Topic N°1 (Oral)

ISOPIESTIC DENSITY LAW OF ACTINIDE NITRATES APPLIED TO CRITICALITY CALCULATIONS

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Criticality calculations need, as input data, the atomic densities of fissile mixtures. Density laws are used to determine them in solution mixtures; they give the solution density knowing the fissile nuclide concentrations and the acidity; the water content is then deduced. Most of the relationships giving density laws are strictly empirical; they are mathematical fittings of assumed polynomial expressions on experimental measurements and analysis. Up to now, this type of density laws were used and applied in and outside their measurement range by criticality safety experts. As it was showed by French studies at ICNC'99, such an approach could be wrong, in some important cases, especially for nitrate solutions [1].
A proposal has been made to correct this possibly wrong approach; a thermodynamic methodology based on the concept of mixtures of binary electrolyte solutions (one electrolyte + water) at constant water activity, so called "isopiestic" solutions, was presented at ICNC'99 [2] and continued. Methodology development and applications are given in the following paper.
Mainly in the spent fuel reprocessing, seven main electrolytes in nitric solutions are concerned, they are HNO_3, $UO_2(NO_3)_2$, $Pu(NO_3)_4$, $Th(NO_3)_4$, $Pu(NO_3)_3$, $Am(NO_3)_3$ and $U(NO_3)_4$. The new "isopiestic" method is applied to these electrolytes and is based on the Zdanovski's rule (Z.S.R.). It states that under specific conditions (same water activity), the volumes of binary solutions can simply be added without volume variation.
It should be added that even if the Z.S.R. rule is not strictly followed, the method can give yet good estimates of the density.

The method has been implemented in CIGALES V2.0 [3], the graphical user interface of the French criticality safety package CRISTAL [4] that calculates the atom densities of nuclides. For that purpose, binary data (concentration, density, water activity) of binary solutions are necessary to know about the density of multinary solutions; these data are provided by literature ($UO_2(NO_3)_2$, HNO_3) or determined by a recent thesis work [5] ($Pu(NO_3)_4$, $Th(NO_3)_4$, $U(NO_3)_4$) on the basis of ternary data (one electrolyte in acidic medium) with the help of the Z.S.R. inverse method.
The validity and restrictions of the method include the binary data limits and also the solubility limits of the nitrate salts. Nevertheless, the concentration in fissile nuclide is determined beyond the solubility limit of the nitrate salt only for the two ternary solutions: plutonium nitrate (HNO_3, $Pu(NO_3)_4$, H_2O) and uranyl nitrate (HNO_3, $UO_2(NO_3)_2$, H_2O). The solution mixture is studied in two steps.
First, the volume of the mixture is obtained by addition of the two individual volumes of the crystal and the saturated solution.
Second, these volumes are homogenized. In other words, the biphasic mixture (crystal + saturated solution) is considered, on the concentration point of view, as a one-phase mixture.

The validation uses at least forty critical benchmarks from ICSBEP handbook (naturally in the solubility range). It consists in comparing the influence of the water density value (and of the mixture density) on the keff between the isopiestic law and the benchmark specifications.
For that purpose, the configuration is calculated for the same fissile nuclide densities as the benchmark, with the water densities determined by the isopiestic law and with the water densities provided by the benchmark. When applied on the uranyl and plutonium nitrate solutions, the qualification results show that the new "isopiestic" density law is in better agreement with the benchmarks than the former ones:

- no bias for the uranium and plutonium solutions has been pointed out,
- solution densities calculated with the isopiestic laws are in good agreement with those provided by the benchmarks.

Moreover, the isopiestic law corrects:

- the observed 1 % overestimation of the keff generated by the empirical Leroy & Jouan density law, for uranium solutions,
- and the observed 3.4 % underestimation of the keff generated by the ARH-600 density law, for plutonium solutions.

For these reasons, the isopiestic density law has been implemented in CIGALES V2.0. It has allowed the author to determine new minimum critical values of nitrate solutions [6].

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