

Introduction to Electrolyte Process Simulation Using PRO/II with PROVISION

Dr. Jungho Cho, Professor
Department of Chemical Engineering
Dong Yang University



Introduction

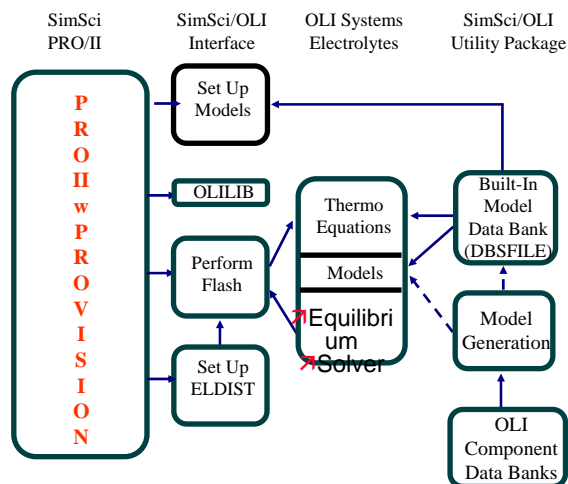
- PRO/II Electrolytes has the full capabilities of SimSci's Conventional PRO/II.
- Electrolyte code from OLI Systems, Inc.,
 - Electrolyte Thermodynamic Methods (Rigorous)
 - Electrolyte Models (Fixed set of components)
 - Chemical and Phase Equilibrium Algorithm
 - Pure Component + Species Interaction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

Slide 3

Implementation



Slide 4

Unit Operations

↗ 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

Slide 5

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

Slide 6

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.

Slide 7

Application Range

- ↗ Aqueous Electrolyte
 - 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

Slide 8

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

Slide 9

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.

Slide 10

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⁺+1mol CL⁻+10⁻⁷ mol OH⁻+10⁻⁷ mol H⁺

➤ Product as Reconstituted Components: 51mol H₂O + 1mol NACL

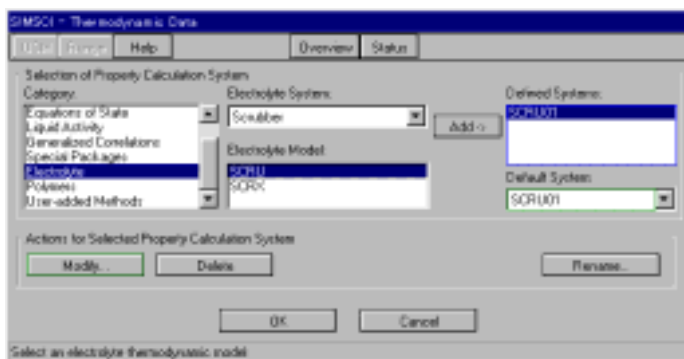
➤ Reconstitution is automatic.

➤ Output gives true and reconstituted values.

Slide 11

Simulation Steps: Predefined Modes

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



Slide 12

Simulation Steps: Predefined Modes

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

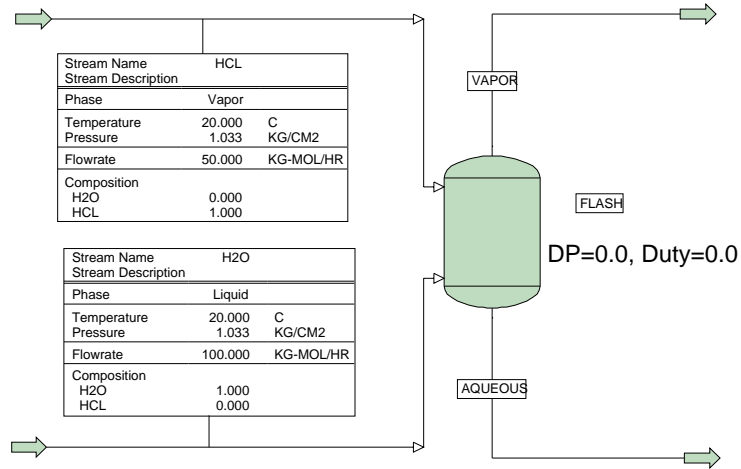
Slide 13

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.

Slide 14

Problem #1: HCL & H2O Solution

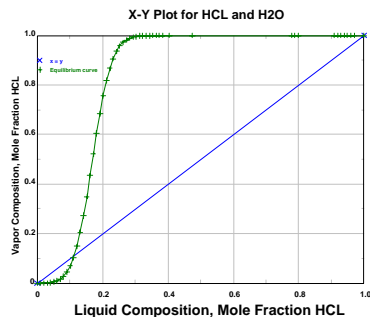


Slide 15

Problem #1: HCL & H2O Solution

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

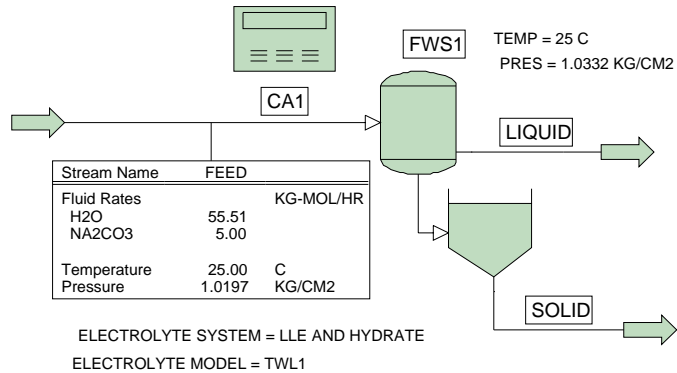
I	J	A(I,J) A(J,I)	B(I,J) B(J,I)	C(I,J) C(J,I)	ALPHAC ALPHAT	UNITS FROM
1	2	0.000000 0.000000	2222.9199 -2037.3400		0.00 0.00	DEG K SIMSCI VLEBANK 0.0000



Slide 16

Problem #2: Na₂CO₃ Solubility in Water

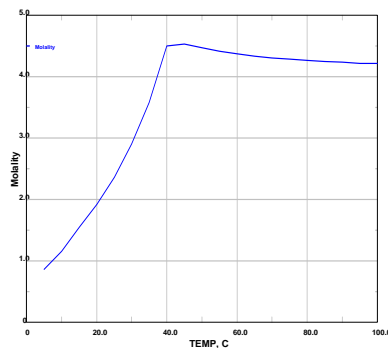
- Employ a Flash Solid model to determine the solubility of Na₂CO₃ in water.



Slide 17

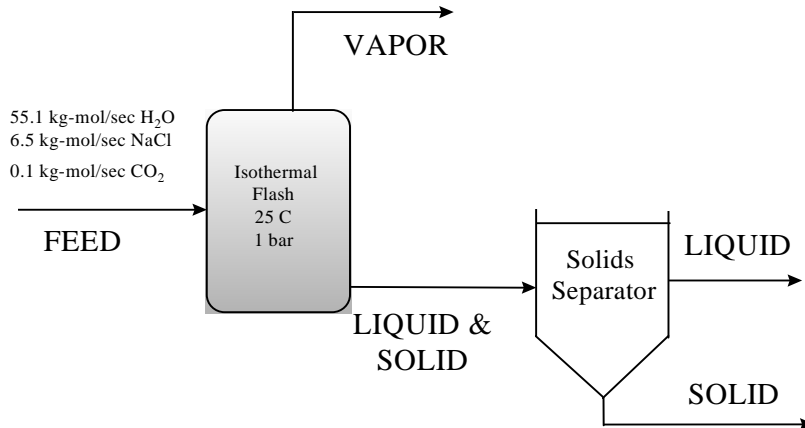
Problem #2: Na₂CO₃ Solubility in Water

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



Slide 18

Problem #3: Sodium Chloride Solution



Slide 19

Problem #3: Sodium Chloride Solution

➤ Part 1:

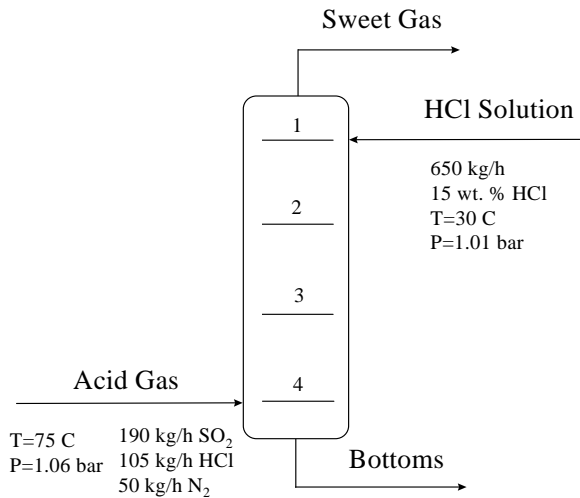
- Is the CO₂ absorbed in the solution and to what extent?
- Is the solution saturated with NaCl?
- Is there an excess of salt, and does it form a solid phase?
- What is the pH of the solution?

➤ Part 2:

- How does increasing the temperature of the flash change the pH and NaCl concentration of the outlet streams?

Slide 20

Problem #4: Acid Gas Absorber



Slide 21

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 is 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?

Slide 22

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.

Slide 23

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 calculations (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 reconstituted species.
 - Once the speciation equations are solved, VLE k-values and its derivatives are computed as a function of T, P, x and y.

Slide 24

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

Slide 25

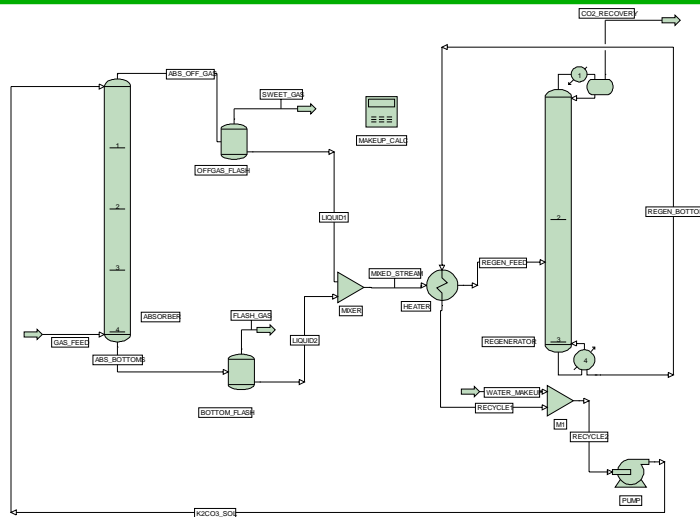
Initial Estimate Generator (IEG)

➤ 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.

Slide 26

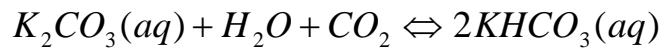
Problem #5: Benfield Process



Slide 27

Problem #5: Benfield Process

➤ Reactions produce potassium bicarbonate and potassium bisulfide:



Slide 28

Problem #5: Benfield Process

↗ You need to answer to followings:

- What are the flowrate and compositions of the sweet gas, CO₂ recovery, and K₂CO₃/KHCO₃ solution stream?
- What is the make-up water flowrate?
- What is the weight percentages of CO₂ in the feed gas and sweet gas stream?

Slide 29

User-added Electrolyte Model

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

Slide 30

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

Slide 31

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

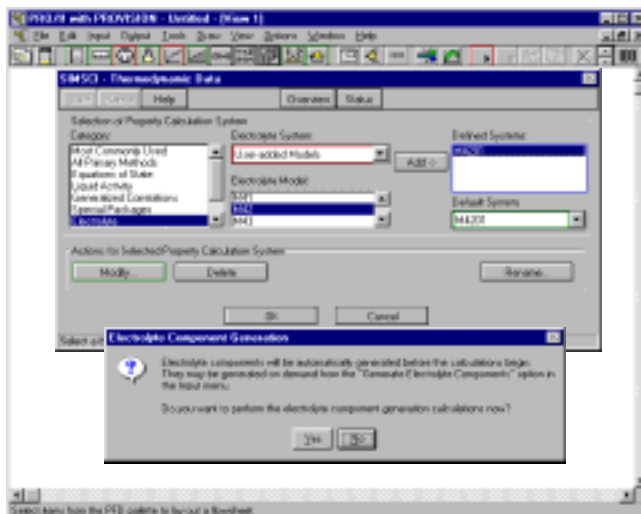
Slide 32

Run PROVISION

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

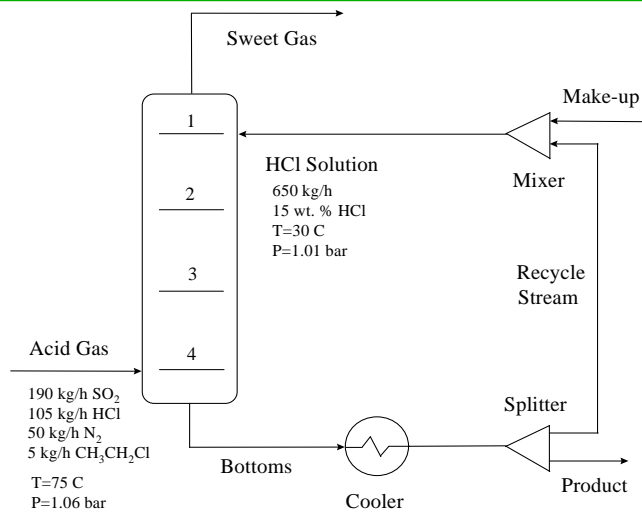
Slide 33

Select “Input” & “Thermodynamic Data”



Slide 34

Problem #6: Acid Gas Absorber using EUP



Slide 35

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?

Slide 36

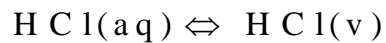
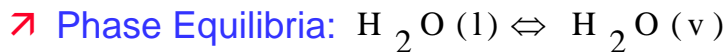
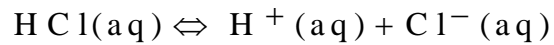
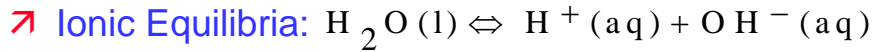
Equilibrium of HCL-H2O System

↗ Components:

- H₂O, HCL

↗ Ionic Species:

- OH⁻, H⁺, CL⁻



Slide 37

Thermodynamic: Equilibrium Expression

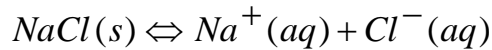
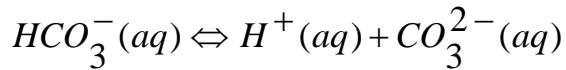
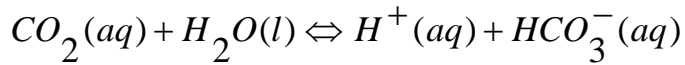
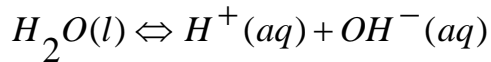
↗ Thermodynamic Equilibrium Constant K:

$$K = \frac{\prod_{iP} [(\gamma_{iP})^{n_{iP}} (m_{iP})^{n_{iP}}]}{\prod_{iR} [(\gamma_{iR})^{n_{iR}} (m_{iR})^{n_{iR}}]}$$

Slide 38

Equilibrium of H₂O-CO₂-NaCl

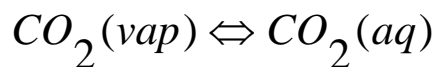
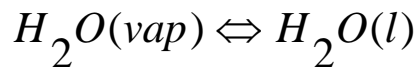
↗ Ionic Equilibrium:



Slide 39

Equilibrium of H₂O-CO₂-NaCl

↗ Vapor-Liquid Equilibrium:



Slide 40

Equilibrium of H₂O-CO₂-NaCl

↗ Ionic Equilibrium Constant Expression:

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

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

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

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

Slide 41

Equilibrium of H₂O-CO₂-NaCl

↗ Vapor-Liquid Equilibrium Constant Expression:

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

$$K_{CO_2} = \frac{\gamma_{CO_2(aq)}^m}{\phi_{CO_2} y_{CO_2} P}$$

Slide 42

Thermodynamic: Equilibrium Expression

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

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

Slide 43

Thermodynamic Framework

- ↗ Ionic Strength is defined by the following equation:

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

Slide 44

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 .

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

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

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 concentrations

Slide 47

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.

Slide 48

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

Slide 49

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

Slide 50

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.

Slide 51

Thermodynamic Framework

↗ Bulk Phase Properties:

- ↗ Old vs. New Framework:
 - Old: Equilibrium constant, K , is temperature dependent (retrieved from PUBLIC databank).
 - New: Equilibrium constant is temperature and pressure dependent (retrieved from PUBNEW databank) Tanger and Helgeson equation used for K calculation.

Slide 52

The End....

Slide 53

Slide 54