

Intermolecular Interactions in Spinel Structures

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ABSTRACT

Calculations of the electron concentration and compaction coefficients for the interaction of oxygen and metals that form oxides are presented. Calculations of the concentration of electrons and the compaction coefficients for the interaction of oxides forming spinel are presented. It is shown that the concentration of electrons and the concentration of nucleons are applicable to characterize the structures of substances. Correlation coefficients are calculated, indicating the relationship between the heat of reaction and the change in the volume of the reacting components.

Key words: electron concentration, density, spinel, structure.

INTRODUCTION

Interatomic and intermolecular interactions lead to the formation of chemical bonds in compounds, and these new bonds determine the properties and structure of new substances. Interaction is a process that is characterized by a simultaneous mutual change in the characteristics of interacting material objects (in our case, molecules). These material objects (molecules) act on each other with different intensities, obeying certain laws, and reproduce new structures with high accuracy. Chemical bonding is a consequence of both interatomic and intermolecular interactions. The concept of composition is quite definite and does not cause confusion. The concept of structure is still controversial due to the choice of structural units. With an equal chemical composition, differences in the properties of substances are determined by the difference in structures. The structure is a consequence of two factors: chemical composition and energy content. An amorphous structure contains more stored energy than a crystalline one. A substance in a gaseous state contains more energy than a liquid.

The physical and chemical properties of substances are determined by the number and location of nucleons and electrons. Interatomic [1- 9] and intermolecular [10- 12] interactions are accompanied by different thermal effects, as well as changes in structure and volumes of the reacting components of a substance. Thermal effects are described by methods of thermodynamics and thermochemistry, while the data on the rearrangement of electron clouds with changes in volume is not sufficient. The density of substances is a complex characteristic. Most mass is concentrated in nucleons, while the volume is due to electron clouds. In the case of interatomic and intermolecular interactions, the total mass of the substance is preserved, and the volume changes. During chemical interactions, electron clouds change their shape and volume.

A classic example of intermolecular interactions is the work of D. I. Mendeleev on mixing water and ethanol [13]. When ethanol is mixed with water, heat is released and the volume of the resulting mixture is less than the sum of the initial volumes of ethanol and water. The largest reduction in the volume of the water-ethanol mixture is achieved at a ratio of ~ 2.96 mole of water per mole of ethanol. Water at 20°C and normal atmospheric pressure is characterized by an electron concentration of 0.555 mole/cm^3 and a nucleon concentration of 0.166 mole/cm^3 . Ethanol under the same conditions has an electron concentration of 0.445 mole/cm^3 and a nucleon concentration of 0.154 mole/cm^3 . An aqueous-ethanol solution with a maximum volume change has an electron concentration of 0.534 mole/cm^3 , and a nucleon concentration of 0.160 mole/cm^3 . Ethanol, from the point of view of its electronic structure, is a more "loose" system compared to water. It should be assumed that the volume change when mixing water and ethanol occurs mainly due to the compression of electronic clouds of ethanol as a result of the intermolecular interaction of these two molecular substances.

To estimate the depth of interaction between atoms or molecules, it is convenient to compare the volumes of substances before the reaction ($V_{\text{component}}$) and volumes of substances after reaction (V_{product}). The resulting value is normalized to the volume of the final product. The result, expressed as a percentage, characterizes the change in the volume of substances during the reaction. Let us to denote this value as the coefficient of consolidation ($K_{\text{consolidation}}$):

$$K_{\text{consolidation}} = \left(\frac{\sum V_{\text{component}} - V_{\text{product}}}{V_{\text{product}}} \right) \times 100\% \quad (1)$$

Formula 1 can be represented as

$$K_{\text{consolidation}} = \left[\frac{\sum V_{\text{component}}}{V_{\text{product}}} - 1 \right] \times 100\% \quad (1a)$$

The space occupied by matter is filled with nucleons and electrons. To estimate the space occupied by matter, it is convenient to use the indicators of electron concentration and nucleon concentration.

$$C_{\text{electron}} = \frac{d}{M} Z \quad (2)$$

where C_{electron} is for the concentration of electrons in a unit of volume, mole/cm^3 ;

d is for substance density in the condensed state, g/cm^3 ;

M is for molecular weight, g/mole ;

Z is for the ordinal number of the element in the Periodic table.

For chemical compounds the electron density is determined through the following expression:

$$C_{\text{electron}} = \frac{\text{number of electrons in compound (in one mole)}}{\text{volume of mole of compound (condensed state)}} \quad (2a)$$

A_aB_b type compound has a concentration of electrons:

$$C_{electron} \approx \frac{aZ_A + bZ_B}{M/d} \quad (2b)$$

A compound of the A_aB_b type has a concentration of nuclei (regardless of their class)

$$C_{nuclei} = \frac{a+b}{\frac{M}{d}} \quad (3)$$

where a is for the subscript of element A,

Z_A is for the ordinal number of element A,

b is for the subscript of element B,

Z_B is for the ordinal number of the element B.

The convenience of structural indicators of electron concentration and nucleon concentration is that they can characterize solid, liquid and gaseous states of substances. For most gases, the volumes under normal conditions are known. Table 1 shows a number of gases and their characteristics of the concentration of electrons and nucleons.

The concentration of electrons is calculated using formula 2. The concentration of nucleons is calculated using formula 3.

For the calculation, data sources were used [14, 15].

Table 1. Structural characteristics of gases under normal conditions

gas	electron concentration mole/m ³	nucleon concentration mole/m ³
He	89.2	44.6
O ₂	713,9	89,24
H ₂	89,2	89,24
N ₂	624,7	89,24
CO	624,7	89,24
NO	669,3	89,24
CO ₂	981,6	133,86
HCl	803,2	89,24
SO ₂	1427,8	133,86
CH ₄	448.4	224.2
Xe	2421.5	44.8
HBr	1628.9	90.5

* Concentrations of electrons and nucleons in the table are normalized to cubic meter.

The concentrations of electrons and nucleons presented in Table 1 are capable of reflecting the differences and similarities in the structures of substances in the gaseous state.

To understand the interactions between atoms, it is necessary to determine their constitutionality, i.e. properties manifested in interactions with other atoms.

The fundamental characteristic of a simple substance is the molar volume, which is the ratio of the molar mass of a substance (M , g/mole) to its density (d , g / cm³) $V_m = M / d$ (cm³ / mole). Even Lothar Meyer [16] presented a graphical dependence of atomic volumes on the mass of an atom, which successfully illustrated the periodic law of D.I. Mendeleev.

Turning to the search for the reasons for the differences in the properties of materials, it is necessary to consider the general concept of the composition-structure-property relationship. The properties of substances and materials depend on the chemical composition and on the mutual arrangement of chemical elements. Everything is based on the electronic structure of the material. To assess the properties of the analyzed object, one should take into account all structural parameters, including at the level of interatomic interaction, since the properties of all materials and, accordingly, their structure are a function of the chemical composition and internal energy of the system.

The separation or movement of some parts of the test specimen relative to other parts of this specimen is associated with the internal structure of the test object. All bodies are composed of atoms, the nuclei of which are five orders of magnitude smaller than the size of an atom. Thus, the interaction of electronic media belonging to different structural groups is overcome. Reference data collected as a result of physical testing of substances characterizes the interaction of electronic media.

METHODS

A group of double oxides with a cubic system and the formula $RO \cdot R_2O_3$ (R - metals) are called spinels. There are 22 connections.

To understand the intermolecular interactions between oxides like RO and R_2O_3 , it makes sense to consider the RO and R_2O_3 groups separately. Determine the similarities and differences of oxides in each group. The RO group consists of eight oxides. The similarity in this group is the ability to crystallize in a cubic system. Some oxides in this group can crystallize in the hexagonal system.

In [1–12], the normalized value of the volume change during chemical reactions (compaction coefficient) is presented, which correlates with thermodynamic characteristics. The compaction coefficient characterizes the intensity of interaction during chemical reactions. The volume is formed by electrons. The quantity "electron concentration" is introduced, which can be used as a structural characteristic of a substance.

The crystal structures of RO -type oxides can, for the most part, have a cubic system. This type of system is the most dense for these oxides. Table 2 presents data showing the result of the interaction of oxygen with metals that form a particular oxide. The concentrations of electrons and nucleons indicate the similarities and differences in their structures.

One mole of oxygen atoms in the homonuclear condensed state occupies a volume of 7.2 cm³ and has an electron concentration of 1.11 mole/cm³, the concentration of nucleons is 0.139

mole/cm³. The density of substances is a complex characteristic. The mass is concentrated in nucleons, and the volume is formed by electron clouds.

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RESULTS

Table 2 summarizes the data for oxides of the RO type. The second column lists the heats of formation of oxides [17]. The third column shows the results of calculations by formula 1. The fourth and sixth show the results of calculations by formula 2. The fifth column shows the results of calculations by formula 3.

Table 2. Interrelation of enthalpy with the concentration of electrons in the metal, the concentration of electrons in the oxide of the RO type and the coefficient of compaction

1	2	3	4	5	6
substance	$-\Delta H_{298}^{\circ}$, kJ/mole	Coefficient of consolidation ($K_{\text{consolidation}}$), %	the concentration of electrons in the oxide, $C_{\text{electrons}}$ mole/cm ³	concentration of nucleons in oxide, mole/cm ³	the concentration of electrons in the metal, mole/cm ³
MgO	601	87	1,77	0,178	0,86
TiO	519	37	2,31	0,154	2,09
MnO	385	9	2,41	0,149	3,39
ZnO	353	14	2,66	0,140	3,28
FeO	271	14	2,72	0,159	3,66
CdO	258	-9	3,54	0,127	3,69
NiO	240	38	3,6	0,133	4,05
CoO	239	24	3,01	0,179	4,05

The critical correlation coefficient for 8 pairs at a confidence level of 0.95 is 0.621.

The correlation coefficient between the heat of formation of the oxide and the compaction during the formation of an oxide of the RO type is (0.709). The compaction coefficient, along with the enthalpy of formation, can reliably characterize the intensity of interatomic interactions.

The correlation coefficient between the heat of formation of the oxide and the concentration of electrons in the RO type oxide is (-0.883). The enthalpy of formation and the concentration of electrons in the reaction product are inversely proportional.

The correlation coefficient between the heat of formation of the oxide and the concentration of electrons in the metal forming the oxide of the RO type is (-0.971). It can be confidently asserted that the higher the electron concentration in the metal forming the RO oxide, the lower the heat of formation of the compound.

The correlation coefficient between the densification and the concentration of electrons in the metal forming the RO type oxide is (-0.775). It can be confidently asserted that the higher the

electron concentration in the metal forming the RO oxide, the lower the heat of formation of the compound.

The correlation coefficient between the concentration of electrons in the metal and the concentration of electrons in the oxide RO is (0.836). It turns out that the higher the concentration of electrons in the metal forming the RO oxide, the higher the concentration of electrons in the oxide, for a given sample.

Table 3 summarizes the data on oxides of the R_2O_3 type. The second column lists the heats of formation of oxides [17]. The third column shows the results of calculations by formula 1. The fourth and sixth show the results of calculations by formula 2. The fifth column shows the results of calculations by formula 3.

Table 3. Relationship of enthalpy with the concentration of electrons in the metal, the concentration of electrons in the oxide of the type R_2O_3 and the coefficient of compaction

1	2	3	4	5	6
substance	$-\Delta H_{298}^0$, kJ/mole	Coefficient of consolidation ($K_{\text{consolidation}}$), %	the concentration of electrons in the oxide , $C_{\text{electrons}}$ mole/cm ³	concentration of nucleons in oxide, mole/cm ³	the concentration of electrons in the metal, mole/cm ³
Al ₂ O ₃	1675	62	1,95	0,195	1,3
Ti ₂ O ₃	1521	33	2,15	0,156	2,09
V ₂ O ₃	1218	24	2,27	0,162	2,76
Cr ₂ O ₃	1141	24	2,47	0,172	3,31
Mn ₂ O ₃	958	4	2,11	0,142	3,39
Fe ₂ O ₃	824	18	2,49	0,164	3,66

The critical correlation coefficient for 6 pairs at a confidence level of 0.95 is 0.729.

The correlation coefficient between the heat of formation of the oxide and the concentration of electrons in the metal forming the oxide is (-0.972). It can be confidently asserted that the higher the electron concentration in the metal forming the R_2O_3 oxide, the lower the heat of formation of the compound.

The correlation coefficient between the heat of formation of the oxide and the coefficient of compaction during the formation of oxide R_2O_3 is (0.872). It can be argued that the effect of heat release and the change in volume during the formation of oxides of the type R_2O_3 are in direct relationship.

The correlation coefficient between the compaction coefficient and the concentration of nucleons in the oxide of the R_2O_3 type is (0.884).

The correlation coefficient between the concentration of electrons in the metal and compaction during the formation of an oxide of the type R_2O_3 is (-0.903). It can be confidently asserted that the higher the electron concentration in the metal forming the R_2O_3 oxide, the less the compaction. The looser the metal, the more reactive it is.

The correlation coefficient between the concentration of electrons in a metal and the concentration of electrons in an oxide of the type R_2O_3 is (0.785).

Table 4. The result of the interaction and the structure of oxides such as RO and R_2O_3 , with the formation of spinels

1	2	3	4	5	6	7
substance	$-\Delta H_{298}^o$, kJ/mole	Compaction coefficient for the interaction of oxides %	The concentration of electrons in spinel mole/cm ³	Concentration of nucleons in spinel mole/cm ³	Electron concentration in metal 1 mole/cm ³	Electron concentration in metal 2 mole/cm ³
MgAl ₂ O ₄	2300	-9.2	1,761	0,176	0,86	1,3
FeAl ₂ O ₄	1982	-9.5	2,059	0,172	3,66	1,3
MnAl ₂ O ₄	2098	-8.7	1,992	0,168	3,39	1,3
CoAl ₂ O ₄	1948	-9.5	2,120	0,175	4,05	1,3
NiAl ₂ O ₄	1915	-8.9	2,191	0,178	4,05	1,3
ZnAl ₂ O ₄	2067	-1.7	2,208	0,176	3,28	1,3
ZnFe ₂ O ₄	1182	-1.4	2,516	0,154	3,28	3,66
MgFe ₂ O ₄	1462	-6.1	2,169	0,158	0,86	3,66
TiFe ₂ O ₄		-2.3	2,262	0,149	2,09	3,66
NiFe ₂ O ₄	1066	-5.4	2,566	0,160	4,05	3,66
MnFe ₂ O ₄	1227	-6.4	2,344	0,151	3,39	3,66
FeFe ₂ O ₄	1117	-4.8	2,471	0,157	3,66	3,66
CdFe ₂ O ₄	1074	-4.50	2,653	0,141	3,69	3,66
MgTi ₂ O ₄		-7.1	1,193	0,152	0,86	2,09
FeV ₂ O ₄		-10.6	2,214	0,149	3,66	2,76
FeCr ₂ O ₄	1439	-7.3	2,392	0,158	3,66	3,31
MgCr ₂ O ₄	1787	-7.7	2,110	0,161	0,86	3,31
NiCr ₂ O ₄	1391	-6.9	2,516	0,163	4,05	3,31
CdCr ₂ O ₄	1437	-5.3	2,703	0,148	3,69	3,31
ZnCr ₂ O ₄	1550	-0,2	2,640	0,168	3,28	3,31
CoCr ₂ O ₄	1431	-7,0	2,457	0,161	4,05	3,31
FeMn ₂ O ₄		-15.2	2,328	0,151	3,66	3,39

The critical correlation coefficient for 18 pairs at a confidence level of 0.995 is 0.590.

The correlation coefficient between the heat of formation of a spinel and the concentration of electrons in the spinel is (-0.835). It can be confidently asserted that the higher the concentration of electrons in the spinel, the lower the heat of formation of the spinel, and vice versa.

The correlation coefficient between the heat of formation of a spinel and the concentration of nucleons in a spinel is (0.828). It can be confidently asserted that the higher the concentration of nucleons in the spinel, the higher the heat of formation of the spinel, and vice versa.

The correlation coefficient between the heat of formation of spinel and the concentration of electrons in the metal oxide of the type R_2O_3 is (-0.912). We can confidently assert that the

higher the electron concentration in the metal oxide of the R_2O_3 type, the lower the heat of spinel formation and vice versa.

The correlation coefficient between the concentration of electrons in spinel and the concentration of electrons in the metal oxide of the RO type is (0.634).

The correlation coefficient between the concentration of electrons in spinel and the concentration of electrons in the metal oxide of the type R_2O_3 is (0.604). It can be confidently asserted that the concentration of electrons in spinel is in the same dependence on the concentration of electrons in metals that form oxides such as RO and R_2O_3 .

The correlation coefficient between the concentration of nucleons in spinel and the concentration of electrons in the metal oxide of the RO type is (-0.757).

The correlation between the heat of formation of spinel and the structural characteristics in the form of the concentration of electrons and nucleons indicates the correct choice of structural parameters.

The interaction between oxides of type RO and type R_2O_3 is accompanied by an increase in volume.

DISCUSSION

The presented calculations reflect the ability to characterize interatomic and intermolecular interactions by calculating the volume change. The compaction ratio reflects the intensity of chemical interactions. Structural indicators at the level of electron concentration and nucleon concentration are able to characterize the similarity and difference in substances.

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