investigation.

5. Conclusions

The mechanism of evaporation of ZnO and HgO with releasing of atomic oxygen (O) as a primary product of decomposition and the mechanism of evaporation of CdO with releasing of molecular oxygen (O_2) was proved by good agreement of experimental values of the E parameters with theoretical values of the enthalpies for corresponding reactions and also, by results of investigation of the retardation effect of oxygen on the evaporation rate of ZnO, CdO and HgO. From the analysis of crystal structure for 12 different oxides, which evaporate with releasing of atomic oxygen, and for 13 compounds, which evaporate with releasing of molecular oxygen, it was revealed that (i) the first mechanism is observed for all oxides with the cubic crystal structure and (ii) the difference in mechanisms is not related with interatomic O–O distances in these oxides. It was proposed that a decisive role here belongs to a local symmetry in the position of O atoms. These conclusions deserve further investigation and application to decomposition studies for other compounds (sulfides, nitrides, etc).

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