Application for Determining the Solubility Limits of Solid Solutions Depending on Temperature

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***Abstract* —** **Application for calculating the miscibility regions of isovalent binary compounds has been designed and developed. The results of the program will be compared with the known experimental data in the NaCl-AgCl and SnO2-TiO2 systems with continuous and limited solid solutions, then the optimization of the software product will be carried out, which will be applied to the SiO2-TiO2 system. The program will be useful for a preliminary assessment of the dependence of the boundaries of solid solutions on temperature.**

***Keywords — binary solid solutions, optimization, heat of mixing, entropy of mixing, isovalent components***

# I. Introduction

Modern scientific and applied materials science requires the emergence of both new materials with the necessary combination of functional properties and optimization of the properties of known compounds that have already proven themselves in practice, with further control by external (growth conditions or post-growth treatments) or internal (isomorphic substitution) impacts. Isomorphic substitution is a powerful and flexible way of realizing a specific property with a targeted change in composition within the desired crystal structure.

To accelerate the process of obtaining materials, substantiate the possibility of realizing solid solutions with the required compositions, and specify the temperature, appropriate software is required. The basis for the development of such software should be the already existing analytical calculation formulas, values of structural parameters (i.e. crystal chemical data) and tabular, calculated or experimental empirical coefficients [1,2].

The main goal of this work is to develop an application for determining the solubility limits of substitutional solid solutions with isovalent components, available for a wide range of researchers.

Because the program should be created not only based on theoretical prerequisites, but it should make maximum use of empirical tabular data obtained from various sources (including experimental), an important stage in the development of the application is to check its efficiency by example systems with the specification of input parameters. Only after such verification and analysis of the results, it is possible to use the developed program for new systems with missing experimental data.

The purpose of this paper is to give an insight into substitutional solid solutions and calculations that will be performed (Section II), describe what functions and how will be implemented in the application (Section III), and give examples of checking the accuracy of the application on systems with existing and non-existent data (Section IV).

# II. Theoretical part

Substitutional solid solutions are phases of variable composition, in which atoms (ions) of one component replace atoms (ions) of another component in the structure. Rules for the formation of continuous solid substitution solutions:

- both components must belong to the same or similar structural types (structural factor);

- the difference between the atomic (ionic) radii of the substituting and substituted atom (ion) in the components should not exceed 15% (the larger radius is taken as 100%) or the difference in the interatomic distances in the components should not exceed 4-5% (at all temperatures) and should be less 8-10% (at temperatures over 100-400 °C) (dimensional factor);

- the substituting and substituted atom (ion) in the components must have close polarization properties, i.e. the same structure of the electron shells, the proximity of the values of electronegativity (the difference should not exceed 0.4 relative units) or ionization potentials and the same formal charge (chemical bonding factor).

The equilibrium state of an isomorphic mixture is determined by the tendency to a minimum of the Gibbs free energy:

ΔGmix=ΔНmix - ТΔSmix (1),

where *ΔНmix* and *ΔSmix* are the heat and entropy of mixing respectively.

Depending on the ratio of *ΔНmix* and *ТΔSmix*, three types of state diagrams are possible:

1. ΔНmix > 0, ΔНmix < TΔSmix,ΔGmix < 0 - continuous solid solutions between components (compounds, phases) at elevated temperatures and the region of immiscibility of components at low temperatures;
2. ΔНmix > 0, ΔНmix > TΔSmix, ΔGmix > 0 – lack of mutual solubility of components in the solid state;
3. ΔНmix > 0, ΔGmix crosses the zero line twice - this indicates the decomposition of the solid solution at the eutectic temperature, i.e. solid solutions with limited solubility are formed by both components.

The values *ΔSmix* and *ΔНmix* are determined by the formulas given in [1,2] for isovalent systems AX-BX (in our case) or AX-AY (A, B and X, Y are isovalent substituting / substituted cations or anions in the system components respectively) subject to Vegard's law:

ΔSmix = ΔSconf + ΔSvib = -kN(*x*1ln*x*1 + *x*2ln*x*2) + . 2.7250*x*1*x*2(ΔR/Rmin) (2),

where *ΔSconf*. and *ΔSvib*areconfigurational and vibrational entropy, *k* and *N* are the Boltzmann's constant and Avogadro's number (*kN* is the universal gas constant), *x1* and *x2* are the number of components in the system: x1 + x2 = 1.

ΔHmix = *x*1*x*2[(332A/R)Δε2 + cmnzAzX(ΔR/R)2] (3),

***The dimensional factor is:***

R = *x*1R1 + *x*2R2 + Rx (4),

where *R* is interatomic distance cation-anion: *R1* and *R2* are substituting / substituted ion radii, *Rx* is radius of a common structural unit in system components [3];

R = *x*1R1 + *x*2R2 (5),

where *R* is interatomic distance cation-anion: *R1* and *R2* are interatomic distances of the first and second components of the system;

***The structural factor is:***

*А* is Madelung's constant, *m* is sum of formula coefficients in components, *n* is coordination number (the same for the substituting and substituted ion);

***The chemical bonding factor is:***

*zA*and *zX*are formal charges of the cation (A) and anion (X) in the components of the system, *с* is empirical coefficient depending on the degree of ionicity of the system [1,2].

The degree of ionicity is estimated by the formula:

ε = 1 – z / n × exp(-Δχ2 × 0.25) (6),

where *z* and *n* are the formal charge and coordination number respectively, Δχ=⏐χi-χx⏐ - the difference between the values of the electronegativities of the cation (A) and anion (X) for each component of the system [1], Δε = |ε1 - ε2| – the difference in the degrees of ionicity of the first and second components of the system.

Mixing energy (energy of interchange, interaction parameter), which is calculated in the subregular approximation:

Qmax = cmnzAzX(ΔR / Rmin)2 (7),

is related to the critical temperature of the decay dome by the relation:

Tcr = Qmax / 2kN (8).

# III. Implementation part

The developed application allows:

* Receive information about atoms, chemical compounds and binary systems of compounds;
* Edit/add data about atoms, ions and compounds, also add new chemical compounds / systems of compounds;
* Solve the problem of approximating the tabular dependence, obtained during the experimental evaluation of the phase boundary of a binary system, by the functional dependence, which theoretically determines the thermodynamic mixing function;
* Assess the sensitivity (influence) of the mixing function parameters on the final result;
* Based on the obtained data by the optimization of the parameters *ΔHmix* (3) and *Qmax* (7), build a graph of the Gibbs free energy in a specific temperature range.

Microsoft Visual Studio is used as an application development tool [4]. The application was developed in the C# programming language using Windows Presentation Foundation (WPF) [5].

The process of developing an application and its "customization" to the specifics of solving specific applied problems includes several stages:

1. Software implementation of the Interactive Periodic Table, which is based on the DataGrid control, displays data in a custom grid.
2. Filling the Interactive Periodic Table by the user with the data necessary for further specific calculations.
3. Development of a module for constructing the thermodynamic mixing function *∆Hmix* and the decay dome by the data of the Interactive Periodic Table.
4. Development of a module for approximating the experimental dependence by changing the parameters of the expression, theoretically determining the thermodynamic mixing function. Optimization of parameters *R1*, *R2*, *Rx*, *χ1*, *χ2*, *χx* is carried out by the gradient minimization method. The criterion of optimality was the residual standard error (RSE).
5. Development of a module for assessing the sensitivity of the parameters of the thermodynamic mixing function to the final calculated or experimental value.
6. Development of a module for constructing a graph of Gibbs free energy by the obtained data from the approximation.

# IV. Experimental part

The calculation according to equations 1-8 will be performed for the systems NaCl-AgCl (structure of the NaCl type) and TiO2-SnO2 (structure of the rutile type TiO2) with known experimental data and for the SiO2-TiO2 system (substitution of Si4+ ions for Ti4+ ions in SiO2 with the structure quartz and the substitution of Ti4+ ions in TiO2 with anatase structure) with unknown phase diagram. The initial data for individual atoms (ions) and compounds, necessary for the calculation, were obtained from the Interactive Periodic Table.

The calculation of the details of the phase diagrams was carried out in two stages:

1. Calculate the enthalpy of mixing - *ΔHmix* and the critical temperature of decomposition of solid solutions - *Tcr*. Variable parameters when calculating *ΔНmix* (3) are *Δε* with possibly variable values *χi* and *χx* (different values for different systems) and *ΔR/R*. Equations (7) and (8) for calculating *Tcr* include variable values *c* = 33.33ε + 8.83 and *ΔR/Rmin*;
2. Build a graph *ΔGmix* (1, 2) by the obtained data in the first stage and, depending on the graph at certain temperatures, draw conclusions about the miscibility of the system components.

# V. Conclusion

Thus, an application has been developed to automate the calculations of the thermodynamic function of mixing and the dome of decay of a binary system of compounds by data from the Interactive Periodic Table. The application allows you to optimize the parameters of these functions to approximate the result to the experiment and, based on the obtained data, build a graph of the Gibbs free energy.

After performing calculations of equations 1-8 on the systems NaCl-AgCl and TiO2-SnO2, it will be possible to understand which of the variable parameters deviates most from the experiment. After that, it will be possible to proceed to the calculations of such systems as SiO2-TiO2, for which there are no phase diagrams, however, knowing which of the parameters and how much to change, it is possible to construct it by theoretical data considering this deviation.

# References

1. V. Urusov "Isomorphic miscibility theory", Science, Moscow, 1977, pp. 252.
2. V. Urusov "Energy crystal chemistry", Science, Moscow, 1975, pp. 335.
3. R.D. Shannon "Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides", Acta Crystallogr. A 32, 1976, pp. 751-767.
4. Microsoft Visual Studio official site [Online]. Available: <https://visualstudio.microsoft.com/>. [Accessed Feb. 25, 2021].
5. WPF tutorial [Online]. Available: <https://www.wpftutorial.net/>. [Accessed Feb. 25, 2021].

Word Count: 1574