ГОСУДАРСТВЕННАЯ КОРПОРАЦИЯ ПО АТОМНОЙ ЭНЕРГИИ «РОСАТОМ»

ESTIMATION OF THERMODYNAMIC PROPERTIES OF INDIVIDUAL SUBSTANCES FOR NUCLEAR FUEL CYCLE TECHNOLOGIES SIMULATION

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Introduction

- Nowadays there is a lot of reference books and databases on properties of individual substances
- On the other hand, when carrying out calculations for the purpose of nuclear fuel cycle chemical technologies modeling commonly encountered problem is a substances data lack
- In this work we suggest the model generalizing the known reference information for missing data forecasting
- One of the modern approaches to constructing such models is QSPR/QSAR – the Quantitative Structure-Property/Activity Relationship

Properties and descriptors relationship

- The intuitive hypotheses can be formulated so:
  - Type and quantity of functional groups determines a compound properties
- The stricter formulation:
  - The model is based on the assumption of descriptors properties additivity
  - Molecular fragments or functional groups with regard to it's chemical bounds and also aggregate state flags play the role of descriptors

$$f = \sum_i n_i w_i$$

f – some property value
n_i – i-th descriptor value for the compound
w_i – i-th descriptor characteristic

Neighborhood descriptors

- Mutual influence of molecular fragments can be described using additive correction:

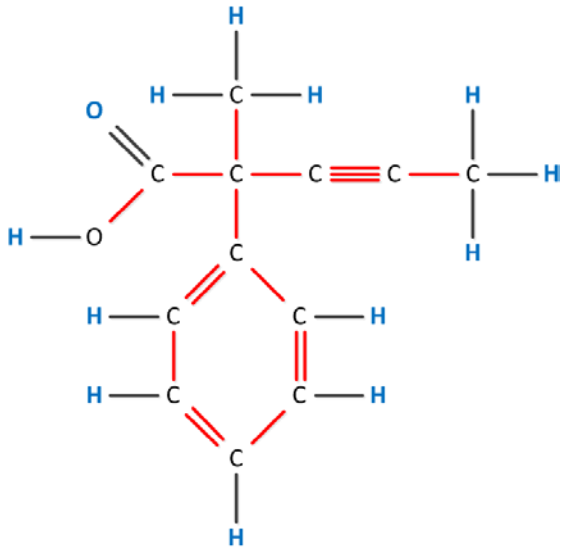
$$f = \sum_i n_i w_i + d$$

$$d = \sum_j m_j z_j$$

d – correction
m_j – quantity of j-th type neighbors pairs
z_j – j-th pair characteristic

Molecular graph segmentation

- Molecular fragments can be found as subgraphs derived from molecular graph by removing all edges not connected with terminal nodes



fragment	quantity
-C(H)(H)H	2
-C(-)=O	1
-O-H	1
-C(-)(-)(-)	1
-C#	2
-C(=)H	5
-C(-)=	1

Blue indicates terminal nodes

Red indicates edges to be removed

- Database batch processing was performed using OPSIN software

  [Daniel M. Lowe, Peter T. Corbett, Peter Murray-Rust, Robert C. Glen // Chemical Name to Structure: OPSIN, an Open Source Solution Journal of Chemical Information and Modeling 2011 51 (3), 739-753
  doi 10.1021/ci100384d]

  And specially developed Matlab-scripts

Descriptors characteristics calculation

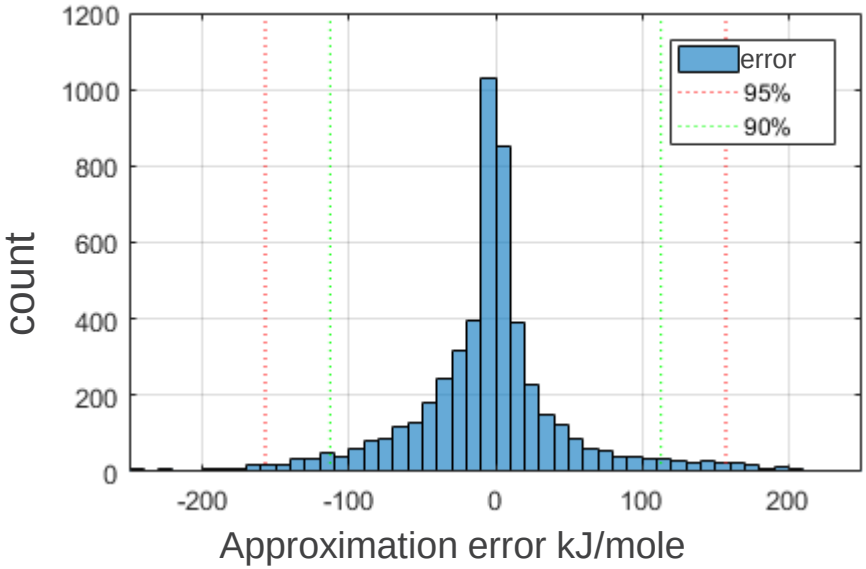
- In the case of compounds set we can write the descriptors properties additivity formula in vector form:

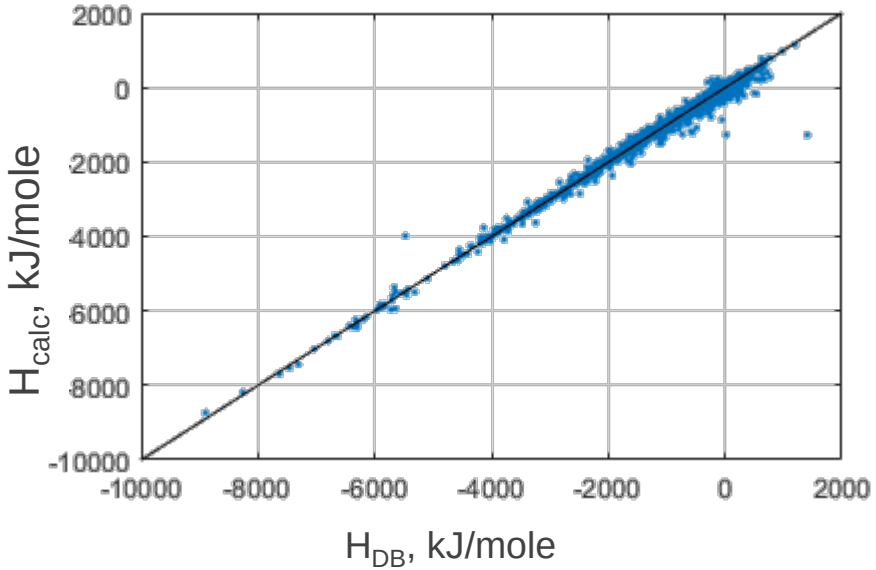
$$F = N \cdot w$$

F – property values vector
N – descriptors matrix, (rows correspond to compounds, columns correspond to descriptors)
w – descriptors characteristics vector.

- Knowing compounds properties (*F*) and related descriptors values (*N*), we can find descriptors characteristics vector (*w*) by solving this equation

Enthalpy approximation quality

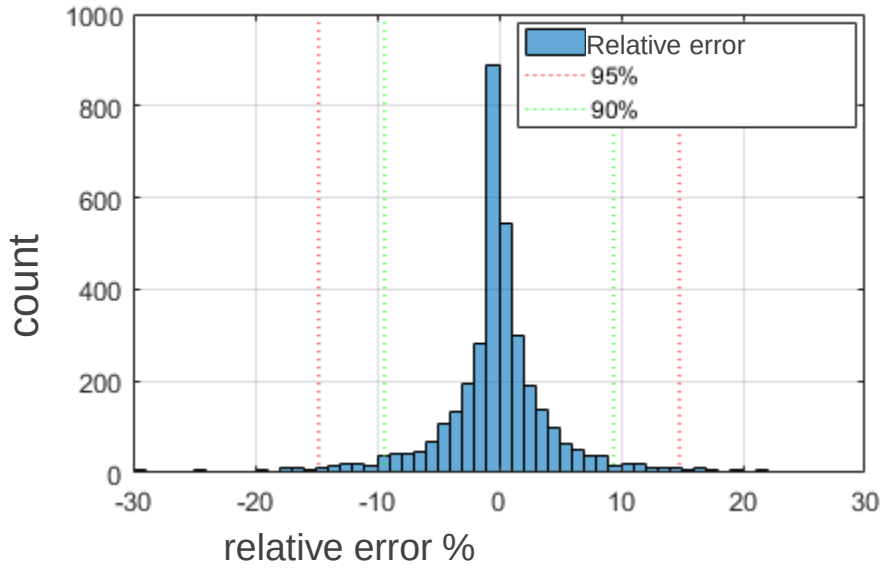


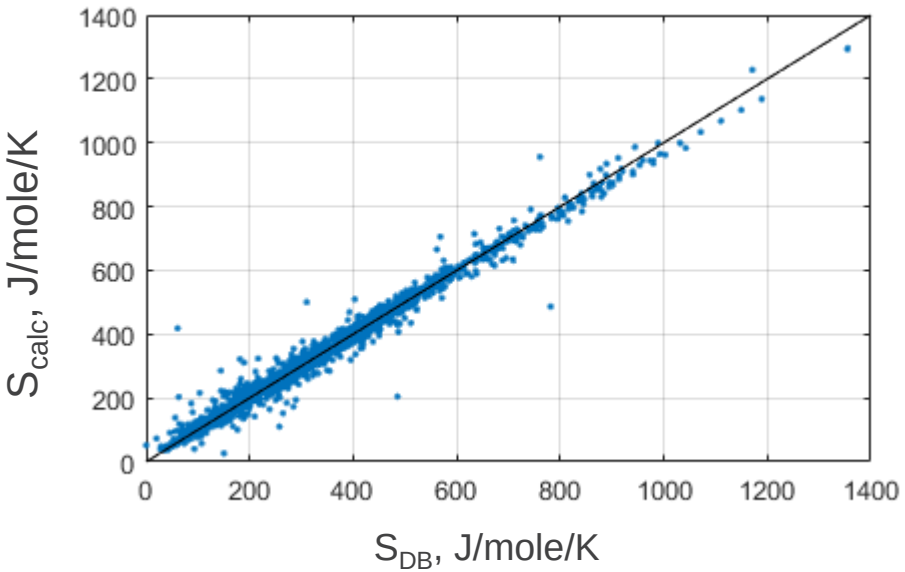


- Sample size **5000**
- $\Delta H_{95\%}$ = **157** kJ/mole
- $\Delta H_{90\%}$ = **113** kJ/mole

- MSE (ignoring neighborhood) **93,5** kJ/mole
- MSE (with neighborhood) **89,2** kJ/mole

Entropy approximation quality

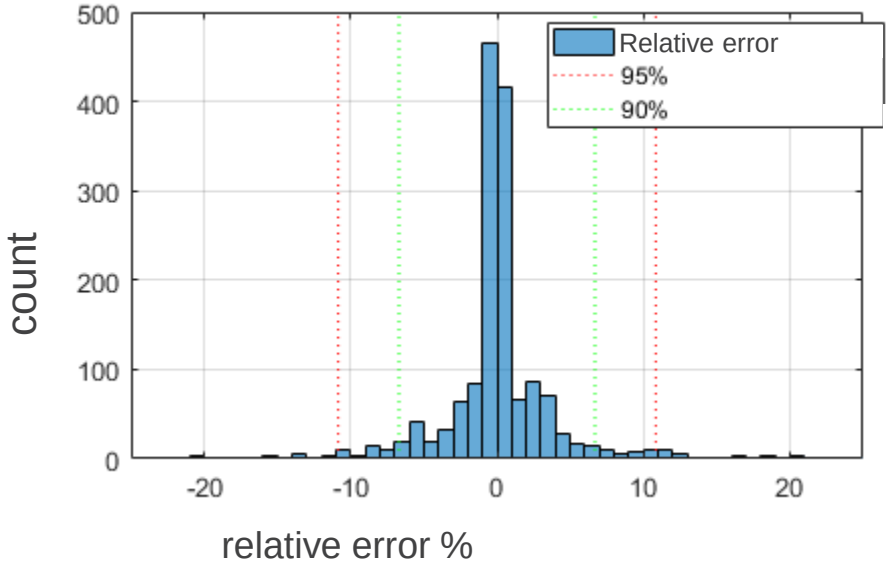


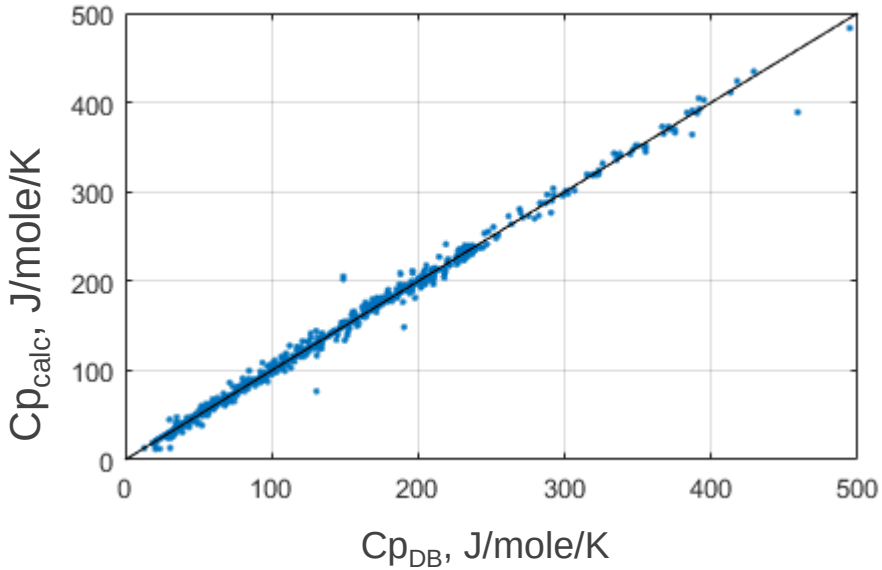


- Sample size **3500**
- $\Delta S_{95\%}$ = **15**%
- $\Delta S_{90\%}$ = **9,4**%

- MSE (ignoring neighborhood) **22,7** J/mole/K
- MSE (with neighborhood) **20,4** J/mole/K

Heat capacity approximation quality



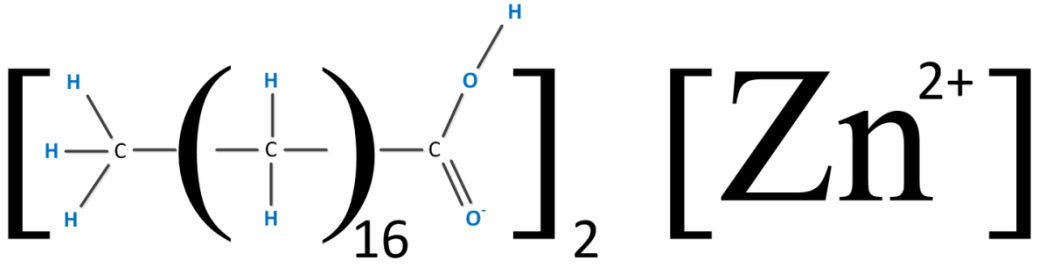


- Sample size **1500**
- $\Delta C_{p\ 95\%}$ = **11**%
- $\Delta C_{p\ 90\%}$ = **6,7**%

- MSE (ignoring neighborhood) **28,2** J/mole/K
- MSE (with neighborhood) **23,0** J/mole/K

Zinc stearate properties estimation

One of the organic compounds used in nuclear fuel fabrication technology is zinc stearate. It is the binding agent for the powder mixture on the nitride synthesis stage. Thermodynamic data was not found in available sources.



descriptor	value	w_H, kJ/mole	w_S, J/mole/K
CH_3	2	-84,95	51,71
CH_2	32	-29,48	34,93
COO^-	2	-497,09	31,67
Zn^{2+}	1	10,33	44,67
estimation		**-2097,16**	**1329,18**

fragm.1	fragm.2	value	w_H, kJ/mole	w_S, J/mole/K
CH_3	CH_2	2	2,57	-7,46
CH_2	CH_2	30	-1,22	0,43
CH_2	COO^-	2	-22,89	-
correction			**-77,29**	**-2,02**

Estimated thermodynamic values:

enthalpy **-2170** kJ/mole

entropy **1330** J/mole/K

Actinides nitrates properties estimation

For inorganic compounds example we can take actinides nitrates used in spent nuclear fuel refabrication. Their thermodynamic properties determines optimal conditions of the microwave denitration process. At the same time thermodynamic data for some nitrates was not found in available sources.

	$Am(NO_3)_3$	$Cm(NO_3)_3$	$NpO_2(NO_3)_2$
NO_3^-	3	3	2
Am^{3+}	1	0	0
Cm^{3+}	0	1	0
Np^{6+}	0	0	1
O^{2-}	0	0	2
Estimation H, kJ/mole	**-1251,06**	**-1253,23**	**-1365,20**
Estimation S, J/mole/K	**284,42**	**304,12**	**253,26**

descriptor	w_H, kJ/mole	w_S, J/mole/K
NO_3^-	-291,23	79,09
Am^{3+}	-377,37	47,15
Cm^{3+}	-379,54	66,86
Np^{6+}	-161,27	80,68
O^{2-}	-310,73	7,20

Conclusion

- The mathematical model was developed for estimation of individual compounds thermodynamic properties
- Model parameters values are calculated
- Estimation errors are
  - enthalpy MSE 89,2 kJ/mole
  - entropy MSE 20,4 J/mole/K
  - heat capacity MSE 23,0 J/mole/K
- Thermodynamic properties of zinc stearate and actinides nitrates estimations are shown as an example of model application

THANK YOU FOR ATTENTION

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Detailed model description and parameters values will be published in the paper:
О. В. Шульц. Оценка термодинамических свойств химических соединений на основе количественных соотношений структура – свойство.
Russian Journal of Physical Chemistry A, 2019, vol 93, № 7
DOI: 10.1134/S0044453719070264

Organic and inorganic compounds proportion

- The sample contains totally about 5,5 thousands unique compounds.
- About 3 thousands do not contains carbon.