Introduction to Electrolyte Process Simulation Using PRO/II with PROVISION

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Introduction

- PRO/II Electrolytes has the full capabilities of SimSci's Conventional PRO/II.
- Electrolyte code from OLI Systems, Inc.,
  - Electrolyte Thermodynamic Methods (Rigorous)
  - Electrolyte Models (Fixed set of components)
  - Chemical and Phase Equilibrium Algorithm
  - Pure Component + Species Interaction Data Banks

Introduction

- SIMSCI's ELDIST algorithm for modeling distillation columns with electrolytes,
- ELECTROLYTE UTILITY PACKAGE
  - User-added Electrolyte Model Generation Program
  - Data Bank Management Program

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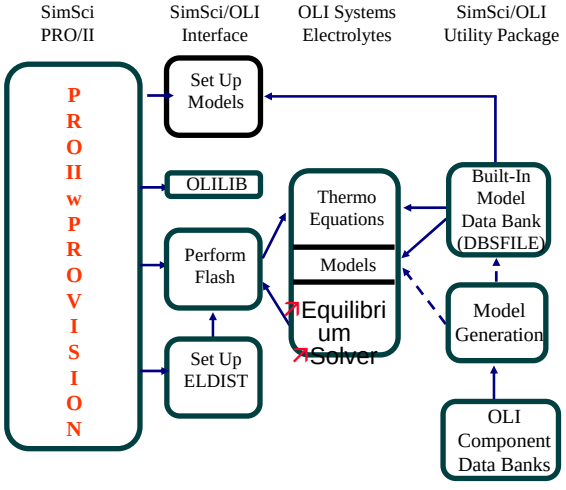
Implementation



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Unit Opeations

- Unit Operation Modules built in PRO/II
  - Flash
  - Calculator
  - Pump
  - Controller
  - Valve, Mixer, Splitter
  - Optimizer
  - Pipe
  - ELDIST Column
  - HEX, LNG HEX
  - Conversion Reactor
  - Stream Calculator
  - Equilibrium Reactor
  - HCURVE
  - Batch Reactor

Thermodynamic Models (I)

- Pregenerated models for 40 systems:
  - Amine systems
  - Caustic systems
  - Acid systems
  - Benfield systems
  - Mixed salt systems
  - Scrubber systems
  - Sour water systems
  - LLE and Hydrate systems

Thermodynamic Models (II)

- User added model can be generated using Electrolyte Utility Package(EUP):
  - Maximum of 60 built-in models allowed
  - Maximum of 50 model components allowed, but 30 component maximum is recommended.

Application Range

- Aqueous Elelctrolyte
  - Temperature: 0 ~ 200 C
  - Pressure: 0 ~ 200 atm
  - Dissolved Gases: 0 ~ 30 mole%
  - Ionic Solutes: 0 ~ 30 ionic strength
- Amine System
  - Pressure: 0 ~ 30 atm
- LLE System
  - Organic Solutes: Max wt% = 10

PRO/II Electrolyte & Conventional PROII

- PRO/II Electrolyte Module takes the followings into account:
  - Chemical and Phase Equilibria
  - Charge Balance
  - Material Balance
- All Thermodynamic Method in Conventional PRO/II tank into account only Phase Equilibria except:
  - SOUR
  - GPSWATER
  - AMINE

Component Reconstitution

- Phase and chemical equilibrium are solved for unknown concentrations of the true species (ionic, neutral) in the aqueous phase.
- A reconstitution procedure is used to calculate apparent concentrations of the model's neutral components that are consistent with the true species concentrations.

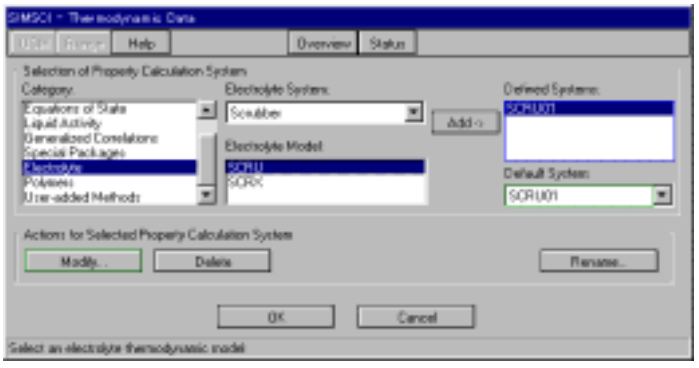
Component Reconstitution

- Example:
  - Models components: H2O, NAOH, HCL, NACL
  - Feed components: 50mol H2O + 1mol NAOH + 1mol HCL
  - Product as True Chemical Species:

    51mol H2O+1mol NA^{+1}+1mol CL^{-1}+10^{-7} mol OH^{-1}+10^{-7} mol H^{+1}
- Product as Reconsitituted Components: 51mol H2O + 1mol NACL
- Reconstitution is automatic.
- Output gives true and reconstituted values.

Simulation Steps: Predefined Modes

1. Description of the simulation
2. Input Unit of Measurement
3. Select Electrolyte Thermodynamic



Simulation Steps: Predefined Modes

4. Component Databank: OLILIB and SIMSCI Bank
5. Build PFD with Unit Operations and Streams
6. Run
7. Generate Output

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Problem #1: HCL & H2O Solution

- Run a simple Flash model for H2O-HCL system using:
  - NRTL Method
  - HCL Electrolyte Method
- And then compare the results.

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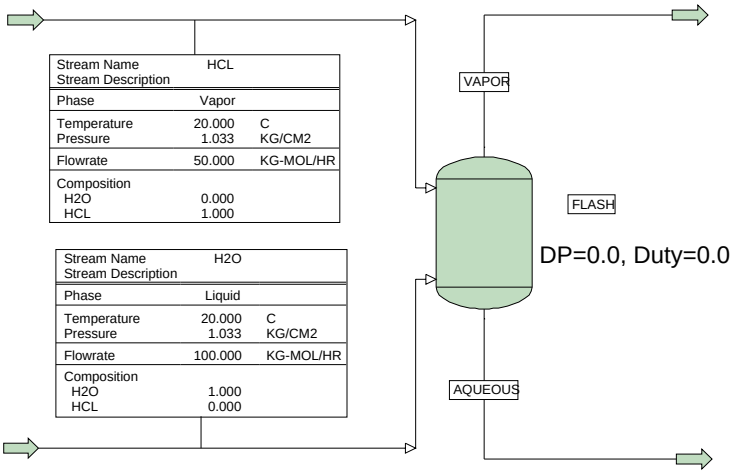
Problem #1: HCL & H2O Solution



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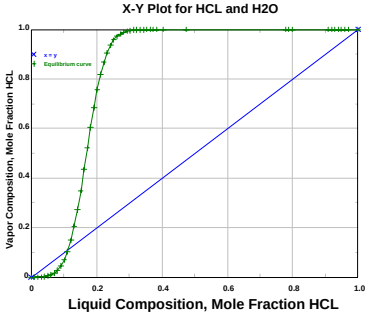
Problem #1: HCL & H2O Solution

VLE LIQUID INTERACTION PARAMETERS FOR H2O-HCL PAIR
NRTL BINARY COEFFICIENTS

I	J	A(I,J) / A(J,I)	B(I,J) / B(J,I)	C(I,J) / C(J,I)	ALPHAC / ALPHAT	UNITS FROM	
1	2	0.000000	2222.9199		0.00	0.2007	DEG K SIMSCI VLEBANK
		0.000000	-2037.3400		0.00	0.0000	



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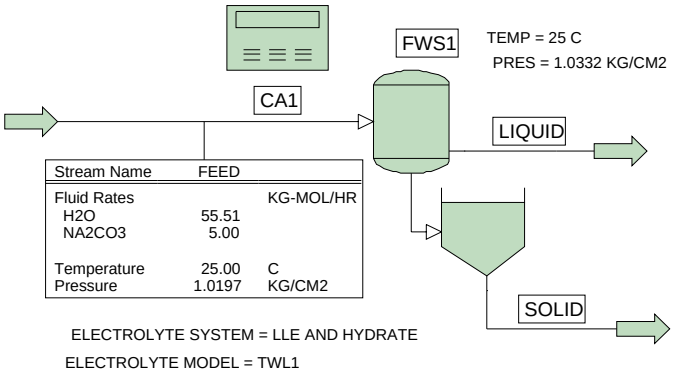
Problem #2: Na2CO3 Solubility in Water

- Employ a Flash Solid model to determine the solubility of Na2CO3 in water.



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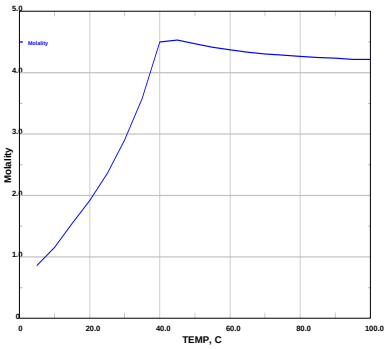
Problem #2: Na2CO3 Solubility in Water

- Employ Case Study option for the followings:
  - Temperature from 5 C to 100 C with step size = 5 C



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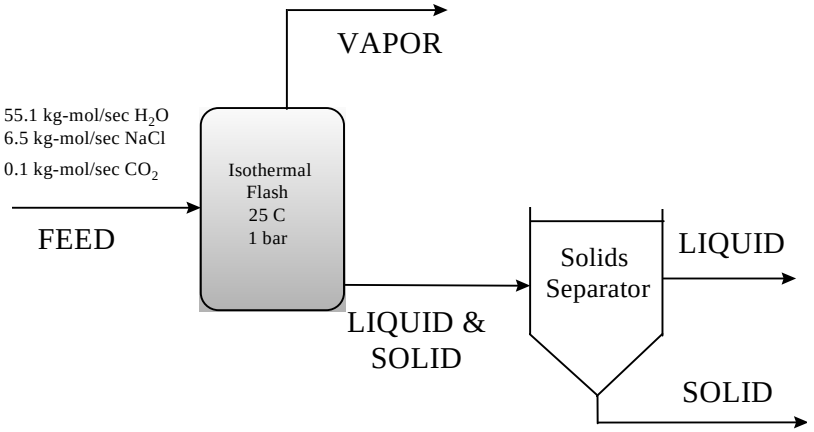
Problem #3: Sodium Chloride Solution



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Problem #3: Sodium Chloride Solution

- Part 1:
  - Is the CO2 absorbed in the solution and to what extent?
  - Is the solution saturated with NaCl?
  - Is there an excess of salt, and does it form a solid phase?
  - What is the pH of the solution?
- Part 2:
  - How does increasing the temperature of the flash change the pH and NaCl concentration of the outlet streams?

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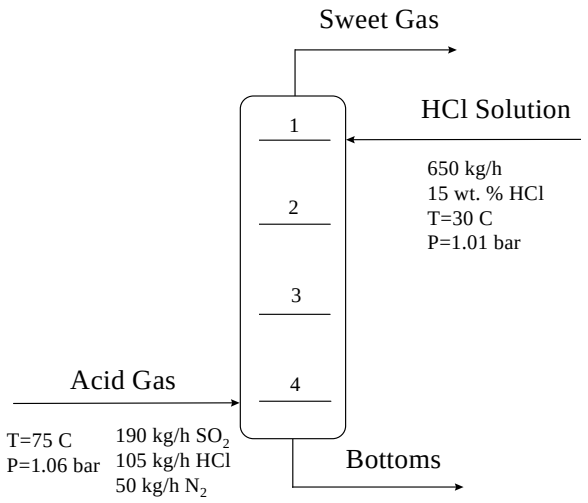
Problem #4: Acid Gas Absorber



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Problem #4: Acid Gas Absorber

- Part 1:
  - How effective is the absorber?
  - What is the weight fraction of HCl in the bottoms stream?
  - What is the pH of the bottoms stream and the HCl solution stream?
  - What is the temperature of the absorber?
- Part 2:
  - What flowrate of HCl wash solution in necessary to reduce the OVHD weight fraction of HCl to 0.1%?
  - What is the weight fraction of HCl in the bottoms stream with the new wash solution flowrate?

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Electrolyte Distillation (ELDIST)

- Electrolyte distillation column equations for component balance and energy balance are solved by Newton-Raphson algorithm in the Outer Loop while liquid phase speciation along the k-value computation are handled by the Inner Loop.

Electrolyte Distillation (ELDIST)

- INNER LOOP:
  - Input to the Inner Loop model are T, P, x and y. T, P and x are needed for speciation calcualations (equations that include equilibrium constants, electroneutrality and independent atom balance equations) and for computation of liquid phase fugacities.
  - Once the true model fraction of aqueous components are determined, they are then translated to reconsitituted species.
  - Once the speciation equations are solved, VLE k-values and its derivatives are computed as a function of T, P, x and y.

Electrolyte Distillation (ELDIST)

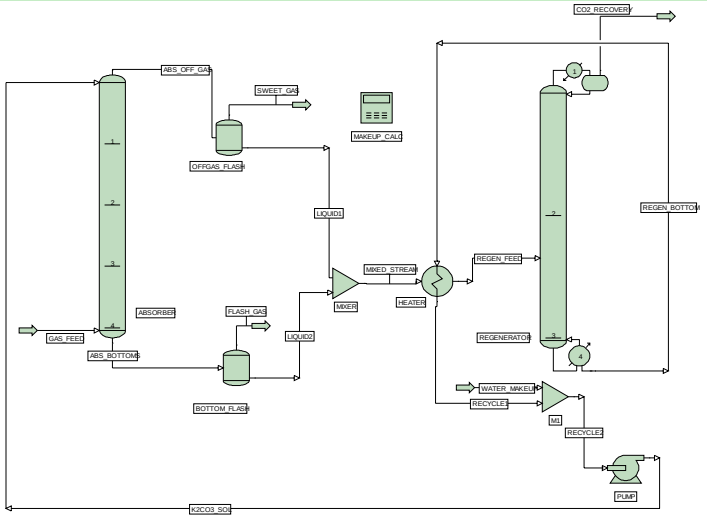
- OUTER LOOP:
  - Outer loop is solved by the Newton-Raphson algorithm.

- The equation to be solved on each tray are:
  - Component balance
  - Vapor liquid equilibrium
  - Energy balance
  - Overall mass balance

Initial Estimate Generator (IEG)

- Given the initial estimates for the column overhead and bottoms flowrate, the top tray temperature, the condenser temperature, and the column pressure, along with the column specifications, the IEG=ELECTROLYTE will then calculate initial estimates for all other column parameters.
- These column parameters are then used by ELDIST to solve the column.

Problem #5: Benfield Process



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Problem #5: Benfield Process

- Reactions produce potassium bicarbonate and potassium bisulfide:

$$K_2CO_3(aq) + H_2O + CO_2 \Leftrightarrow 2KHCO_3(aq)$$

$$K_2CO_3(aq) + H_2S \Leftrightarrow KHCO_3(aq) + KHS(aq)$$

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Problem #5: Benfield Process

- You need to answer to followings:
  - What are the flowrate and compositions of the sweet gas, CO_2 recovery, and $K_2CO_3/KHCO_3$ solution stream?
  - What is the make-up water flowrate?
  - What is the weight percentages of CO_2 in the feed gas and sweet gas stream?

User-added Electrolyte Model

- Look up the component name for EUP using PRO/II Component Utility Program.

Electrolyte Utility Package (EUP)

- Use the electrolyte utility package (EUP) to generate model's FORTRAN routines.
- Equations for Mass and Charge Balance
- Equations for Chemical and Phase Equilibria and to generate model's data block.
- Data on Pure Species and Species Interactions

Created Files from EUP

- The following files are generated from EUP:

• DBS	Model database file
• MDL	Inflow file
• MOU	Inflow log file
• MOD	Model definition file
• EQN	Equation file
• OUT	Summary of Generated model
• ERR	Log/Error File

Run PROVISION

- From “File” Select “New”
- From “View” Select “Thermodynamic Data”
- Select Electrolytes
- Select User Models
- Select desired model

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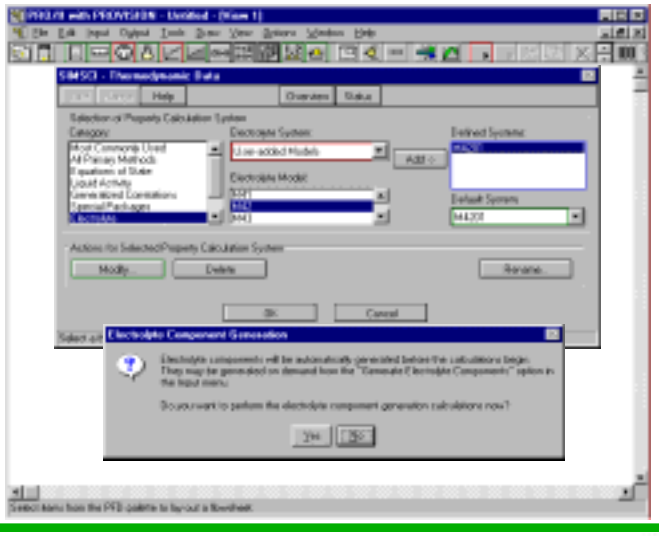
Select “Input” & “Thermodynamic Data”



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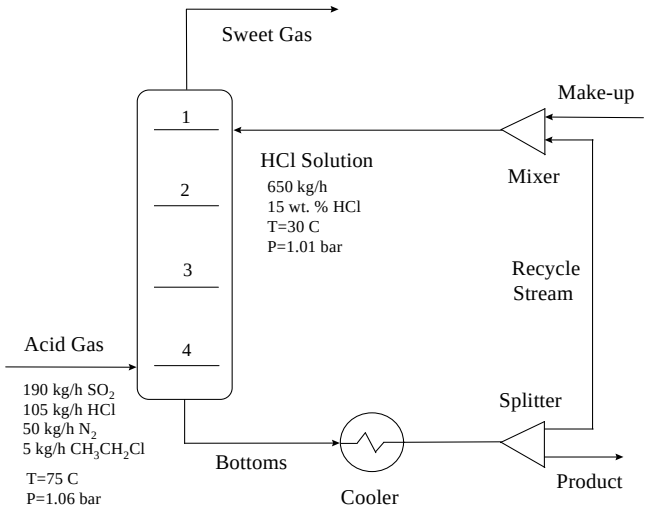
Problem #6: Acid Gas Absorber using EUP



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Problem #6: Acid Gas Absorber using EUP

- Part 1:
  - Use the EUP to generate a new model that combines SO2, N2, HCl, H2O and CH3CH2Cl.
- Part 2:
  - How does the ethyl chloride distribute in the system?
  - Is it absorbed by the HCl solution or does it remain in the gas stream?

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Equilibrium of HCL-H2O System

- Components:
  - H2O, HCL
- Ionic Species:
  - OH-1, H+1, CL-1
- Ionic Equilibria: $H_2O(l) \Leftrightarrow H^+(aq) + OH^-(aq)$

  $HCl(aq) \Leftrightarrow H^+(aq) + Cl^-(aq)$
- Phase Equilibria: $H_2O(l) \Leftrightarrow H_2O(v)$

  $HCl(aq) \Leftrightarrow HCl(v)$

Thermodynamic: Equilibrium Expression

- Thermodynamic Equilibrium Constant K:

$$K = \frac{\prod_{iP} \left[(\gamma_{iP})^{n_i P} (m_{iP})^{n_i P} \right]}{\prod_{iR} \left[(\gamma_{iR})^{n_i R} (m_{iR})^{n_i R} \right]}$$

Equilibrium of H2O-CO2-NACL

- Ionic Equilibrium:

$$H_2O(l) \Leftrightarrow H^+(aq) + OH^-(aq)$$

$$CO_2(aq) + H_2O(l) \Leftrightarrow H^+(aq) + HCO_3^-(aq)$$

$$HCO_3^-(aq) \Leftrightarrow H^+(aq) + CO_3^{2-}(aq)$$

$$NaCl(s) \Leftrightarrow Na^+(aq) + Cl^-(aq)$$

Equilibrium of H2O-CO2-NACL

- Vapor-Liquid Equilibrium:

$$H_2O(vap) \Leftrightarrow H_2O(l)$$

$$CO_2(vap) \Leftrightarrow CO_2(aq)$$

Equilibrium of H2O-CO2-NACL

↗ Ionic Equilibrium Constant Expression:

$$K_{H_2O(aq)} = \frac{\gamma_{H^+} m_{H^+} \gamma_{OH^-} m_{OH^-}}{a_{H_2O}}$$

$$K_{CO_2(aq)} = \frac{\gamma_{H^+} m_{H^+} \gamma_{HCO_3^-} m_{HCO_3^-}}{\gamma_{CO_2(aq)} m_{CO_2(aq)} a_{H_2O}}$$

$$K_{HCO_3^-(aq)} = \frac{\gamma_{H^+} m_{H^+} \gamma_{CO_3^{2-}} m_{CO_3^{2-}}}{\gamma_{HCO_3^-} m_{HCO_3^-}}$$

$$K_{NaCl(s)} = \frac{\gamma_{Na^+} m_{Na^+} \gamma_{Cl^-} m_{Cl^-}}{a_{NaCl(s)}}$$

Equilibrium of H2O-CO2-NACL

↗ Vapor-Liquid Equilibrium Constant Expression:

$$K_{H_2O} = \frac{a_{H_2O}}{\phi_{H_2O} y_{H_2O} P}$$

$$KCO_2 = \frac{\gamma_{CO_2(aq)} m_{CO_2(aq)}}{\phi_{CO_2} y_{CO_2} P}$$

Thermodynamic: Equilibrium Expression

- Assuming a constant heat capacity of reaction, the equilibrium constant are determined by the following:

$$\ln K(T) = -\frac{\Delta G^0}{RT_r} - \frac{\Delta H^0}{R}\left[\frac{1}{T} - \frac{1}{T_r}\right] - \frac{\Delta Cp^0}{R}\left[\ln\frac{T_r}{T} - \frac{T_r}{T} + 1\right]$$

Thermodynamic Framework

- Ionic Strength is defined by the following equation:

$$I = \frac{1}{2}\sum_{i=1}^{nI}\left(z_i^2 m_i\right)$$

Thermodynamic Framework

- For example, a 1.0 molal solution of $CaCl_2$ has 1.0 moles of Ca^{+2} ion and 2.0 moles of Cl^{-1} ion per Kg of H_2O.

$$I = \frac{1}{2}\left(\left(Z_{Ca^{+2}}\right)^2\left(m_{Ca^{+2}}\right) + \left(Z_{Cl^{-1}}\right)^2\left(m_{Cl^{-1}}\right)\right)$$

$$I = \frac{1}{2}\left((2)^2(1.0) + (-1)^2(2.0)\right) = 3.0$$

Thermodynamic Framework

- Aqueous Phase:
- The key to successful simulation of aqueous systems I sto accurately predict:
  - Activity coefficients of ions in solution
  - Activity coefficients of molecules in solution
  - Activity of water

Thermodynamic Framework

- **Aqueous Phase:**
- For activity coefficients of ions in solution the formulation is made up of 3 terms:
  - The Debye-Huckel term for long-range, ion-ion interactions
  - The Bromley-Zemaitis term for short-range, ion-ion interactions
  - The Pitzer term for short-range, ion-molecular interactions

Note: Long-range is for moderately dilute solutions, short-range is for increased concentractions

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Thermodynamic Framework

- **Aqueous Phase:**
- For activity coefficients for molecules other than water in solution, the Setschenow equation is used.
- For activity of water in a multicomponent system the Meissner and Kusik mixing rule equation is used.

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Thermodynamic Framework

- **Vapor Phase:**
- To calculate vapor liquid equilibrium, vapor phase fugacity coefficient methods are used which are strong functions of temperature, pressure and composition, particularly at elevated pressures. The methods are:
  - Ideal, all fugacity coefficients are assumed to be 1.0
  - Nothnagel method, valid up to 20 atmospheres
  - Nothnagel method, valid up to 200 atmospheres
  - SRK method, valid for wider range of conditions and for vapor-phase nonideality

Thermodynamic Framework

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Thermodynamic Framework

- **Non-Aqueous Phase:**
- Normally strong functions of temperature and composition and weaker function of pressure.
- Activities of components in the organic liquid phase are determined from SRK Kabadi-Danner equation of state.

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Thermodynamic Framework

- **Bulk Phase Properties:**
- Old vs. New Framework:
  - Old: Equilibrium constant, K, is temperature dependent (retirived from PUBLIC databank).
  - New: Equilibrium constant is temperature and pressure dependent (retrieved from PUBNEW databank) Tanger and Helgeson equation used fro K calculation.

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The End….