OCT.14.2020

AVEVA™ Thermodynamics

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Agenda

1. **Roadmap Overview**
2. **Highlighted topics**
   - gE-type mixing rules (such as PSRK) and association theories (such as ePC-SAFT and CPA) for modeling high pressure chemical processes
   - Combination of reaction equilibrium and phase equilibrium (including Electrolyte) making the most of Fluid Feature on AVEVA Process Simulation
   - Solid-fluid in equilibrium and its usage for the Chemical industry, Prediction of solid and gas hydrate occurrence in the Oil & Gas industry
   - Usage of newly emerging technologies such as quantum chemistry calculation and AI
3. Further discussions

AVEVA

Roadmap Overview of AVEVA™ Thermodynamics

Customer Benefits

Primarily Goals	*Key highlights*

High **Accuracy** and Wide Range of **Applicable Substances**	• Short-term (being delivered): **Chemicals**
	  • Methods for Chemicals (SRKH, LK, HF-thermo, e-NRTL)
	  • User-added thermo interface
	  • Basic solid features for Chemicals
	• **Extension for Chemicals**
	  • Electrolyte with species propagation and databank
	  • Method for high pressure non-ideal systems (PSRK, CPA, ePC-SAFT)
	  • Polymers methods and architecture
	  • Extended solid feature for Chemicals
	• **Oil and gas**
	  • Basic refinery features on AVEVA™ Process Simulation
	  • Solid for upstream, hydrate (applicable to RTO), asphaltene

Ready for **EO** and **Dynamic**, on **Cloud**	• **Fast and robust VLLE** • Equilibrium algorithm improvements including those for a large number of components • Making the most of the new computer technologies such as multi-CPU/multi-thread calculations
Ease of use	• Supportive features for thermo merger /converting • Thermo dynamic diagrams: Ternary diagrams, Binary LLE, Advanced Phase Envelopes • Interface with external manage tools like DPP and DDBSP • Native REGRESS on AVEVA Process Simulation which covers reaction constants

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Overview of Roadmap of AVEVA Thermodynamics

	Delivered	In development	Future (long range)
Goals	**AVEVA Process Simulation (SimCentral)** • Chemical Process Simulation **AVEVA Dynamic Simulation (Dynsim)** • Key items for OTS projects **AVEVA PRO/II Simulation(PRO/Ii)** • Defect fixing	**AVEVA Process Simulation (SimCentral)** • **Chemical Process Simulation Improvements** • Committed key items **AVEVA Dynamic Simulation (Dynsim)** • **Key items for OTS projects** **AVEVA PRO/II Simulation(PRO/II)** • Committed key items	**AVEVA Process Simulation (SimCentral)** • **Chemical Process Simulation Improvements** • **Downstream, Upstream Process Simulation** **AVEVA Dynamic Simulation (Dynsim)** • **Key items for OTS projects** **AVEVA PRO/II Simulation(PRO/II)** • Committed key items

Initiatives	**AVEVA Process Simulation (SimCentral)**
	• **Thermo Methods**
	  • **Major LACT and EOS(SRK, PR, SRKM with the latest alpha and BIPs), Hayden O'Connell, Gamma Phi, Specific Electrolyte**
	• **Thermo Diagrams**
	  • **Heat Curve Diagrams, BVLE Diagrams**
	• **Thermo Data**
	  • **Integration with TDM, DIPPR Public Database, UNIFAC Data Manage on TDM, Search by CARN**
	  • **Extended temperature dependency equations**
	• **Thermo Architecture and Flash**
	  • **Fluid Reaction Models , Fluid Concept combines Method, Data, Chemistry**
	  • **Thread Safety for multi core solution, VLE ,VLLE, VLWE (beta)**
	AVEVA Dynamic Simulation (Dynsim)
	• **Extensive support on use of Local Thermo**
	AVEVA PRO/II Simulation (PRO/II
	• **BWRS 11 Parameters**
		AVEVA Process Simulation (SimCentral)
		• **Thermo Methods**: **SRK Huron-Vidal (SRKH)**, **LK**, **e-NRTL**, HF-Thermo, **Transport prop. mixing rules**, IF97 Transport prop.
		• **Thermo Diagrams**
		  • **Liquid-Liquid Diagrams, Ternary Diagrams**
		• **Thermo Data Override (NRTL, Pure Comp. and Henry)**
		• **Integration/Interface**
		  • **User Added Thermo Interface**
		  • Thermo Access Interface
		  • **Improve PPDX import/export**
		  • **Data export for HTRI**
		• **Thermo Data**: FILL options
		• **Thermo Architecture and Flash**
		  • VLLE Update
		  • **Non-Equilibrium Solids**
		  • **Electrolyte Precipitates**
		AVEVA Dynamic Simulation (Dynsim)
		• Fast and robust VLLE and other supports for OTS projects
		AVEVA PRO/II Simulation(PRO/II)
		• **HF-Thermo**
		• **REFPROP 10 interface**
			AVEVA Process Simulation (SimCentral)
			• **Thermo Methods**
			  • EOS: PSRK, CPA, BWRS, PC-SAFT
			  • RIPs, Amine Methods, Wax and asphaltene model
			• **Thermo Diagrams**
			  • Unified Fluid Editor with REGRESS
			  • Phase Envelope Diagrams
			• **Integration/Interface**
			  • Interface with Spiral Crude database
			  • Assay/feed data import from external sources
			• **Thermo Data**
			  • Electrolyte Component (Species) and Reaction Data
			  • More FILL options
			  • Heavy Oil, Water and gas Solubility, new API methods
			• **Thermo Architecture and Flash**
			  • Distillation curves, Crude Assay Characterization
			  • Updated hydrate and solid
			  • Polymer
			AVEVA Dynamic Simulation (Dynsim)
			• Usage of new computer architecture and technologies
			AVEVA PRO/II Simulation(PRO/II)
			• Committed key items

Yearly update of **DIPPR, UNIFAC databanks**

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New Features

Electrolyte NRTL on AVEVA Process Simulation

Objectives/Background

- Chemical users need to simulate processes such as sulfuric acid production
- Chen's Electrolyte NRTL (e-NRTL) has been used by many chemical users who like to keep using it.

Solutions

- Implement e-NRTL on AVEVA Process Simulation
- Enable to apply e-NRTL to activity coefficient of species
- At the first version, databank (scalable) should have a small set of parameters
- In the future, REGRESS should have access to not only Pitzer parameters but also reaction constants

Delivery

- Implemented on AVEVA Process Simulation 4.3

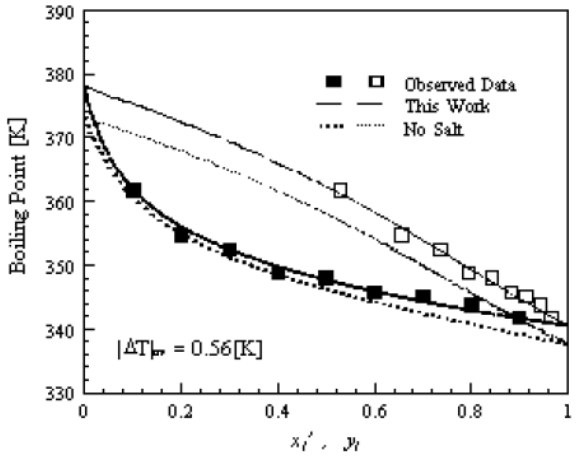
$$\ln\gamma_m = \frac{\sum_j X_j G_{jm}\tau_{jm}}{\sum_k X_k G_{km}} + \sum_{m'} \frac{X_{m'} G_{mm'}}{\sum_k X_k G_{km'}} \left(\tau_{mm'} - \frac{\sum_k X_k G_{km'}\tau_{km'}}{\sum_k X_k G_{km'}} \right)$$

Non-electrolyte term

$$+ \sum_c \sum_{a'} \frac{X_{a'}}{\sum_{a''} X_{a''}} \frac{X_c G_{mc,a'c}}{\sum_k X_k G_{kc,a'c}} \left(\tau_{mc,a'c} - \frac{\sum_k X_k G_{kc,a'c}\tau_{kc,a'c}}{\sum_k X_k G_{kc,a'c}} \right)$$

$$+ \sum_a \sum_{c'} \frac{X_{c'}}{\sum_{c''} X_{c''}} \frac{X_a G_{ma,c'a}}{\sum_k X_k G_{ka,c'a}} \left(\tau_{ma,c'a} - \frac{\sum_k X_k G_{ka,c'a}\tau_{ka,c'a}}{\sum_k X_k G_{ka,c'a}} \right)$$

Electrolyte terms



Methanol-water-$CaCl_2$ system at 101.3kPa

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New Features

Transport Property Mixing Rules on AVEVA Process Simulation

Objectives/Background

- Accurately predict transport properties which give impact on sizing of heat exchangers and mass-transfer devices such as distillation columns.

Challenges

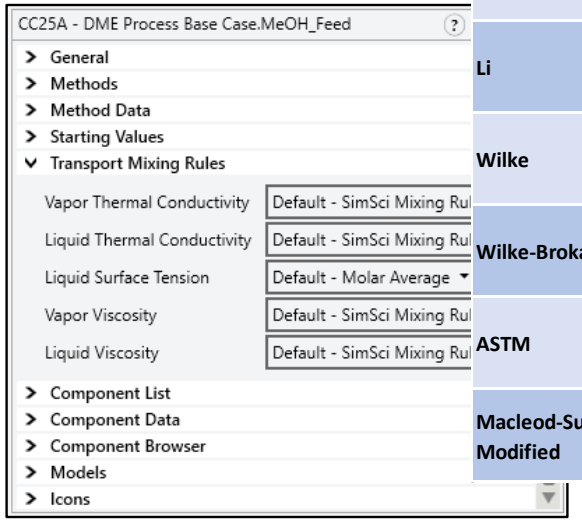
- High non-linearity with respect to composition; simple molar average does not work

Solutions

- Equip AVEVA Process Simulation with advanced mixing rules; Fluid Editor now has section to set
  - Vapor Thermal Conductivity, λ_V
  - Liquid Thermal Conductivity, λ_L
  - Vapor Viscosity, η_V
  - Liquid Viscosity, η_L
  - Surface Tension (σ)

Delivery Plan

- AVEVA Process Simulation Version 5.0 (October 2020)
- (Pressure correction and TRAPP are proposed for 2021-2022)



Snapshot of AVEVA Process Simulation 5.0

Name	Example equation	λV	λL	ηV	ηL	σ
SimSci	$\eta_m = \left[\sum_i x_i \sqrt[3]{\eta_i}\right]^3$	✓✓	✓✓	✓✓	✓✓	
Molar Average	$P_m = \sum_i x_i P_i$	✓	✓	✓	✓	✓✓
Log Molar Average	$\ln(P_m) = \sum_i x_i * \ln(P_i)$	✓	✓	✓	✓	✓
Power Molar Average	$(P_m)^r = \sum_i x_i (P_i)^r$	✓		✓	✓	✓
Vredeveld (same as Power Molar Average)			✓			
Lambda	$\lambda_m = 0.5 \cdot \left(\sum_i x_i \cdot \lambda_i + \frac{1}{\sum_i \frac{x_i}{\lambda_i}}\right)$	✓				
Wassijewa-Mason-Saxena	$\lambda_m = \sum_i \frac{x_i \lambda_i}{\sum_i x_i F_{ij}}$ $F_{ij} = \frac{\left[1 + \sqrt{\frac{\eta_i}{\eta_j}} \cdot \sqrt{\frac{x_j}{x_i}}\right]^2}{\sqrt{8\left(1 + \frac{x_i}{x_j}\right)}}$	✓				
DIPPR	$\sigma_m = \left[\frac{\sum_i x_i V_i \sqrt[4]{\sigma_i}}{\sum_i x_i V_i}\right]^4$		✓			✓
Li	$\lambda_m = \sum_i \sum_j \Phi_i \Phi_j \lambda_{ij}$,		✓			
Wilke	$\eta_m = \sum_i \frac{x_i \eta_i}{\sum_j x_j F_{ij}}$ $F_{ij} = \frac{\left[1 + \sqrt{\frac{\eta_i}{\eta_j}} \cdot \sqrt{\frac{x_j}{x_i}}\right]^2}{\sqrt{8\left(1 + \frac{x_i}{x_j}\right)}}$			✓		
Wilke-Brokaw				✓		
ASTM	$log_{10}(log_{10}(1000\eta_m + f)) = \sum_i w_i \, log_{10}(log_{10}(1000\eta_i + f))$				✓	
Macleod-Sugden Modified	$(\sigma_m)^{0.25} = \sum_i \frac{V_i x_i (\sigma_i)^{0.25}}{V_i}$					✓

✓✓ = Default

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New Features

Themro Override on AVEVA™ Process Simulation

Objectives/Background

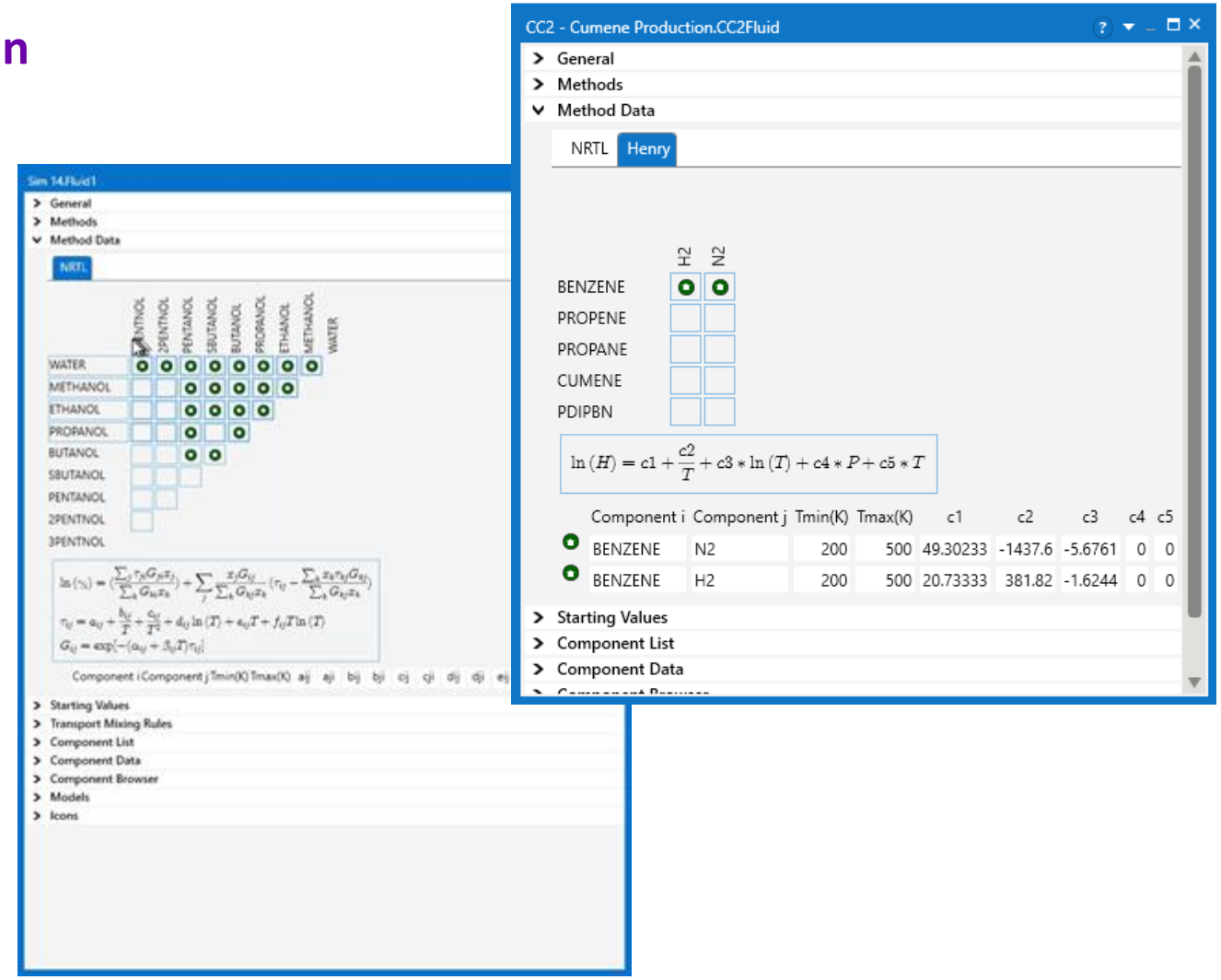
- Quickly see effect thermo parameter changes on the simulation.

Solutions

- Fluid Editor contains thermo data to override TDM Library (Updating lb1 and lb2 files no longer required.)
- Thermodynamics specialists may share Fluid with other users in their company.

Delivery Plan

- NRTL binary data override: (done)
- Pure and Henry's parameters: (done)
- Transport properties: Version 5.0 (Oct 2020)
- More methods: after Version 5.0 (Oct 2020)



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New Features

API for Interface with 3rd Party Thermo Package

Objectives/Background

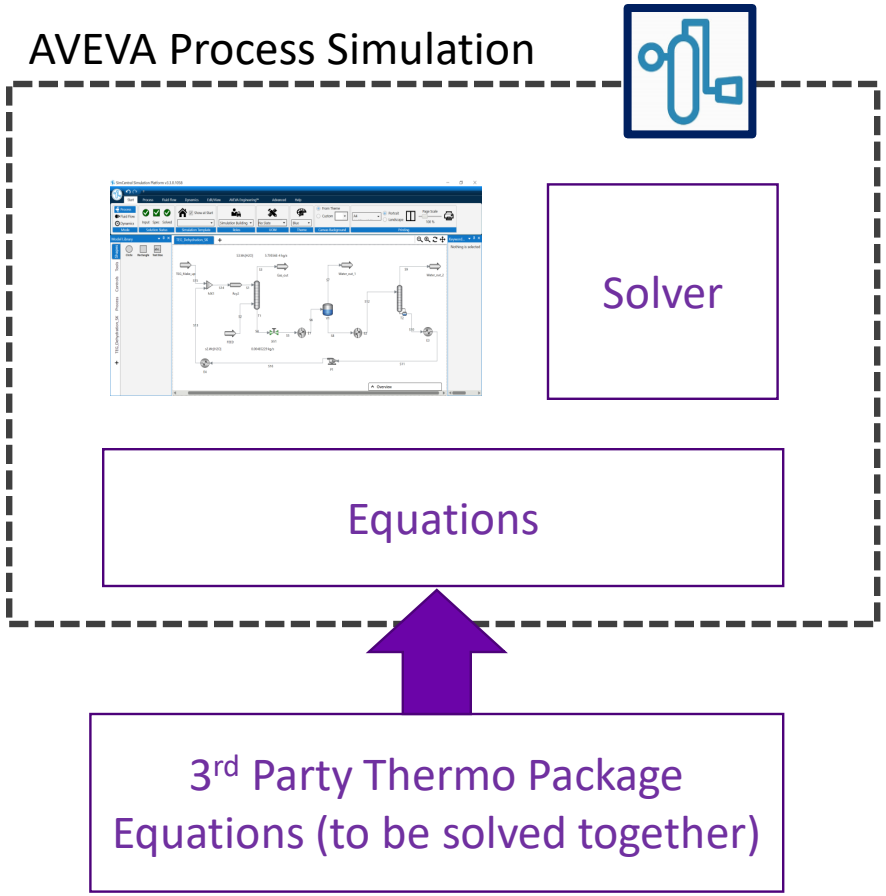
- Some customers have their proprietary thermo engines as well as data, which most of their process simulations need to use.
- Some 3rd party thermo engines are well accepted by the market, which our customers want to use in process simulation.

Solutions

- Create standard APIs on AVEVA Process Simulation to access external thermo engines.

Delivery Plan

- The 1st version was delivered with AVEVA Process Simulation 4.2
- Enhancements are being planed in 2020-2021



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New Features

User-defined UNIFAC Groups

Objectives/Background

- Large chemical companies have their own UNIFAC parameter values for ranges of components of their interests.
- The users' values are better than versatile values in the range, and need to be applied for process simulation. (Interpolation with respect to molecular structure)

Challenges

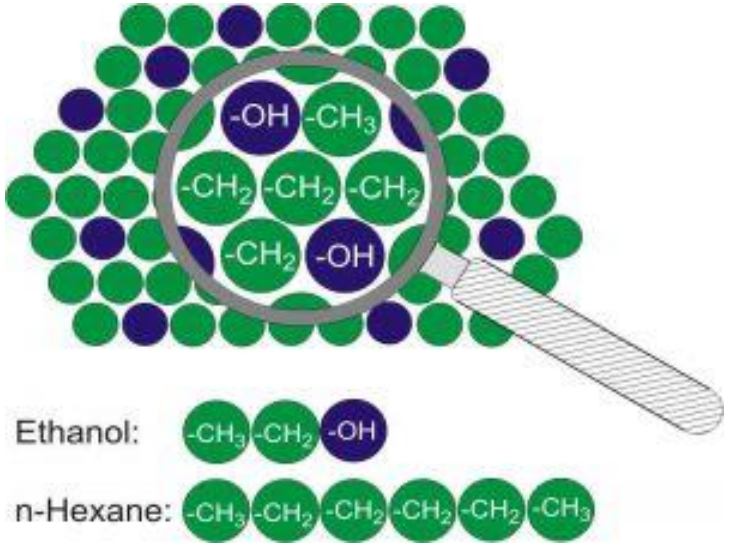
- Currently our products do not allow to modify or add UNIFAC parameters on GUI. (Tedious procedure through xml-files is needed)

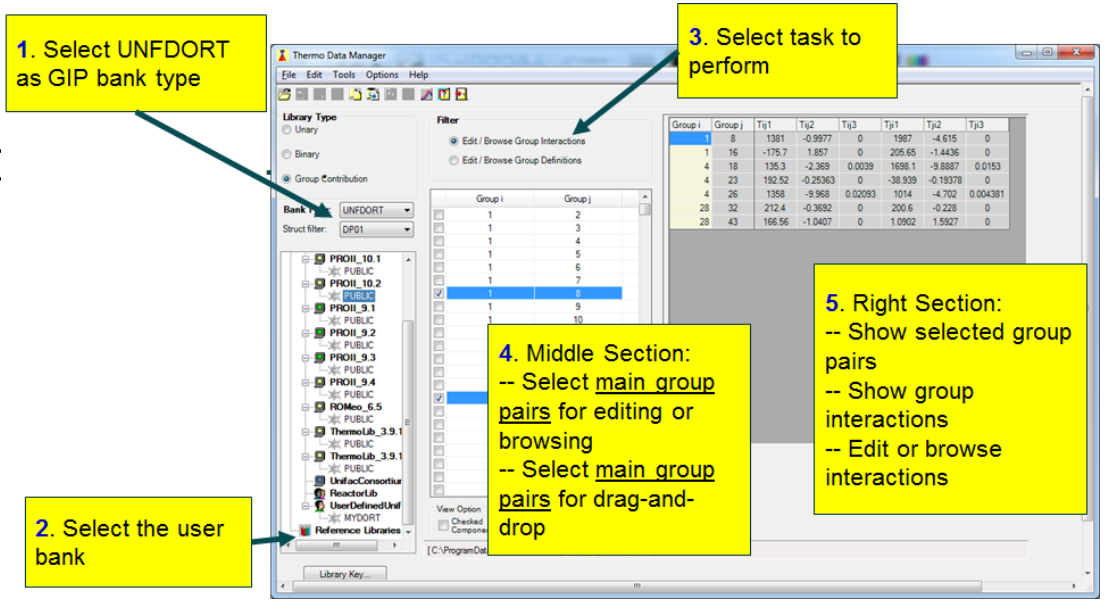
Solutions

- Equip TDM with GUI for add/edit UNIFAC group, Group parameter values, and group-group interaction parameters.

Status and plan

- Done (2019)





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In Progress

Robust and fast VLLE and VLWE

Objectives/Background

- Design of CDU and azeotropic distillation requires robustly solving VLWE and VLLE respectively on AVEVA Process Simulation
- OTS of CDU and azeotropic distillation requires robustly solving VLWE and VLLE respectively on AVEVA Dynamic Simulation

Challenges

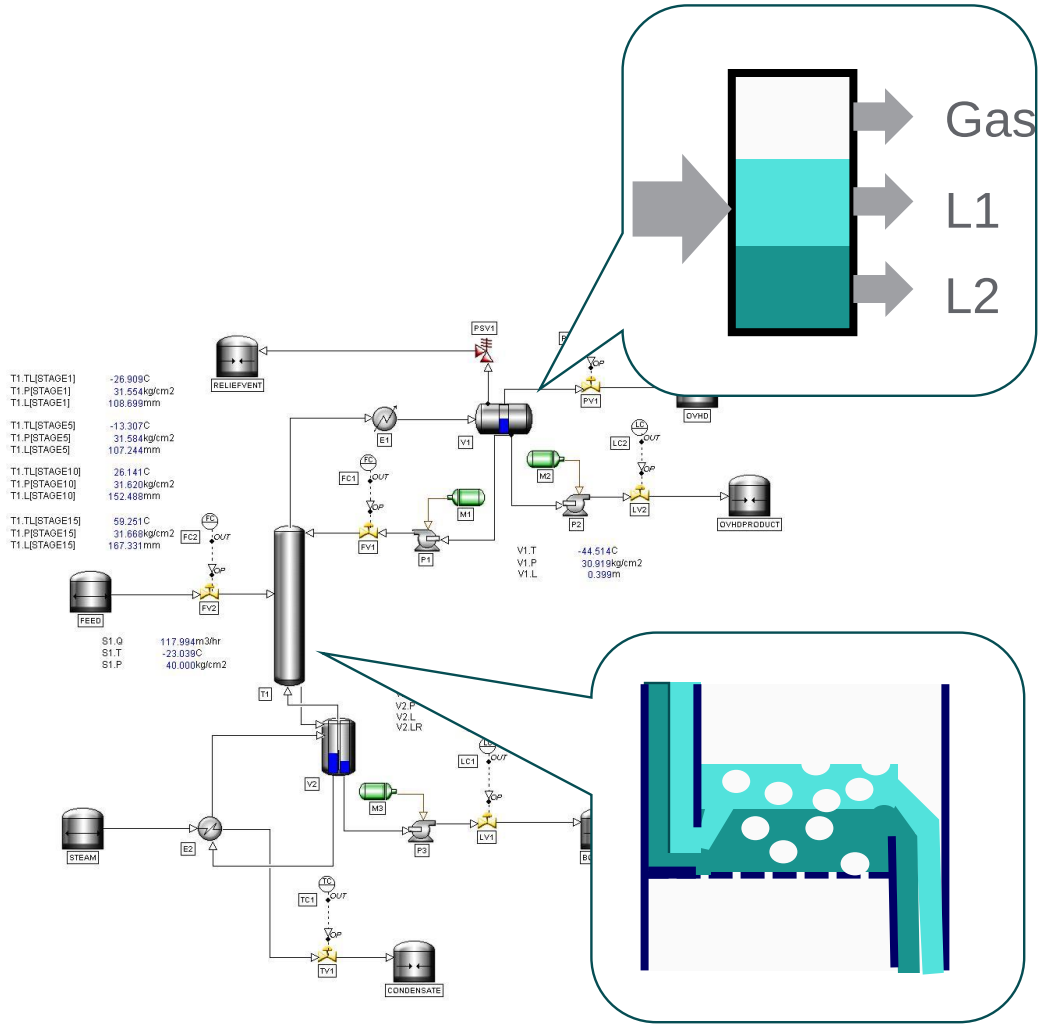
- Each phase may appear and disappear depending on conditions

Solution

- New flash algorithms which works well on open-form architecture

Status and plan

- VLLE on AVEVA Process Simulation is being improved. Multiple initiatives are in progress.
- AVEVA Dynamic Simulation is also equipped with an improved VLLE algorithm in 2020



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In Progress

Interface APIs for 3rd Party Thermodynamic Data Management/Regression Programs

Objectives/Background

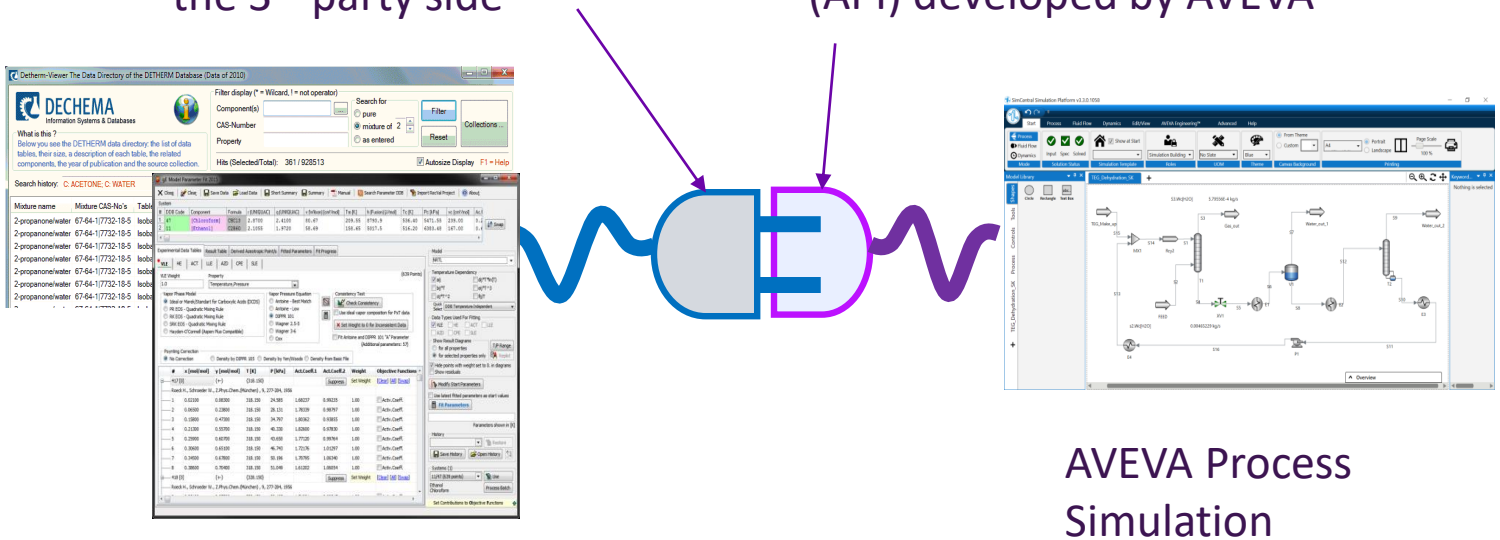
- Enables users to manage/ determine parameters of thermodynamic methods in AVEVA Process Simulation applying 3rd party tools which are widely accepted in the market

Solution

- Create APIs of AVEVA Process Simulation so that the 3rd party tool has access to thermodynamic calculation in AVAVE Process Simulator

Delivery Plan

- The APIs will be coming with AVEVA Process Simulation in early next year



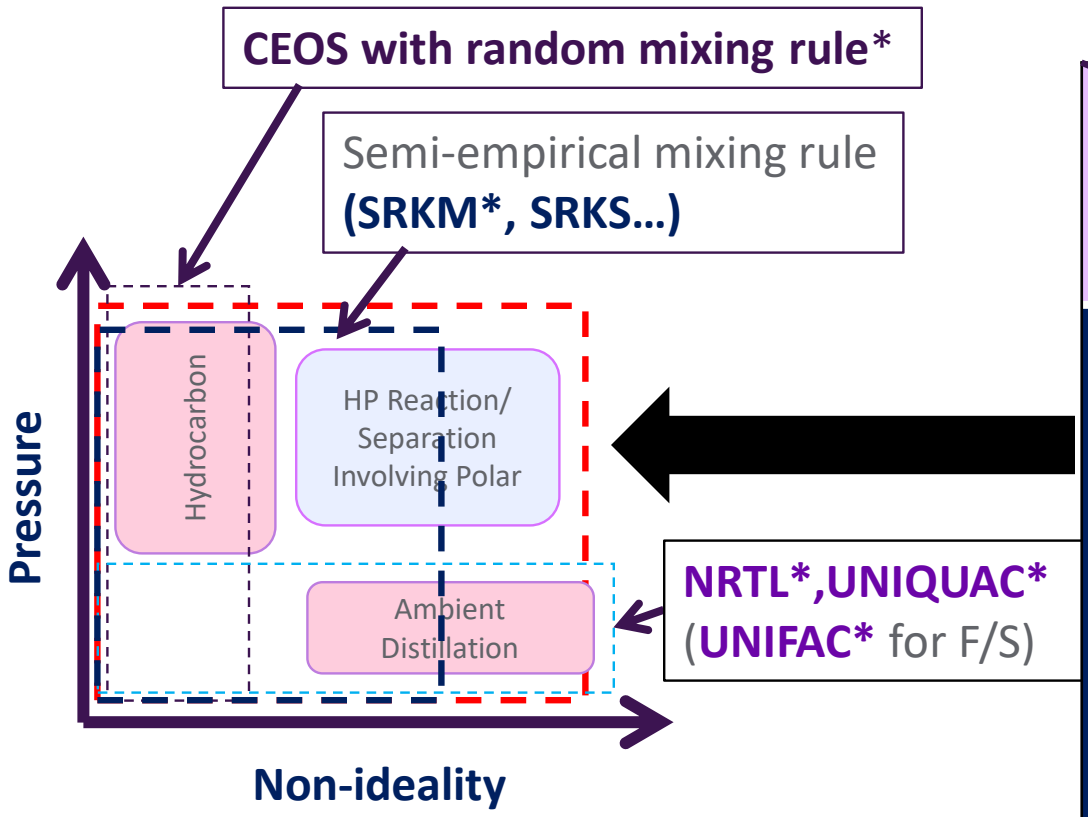
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Agenda

1. **Roadmap Overview**
2. **Highlighted topics**
   - gE-type mixing rules (such as PSRK) and association theories (such as ePC-SAFT and CPA) for modeling high pressure chemical processes
   - Combination of reaction equilibrium and phase equilibrium (including Electrolyte) making the most of Fluid Feature on AVEVA Process Simulation
   - Solid-fluid in equilibrium and its usage for the Chemical industry, Prediction of solid and gas hydrate occurrence in the Oil & Gas industry
   - Usage of newly emerging technologies such as quantum chemistry calculation and AI
3. Further discussions

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Thermo Methods for Non-Ideal Mixtures



Schematic Diagram for Applicable Range of Thermo Methods

Currently Published Methods for High Pressure Non-ideal Mixtures

		Type of Equation of State	
		Cubic	Non-Cubic
Type of non-ideality expression	gE-type	Hüron-Vidal* PSRK**(MHV-1), VTPR****, MHV-2, Wang-Sandler Twu-Bluck-Coon	(none)
	Association	Cubic Plus Association (CPA)***	PC-SAFT***

*:Already implemented in AVEVA Process Simulation
**:Discussed in the next slide
***:In the roadmap
****:To be discussed

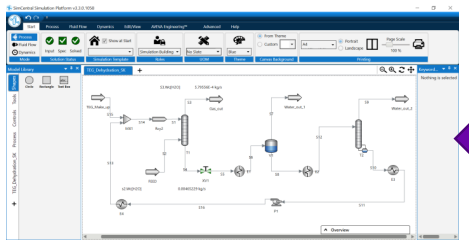
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Use of SRK+ Holderbaum-Gmehling Mixing Rule (SRK-HG)

Mixing Rule of PSRK. Often uses g^E of NRTL and its parameters determined using experimental data.

Process Simulations

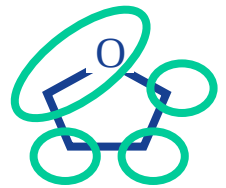


Holderbaum-Gmehling (HG) Mixing Rule*

$$\frac{a_m}{b_m} = \frac{g^E}{C} + \frac{RT}{C}\sum_i x_i \ln\left(\frac{b_m}{b_i}\right) + \sum_i^{Nc} \frac{a_i}{b_i} x_i$$

g^E of UNIFAC

Molecular Structure



g^E of NRTL**

$$g^E = \sum_i x_i \frac{\sum_j x_j G_{ji} \tau_{ji}}{\sum_k x_k G_{ki}}$$

$$G_{ji} = exp(-\alpha_{ji}\tau_{ji})$$

$$\alpha_{ii} = 0, \tau_{ii} = 0$$

UNIFAC FILL

NRTL Bank

Experimental data

PSRK (SRK-HG + UNIFAC g^E)

SRK-HG + g^E of NRTL

- **AVEVA implemented PSRK (g^E of UNIFAC) in AVEVA PRO/II Simulation and AVEVA Dynamic Simulation**
- **Will be implementing SRK-HG + g^E of NRTL also in AVEVA Process Simulation**

* Holderbaum ,T and Gmehling,J.; Fluid Phase Equilibria, 70,2-3, (1991), 251-265

** Renon H., Prausnitz J. M.; AIChE J., 14(1), S.135–144, 1968

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Fill Options for BIPs on AVEVA Process Simulation

FILL OPTION	Target pairs	Methods	Industry	Implementation timing
Water Correlation	water-hydrocarbon (or petro) pairs	CEOS	Common	Phase-1
MW Correlation	light gas-hydrocarbon(or petro) pairs	CEOS	Common	Phase-1
H2 Correlation	hydrogen-hydrocarbon(or petro) n pairs	CEOS	Common	Phase-1
Sulfur Correlation	Sulfur components-hydrocarbon(or petro) pairs	CEOS	Oil/gas	Phase-2
Glycol Correlation	glycol-petro pairs (invented by AVEVA)	CEOS	Oil/gas	Phase-2
Methanol Correlation	methanol-hydrocarbon(or petro) pairs	CEOS	Oil/gas	Phase-2
Azeotrope Fill	all component pairs which has azeotrope	NRTL, UNIQUAC	Chemical	done
Fill from infinite dilute activiy coefficient	component pairs which has infinite dilution activity coeff.	NRTL, UNIQUAC	Chemical	at the timing of REGRESS
Fill from mutual solubility	component pairs which has mutual solubility	NRTL, UNIQUAC	Chemical	at the timing of REGRESS
UNIFAC Fill for LACT	All the component pairs, of which components have UNIFAC structure, and petroleum comp. (DDBST UNIFAC Consortium members should be able to apply Consortium databank)	NRTL, UNIQUAC	Chemical	Phase-1
FILL from RS and FH		NRTL, UNIQUAC	Chemical	(non, scarcely used)
C1/C2 GOR	C1/C2-other hydrocarbons(or petro) pairs	CEOS	Oil/gas	(non, PPR78 is better)
Modified Gao	C1/C2/C3-other hydrocarbons(or petro) pairs	CEOS	Oil/gas	(non, PPR78 is better)
Modified Chueh-Prausnitz	hydrocarbon(or petro) -hydrocarbon(or petro)	CEOS	Oil/gas	Phase-1
PPR78 Fill Option	hydrocarbon(or petro) -hydrocarbon(or petro)	CEOS	Oil/gas	Phase-2
UNIFAC FILL for EOS	Invented by AVEVA	SRKM, SRKH	Chemical	(after PSRK)

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PC-SAFT Update

Objectives

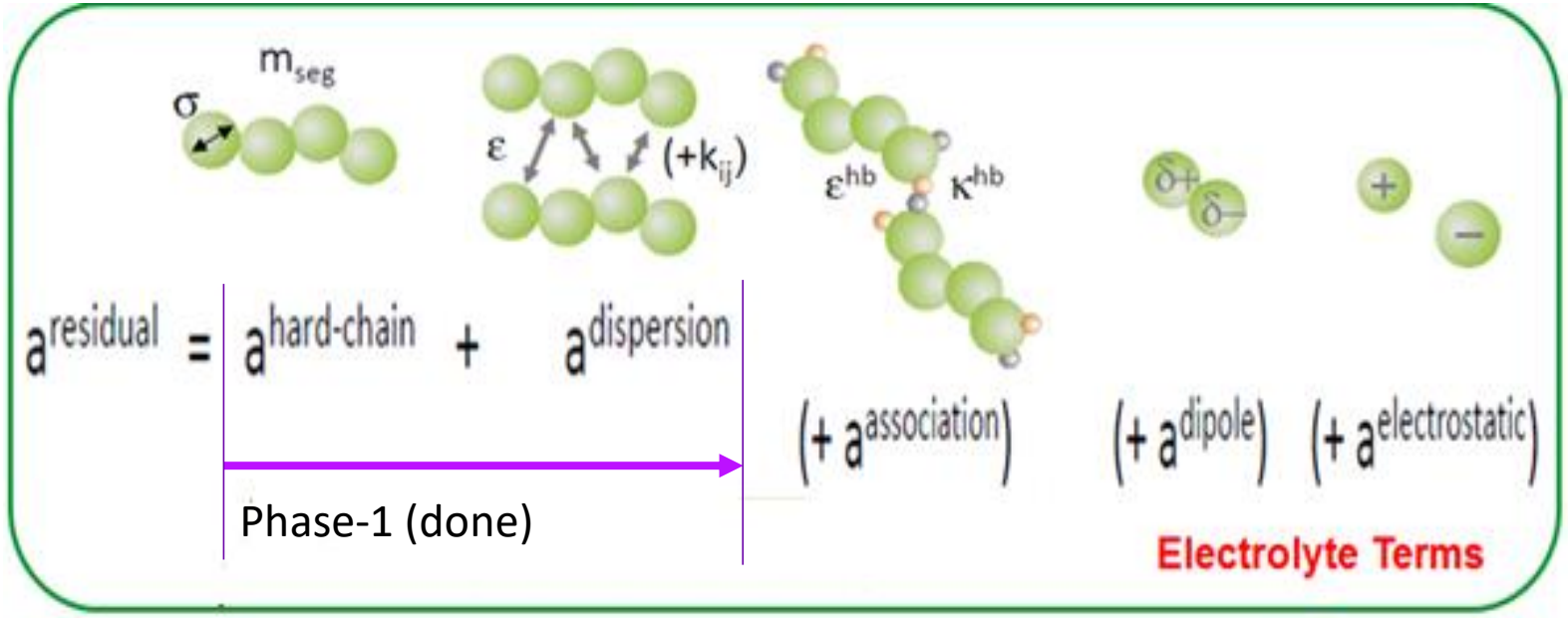
- Establish reliable thermo model to cover mixtures with polar and/or electrolyte polymer at elevated pressures

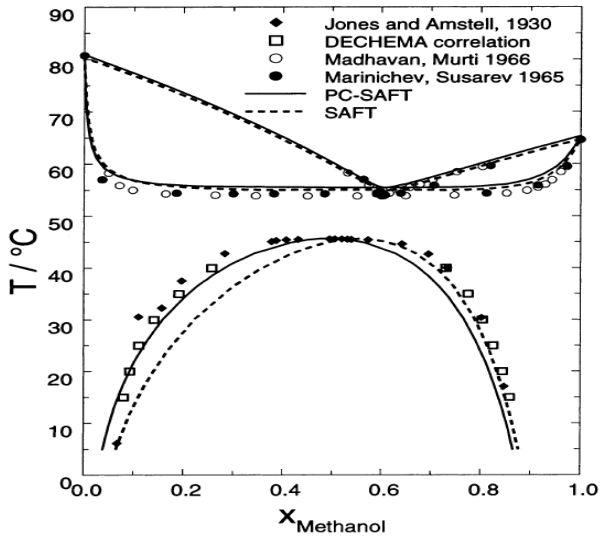
Solution

- Add association term for chemical application
- Add electrolyte terms for ions
- Mixing rule for copolymers

Status and plan

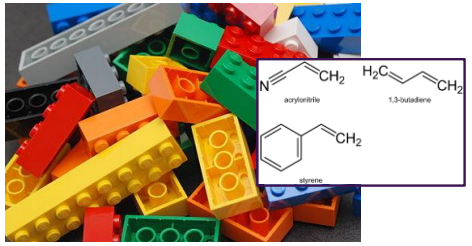
- Collaboration with Dortmund Technical University is **on-going**
- Implementation on SimCentral is being discussed





Methanol-Cyclohexane system

Polymers



Butylaminoethyl Methacrylate Copolymer

(http://www.goodguide.com/ingredients/165406-butylaminoethyl-methacrylate-copolymer-ingredient-information-reviews)

ABS resin





SBR resin

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AVEVA Invests in Improving Electrolyte PC-SAFT of TU Dortmund

Original Debye-Huckel (1923)



PHYSIKALISCHE ZEITSCHRIFT

No. 9. 1. Mai 1923. Redaktionsschluß für No. 11 am 10. Mai 1923. 24. Jahrgang.

INHALT:

Originalmitteilungen:
P. Debye u. E. Hückel, Zur Theorie der Elektrolyte. S. 185.

Vorlesungsverzeichnis für das Sommersemester 1923. S. 206.
Personalien. S. 208.

ORIGINALMITTEILUNGEN.

Zur Theorie der Elektrolyte.

I. Gefrierpunktserniedrigung und verwandte Erscheinungen.

Von P. Debye und E. Hückel[1]).

§ 1. Einleitung.

Bekanntlich deutet die Arrheniussche Dissoziationshypothese die bei den Elektrolytlösungen beobachteten abnormal großen Werte von osmotischem Druck, Gefrierpunktserniedrigung usw., durch die Existenz freier Ionen und der damit Hand in Hand der Einzelteilc

hiermit eingeführte „osmotische Koeffizient" f_0, unabhängig von jeder Theorie, jene Abweichungen messen soll und als Funktion von Konzentration, Druck und Temperatur beobachtbar ist. In Wirklichkeit beziehen sich solche Beobachtungen nicht unmittelbar auf den osmotischen Druck selber, sondern auf Gefrierpunktserniedrigung, bzw. Siedepunktserhöhung, welche beide aus thermodynamischen Gründen mit Hilfe desselben osmotischen Koeffizienten f_0 aus ihren nach dem van't Hoffschen Gesetz für vollkommene Dissoziation folgenden Grenzwerten ableitbar sind.

AVEVA Solutions Your Industry Resources Services & Support

PRESS RELEASE

AVEVA ANNOUNCES WINNERS OF FIRST UNIVERSITY RESEARCH AND DEVELOPMENT PROGRAMME

March 27, 2018

TU Dortmund University and West Virginia University were each awarded research funds to focus on next generation engineering simulation capabilities

AVEVA, a global leader in engineering and industrial software, today announced the selection of the first winners of its university research programme. Awards will be granted to TU Dortmund and West Virginia Universities to fund research programmes tied to engineering design and simulation. Winners were selected from 20 submittals. Funds will be used for research that provides proof of concepts, demonstrations of feasibility and related activities.

"Deepening our relationships with the academic community is a major priority for AVEVA as it enables Research and Development collaboration in key areas of our business, including machine learning, analytics, product speed and statistical confidence, among other attributes," said Dr. Ravi Gopinath, COO at AVEVA. "As AVEVA continues to advance how industrial and infrastructure organisations embrace a digital twin strategy to model and optimise engineering processes, we are increasingly building partnerships with the academic community to invest in tomorrow's problems today."

"We are very pleased to have been selected as a first-year recipient of AVEVA's Research and Development programme," said Professor Gabriele Sadowski, Chair of Thermodynamics at Technical University (TU) Dortmund. "We will apply and improve the ePC-SAFT model within the Unified Simulation Platform (SimCentral), which will lead to faster and more accurate thermodynamic results. Having a single simulator for the entire life cycle of a process fascinates us."



Professor Gabriele Sadowski,
Technical University (TU) Dortmund,
award winner



Professor Christoph Held,
Technical University (TU) Dortmund,
award winner

ePC-SAFT is equipped with a Helmholtz energy term derived in the original paper of Debye-Huckel which considers the size of ions; LiCl is distinguished from NaCl.
(The currently well-known Debye-Huckel is a (over) simplified version which ignores effects of the size of ions.)

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Overview of Modeling Acid Gas Removal System using ePC-SAFT

Combination of reaction equilibrium model and reaction equilibrium

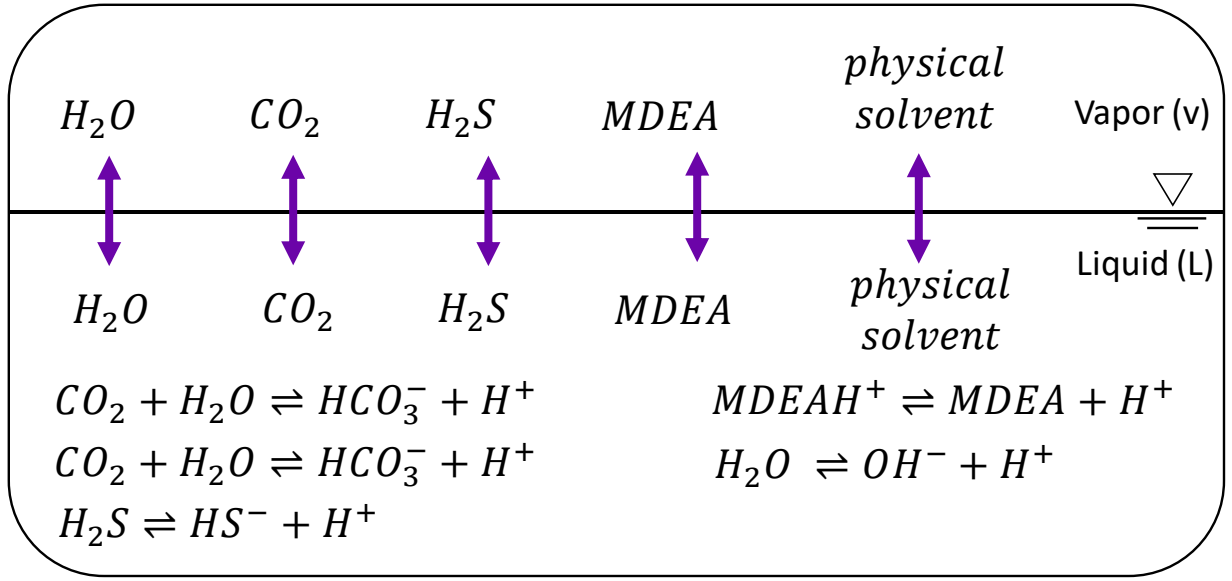
- Equilibrium conditions
  - Pressure: $P^L = P^V$
  - Temperature: $T^L = T^V$
  - Physical (phase)equilibrium:

$$x_i^L \cdot \varphi_i^L = x_i^V \cdot \varphi_i^V$$

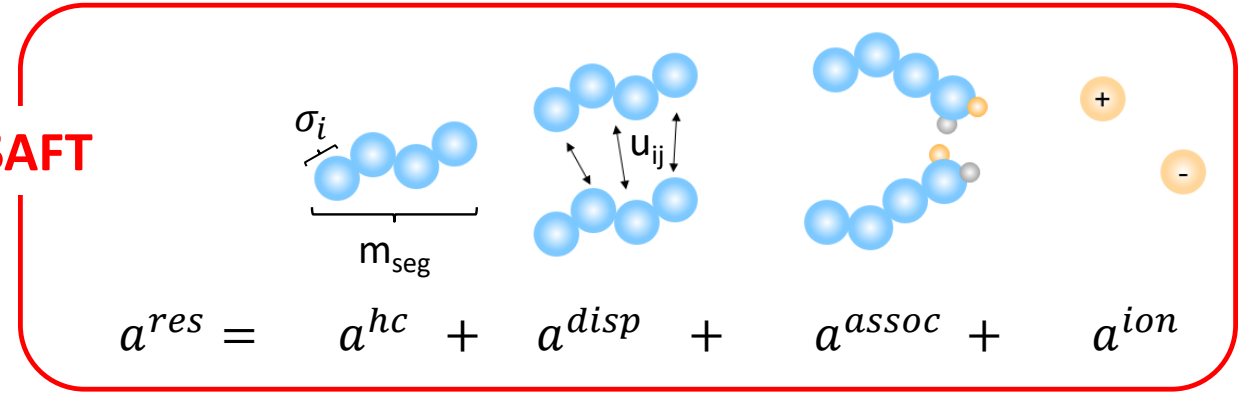
  - Chemical (reaction) equilibrium for A+B=C+D:

$$K_{th} = \prod_i a_i^{\nu_i} = \frac{a_C * a_D}{a_A * a_B}$$

$$a_i = x_i \cdot \gamma_i$$



ePC-SAFT



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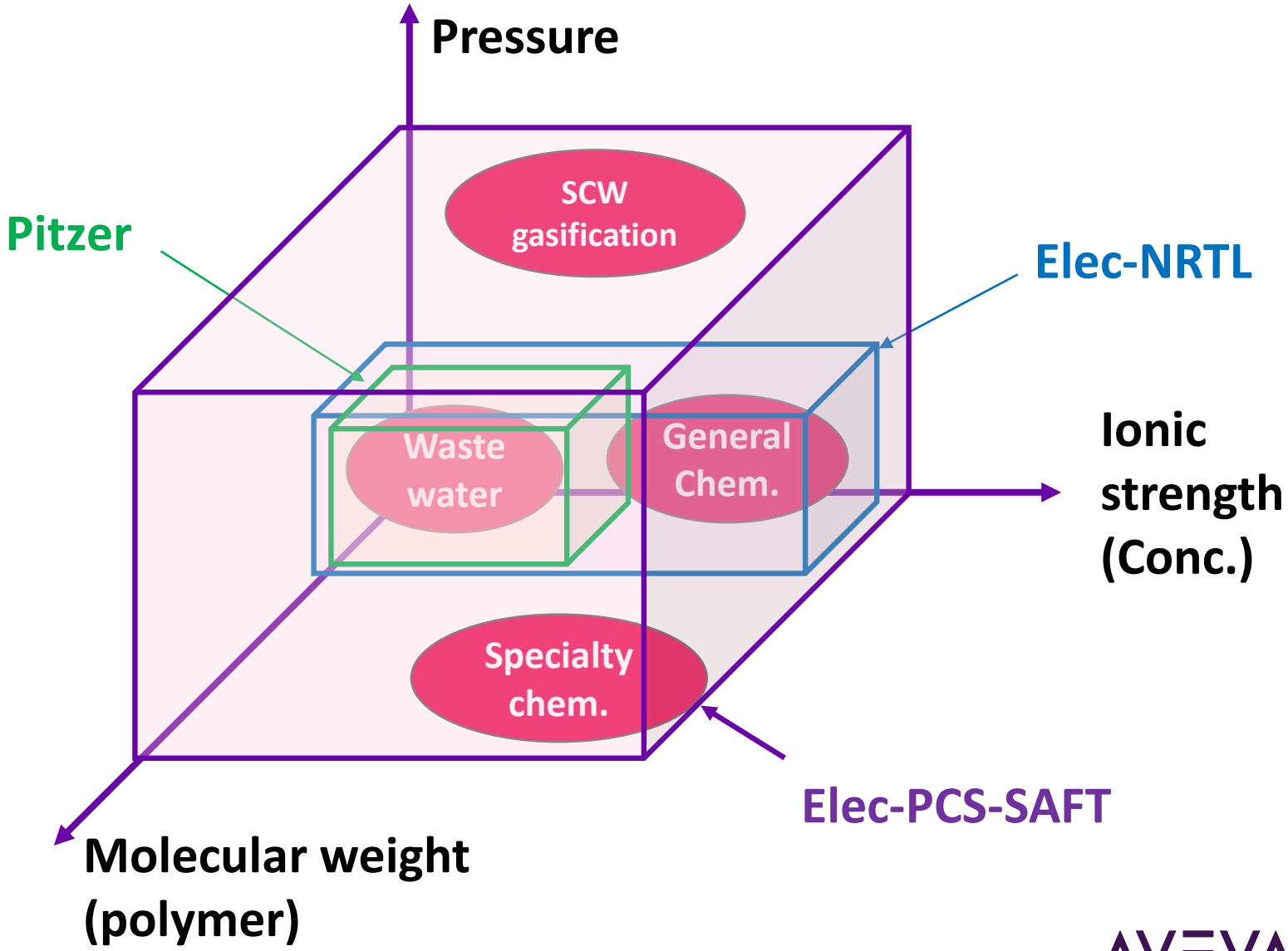
Coverage of Each Electrolyte Method for Expected Applications

- Bosen and Engels (Done)

Pitzer
- Ionic strength: up to 10
- Aqueous electrolyte
- Low to medium press.
- Monomer

Elec. NRTL (done)
- Covers very high ionic strength
- Mixed solvent
- Low to medium press.
- Monomer

Elec.PC-SAFT(proposed)
- Covers very high ionic strength
- Mixed solvent
- Covers high pressure
- Covers elec. polymers



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Three Phase Electrolyte Plan

Phase 1 – Proof of Approach (Complete)

Feature	Status
Prove Fluid Reaction Model approach.	*Complete*
Deliver H2SO4 components and reaction fluid.	*Complete*
Allow customers to extend to their own systems	*Complete*

Prove

Objective is to demonstrate that electrolytes can be solved in a rapid solution using an EO approach and deliver a typical system such as H2SO4.

Phase 2 – Functional Expert Use (In progress for completion in 2020)

Feature	Status
Develop Pitzer Method	*Code completed*
Create typical Reaction Model	*Underway*
Create e-NRTL Method	*Complete*
Solids/Precipitation Handling	*Complete*

Functional

Get 80% of most users functionality although there is a burden on users to supply data and reactions if is not one of the typical ones we deliver.

Pitzer is a common reference system that requires many of the same features as e-NRTL so we decided to do it first.

We chose e-NRTL since many customers already have data for it so that regression for a new method is not required.

Phase 3 – Generalized Use (2021+)

Feature	Status
Extended Literature Component Data	*proposed*
Create framework to automatically populate species and reactions	*proposed*
Add Regression Capability	*proposed*
Consider e-PCSAFT	*Research phase (collaboration with University)*

Generalized

Extend to be a generalized electrolyte system with many built in component data and reaction data so that less expertise is required to construct the Fluid Reaction Model.

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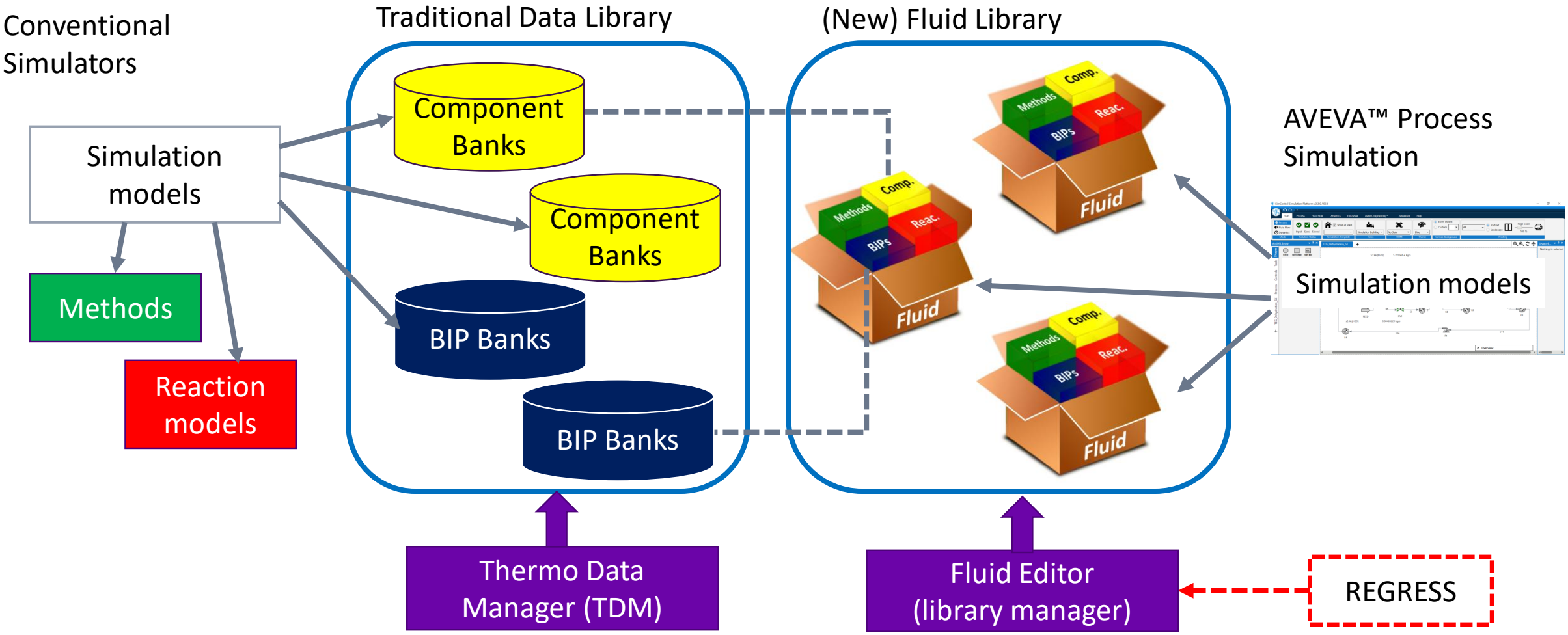
AVEVA

Agenda

1. **Roadmap Overview**
2. **Highlighted topics**
   - gE-type mixing rules (such as PSRK) and association theories (such as ePC-SAFT and CPA) for modeling high pressure chemical processes
   - Combination of reaction equilibrium and phase equilibrium (including Electrolyte) making the most of Fluid Feature on AVEVA Process Simulation
   - Solid-fluid in equilibrium and its usage for the Chemical industry, Prediction of solid and gas hydrate occurrence in the Oil & Gas industry
   - Usage of newly emerging technologies such as quantum chemistry calculation and AI
3. Further discussions

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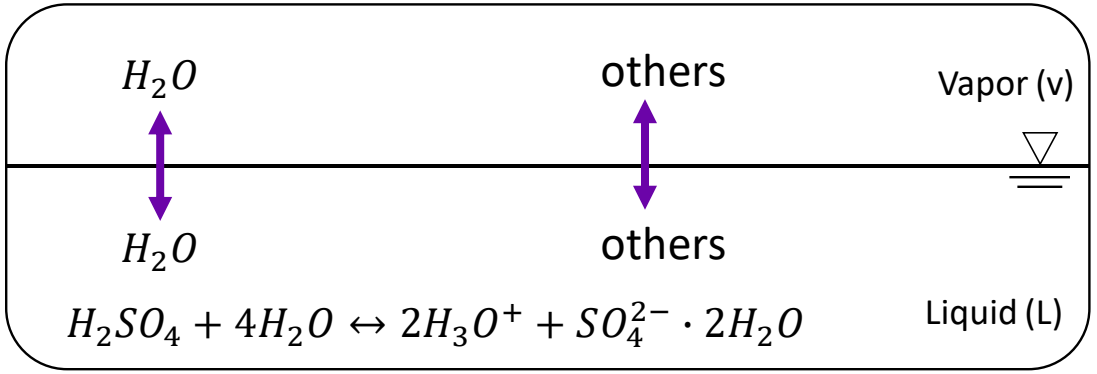
“Fluid” Concept on AVEVA Process Simulation (SimCentral)



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Bosen and Engels

Simple but Practical Electrolyte Model for Sulfuric Acid: The first electrolyte on AVEVA Process Simulation



Objectives

- Model processes which use mixtures of sulfuric acid and water

Solutions

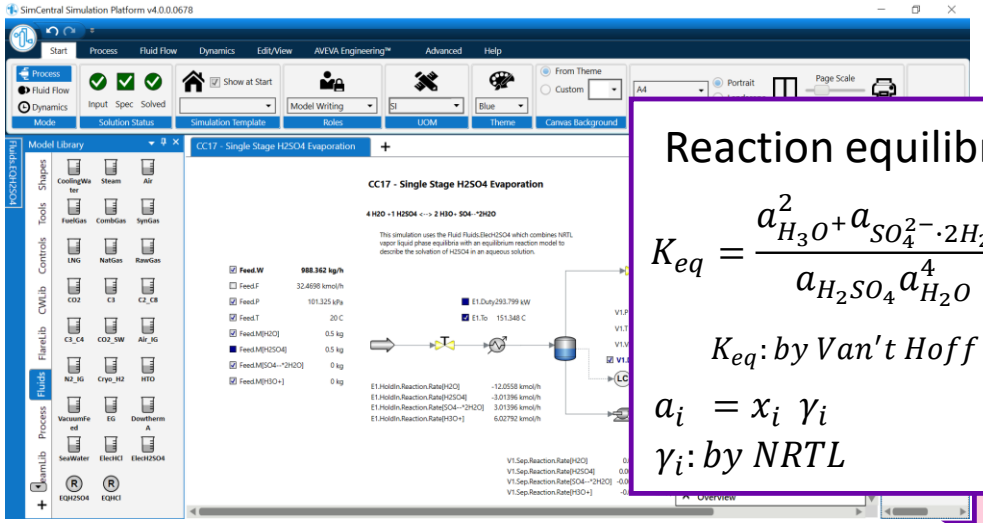
- Equip simple model of Bosen, A. and Engels*, which is widely accepted by the market.
- Reaction equilibrium model is incorporated in "Fluid" of AVEVA Process Simulation
- Activity coefficient of each species is calculated by NRTL

Reactions considered

$$H_2SO_4 + 4H_2O \leftrightarrow 2H_3O^+ + SO_4^{2-} \cdot 2H_2O$$

Delivery

- Equipped in library of AVEVA Process Simulation



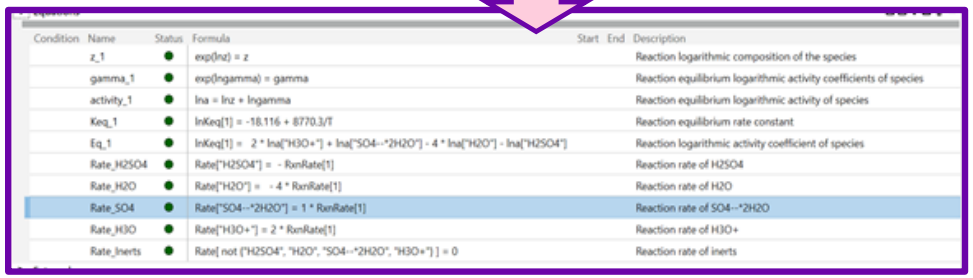
Reaction equilibrium equation

$$K_{eq} = \frac{a_{H_3O^+}^2 a_{SO_4^{2-}\cdot 2H_2O}}{a_{H_2SO_4} a_{H_2O}^4}$$

K_{eq}: by Van't Hoff type equation ($K_{eq} = A + \frac{B}{T}$)

$a_i = x_i \ \gamma_i$

γ_i: by NRTL



*Bosen, A. and Engels, H., "Description of the Phase Equilibrium of Sulfuric Acid with the NRTL Equation and a Solvation Model in a wide Concentration and Temperature range," Fluid Phase Equilib. 43(2–3):213–230, 1988

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Thermo Methods for HF-Mixtures

Reaction model combined with EOS and Activity Coefficient Method (when needed)

Objectives

- Modeling processes which uses HF at elevated pressures, such as HF alkylation in refineries

Solutions

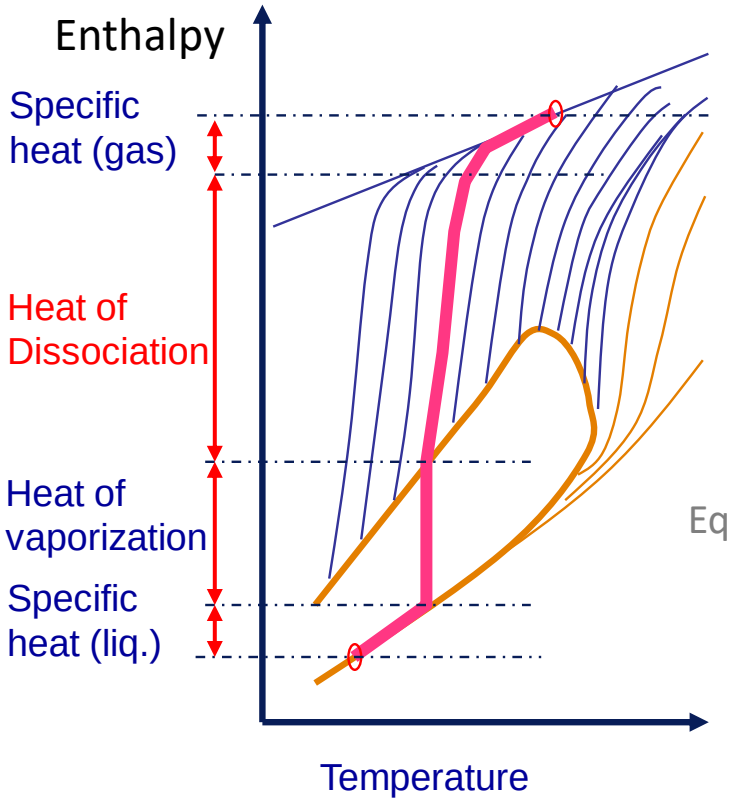
- (Conventional) Implement HEXAMER model of Twu, which is a combination of reaction equilibrium with SRKS EOS
- (AVEVA Process Simulation) Enable SRKM to work with reaction equilibrium
- Both work with activity coeff. (gamma-phi) considering reaction ($y_{HFm,sat,o,1}$)

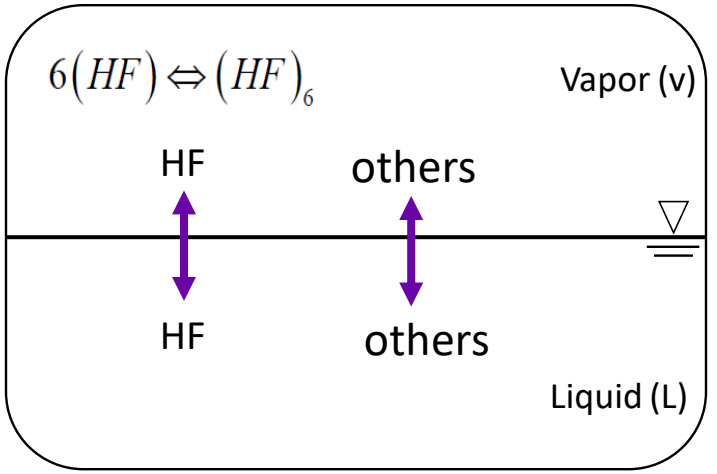
Reaction considered

$$6(HF) \Leftrightarrow (HF)_6$$

Delivery

- Hexamer has been available in AVEVA PRO/II Simulation and AVEVA Dynamic Simulation
- AVEVA PRO/II Simulation 2020.1 was equipped with gamma-phi feature
- AVEVA Process Simulation will be equipped with HF-Thermo (gamma-phi) in early 2021





Equilibrium conditions

- Pressure: $P^L = P^V$
- Temperature: $T^L = T^V$
- Physical (phase)equil.: $f_i^L = f_i^V$
- Chemical (reaction) equilibrium

$$K(T) = \frac{\phi_6}{\phi_1^6}\frac{z_6}{z_1^6}\frac{1}{P^5}$$

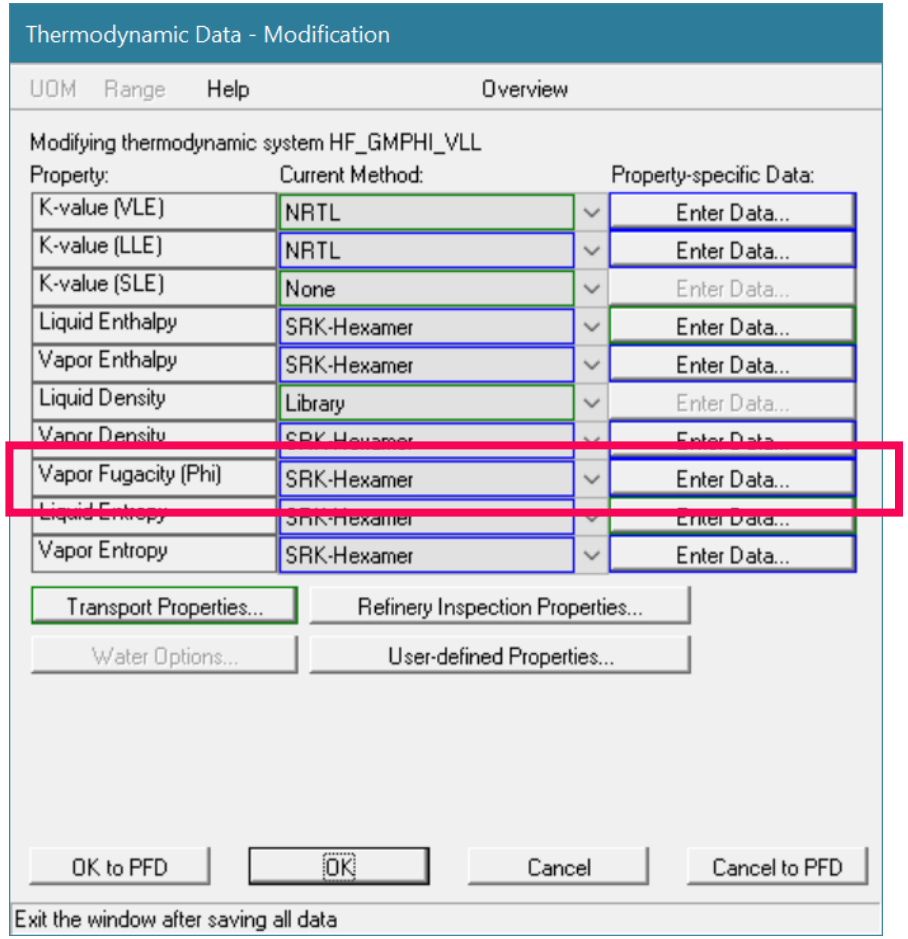
Equation for gamma-phi

$$y_1 \emptyset_{V,1} P = x_1 \gamma_1 P_{sat,o,1} \emptyset_{L,sat,o,1} y_{HFm,sat,o,1} (Poynting)$$

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The Hexamer-NRTL gamma-phi approach now works on AVEVA PRO/II Simulation 2020.1 (released in August 2020)



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Model for Formaldehyde Water Mixtures*

AVEVA (former SIMSCI) conducted a project of implementing UAS for PRO/II for a client

Objectives

- Modeling chemical processes

Solution

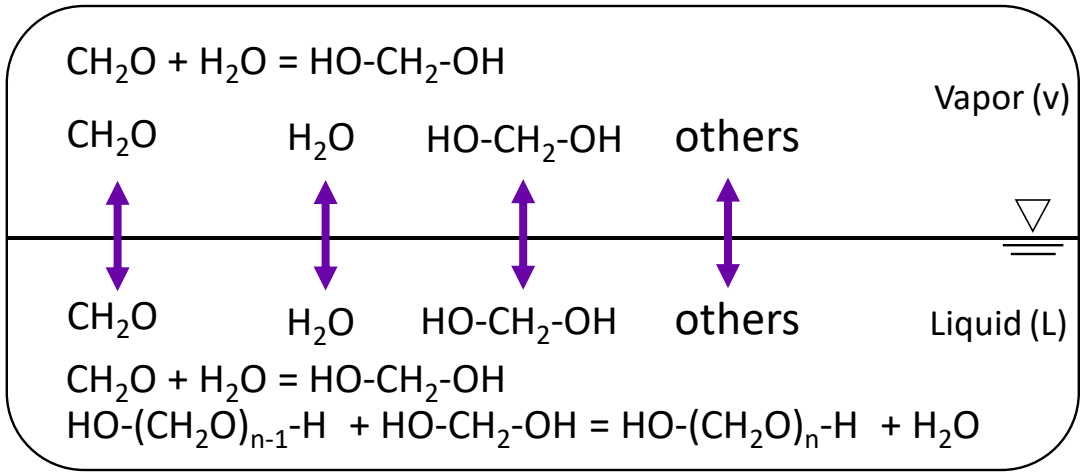
- Project work for implementing a user-added subroutine (UAS) which works on PRO/II

Reaction considered

1. Formation of methylene glycol
   $CH_2O + H_2O = HO\text{-}CH_2\text{-}OH$
2. Formation of polyoxymethyelen (n>1)
   $HO\text{-}(CH_2O)_{n-1}\text{-}H + HO\text{-}CH_2\text{-}OH = HO\text{-}(CH_2O)_n\text{-}H + H_2O$
3. Cannizzaro-reaction
   $2CH_2O + H_2O = CH_3OH + HCOOH$
4. Formation of methylal
   $2CH_3OH + CH_2O = CH_3OH\text{-}CH_2\text{-}OH$
5. Formation of higher hemiformals (n>1)
   $CH_3O\text{-}(CH_2O)_{n-1}\text{-}H + CH_3OH\text{-}CH_2\text{-}OH = CH_3O\text{-}(CH_2O)_{n-1}\text{-}H + CH_3OH$
6. Tischenko-Reaction
   $HO\text{-}(CH_2O)_2\text{-}H = HCOOCH_3 + H_2O$
7. Decomposition reaction (T/K=420)
   $2CH_2O = CH_3OH + CO$

Delivery

- UAS for PRO/II was delivered to the client (IP of the client)
- Proposed to cover using FLUID on AVEVA Process Simulation



- Equilibrium conditions
  - Pressure: $P^L = P^V$
  - Temperature: $T^L = T^V$
  - Physical (phase)equilibrium: $f_i^L = f_i^V$
  - Chemical (reaction) equilibrium for A+B=C+D:

$$K_{th} = \prod_i f_i^{\nu_i} = \frac{f_C * f_D}{f_A * f_B}$$

*Mauer, G. of BASF; "Vapor-Liquid Equilibrium of Formaldehyde and Water-Containing Multicomponent Mixtures", AIChE J. 32(6)932-948 (1986)

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REGRESS on AVEVA Process Simulation

Objectives

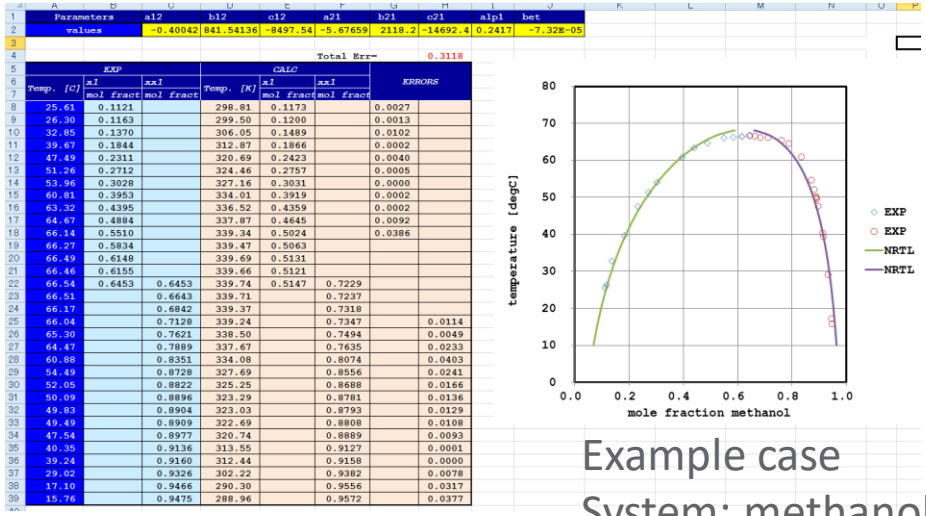
- To improve accuracy of simulation, parameters need to be adjusted based on newly obtained experimental data.

Known demands:

- Determine binary interaction parameters using plural types of experimental data **(TPXY, PXY, TXY, TXX, heat of mixing, density, excess volume ...)** at the same time.
- Enhance types of parameters that can be determined by REGRESS: For Electrolyte, amine..., reaction equilibrium constants may also be parameters to be adjusted
- Regression process should be visible to users.
- Plot with a variable range and variable resolution for each parameter
- Diagnose binary parameters in terms of uniqueness of phase equilibrium solutions

Status and plan

- Being discussed

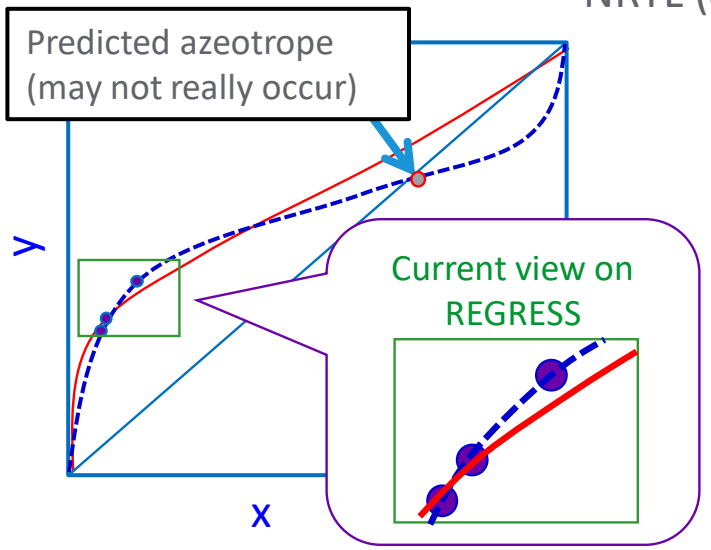


Parameters	a12	b12	c12	a21	b21	c21	alp1	bet
values	-0.40042	841.54136	-8497.54	-5.67659	2118.2	-14692.4	0.2417	-7.32E-05

Total Err= 0.3118

EXP			CALC			ERRORS	
Temp. [C]	x1 mol fract	xx1 mol fract	Temp. [K]	x1 mol fract	xx1 mol fract		
25.61	0.1121		298.81	0.1173		0.0027	
26.30	0.1163		299.50	0.1200		0.0013	
32.85	0.1370		306.05	0.1489		0.0102	
39.67	0.1844		312.87	0.1866		0.0002	
47.49	0.2311		320.69	0.2423		0.0040	
51.26	0.2712		324.46	0.2757		0.0005	
53.96	0.3028		327.16	0.3031		0.0000	
60.81	0.3953		334.01	0.3919		0.0002	
63.32	0.4395		336.52	0.4359		0.0002	
64.67	0.4884		337.87	0.4645		0.0092	
66.14	0.5510		339.34	0.5024		0.0386	
66.27	0.5834		339.47	0.5063			
66.49	0.6148		339.69	0.5131			
66.46	0.6155		339.66	0.5121			
66.54	0.6453	0.6453	339.74	0.5147	0.7229		
66.51		0.6643	339.71		0.7237		
66.17		0.6842	339.37		0.7318		
66.04		0.7128	339.24		0.7347		0.0114
65.30		0.7621	338.50		0.7494		0.0049
64.47		0.7889	337.67		0.7635		0.0233
60.88		0.8351	334.08		0.8074		0.0403
54.49		0.8728	327.69		0.8556		0.0241
52.05		0.8822	325.25		0.8688		0.0166
50.09		0.8896	323.29		0.8781		0.0136
49.83		0.8904	323.03		0.8793		0.0129
49.49		0.8909	322.69		0.8808		0.0108
47.54		0.8977	320.74		0.8889		0.0093
40.35		0.9136	313.55		0.9127		0.0001
39.24		0.9160	312.44		0.9158		0.0000
29.02		0.9326	302.22		0.9382		0.0078
17.10		0.9466	290.30		0.9556		0.0317
15.76		0.9475	288.96		0.9572		0.0377

Example case
System: methanol-octane
NRTL (8 parameters)



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Question

Indicating Gmix Chart useful for you?

Objective

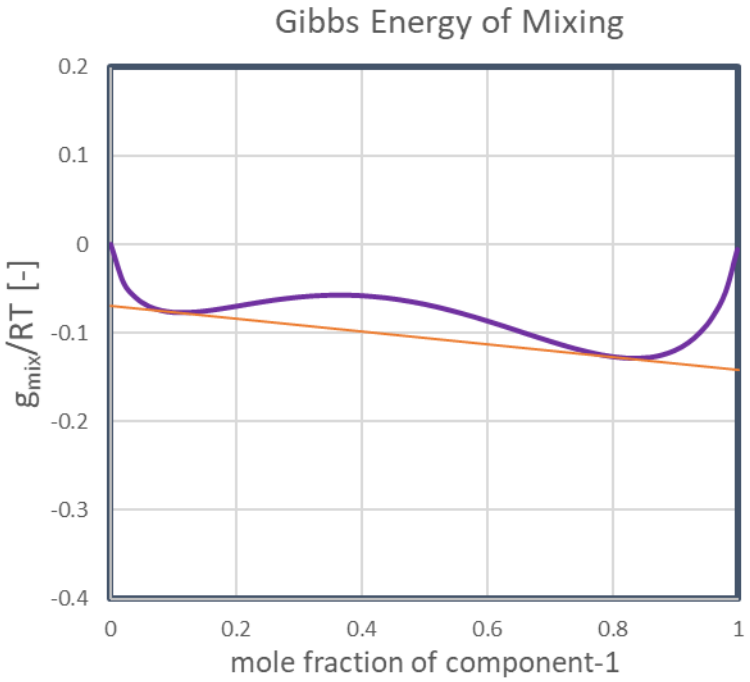
- To diagnose binary interaction parameters have expected number of solutions for binary phase equilibrium (especially LLE)

Solution

- Indicate Gmix chart for each binary system
- Conduct automated stability analysis for each binary system to check possible number of solution

Status

- Being discussed



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AVEVA™ Thermodynamics

Questions:

- Do you like the demonstrated feature of Gmix to diagnose binary interaction parameters?”

(#AVEVA1014)

1. **Yes, I like it**
2. **No, I am not interested in it**

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Agenda

1. **Roadmap Overview**
2. **Highlighted topics**
   - gE-type mixing rules (such as PSRK) and association theories (such as ePC-SAFT and CPA) for modeling high pressure chemical processes
   - Combination of reaction equilibrium and phase equilibrium (including Electrolyte) making the most of Fluid Feature on AVEVA Process Simulation
   - Solid-fluid in equilibrium and its usage for the Chemical industry, Prediction of solid and gas hydrate occurrence in the Oil & Gas industry
   - Usage of newly emerging technologies such as quantum chemistry calculation and AI
3. Further discussions

AVEVA

Possible 3 Phases Plan for Solid for Chemicals

AVEVA Process Simulation

Phases	Phase-1	Phase-2	Phase-3
Timeframe	2020	To be decided (2022+)	To be decided (long term)
Targets/ Objectives	• Committed Features • Defining minimum market requirements	Minimum market requirements	Advanced
Equilibrium	• Non-equilibrium solid • Electrolyte (solubility product) • Simple SLE for non-electrolyte	• **SLE based on activity coefficient methods (such as NRTL)** • Detection of solid occurrence applying EOS to fluid phase	• **General Fluid-Solid Equilibrium (SLE, SVE, SFE)**
Solid properties	• Enthalpy, entropy, density	• Fugacity	• **Particle size distribution for each component** • Slurry property (non-Newtonian viscosity behavior)
Unit Operation	• Simple equilibrium flash unit • Reactors	• Crystallizer and mechanical Separation • Solid warning	• Predict particle size distribution and its effect • General Solid Warning in upstream industry

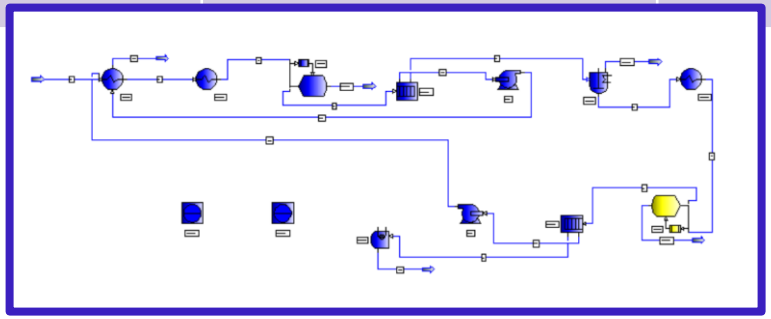
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Users' Feedbacks on Solid Thermo on AVEVA PRO/II Simulation

Category	Features on AVEVA PRO/II Simulation	Feedback of users	Actions taken
Electrolyte solid	OLI Electrolyte Package: applicable to most units (but not to Crystallizer)	Cannot change parameters of Elec. Thermo	(AVEVA Process Simulation) applies AVEVA's native Elec. in Phase-1, which enables this feedback)
Upstream solid	Limited to CO2, water, and benzene	Apply to around 25 components in LNG	JIP Project was conducted. Enhanced to cover 25 comp. (2015-2020)
Chemical (organic) solid	• van't Hoff theory for limited units, in which liquid phase is always ideal solution (gamma=1) • Genetic solubility correlation (polynomial) for limited units (single solute and single solvent)	Gamma=1 is too limited. Should apply **LACT or EOS** to the liquid phase	**(AVEVA Process Simulation to cover in Phase-2)**

$$\ln x_{eq} = -\ln \gamma_{eq} + \frac{\Delta H^{f}(T_m)}{R}\left[\frac{1}{T_m} - \frac{1}{T}\right] - \frac{q}{R}\left[\ln\left(\frac{T_m}{T}\right) - \frac{T_m}{T} + 1\right]$$



Should be considered!

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Solid Warning Needed for Flow Assurance and Avoiding Fouling

Category	Components	Typical location	Remarks on simulation	Applicable theories
Pure solids	CO2 and H2S, 20 hydrocarbons	Cryogenic in gas process	Not hydrate (may happen without water) JIP Project extensively covers the class of components	Solve $f_{\text{each comp., gas/liq}} = f_{\text{each comp., solid}}$ • $f_{\text{each comp., gas/liq}}$: fugacity of each solid comp. in gas/liq using EOS • $f_{\text{each comp., solid}}$: fugacity in each solid (pure comp.) using correlation
	water (ice)	pipe-line (gas)		
	sulfur	pipe-line (gas)	Need to model the reaction; H2S+(1/2)O2->H2O+S	Kinetic reaction model (looking for data for data regression)
Hydrates	Hydrate of gas mixtures (mainly methane, ethane, CO2….)	pipe-line(gas)/ cryogenic	Water is needed for hydrate to occur. Need to predict effect of gas dryer/inhibitor	Solve $f_{\text{water, gas/liq}} = f_{\text{water, hydrate}}$ • $f_{\text{water, gas/liq}}$:fugacity of water in gas/liq calculated using EOS • $f_{\text{water, hydrate}}$: fugacity of water in hydrate using Solid Solution Theory
Salts	ammonium hydrosulfide	Hydrotreater HX	precipitate from gas containing NH3 and H2S	Electrolyte
	ammonium chloride	VDU condenser	precipitate from gas containing NH3 and HCl	Electrolyte
Heavy oil	Asphaltene (crude)	pipe-line (oil)	(Many authors model asphaltene as liquid)	CEOS, RS,PC-SAFT, sac-NRTL
	Asphaltene (cracked oil)	thermal crackers	Kinetic model need to be combined	Dr.Takatsuka's theory (modified RS + kinetic model)

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Joint Industrial Project (JIP) for Solid in LNG

Objective

- Establish reliable thermodynamic base for LNG with focus on solid prediction

Project members: AVEVA, TOTAL, and TechipFMC

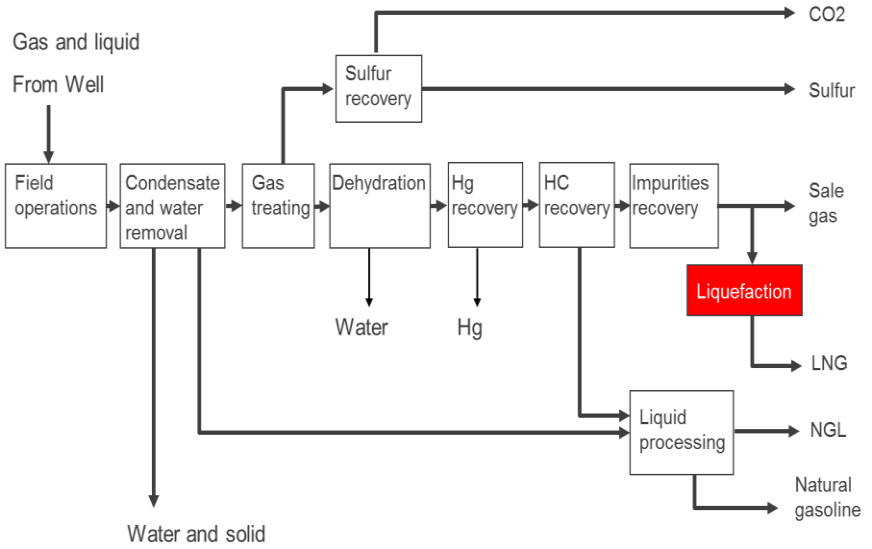
Scope of the works:

- Model: CEOS (SRK/PR) for fluid side. Currently 25 components (scalable)
- Update correlation for solid fugacity, alpha param., BIPs
- Establish flash algorithms:
  - AVEVA PRO/II Simulation: VLL-multi. S
- Physical Properties: Fluid: enthalpy, entropy, and density, solid: enthalpy and density
- Deliverables
  - Thermo enhancement for AVEVA PRO/II Simulation
  - Equations and databank for future usage for all products
- Technical detail was presented by Total at AWC Europe 2019

Status and plan

- Will be available on AVEVA PRO/II Simulation
- Will be Applying to solid worming on AVEVA Process Simulation





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Plan for Hydrate Prediction

Items		Conventional on AVEVA PRO/II Simulation	Phase-1 (Simple) on AVEVA Process Simulation	Phase-2 (Ultimate) on AVEVA Process Simulation (2022+)
Predict effect of water content in gas stream		No	Yes	Yes
Predict effect of inhibitors	When only feed T,P,z are known	No	Yes	Yes
	When inhibitor fract. in liq. are known	Yes	Yes	Yes
Warning of hydrate occurrence	Give warning message hydrate	No	Yes	Yes
	Tell hydrate forming Tor P	No	Yes	Yes
	Draw plots of hydrate forming T-P	Yes	No (not needed)	Yes
Usage of hydrate as constraint for optimization	Tell how close to hydrate formation	No	Yes	Yes
	Solve hydrate module as a part of EO	No	Yes	Yes
	Use parameters for data-reconciliation	No	Yes	Yes
Flash calc. considering hydrate		No	No	Yes
Allow data regression for fitting to customer data		No	Yes (stand-alone tool)	Yes
Hydrate types considered	I (natural gas)	Yes	Yes	Yes
	II	Yes	no	Yes
	H	No	no	Yes
Hydrate guest component considered	Main components in natural gas	Yes	Yes	Yes
	Minor components in natural gas	Yes	No (can be added)	Yes
	Olefins: (ethylene, propylene)	Yes	no	Yes
	Heavier hydrocarbons	no	no	Yes
	Gases for chemicals, noble gases	(depends on)	no	Should cover a lot
Calculation method		Rigorous (direct)	Semi-Rigorous	Rigorous (I/O approach)

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Usage of Solid Solution Theory on EO Architecture for Hydrate Prediction

Fugacity of water

Hypothetical vacant hydrate cage
(β-phase)

Difference between β and pure liq. $(\Delta_{\beta L,T,P})$

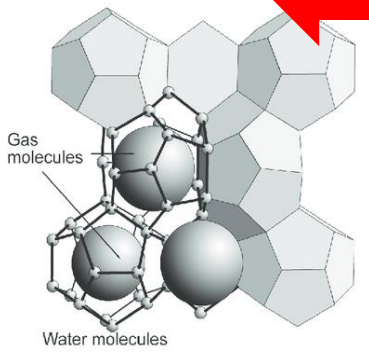
Saito's approach of using exp. data inherited by Sloan and Prauznitz

Stabilize by guest molecule $(\Delta_{H\beta,T,P})$

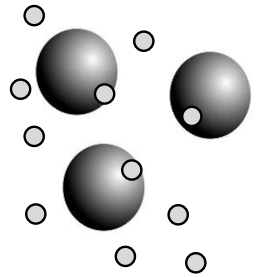
- Apply I/O-type approach for EO
- Simple temp. dependent equation for cell-guest interaction parameters, adjusted by rigorous theory

- Rigorous theory based on integration of inter-molecular potential such as Kihara, or L-J at each cell

$f_{H2O,hy}$:fugacity of at actual hydrate **(hydrate phase)**



$f_{H2O,G/L}$: Fugacity of water in Gas or Liquid



Pure liquid water
(L-phase)

EOS

EOS

Ideal gas pure water at ref. pressure at the temperature of interest

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Agenda

1. **Roadmap Overview**
2. **Highlighted topics**
   - gE-type mixing rules (such as PSRK) and association theories (such as ePC-SAFT and CPA) for modeling high pressure chemical processes
   - Combination of reaction equilibrium and phase equilibrium (including Electrolyte) making the most of Fluid Feature on AVEVA Process Simulation
   - Solid-fluid in equilibrium and its usage for the Chemical industry, Prediction of solid and gas hydrate occurrence in the Oil & Gas industry
   - Usage of newly emerging technologies such as quantum chemistry calculation and AI
3. Further discussions

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Physical Property Prediction with 1st Principle Approaches

Brainstorming

Market information

- Thanks to recent expansion of computer power, molecular dynamics (MD), molecular Monte Carlo (MC) simulation, COSMO-SAC, QSPR approaches are coming into the scope of industrial usage.
- The approaches are based on quantum chemical calculations such as electron distribution bases on Density Functional Theory (DFT)
- Some famous research institutes have started to extensively use MD to fill physical properties in combination with experimental data, after critical evaluations.
- Some chemical companies started to apply the approach for conceptual design
- DDBST created data base for sigma-profile for COSMO-SAC method: http://www.ddbst.com/ddb-sigma.html

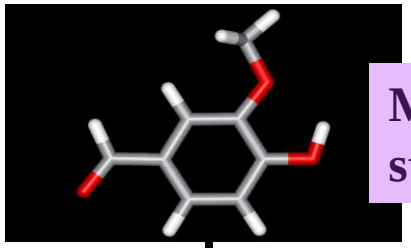
AVEVA's current status

- AVEVA wishes to learn from customers about the needs/status of the new approaches, so that AVEVA better serve the customers
- AVEVA has been talking with some 3rd parties and University Professors who have been pioneer in this field.

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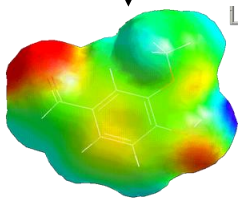
Physical Property Prediction with 1st Principle Approaches

Example: Concept of COSMO-SAC method



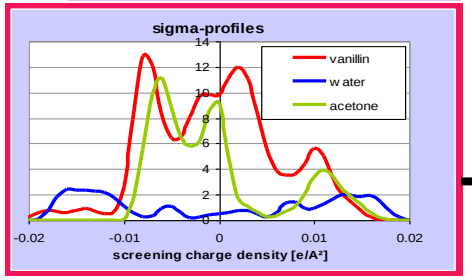
Molecular structure

Ab initio calc.



Energy and charge distribution

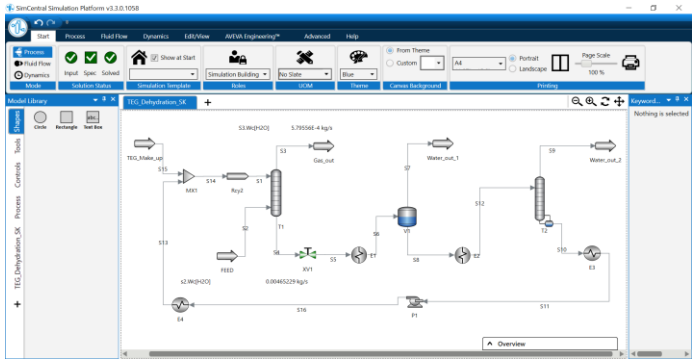
σ-Profile



Source:Web-page of Cosmo Logic

Physical Properties

VLE, LLE, enthalpy, entropy,..



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Agenda

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AVEVA™ Thermodynamics

Questions:

- Are you ever used or interested in using quantum chemistry features (such as DFT, COSMO-sac, ..etc) in commercial projects to predict physical properties without experimental data?

  - **Yes, I have used it. It was very useful**
  - **Yes, I have used it. But it was not very useful**
  - **No, I have not used it. But I am interested in it**
  - **No, I have not used it. I am not interested in it**

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AVEVA™ Thermodynamics

Questions:

- Have you ever conducted data regression for physical properties (such as binary interaction parameters for NRTL) using actual plant operation data rather than laboratory data?
  - **Yes, I have used it. It was very useful**
  - **Yes, I have used it. But it was not very useful**
  - **No, I have not used it. But I am interested in it**
  - **No, I have not used it. I am not interested in it**

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AVEVA™ Thermodynamics

Questions:

- What is the biggest challenge in using thermodynamics in current works/projects?

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Thank you !

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ABOUT AVEVA

AVEVA is a global leader in engineering and industrial software driving digital transformation across the entire asset and operational life cycle of capital-intensive industries.

The company's engineering, planning and operations, asset performance, and monitoring and control solutions deliver proven results to over 16,000 customers across the globe. Its customers are supported by the largest industrial software ecosystem, including 4,200 partners and 5,700 certified developers. AVEVA is headquartered in Cambridge, UK, with over 4,400 employees at 80 locations in over 40 countries.

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