

PRECIPITATION OF YTTRIA DOPED ZIRCONIA IN AQUEOUS SOLUTION: THERMODYNAMIC REVIEW

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ABSTRACT

The literature on the subject pointed out that yttria stabilized zirconia is stable at both room temperature and saturated-vapor autoclave conditions but that there wasn't any datum for the free-energy of formation of this solid solution, hindering this way any trying of thermodynamic analysis of the chemical precipitation process for obtaining the same species from aqueous solution. This paper deals with the computation of such thermodynamic datum for room temperature starting from available phase diagram, using the well know correlation between free energy – composition diagram and temperature – composition phase diagram. Additional calculations of the molar entropy and heat capacity of the referred species allowed calculating and to construct Potential-pH and activity-pH diagrams for selected temperatures in the range 25-300°C. The conclusions given by the thermodynamic calculation is that excess enthalpy of mixing in the formation of 9 mol% yttria doped zirconia from their single oxides should be in the range from -99.000 kcal.mole⁻¹ to -371.000 kcal.mole⁻¹ of Y₁₈Zr₉₁O₂₀₉, while de constructed diagrams revealed that yttria-doped zirconia becomes less stable when the temperature rises, matching to the behavior reported in the literature.

INTRODUCTION

With more than 9 mole percent of Y₂O₃ in the yttria-doped zirconia, a homogeneous cubic solid solution zirconia forms (Stevens R., 1986) which is stable from room temperature to the melting temperature. From other hand, Hettiarachchi and Macdonald (1984) found out that yttria-doped zirconia was good as ceramic membranes for precise pH measurements in high temperature aqueous environments, according to experiments carried out at 175°C to 175°C at 25°C intervals. Therefore, there isn't any doubt about the stability of the yttria-doped zirconia

at room temperature and under water vapor saturated autoclave conditions.

Despite of this, when electrochemical potential-pH diagrams are calculated and constructed using thermodynamic data provided by published databases, yttria-doped zirconia doesn't appear as a predominant species, as may be seeing in Figures 1 to 4. Figures 1 and 2 point out that monoclinic zirconia is the predominant solid zirconia species, while Figures 3 and 4 point out that Y₂O₃•2ZrO₂ compound (not solid-solution) is the predominant species. Why this happens? The answer is simple: there isn't thermodynamic data on yttria-doped zirconia solid solution. In view of this picture, the authors of this paper decided to calculate the desired thermodynamic data (S, H, G, c_p) for the 9 mol% yttria-doped zirconia and use them to construct electrochemical potential-pH and activity-pH diagrams.

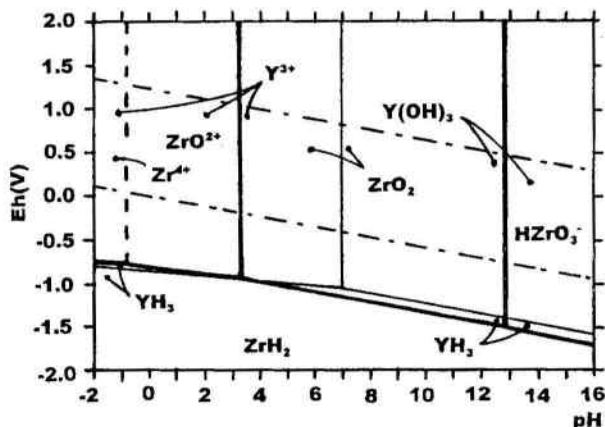


Figure 1 – Eh-pH diagram of the Zr-Y-H₂O system at 25°C for a_Y = 0.1 a_{Zr} and 1 molar Zr activity in the aqueous solution, with thermodynamic data provide by published databases.

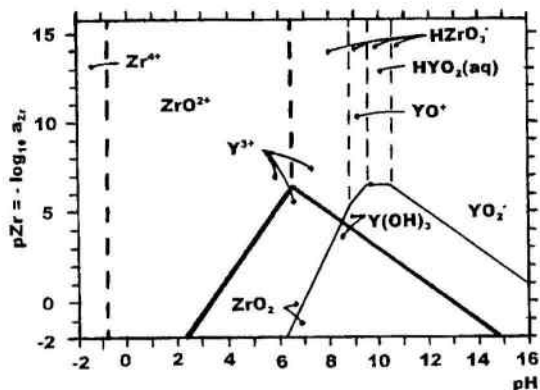


Figure 2 – pZr-pH diagram of the Zr-Y-H₂O system at 25°C for $a_Y = 0.1$ a_{Zr} and well aired aqueous solution, constructed with thermodynamic data provide by published databases.

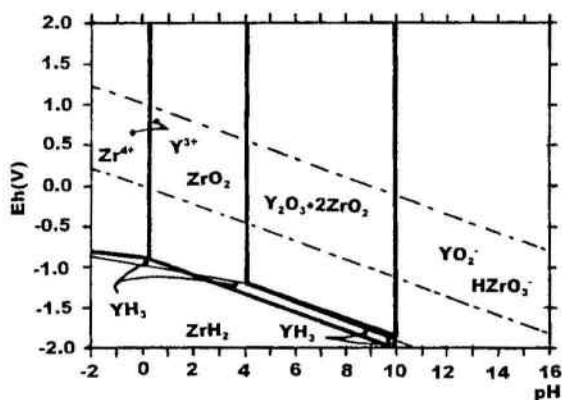


Figure 3 – Eh-pH diagram of the Zr-Y-H₂O system at 300°C for $a_Y = 0.1$ a_{Zr} and 1 molar Zr activity in the aqueous solution, with thermodynamic data provide by published databases.

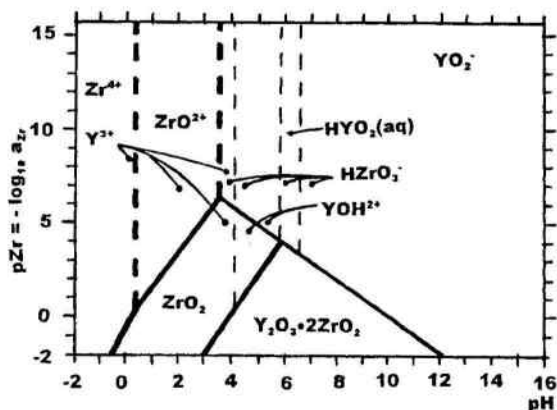


Figure 4 – pZr-pH diagram of the Zr-Y-H₂O system at 300°C for $a_Y = 0.1$ a_{Zr} and 1.777 atm O₂ pressure in the aqueous solution, constructed with published thermodynamic data.

THERMODYNAMIC DATA

Stevens R. (1986) gives a good version of the temperature-composition phase diagram for the Y₂O₃-ZrO₂ system, where it can be seen that cubic solid-solution zirconia is stable from room temperature up to the melting temperature for composition with more than 9 mole of yttria. Originally, this diagram was generated by Scott M. G (1975) and modified by Miller, Smialek and Garlick (1981).

The use of such a phase diagram as the source for free energy-composition diagram is straightforward and its principle may be found out elsewhere (e.g., Kingery, Bowen and Uhlmann, 1976). Following this principle, ideal entropy of mixing ($\Delta S_{id} = 60.114 \text{ cal.mole}^{-1}\text{K}^{-1}$), the entropy of the mixture ($S^M = 1308.03 \text{ cal.mole}^{-1}\text{K}^{-1}$), the enthalpy of the mixture ($-27967 \text{ kcal.mol}^{-1}$), the free-energy of the mixture ($G^M = -28357.2 \text{ kcal.mole}^{-1}$), and the entropy of the regular solution were calculated. ($1368.11 \text{ cal.mole}^{-1}\text{K}^{-1}$). The lacking datum is the excess enthalpy for formation of the solution ($\Delta H^{XS} = ?$). The key-rules for obtaining the desired value of ΔH^{XS} are: a) the maximum value of ΔH^{XS} should at least allow the appearance of the Y₁₈Zr₉₁O₂₀₉ = 9Y₂O₃•91ZrO₂ as a stable species in the Eh-pH and activity-pH diagram of the Y-Zr-H₂O system at 25°C; and b) the maximum value of ΔH^{XS} should allow the exclusion of the ZrO₂ as a stable species in the Eh-pH and activity-pH diagram of the Y-Zr-H₂O system at 25°C.

Thermodynamic data of other species of the Zr-Y-H₂O system were found out in the Main-Database of the HSC Chemistry for Windows 4.0 (Outokumpu Oy, Finland), licensed to UFRJ/COPPE PEMM.

The construction of the Eh-pH diagrams was performed using the Potential-pH section of the Software HSC Chemistry for Windows 4.0. These constructions were carried out for several pairs of the yttrium and zirconium activities in the aqueous solutions, for each temperature. From each Eh-pH diagram, couples of values of (activity of Zirconium and pH) corresponding to each limit of predominance domain of the stable species were taken and used in order to construct the pZr-pH diagram (where $pZr = -\log_{10} a_{Zr}$) for well aired aqueous solutions.

PRESENTATION AND DISCUSSION OF THE RESULTS

The try and error procedure conducted to the determination of $\Delta H^{XS} = -99 \text{ kcal.mole}^{-1}$ is the maximum value of ΔH^{XS} should at least allow the appearance of the $Y_{18}Zr_{91}O_{209} = 9Y_2O_3 \cdot 91ZrO_2$ as a stable species in the Eh-pH and activity-pH diagram of the Y-Zr-H₂O system; the corresponding value of enthalpy of this solution is $H^S = -28066 \text{ kcal.mole}^{-1}$. Using this value of H^S figure 5 illustrates the Eh-pH of the Zr-Y-H₂O system at 25°C for $a_Y = 0.1 a_{Zr}$; it is seen that $Y_{18}Zr_{91}O_{209}$ predominates in the range $7 < \text{pH} < 13$ for a well aired water solution, while zirconia appears as the stable solid phase for $3 < \text{pH} < 7$. Is it possible to synthesize $Y_{18}Zr_{91}O_{209}$ by co-precipitation even with ZrO_2 existing as the predominant solid phase in the way from the starting acid solution to the final $Y_{18}Zr_{91}O_{209}$? The answer is that crystallization of precipitates takes time (for aging) and that the first precipitate may be amorphous solid (in the present case a mixture of zirconium and yttrium hydroxides) which will convert into $Y_{18}Zr_{91}O_{209}$ once the pH value of the aqueous suspension of precipitates is lying in the range from 7 to 13. Of course, if the pH of the system is in the range from 3 to 7, then monoclinic ZrO_2 plus Y^{3+} in the aqueous solution will be the final stable species of zirconium and yttrium.

Again, the try and error procedure used to the determination of $\Delta H^{XS} = -371 \text{ kcal.mole}^{-1}$ as the maximum value of ΔH^{XS} should allow the exclusion of the ZrO_2 as a stable species in the Eh-pH and activity-pH diagram of the Y-Zr-H₂O system at 25°C. The corresponding value of the H^S of the $Y_{18}Zr_{91}O_{209}$ solid solution is $-28228 \text{ kcal.mol}^{-1}$

Using this value of the H^S figures 6 and 7 present the Eh-pH and pZr-pH diagrams of the Zr-Y-H₂O system at 25°C. It can be seen that effectively monoclinic ZrO_2 no more appears in the diagram. The pH range for the least solubility of $Y_{19}Zr_{91}O_{209}$ (about 10^6 molar of zirconium and 10^{-7} molar of yttrium) is $6.3 < \text{pH} < 9$. The prediction of these diagrams is that an aqueous acid solution of zirconium and yttrium may be progressively titrated with a base ($NH_4OH + NaOH$) up to $6 < \text{pH} < 9$ to achieve $Y_{18}Zr_{91}O_{209}$ without any risk of monoclinic zirconia crystallization at 25°C.

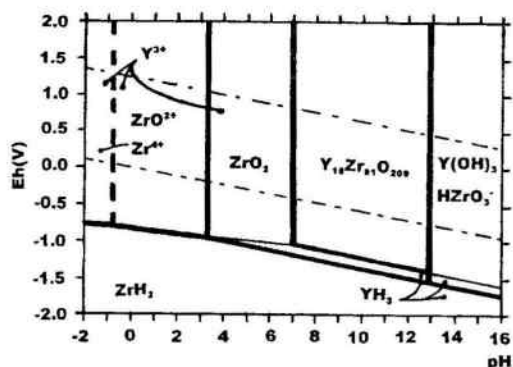


Figure 5 – Eh-pH diagram of the Zr-Y-H₂O system at 25°C for $a_Y = 0.1 a_{Zr}$ and 1 molar activity of zirconium in the aqueous solution, with $\Delta H^{XS} = -99 \text{ kcal.mole}^{-1}$.

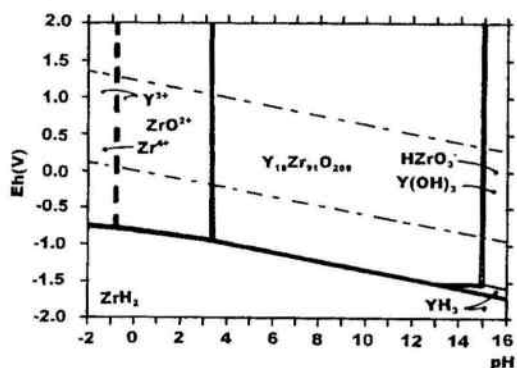


Figure 6 – Eh-pH diagram of the Zr-Y-H₂O system at 25°C, $a_Y = 0.1 a_{Zr}$ and 1 molar Zr activity in the aqueous solution, with $\Delta H^{XS} = -28338 \text{ kcal.mole}^{-1}$.

Figures 8 and 9 present Eh-pH diagrams of the Zr-Y-H₂O system at 200°C and 300°C, for $a_Y = 0.1 a_{Zr}$ and 1 molar activity of zirconium in the aqueous solution. The stability domain of the $Y_{18}Zr_{91}O_{209}$ continues predicted for these 2 temperatures, but monoclinic zirconia shares the pH range of the zirconia containing solid species.

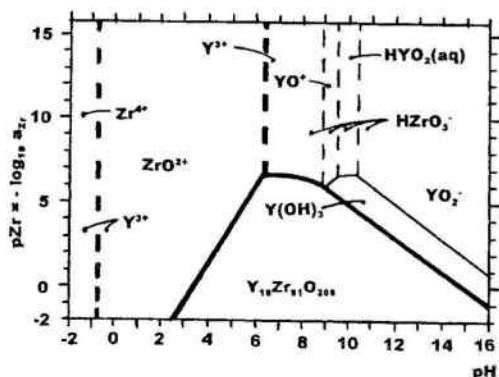


Figure 7 – pZr-pH diagram of the Zr-Y-H₂O system at 25°C, $a_Y=0.1, a_{Zr}$ and well aired aqueous solution, constructed with $\Delta H^{XS} = -28338 \text{ kcal.mole}^{-1}$

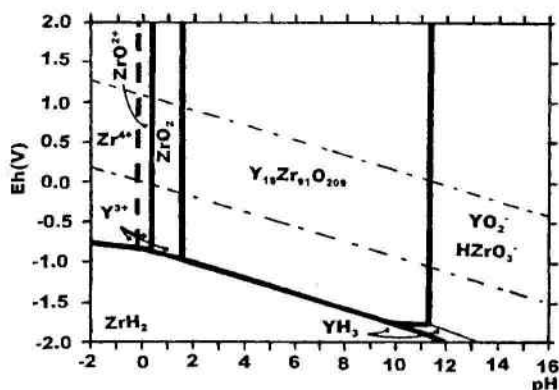


Figure 8 – Eh-pH diagram of the Zr-Y-H₂O system at 200°C for $a_Y = 0.1$, $a_{Zr} = 1$ and 1 molar Zr activity in the aqueous solution, $\Delta H^{XS} = -28338$ kcal.mole⁻¹.

The pH range for which monoclinic zirconia is stable grew with the temperature rise from 200°C to 300°C. This feature agrees well with the reported (Stevens R, 1986) degrading behavior of yttria-doped zirconia at high temperature in water vapor environments. Indeed, Stevens R. (1986) pointed out that yttria-doped zirconia is sensitive to high temperature aqueous environments and caused concern which has led to the development of the ZrO₂-CeO₂ ceramics (Lange F.F, 1982; Coyle, Coblenz and Bender, 1983; Tsukuma and Shimada, 1985).

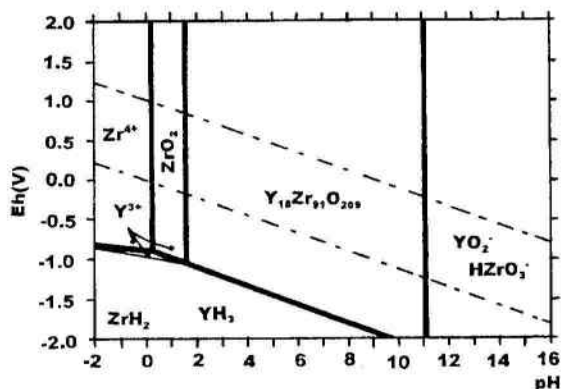


Figure 9 – Eh-pH diagram of the Zr-Y-H₂O system at 300°C, $a_Y = 0.1$, $a_{Zr} = 1$ and 1 molar Zr activity in the aqueous solution, with $\Delta H^{XS} = -28338$ kcal.mole⁻¹.

Now, the relative magnitude of the ΔH^{XS} deserves further analysis. Equation 1 represents the formation of the $Y_{18}Zr_{91}O_{209}$ solid solution from Y_2O_3 and ZrO_2 , while 2 represents the relative magnitude of ΔH^{XS} with reference to the sum of the H° of the reactants multiplied by their number of moles taking place in the reaction 1. Equation 3 represents the formation of the compound $Y_2O_3 \bullet 2ZrO_2$ from Y_2O_3 and ZrO_2 and Equation 4 represents the relative

magnitude of the ΔH^R with reference to the H° of the reactants multiplied by their number of moles taking place in the reaction 3.



$$R(1) = [\Delta H^{XS} / (9 H^\circ_{Y_2O_3} + 91 H^\circ_{ZrO_2})] \quad (2)$$



$$R(3) = [\Delta H^R / (H^\circ_{Y_2O_3} + 2 H^\circ_{ZrO_2})] \quad (4)$$

Table I show that R(1) values in both selected conditions is comparable to that of the R(3) for the formation of $Y_2O_3 \bullet 2ZrO_2$ from Y_2O_3 and ZrO_2 . Additional experimental features will be required in order to determining which of the two restrictions gives the best value of the ΔH^{XS} . For this task it is important to note that cubic structure yttria-doped zirconia solid solution will exist from 9 mole % Y_2O_3 up to a upper solubility limit of Y_2O_3 in zirconia (20 mole% Y_2O_3 , for instance). Stevens R (1986) reported $Y_4Zr_3O_{12}$ solid solution as experimentally observed, but this composition corresponds to 40 mole % of Y_2O_3 in the solid solution, while 33.33 mole% of Y_2O_3 is the yttria content of the $Y_2O_3 \bullet 2ZrO_2$ compound. Therefore, the higher yttria content solubility limit of the yttria-doped zirconia has to be precisely determined prior to future evolution in Eh-pH and activity-pH diagrams of the Zr-Y-H₂O system.

Table I – Relative magnitudes of R(1) and R(3).

ΔH^{XS} or ΔH^R kcal.mole ⁻¹	$\sum(n_i H^\circ_i)$ kcal.mole ⁻¹	R(1) or R(3)
$\Delta H^{XS} = -99.0$	-27967.0	R(1) = 0.00354
$\Delta H^{XS} = -371.0$	-27967.0	R(1) = 0.0133
$\Delta H^R = -5.274$	-980.0	R(3) = 0.00538

CONCLUSIONS

(a) $\Delta H^{XS} = -99$ kcal.mole⁻¹ is the maximum value of ΔH^{XS} should at least allow the appearance of the $Y_{18}Zr_{91}O_{209} = 9Y_2O_3 \bullet 91ZrO_2$ as a stable species in the Eh-pH and activity-pH diagram of the Y-Zr-H₂O system; the corresponding value of enthalpy of this solution is $H^S = -28066$ kcal.mole⁻¹.

(b) $\Delta H^{XS} = -371$ kcal.mole⁻¹ is the maximum value of ΔH^{XS} which allows the exclusion of the ZrO_2 as a stable species in the Eh-pH and activity-pH diagram of the Y-Zr-H₂O system at 25°C. The corresponding value of the H^S of the $Y_{18}Zr_{91}O_{209}$ solid solution is -28228 kcal.mole⁻¹.

(c) Potential-pH and pZr-pH diagrams developed in this work pointed out a decreasing stability of the $Y_{18}Zr_{91}O_{209}$ with the temperature rise from 25°C to 300°C, which agreed well with the yttria-doped zirconia at high temperatures reported in the literature.

(d) Additional investigation will be necessary toward the upper solubility limit of yttria in zirconia solid solution, in order to completely set up Eh-pH and activity-pH diagrams for the Zr-Y-H₂O in aqueous solutions from room temperature to water vapor saturated autoclave conditions.

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