MSE 495 – Advanced Ceramics Technology

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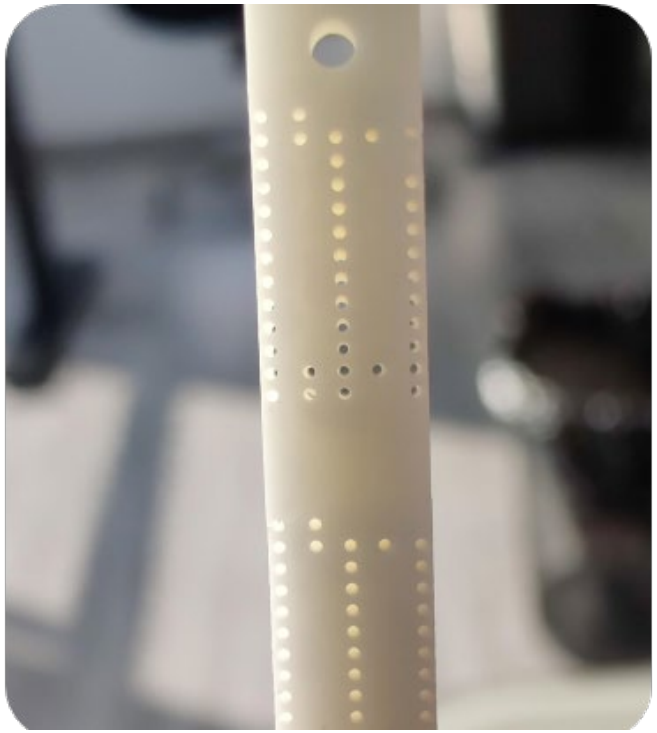
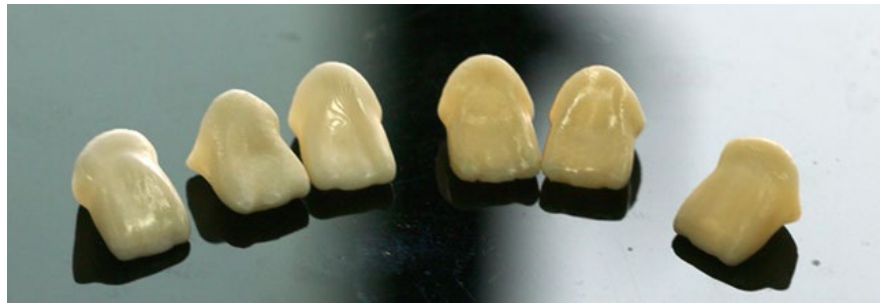
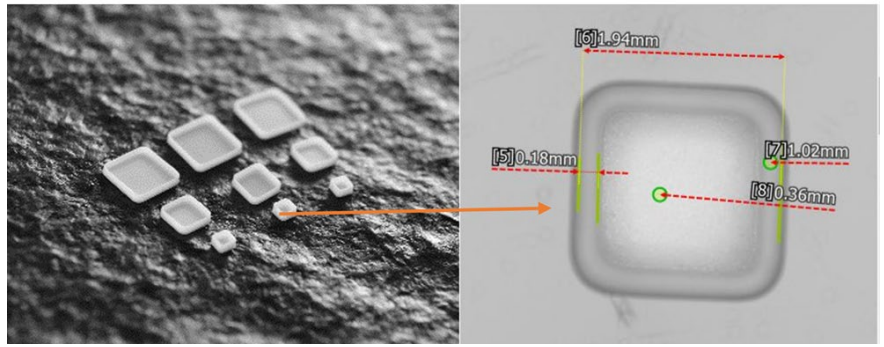
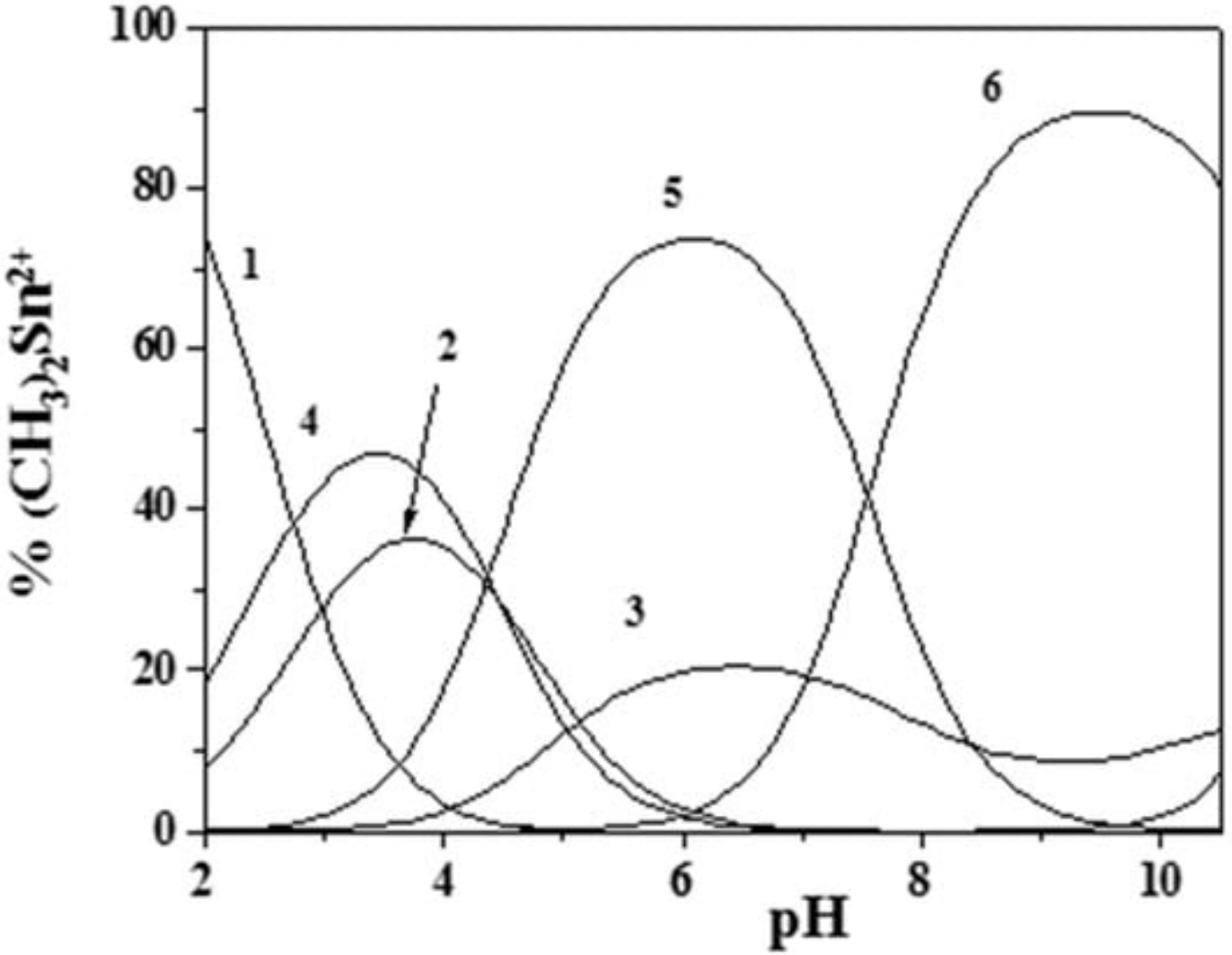
Week 7 – Computational tools







Chemical speciation via computational tools



Tools

Free software:

PHREEQC (US)
https://www.usgs.gov/software/phreeqc-version-3
https://water.usgs.gov/water-resources/software/PHREEQC/index.html

GEMS (PSI)
https://gemshub.github.io/site/

Commercial:

OLI Sythem (trial version 30 days possible)
https://www.olisystems.com/

Example and exercise

Example 1: Speciation and its importance for pH calculations
Example 2: Determining the Solubility of Calcite ($CaCO_3$); Aragonite ($CaCO_3$); Dolomite ($CaMg(CO_3)_2$)

Example 1 – $FeCl_3$, 1 molal, single point, isothermal (25°C)

Resulting pH: ≈2.2

Why is it so low?

Speciation Reactions

First iron (III) chloride dissociates:

$$FeCl_3 \rightarrow Fe^{3+} + 3Cl^-$$

Then the Fe^{3+} interacts with water; hydrolysis reaction:

$$Fe^{3+} + H_2O \rightarrow FeOH^{2+} + 2H^+$$

Then another water molecule enters into the reaction:

$$FeOH^{2+} + H_2O \leftrightarrow Fe(OH)_2^+ + H^+$$

These last two reactions take up the **OH^-** from solution, and release **H^+** into the solution

More speciation reactions occur, but the reactions above where shown as an illustration. The following is a list of all the species that are formed in the aqueous phase:

Fe^{+3}	$FeCl_2^{+1}$	$Fe(OH)_3^0$	H_2O^0
$FeCl^{+2}$	$Fe(OH)_2^{+1}$	OH^{-1}	HCl^0
$FeOH^{+2}$	H^{+1}	$FeCl_4^{-1}$	$Fe_2(OH)_2^{+4}$
Cl^{-1}	$FeCl_3^0$	$Fe(OH)_4^{-1}$	

pH Calculation

The pH is calculating using the following formula:

$$pH = -\log(m_{H^+}\gamma_{H^+})$$

For the pH calculation the molality and the activity coefficient of the H^+ species is needed. To reveal the activity coefficients calculated by software follow the steps below.

Speciation: H^+

H+1	5.26667e-3	5.26667e-3

Activity coefficients:

H+1	1.23481	1.15212	

Thus, the pH is:

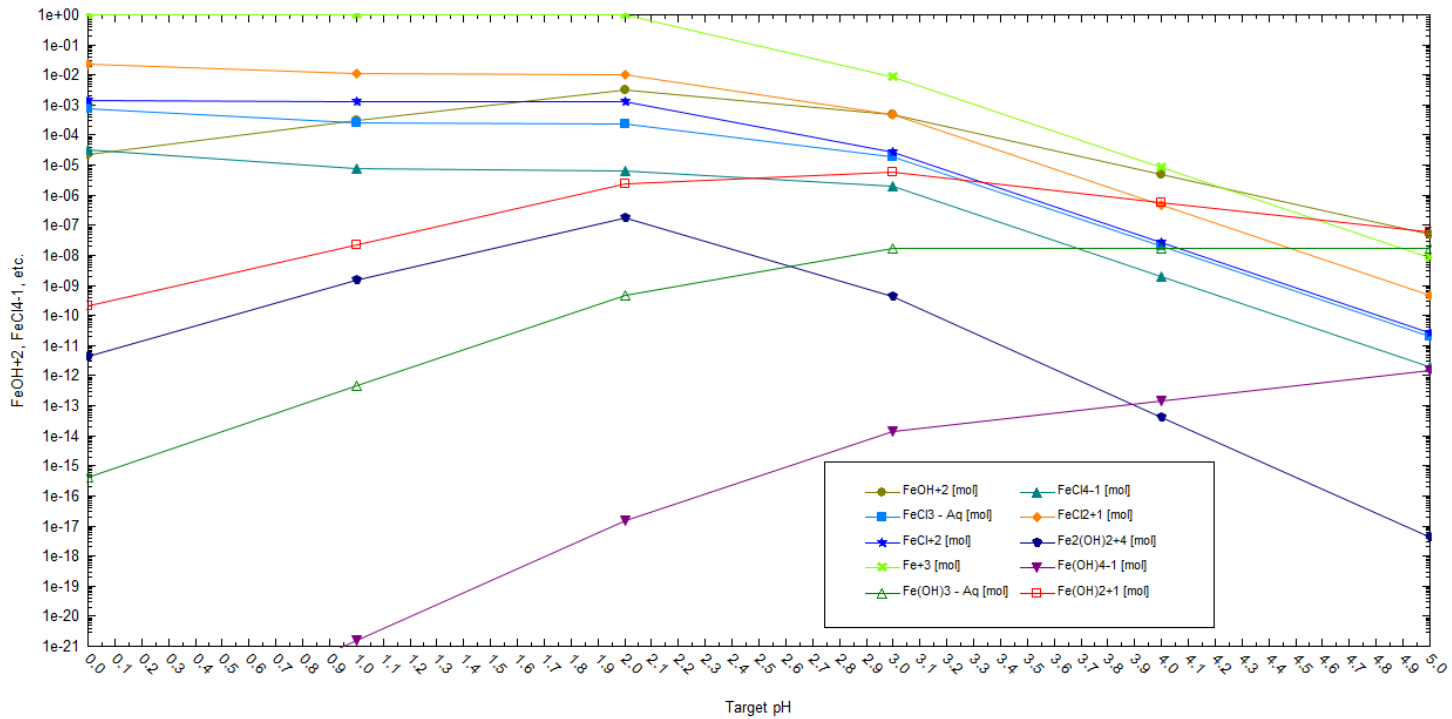
$$pH = -\log(m_{H^+}\gamma_{H^+})$$

$$pH = -\log[(5.28940 \times 10^{-3})(1.15211)]$$

$$pH = -\log[6.094 \times 10^{-3}]$$

$$\boldsymbol{pH = 2.2151}$$

Speciation in the range pH range 0-5



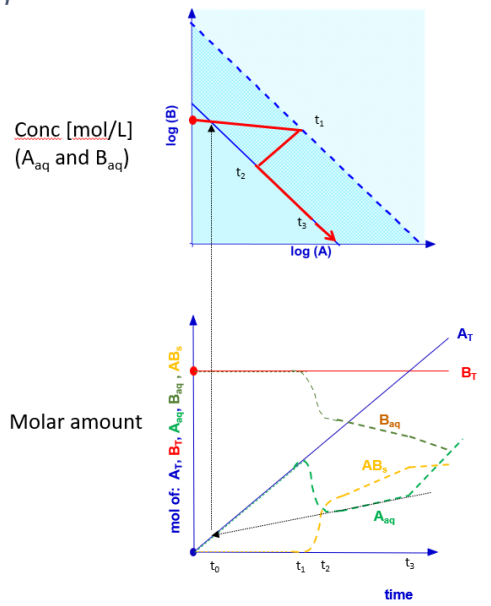
Example 2 – $CaCO_3$, single point, isothermal (25°C)

Precipitation Point Calculation			
Calculation Settings		**Stream Composition and Conditions**	
Calculation Type	Single Point Calculation	Stream Amount	Default - 1 kg
Calculation Sub-type	Precipitation Point	Temperature	25 °C
Stream Name	Solubility of CaCO3 – Precipitation Point	Pressure	1 atm
Name Style	Display Formula	H2O	Calculated
Unit Set	Metric, Mass Fraction (ppm (mass))	CaCl2	10870 ppm (mass)
Framework	AQ	MgCl2	9325 ppm (mass)
		CO2	431 ppm (mass)
		CaCO3	0 ppm(mass)

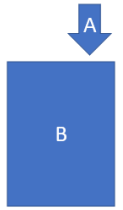
Calcite: 412 ppm
Aragonite: 552 ppm
Dolomite: 246 ppm

Example 3: $CaCO_3$ titration experiment

Recall... 1



$A_{aq}+B_{aq} \leftrightarrows AB_S$



Two chemical species: A_{aq} and B_{aq}
One solid species: AB_s

Mass balance:
$A_{tot} = A_{aq} + AB_S$
$B_{tot} = B_{aq} + AB_S$

In the presence of solid:
$A_{aq} \times B_{aq} = Ksp_{AB}$

Conditions:

B: Na_2CO_3, 0.01 M
A: $CaCl_2$, 0.01 M

pH: 10, using NaOH
T: 25 °C

And then, let's use our fantasy!