

Ab-initio determination of thermodynamic properties of HNO₃-H₂O mixtures

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ABSTRACT

Corrosion due to nitric acid in concentrated mediums is an active domain of investigations in nowadays-nuclear fuel reprocessing plants[1], [2], [3]. However, the complexity of the medium, due to the presence of strong electrolytes and thus heavy deviations from ideal behaviour, hinders the determination of species activities required to predict speciation of the system. Empirical models exist in the literature[4], [5], but require the use of, sometimes many, adjustable parameters. We thus develop an ab-initio numerical approach, based on DFT simulations of liquid HNO₃-H₂O mixtures, to reproduce some thermodynamic functions and properties, without having to rely on parameters-heavy empirical models of electrolytes solution.

References

- [1] P. Fauvet, « Corrosion issues in nuclear fuel reprocessing plants », in *NUCLEAR CORROSION SCIENCE AND ENGINEERING*, n° 22, D. Feron, Éd., in Woodhead Publishing Series in Energy. , Cambridge: Woodhead Publ Ltd, 2012, p. 679-728. Consulté le: 28 février 2024. [En ligne]. Disponible sur: <https://www.webofscience.com/wos/woscc/full-record/WOS:000311568600020>
- [2] D. Sicsic, F. Balbaud-Célérier, et B. Tribollet, « Mechanism of Nitric Acid Reduction and Kinetic Modelling », *European Journal of Inorganic Chemistry*, vol. 2014, n° 36, Art. n° 36, déc. 2014, doi: 10.1002/ejic.201402708.
- [3] F. Balbaud-Célérier, N. Gruet, B. Gwinner, et P. Laghoutaris, « Corrosion behavior of stainless steels in nitric acid in the context of nuclear fuel reprocessing plants », in *Nuclear Corrosion*, Elsevier, 2020, p. 301-340. doi: 10.1016/B978-0-12-823719-9.00008-1.
- [4] S. Balasubramonian, N. K. Pandey, K. Shekhar, et R. V. Subba Rao, « Thermodynamic Modeling of Nitric Acid Speciation Using eUNIQUAC Activity Coefficient Model », *J Solution Chem*, vol. 50, n° 11, p. 1300-1314, déc. 2021, doi: 10.1007/s10953-021-01124-0.
- [5] A. Ruas, P. Pochon, J.-P. Simonin, et P. Moisy, « Nitric acid: modeling osmotic coefficients and acid–base dissociation using the BIMSA theory », *Dalton Trans.*, vol. 39, n° 42, p. 10148-10153, oct. 2010, doi: 10.1039/C0DT00343C.