



# Enabling process simulation of reactive electrolyte mixtures using CAPE-OPEN

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## Background: Bjørn Maribo-Mogensen

- Part of CAPE-OPEN **Thermo SIG** working group
- PhD in **electrolyte thermodynamics** 2010-2014
- Software manager **DTU** Institute of Chemical Engineering (CERE) 2010-2014
- Physical property specialist **Linde Engineering** 2014-2016
- Co-founder **Hafnium Labs** since 2016
  - Developing software to bring **state-of-the-art research** to industrial application
  - **Q-props**: World's most accurate predictions of **physical properties** for pure components and mixtures
  - **Epsilon**: Next-generation – predictive – thermodynamic model for **electrolytes**

## Topics for today

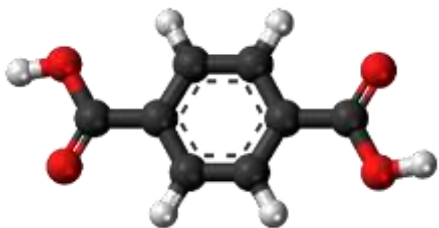
- Reactive electrolyte systems are **challenging** to model
  - No predictive models exist → Parameters needed for **each system**
  - Process simulators **support many** such systems
  - But often we have to implement custom thermodynamic models
  - Integrating a custom model is **simulator-specific** today (native or COM)
- ! New CAPE-OPEN standard **improves support** for reactive electrolyte systems
- ? How will we **drive adoption** by PME vendors?

# Electrolytes are important but hard to model accurately

## Electrolytes are small and not top of mind ...

### Electrolytes are small molecules that

- Carry electrical charge
- Can e.g. form by reaction of neutral compounds + H<sub>2</sub>O
- Disproportionately affect process properties



### They are often neglected in process design as they

- Are present in trace amounts
- Are assumed unimportant
- Appear unexpectedly

## ... but they are crucial to get right ...

### Surprises can be extremely expensive

- Corrosion and deposits
- Wrong material choice
- Unexpected reactions
- Wrong process design
- Pollutants in gas and water

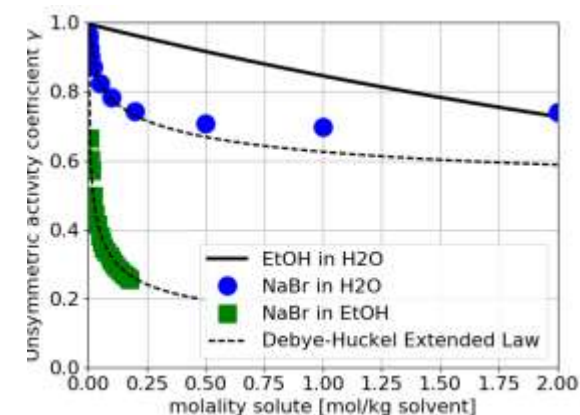


### In addition, electrolytes often serve a function in a process

- Separation processes
- Organic synthesis
- Electrocatalytic reduction
- Crystallization

## ... and very difficult to model accurately

### Electrolytes show extreme non-ideality



### They are more complex than they seem

- H<sub>2</sub>O + CO<sub>2</sub>  
= 6 species, 3 reactions, 3 solids
- H<sub>2</sub>O + CO<sub>2</sub> + NH<sub>3</sub>  
= 9 species, 6 reactions, 8 solids

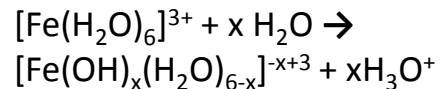
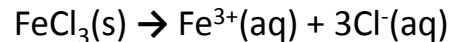
**... and complexity grows exponentially with additional reactive components**

# What makes electrolytes so difficult?

## True chemistry is easily overlooked

Mix 1 kg water + 1 mol FeCl<sub>3</sub>

- Resulting pH = 2... Why?
  - Dissolution
  - Hydration
  - Hydrolysis



### New compounds may form

- Some charged, some not
  - [Fe(CN)<sub>6</sub>]<sup>3-</sup>
  - [Fe(SCN)<sub>3</sub>]
- New compounds may form that are not stable in gas
  - E.g. NH<sub>2</sub>COO<sup>-</sup>

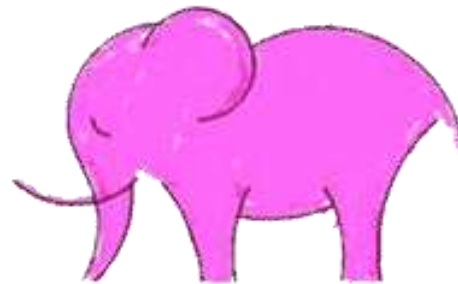
## Parameterization and experimental data

Each compound requires its own set of parameters

- T and P dependence?
- Interaction parameters?
- Do we have enough data?

*Give me four parameters, and I will draw an elephant for you; with five I will have him raise and lower his trunk and his tail*

**Friedrich Gauss (1777-1855)**



A 4-term elephant function

<http://levenspiel.com/octave/elephant.htm>

## Challenge for existing tools and algorithms

Robust and efficient flash algorithms exist for non-reactive systems

- Generic multi-phase flash using Gibbs phase stability criterion
- Used in most simulators and property packages
- e.g. Multiflash (KBC/Infochem)

But reactive systems give new challenges

- Cannot use K-values in the general case
- Reactions must be solved simultaneously or in inner loop
- Double precision may not be enough (roundoff errors)
- Are existing solutions robust?



# No predictive model exists → Specific systems must be fitted

## Example:

Extended UNIQUAC is fitted to many systems – *but far from all*

	H <sub>2</sub> O	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	NH <sub>3</sub> /NH <sub>4</sub> <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Cu <sup>+</sup>	Al <sup>3+</sup> /AlO <sub>2</sub> <sup>-</sup>	Cu <sup>2+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	NH <sub>3</sub> /NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Na <sup>+</sup>	Li <sup>+</sup>	H <sub>2</sub> O	
H <sub>2</sub> O	x																	
Li <sup>+</sup>		x																
Na <sup>+</sup>			x															
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NH <sub>3</sub> /NH <sub>4</sub> <sup>+</sup>					x													
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Al <sup>3+</sup> /AlO <sub>2</sub> <sup>-</sup>									x									
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H <sub>3</sub> PO <sub>4</sub> /H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> /HPO <sub>4</sub> <sup>2-</sup> /PO <sub>4</sub> <sup>3-</sup>	x																	
CO <sub>2</sub> /HCO <sub>3</sub> <sup>-</sup> /CO <sub>3</sub> <sup>2-</sup>	x																	
SO <sub>2</sub> /HSO <sub>3</sub> <sup>-</sup> /SO <sub>3</sub> <sup>2-</sup> /S <sub>2</sub> O <sub>5</sub> <sup>2-</sup>	x																	
OH <sup>-</sup>	x																	
NO <sub>3</sub> <sup>-</sup>	x																	
HSO <sub>4</sub> <sup>-</sup> /SO <sub>4</sub> <sup>2-</sup>	x																	
Br <sup>-</sup>	x																	
Cl <sup>-</sup>	x																	
HF/F <sup>-</sup>	x																	
Sr <sup>2+</sup>	x																	
Ba <sup>2+</sup>	x																	
Co <sup>2+</sup>	x																	
Mn <sup>2+</sup>	x																	
Fe <sup>2+</sup>	x																	
Zn <sup>2+</sup>	x																	
H <sup>+</sup>	x																	
Fe <sup>3+</sup>	x																	
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Li <sup>+</sup>	x																	
H <sub>2</sub> O	x																	

x = System fitted  
= Missing parameters



# Process simulators support many electrolyte systems today

- Examples -  
Not exhaustive list

Many PME implementations

Purpose built – high accuracy

General purpose – high applicability

<ul style="list-style-type: none"><li>• DBRAmine</li><li>• Sour PR</li></ul>	<ul style="list-style-type: none"><li>• OLI</li></ul>
<ul style="list-style-type: none"><li>• VMG gas sweetening</li><li>• BASF OASE</li><li>• ProTreat</li><li>• ChemCAD</li><li>• mNRTL</li></ul>	<ul style="list-style-type: none"><li>• Pitzer</li><li>• Extended UNIQUAC</li><li>• Electrolyte NRTL</li></ul>

Few PME implementations

Few

Compounds supported

Many

# Two options exist when your system is not supported

## 1 Extend model already implemented in your process simulator

- + Easier if possible, but ...
- ÷ Model may not be easily extensible
  - Component list not extensible
  - Physical model cannot be fitted to match experimental data
  - Involving vendor can be expensive
- ÷ Fitting electrolyte models is not simple
  - Requires a lot of experimental data
  - Labor intensive
  - Can prove impossible due to lack of control; e.g. black box model with no access to code, fitting tools, etc.

## 2 Build custom thermodynamic model

- + Always possible, but ...
- ÷ Model often needs to be build from scratch
  - Defining a model that fits the physical system well can be an expert task
  - Fitting model is time consuming
- ÷ **Model needs to be integrated in process simulator**
  - **Integrations are simulator-specific**
  - **May need reactive electrolyte flash**
  - **Handle apparent vs. true components**

Focus today

**New CAPE-OPEN standard improves support for integrating custom electrolyte models in process simulators**





# Even when a model is available, it is challenging to implement custom electrolyte models in process simulators

## Limited support for reactive systems

- **Few** simulators support a generic reactive flash for custom thermodynamic model extensions
- w/o native support for reactions and solids, the PMC must have a **reactive electrolyte flash**
  - Must be sufficiently robust and fast
  - May use cached result
- **Reactions changes mole balance (in  $\neq$  out)**
  - **Implicit assumption** of component molar balances lead to convergence errors
  - True to apparent components conversion is necessary
  - May not always be possible (e.g. when salts not present in input stream precipitate)

## True vs. Apparent components

Compound	Apparent	True
H <sub>2</sub> O	55.5	55.5
NaCl	1	0
Na <sup>+</sup>	0	1
Cl <sup>-</sup>	0	1
H <sup>+</sup>	0	1e-4
OH <sup>-</sup>	0	1e-4
Total	<b>56.5</b>	<b>57.5</b>

(in  $\neq$  out)



# What's new in the Chemicals Reaction Interface Specifications related to electrolyte simulations

- Fully compatible with 1.1 Thermodynamic and Physical Property Interfaces
  - No changes in these interfaces – only new interfaces are added
- Support returning the ratio of total number of moles before/after the reactions
  - ***ICapeThermoEquilibriumRoutinell***
  - [Chemicals Reaction Interface Specifications Chapter 5: Reactive Phase Equilibria]
- Saving of cached calculation results (to improve calculation speed)
  - ***ICapeThermoMaterialCustomData***
  - [Material Object Custom Data Interface Specifications Chapter 3.4: Interface Specifications]
- Multiple compound slates (support true and apparent components)
  - ***ICapeThermoCompoundSlates***
  - ***ICapeThermoCompoundSlateUtilities***
  - [Chemicals Reaction Interface Specifications Chapter 6: Compound Slates]



# CAPE-OPEN introduces new interfaces to support reactive electrolyte systems – reactive flash and custom data store

## **ICapeThermoEquilibriumRoutineI**

- CAPE-OPEN 1.1 Property Packages use *ICapeThermoEquilibriumRoutine* ::CalcEquilibrium() to perform flash
  - Saves the flash result for each phase on the material object in mole fractions
- As total molar flow may change, *ICapeThermoEquilibriumRoutineI* ::CalcEquilibrium() also returns:

$$reactionMoleRatio = \frac{n_{eq}}{n_{in}} = \frac{M_{in}}{M_{eq}}$$

- **Must be implemented and supported by material object (PME)**

## **ICapeThermoMaterialCustomData**

- Simultaneous chemical and phase equilibrium is computationally expensive
- By saving the result from the previous calculation, one can significantly speed up calculations
- Defines how storage can be created on the MO and used by the PP
- MOs supporting reactions **should** implement the interface – but it is not a strict requirement



# CAPE-OPEN introduces new interfaces to support reactive electrolyte systems – compound slates (true vs apparent)

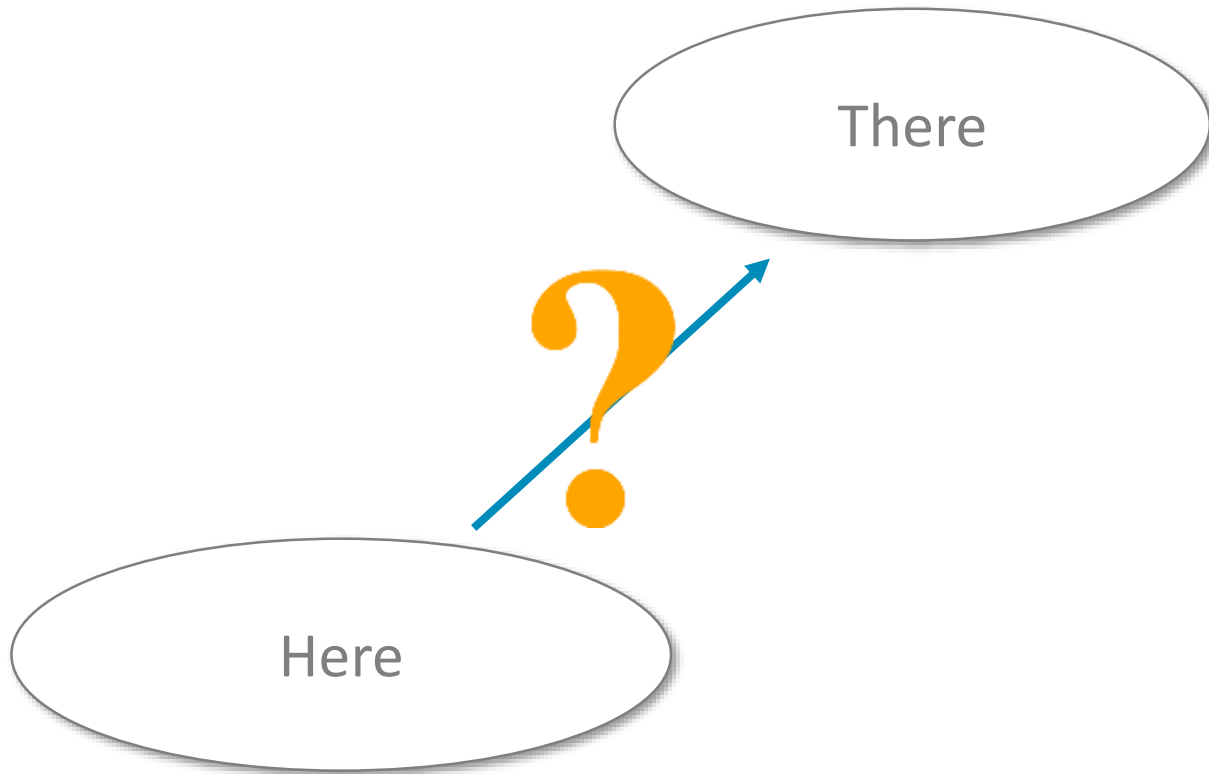
## **ICapeThermoCompoundSlates**

- All CAPE-OPEN 1.1 PPs provide their primary compound slate through *ICapeThermoCompounds*
- Additional compound slates use *ICapeThermoCompoundSlates*
- `SetActiveCompoundSlate()` is used to make a compound slate active – all compositions and properties use this compound slate
- A material object that supports multiple compound slates **must** implement support for *ICapeThermoMaterialCustomData* (requirement open for discussion)

## **ICapeThermoCompoundSlateUtilities**

- Includes a single utility function: `ConvertFractionSinglePhase()`
- Allows conversion between source and target compound slates
- May fail
- **Must** be implemented by a property package that supports multiple compound slates

# How will we drive adoption by PME vendors?



**Push**: Support PMC vendors in using new standard?

**Pull**: Create demand from customers for PME adoption?

**Other?**

Where do we focus our efforts?

# Hafnium Labs is building Epsilon, a predictive electrolyte model that will support new CAPE-OPEN interfaces

## Epsilon is a predictive electrolyte model based on novel science ...



- ✓ Based on novel science and cutting-edge computational tools & software practices
- ✓ Providing good predictions without requiring new experimental measurements
- ✓ Applicable to all systems: Solvents, ions, T, P, phases etc.
- ✓ Supports new CAPE-OPEN interfaces and integrated with leading process simulation tools
- ✓ Easy to use and interpret for both chemists and engineers

## ... and large scale quantum chemistry via our property prediction tool, Q-props

### Motivation

- Garbage in = Garbage out
- Experimental data is scarce and not always reliable
- Prediction methods are inaccurate and/or difficult

### Q-props advantages

- Unprecedented **accuracy** and **specific uncertainty**
  - Using thousands of quantum chemical (QC) calculations for each prediction
- **Easy**; no quantum chemistry expertise needed
- **Cloud-based**; no in-house compute needed
- **Pay-per-use**; no licenses

### Preparing for closed beta (demo available)

- Reach out if you're interested

**H2020 call: "Adopting materials modelling to challenges in manufacturing processes"**  
**Deadline: 22/1/19 – last H2020 call relevant to process simulation. Interested in collaborations**



# Summary

- Many electrolyte implementations **exist** and can be **extended** to other systems
- But **custom thermodynamic models** are frequently required
- New CAPE-OPEN interfaces give **better support for reactive electrolyte systems**
- CAPE-OPEN community needs to find ways to **drive vendor adoption**
- Hafnium Labs will **adopt the new standard** with Epsilon, our predictive electrolyte EoS