REVIEW

by Assoc. Prof. Aleksandar Nikolov Dimitrov, PhD
"Prof. Dr. Assen Zlatarov" University – Burgas

of the PhD Thesis for awarding of the Educational and Scientific Degree "Doctor"
Scientific field: 4. Natural Sciences, Mathematics and Informatics, Professional area: 4.2. Chemical Sciences, Doctoral program: Inorganic Chemistry
Shumen University "Bishop K. Preslavski".
Author of the PhD thesis: **Tsvetan Vassilev Tsenov**
Title: "**Thermodynamics of electrolyte solutions. Experimental and modeling studies**"

I have been appointed as a member of the Scientific Jury, according to the order № RD 16-017/19.02.2024 of the Rector of the Shumen University "Bishop K. Preslavski". At the first meeting of the Scientific Jury held on 29.02.2024 I was elected as a reviewer. I received all the dissertation materials on electronic media.

1. Biographical data

Tsvetan Vassilev Tsenov was born in 1989. He graduated in "Medical Chemistry", BSc and "Chemistry - Ecological Chemistry", MSc at Shumen University "Bishop Konstantin Preslavsky". He was admitted for full-time PhD studies on 1.02.2021 at the Department of Chemistry, Faculty of Natural Sciences, Shumen University. He completed his doctoral studies with the right to defense on 1.02.2024.

2. Submissions on the implementation of the legislation

In accordance with Article 35 of the Academic Staff Development Act in the Republic of Bulgaria and its Implementing Rules, all required documents have been submitted:

- PhD thesis containing theoretical generalizations and solutions to scientific and applied problems that correspond to contemporary achievements and represent a significant and original contribution to science - a requirement of the Academic Staff Development Act in the Republic of Bulgaria (127 pages);

- abstract in Bulgarian (37 pages) and English (27 pages);

- professional curriculum vitae;

- list of the doctoral candidate's publications;

- declaration of authorship;

- reference to the scientific contributions of the dissertation.

3. Science metrics. Fulfillment of the minimum national requirements for the PhD.

According to the data in the submitted materials and the reference with data from world databases [Web of Science (WOS), Scopus], the doctoral student's points (90) exceed the required number of points according to the minimum national requirements for doctoral studies in the field of higher education 4.2 Chemical sciences: total number of points - 80, including 50 points from the dissertation for the degree of Doctor of Science (group A) and 30 points from the scientific publications (group D).

According to the received documents, the list of publications (WOS, Scopus), with which Tsvetan Tsenov participates for obtaining the PhD, is 2, both are in quartile Q2 (one based on the quartile for 2021 and 2022), i.e. the number of points in indicator group D is 40. In one publication the PhD student is first author.

The PhD student also submits a list of other publications in journals included in a "secondary" database, full-length publications in peer-reviewed conference proceedings, and contributed papers.

The submitted abstract objectively reflects the structure and content of the dissertation.

4. PhD thesis

The main objective of this dissertation is to establish comprehensive and accurate pH-concentration-temperature varying, well-validated and thermodynamically-based models for stable and meta-stable phase equilibria in natural and industrial systems with particular relevance to ecology and industry.

The thesis has a total length of 127 pages and contains 23 tables and 45 figures. The bibliography consists 105 references.

The PhD thesis includes the following main paragraphs:

- Introduction, in which the aims and objectives of the dissertation are formulated, as well as the relevance and importance of the scientific issues (pp. 8-11).

- An analysis of the state of research on the problem: an analysis of geochemical nuclear waste storage programmes (pp. 11-14).

- Scientific research methodology (pp. 14-27): 1) Pitzer approach to inter-ion interaction in electrolyte systems; 2) approaches for selection and determination of model parameters for binary systems; 3) model technology for determination of mixing parameters and thermodynamic characteristics of crystallizing solid phases; 4) relative humidity of liquefaction.

- Obtained results and discussion (pp. 27-109):

Model studies (pp. 28-76)

Tsvetan Tsenov's development of thermodynamic models is based on the inter-ion interaction approach developed by Pitzer, which is one of the most widely used in thermodynamic research. This allows different types of data to be used in the determination of model parameters and the calculation of other thermodynamic functions. Validation of the corresponding model involves a comparison between model predictions and such data that were not used in the selection of model parameters.

The model studies described in this dissertation include:

(a) Model studies for binary systems (acetate, rubidium, cesium and selenate) from low to very high concentrations at 25ºC (new models). Values of important thermodynamic characteristics of solid phases crystallizing from saturated solutions in acetate, selenate, rubidium and cesium systems at 25ºC have been calculated. A comparison is made between model-calculated osmotic coefficients and activity coefficients for acetate, selenate, rubidium, and cesium electrolytes in their binary solutions as a function of the molality of the solutions at 25ºC and those given in the literature.

(b) Determination of solid-phase thermodynamic characteristics of saturated solutions in mixed rubidium, cesium, and selenate systems: the natural logarithm of the thermodynamic solubility product, the standard molar free energy of formation (Gibbs), and the standard molar free energy of the synthesis reaction from simple salts.

c) Development and validation of thermodynamic models for solution behaviour and solid-liquid equilibrium in acetate systems of type 2-1: $Ba(CH_3COO)_2$-H_2O, $Mg(CH_3COO)_2$-H_2O

Experimental laboratory studies (pp. 100-109):

The solubilities in the LiBr-$CaBr_2$-H_2O system were determined at 35ºC and 50ºC. The selenate solid phases Na_2SeO_4. H_2SeO_3 и $Na_2Cd(SeO_4)_2.2H_2O$ were synthesized and fully characterized. Experimental methodology, experimental setup, and results are described and analyzed.

- Main scientific contributions (pp. 109-112)

In the scientific work of Tsvetan Tsenov the following main contributions are outlined:

1) Thermodynamic models have been developed and validated for 24 binary and 10 mixed systems at 25ºC.

The models were developed based on Pitzer's approach to inter-ion interaction, and were constructed by applying different parameterization approaches to achieve maximum accuracy and excellent agreement with the available experimental data.

The values of important thermodynamic characteristics of solid phases crystallizing from saturated solutions in acetate, selenate, rubidium, and cesium systems at 25ºC have been calculated: the natural logarithm of the thermodynamic solubility product, the relative humidity of liquefaction, and the standard molar free energy of formation (Gibbs). Very good agreement between model and experiment was obtained.

The resulting thermodynamic database can be applied in many industries, such as the optimization of marine mineral production technology (Lithium, Rubidium, Cesium), the optimization of certain processes in the development of new sources of geothermal energy, oil and gas; the development, treatment and utilization of geothermal spring waters for the production of valuable mineral additives, etc.

The development of solid-liquid equilibrium models in acetate and selenate systems is also relevant to the production and purification of acetate and selenate compounds required for industry and medicine.

2) The solubilities in the $LiBr-CaBr_2-H_2O$ system were experimentally determined at 35ºC and 50ºC. The studies are of increased interest in the production of lithium carbonate from marine lyes.

3) Selenate solid phases $Na_2SeO_4.H_2SeO_3$ and $Na_2Cd(SeO_4)_2.2H_2O$ were synthesized and characterized.

4) Modern physicochemical methods of analysis - Infrared spectroscopy, X-ray phase and Thermal analysis were used. Quantum chemical computer calculations were also carried out.

5. Critical comments, recommendations and questions:

- Critical comments on the layout of the thesis and recommendations - It is appropriate to start each main point (chapter) on a new page!!! Presentation of

figures and tables - many of them are cluttered, the text in them should be in Bulgarian.

- I have the following question for the PhD student Tsvetan Tsenov: Will he continue his scientific work in this field since the topic is actual?

I recommend that the scientific work be published as a monograph in order to promote it.

CONCLUSION

I consider that the PhD Thesis submitted to me for a review is a dissertable and it and the abstract meet the requirements of the Academic Staff Development Act in the Republic of Bulgaria and the Regulations for its implementation and I recommend the Scientific Jury **to award the degree of "Doctor" to Tsvetan Vassilev Tsenov** in the field of higher education 4. Natural Sciences, Mathematics and Informatics, professional area 4.2. Chemical Sciences, doctoral programme Inorganic Chemistry.

04.04.2024 г. **Reviewer:**

Assoc. Prof. Aleksandar Dimitrov, PhD