Process Simulation with ASPEN PLUS

CHE654 Course Notes

Section 7: ASPEN PLUS

Physical Properties

These course materials are applicable to Version 8.4 of ASPEN PLUS

Physical Properties: "Soul" of Simulation

Topics:

- Overview
- Choosing a Property Method
  - Activity coefficient models
  - Equation of state models
  - Special models
- Specifying Property Methods
- Property Parameters
  - Requirements
  - Databanks
  - Input

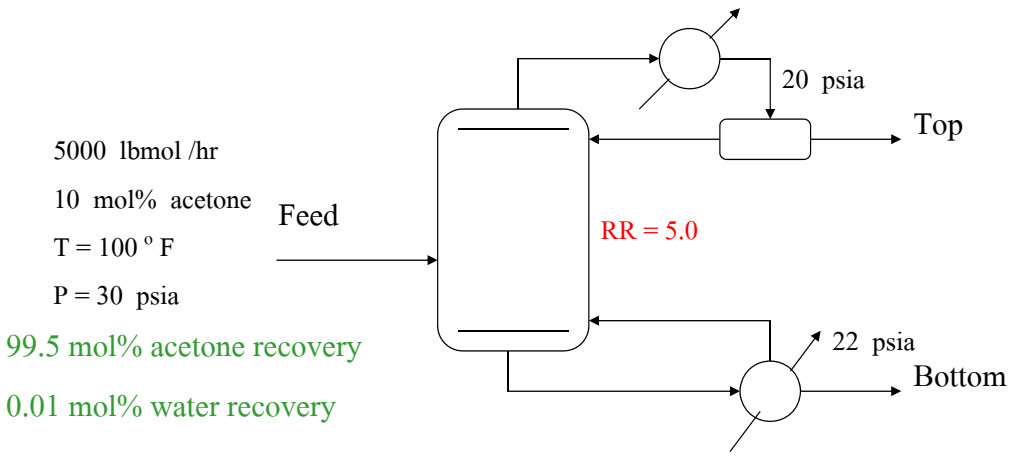
Topics (Cont'd):

- Special Topics
  - Tabular data
  - Parameter estimation (PCES)
- Property Reporting
  - Property Analysis
  - Property sets (PROP-SET)

Overview of Physical Property System in ASPEN PLUS

Overview

- Accurate representation of physical properties is the key to meaningful simulation results.
- Example: Acetone recovery column

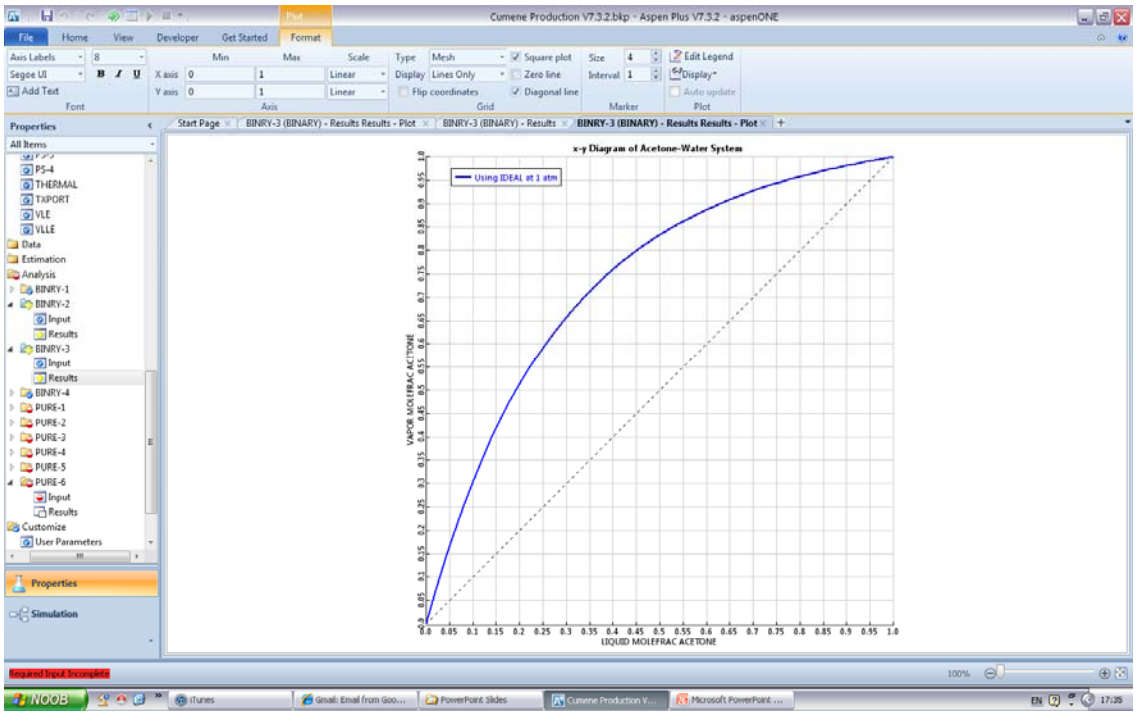


Overview (Cont'd)

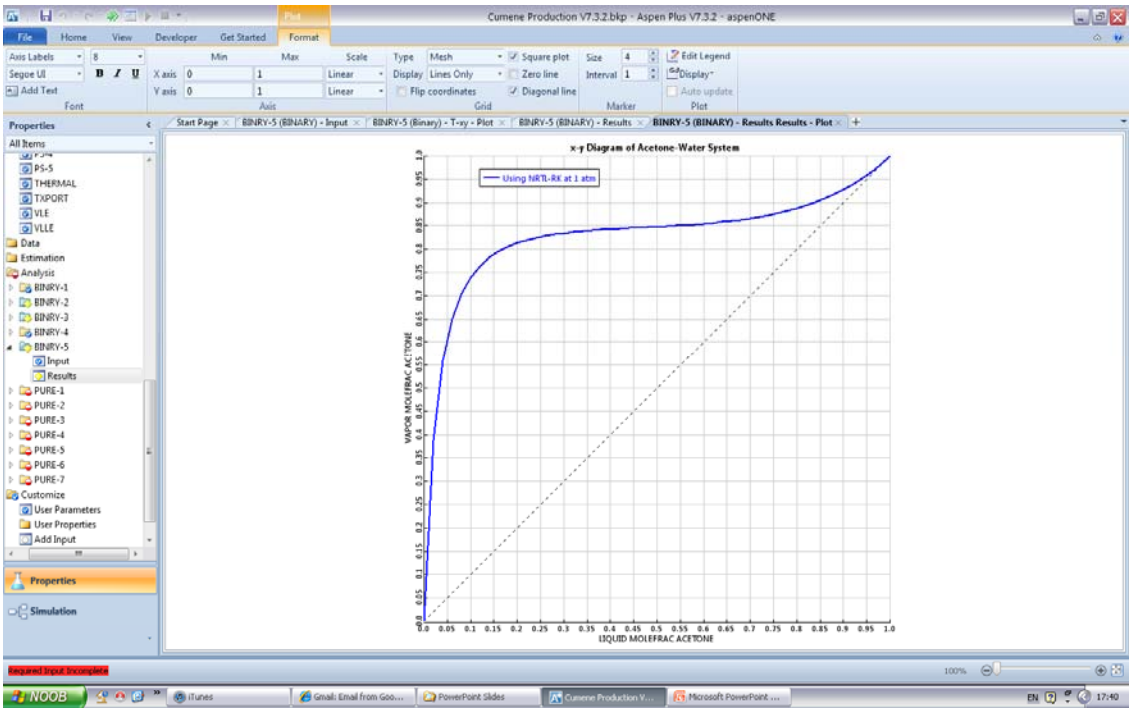
- Simulation results of the acetone recovery column using DSTWU
- 3 property methods were used

	No. of Stages	Condenser Duty (MMBtu/hr)	Reboiler Duty (MMBtu/hr)
IDEAL	14	37.7	49.5
Ideal gas/solution (no binary parameters)			
NRTL-RK	52	37.4	50.7
γ model (binary parameters from databanks)			
LK-PLOCK	11	38.2	52.1
EOS model (binary parameters estimated)			

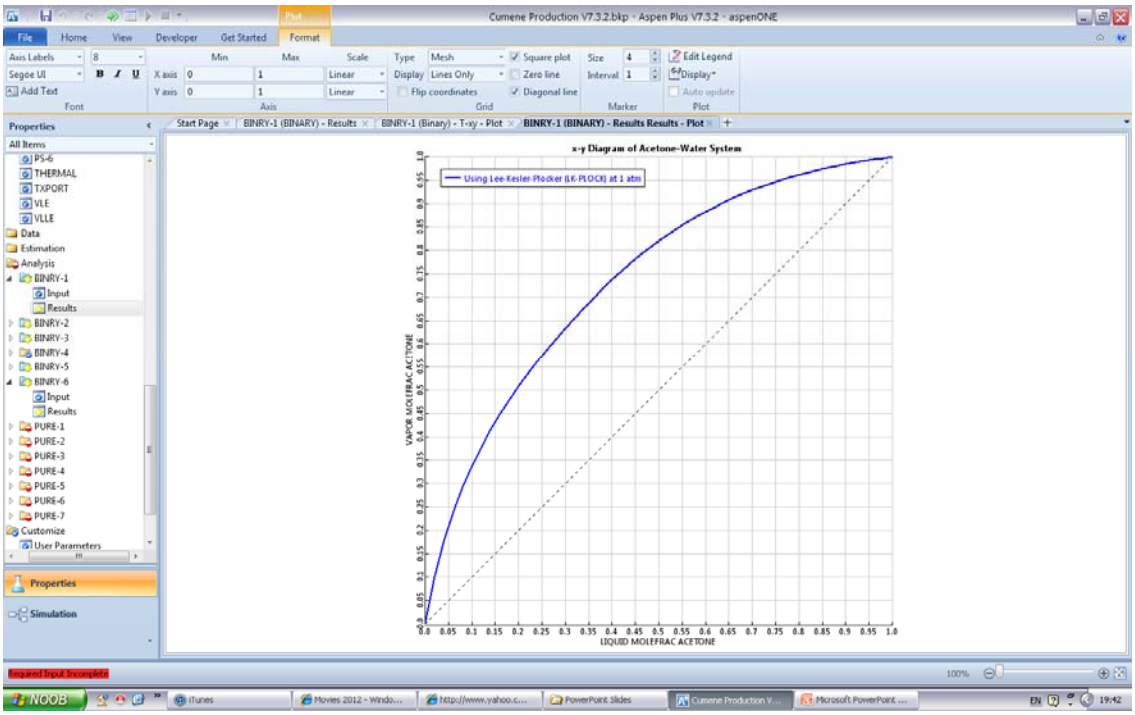
x-y Diagram of Acetone/Water Using IDEAL



x-y Diagram of Acetone/Water Using NRTL-RK



x-y Diagram of Acetone/Water Using LP-PLOCK



Overview (Cont'd)

- The ASPEN PLUS property system supplies thermodynamic and transport properties for unit operation and stream calculations.
- This is done through a base property method, which is a collection of models and methods for calculating properties.

Property	Purpose
K-values	VLE, LLE calculations
Enthalpy	Energy balance, heat duties
Entropy	Work, efficiencies
Free energy	Chemical equilibrium, phase stability
Molar volume	Sizing
Transport properties	Sizing

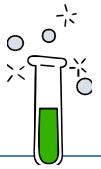
Example of a Base Property Method

- IDEAL Method
  - Assumes ideal gas for vapor calculations
  - Assumes ideal liquid for liquid calculations

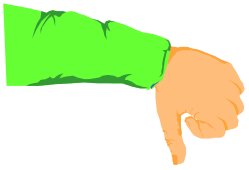
Property	Method	Model
K-values	$K_i = P_{VAP,i}/P$ (Raoult's law)	Antoine
Enthalpy	$H_V = H_{IG}$	Ideal gas heat capacity
	$H_L = H_{IG} - \sum x_i \Delta H^o_{VAP,i}$	Watson
Entropy	-----	Ideal gas
Free energy	-----	Watson
Volume	-----	Rackett

ASPEN PLUS Property Methods

- There are over 60 property methods in ASPEN PLUS.
- There is always at least 1 method suitable for any chemical system and under any operating condition.
- Can be broadly divided into 2 categories
  - Activity coefficient models (often called γ models)
  - Equation of state models (EOS models)
- The rest are special models, such as steam tables, amine package, sour water package, etc.



Choosing a Property Method in ASPEN PLUS



Property Methods

- Activity Coefficient Models (γ Models)

  VLE: $\varphi_i^V y_i = \gamma_i \varphi_i^{OL} x_i$

  Enthalpy: h^V from EOS

  $h^L = \sum x_i (h^{O,IG} + \Delta h^{O,L}) - RT^2 \sum x_i (\partial \ln \gamma_i / \partial T)$

  Volume: V^V from EOS

  V^L from Rackett model

- In essence, a γ model uses 2 methods to calculate properties - EOS for vapor properties and γ for liquid properties.

Essential Aspects of γ Models

- Consists of 2 property methods - one for vapor and one for liquid
- Uses Henry's law to represent the VLE behavior of dissolved gases (supercritical components)
  - Henry's law parameters are available in A+ databanks.
  - The parameters are needed to predict the solubilities of dissolved gases.
- Contains binary interaction parameters which are essential for accurate VLE representations
  - A+ contains interaction parameters for thousands of component-pairs in its databanks.

γ Models in A+

- IDEAL method is a good example.
  - Uses ideal gas law to calculate T, P, and V of vapor
  - Uses Raoult's law to calculate properties of liquid
- Important γ models in A+ are:

  1. IDEAL
  2. CHAO-SEA

  - Chao-Seader correlation
  - Appropriate for systems with hydrocarbons and light gases such as CO_2 and H_2S but with the exception of H_2 in crude towers and vacuum towers of refinery plants

γ Models in A+ (Cont'd)

3. GRAYSON
   - Grayson-Streed correlation
   - Same applications as in Chao-Seader but can handle H_2.
4. NRTL, NRTL-RK, NRTL-NTH, NRTL-HOC
   - Belong to the family of the NRTL model (Non-Random Two-Liquid)
   - Appropriate for mixtures containing polar and non-polar compounds, up to very strong nonideality
   - Can accurately describe the VLE and LLE of highly nonideal solutions
   - NRTL-xxx where xxx is an EOS for vapor side

     NRTL uses ideal gas for vapor, RK = Redlich-Kwong EOS,

     NTH = Nothnagel , HOC = Hayden-O'Connell

γ Models in A+ (Cont'd)

5. UNIQUAC, UNIQ-RK, UNIQ-NTH, UNIQ-HOC
   - Belong to the family of the UNIQUAC model
   - Same applicability as the NRTL model
   - Can accurately describe the VLE and LLE of highly nonideal solutions
   - Contains the same variations as those of NRTL for the vapor
6. WILSON, WILS-RK, WILS-NTH, WILS-HOC, WILS-GLR, WILS-LR, WILS-HF
   - Belong to the family of the Wilson model
   - Same applicability as the NRTL and UNIQUAC models, except it cannot handle 2 liquid phases

γ Models in A+ (Cont'd)

6. WILSON, WILS-RK, WILS-NTH, WILS-HOC, WILS-GLR, WILS-LR, WILS-HF (Cont'd)
   - WILS-HF uses a special HF EOS and is good for mixtures containing hydrogen fluoride, which associate strongly in the vapor phase to form hexamers and other-mers, affecting VLE and enthalpy
   - WILS-GLR allows either ideal gas or liquid as the enthalpy reference state.
   - WILS-LR uses the liquid enthalpy reference state.
   - Both GLR and LR use ideal gas for the vapor side.

Note: In all property methods of A+ (except those mentioned otherwise), the reference state for enthalpy is ideal gas at 25 ^{o}C and 1 atm.

γ Models in A+ (Cont'd)

7. VANLAAR, VANL-RK, VANL-NTH, VANL-HOC
   - Belong to the family of the Van Laar model
   - Similar applicability as NRTL, UNIQUAC, and WILSON, except it is less accurate.
   - Not recommended because of missing binary interaction parameters from A+ databanks

8. UNIFAC, UNIF-LL, UNIF-DMD, UNIF-HOC, UNIF-LBY
   - Belong to the family of UNIFAC model, a group-contribution approach
   - Predictive => will estimate the binary interaction parameters between every component pair, except dissolved gases and solvents.
   - Same applicability as the other γ models, but should only be used for
   - preliminary design calculations but not for final.

γ Models in A+ (Cont'd)

8. UNIFAC, UNIF-LL, UNIF-DMD, UNIF-HOC, UNIF-LBY (Cont'd)
   - UNIFAC uses RK EOS for the vapor.
   - The original version of UNIFAC can predict both VLE and LLE.
     So UNIFAC is good for VLE and UNIF-LL is good for LLE.
   - Two modifications to the original UNIFAC

     Named after the location of the universities where they were developed

     1. Lyngby in Denmark
     2. Dortmund in Germany - activity coefficient at infinite dilution is improved.

   - The modifications are as follows:
     - Include more temperature-dependent terms of the group-group interaction parameters
     - Predict VLE and LLE with a single set of parameters
     - Predict heats of mixing better

Characteristics of γ Models

- Advantage
  - Ability to represent highly nonideal liquid mixtures
- Disadvantages
  - Many parameters required and they are highly temperature dependent
  - Cumbersome for supercritical components
  - Inconsistent in critical region; hence, only accurate at low and moderate pressures

Another Class of Property Methods

- Equation of State Models (EOS Models)

VLE: $\varphi_i^V y_i = \varphi_i^L x_i$

Enthalpy: $h^V = h^{IG} + \Delta h^V$

$h^L = h^{IG} + \Delta h^L$

Volume: V^V from EOS

V^L from EOS

- In essence, an EOS model uses only one method to calculate properties of both vapor and liquid

EOS Models in A+

Important EOS models in A+ are:

- Traditional EOS Models

1. BWR-LS
   - BWR-Lee-Starling virial-type equation of state
2. LK-PLOCK
   - Lee-Kesler-Plocker virial-type equation of state

EOS Models in A+ (Cont'd)

3. RK-SOAVE, RKS-BM
   - Based on the Redlich-Kwong-Soave cubic equation of state
   - Appropriate for non-polar and mildly polar compounds in gas processing, refinery, and petrochemical applications
   - RKS-BM contains the Boston-Mathias modification, making it more accurate for light gases at highly reduced temperature (> 5).
4. PENG-ROB, PR-BM
   - Based on the Peng-Robinson cubic equation of state
   - PR-BM contains the same modification as in RKS-BM.

EOS Models in A+ (Cont'd)

- All 4 EOS models are appropriate for non-polar and mildly polar mixtures, such as hydrocarbons and light gases (e.g. CO_2 , H_2 S, and H_2)
- All 4 models give comparable results but RKS and PR are more accurate. Accuracy PR > RKS > BWR-LS > LK-PLOCK
- All models contain at least 1 binary interaction parameter.
- Built-in parameters are available in A+ databanks for all above EOS methods.
- If built-in parameters are missing in databanks, only LK-PLOCK has built-in correlations to estimate the binary parameters.

Characteristics of Traditional EOS Models

- Advantages
  - Fewer binary parameters than γ models
  - Some degree of nonideal behavior without binary parameters
  - Unencumbered by the presence of supercritical components
  - Consistent in critical region; hence, accurate even at high pressures
- Disadvantage
  - Limited in ability to represent highly nonideal behavior

Flexible and Predictive EOS Methods

- Combine the best characteristics of both γ and EOS methods
- Can handle highly nonideal mixture with high accuracy; at the same time, work well near critical region of mixtures (high-pressure and temperature conditions)
- Can handle liquid-liquid separation at high pressures too
- Different from traditional EOS in that binary interaction parameters can be estimated using various mixing rules

Flexible and Predictive EOS Methods (Cont'd)

- There are 3 main types of EOS under this predictive category:
  1. RKSMHV2, RKSWS, PSRK
  2. PRMHV2, PRWS
  3. SR-POLAR

PSRK, RKSMHV2, RKSWS

- All are extensions of the Redlich-Kwong -Soave EOS.
- The following mixing rules are used to predict interactions at any pressure for each EOS:

Predictive EOS	Mixing Rules
RKSMHV2	MHV2
RKSWS	Wong-Sandler
PSRK (Predictive RKS)	Holderbaum-Gmehling

PRMHV2, PRWS

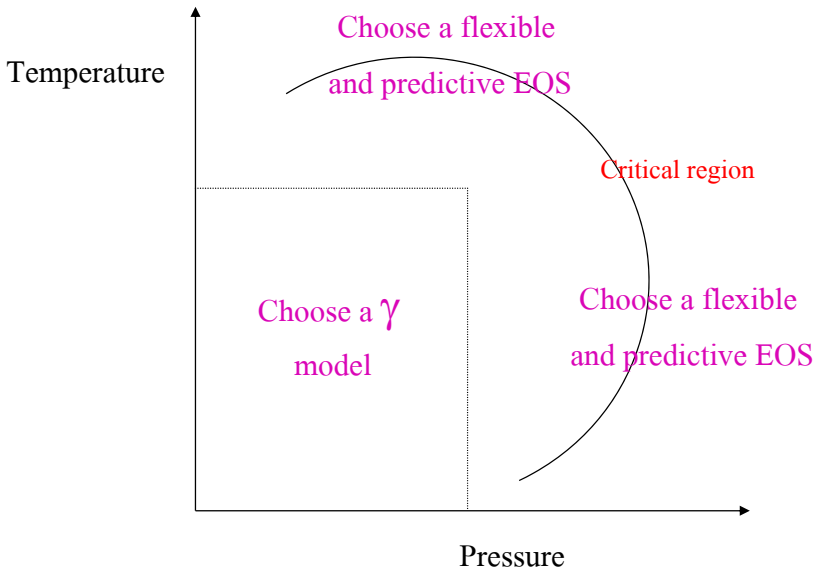
- All are extensions of the Peng -Robinson EOS.
- The following mixing rules are used to predict interactions at any pressure for each EOS:

Predictive EOS	Mixing Rules
PRMHV2	MHV2
PRWS	Wong-Sandler

SR-POLAR

- Based on an equation-of-state model by Schwarzentruber and Renon, which is an extension of the Redlich-Kwong-Soave equation of state
- Can apply the method to both non-polar and highly polar components, and to highly nonideal mixtures.
- Recommended for high temperature and pressure applications
- If you do not enter binary parameters, A+ estimates them automatically using VLE data generated from the UNIFAC group contribution method.

Choosing a Property Method for Nonideal Systems



Special Property Methods

- Steam Tables for pure water and steam systems

1. STEAM-TA
   - 1967 ASME steam table correlations
   - 273.15 K < T < 1073 K
   - Maximum pressure = 1000 bar
2. STEAMNBS
   - 1984 NBS/NRC steam table correlations
   - 273.15 K < T < 2000 K
   - Maximum pressure = 10000 bar

Special Property Methods (Cont'd)

- Crude oil and petroleum refinery

3. BK-10
   - Uses the Braun K-10 K-value correlations
   - All parameters for BK-10 are built-in
   - Developed from the K10 charts for both real components and oil fractions
   - The real components include 70 hydrocarbons and light gases
   - The oil fractions cover boiling ranges 450 – 700 K (350 – 800 ^{o}F)
   - Suited for vacuum and low pressure applications (up to several atm)
   - For higher pressures, use CHAO-SEA or GRAYSON instead

Exercises in Choosing an Appropriate Property Method

	Chemical System	Operating Condition	Suitable Methods
1.	Acetone, water	1 atm	???
2.	C_1- C_6 , H_2 , CO_2	Any pressure	???
3.	Benzene, toluene, xylenes	2 atm	???
4.	Hydrocarbons, N_2, H_2 S, CO, CO_2	1-3 atm	???
5.	Ethanol, water, acetic acid	1-2 atm	???

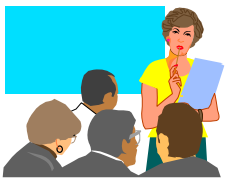
Exercises (Cont'd)

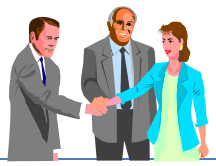
	Chemical System	Operating Condition	Suitable Methods
6.	Hydrocarbons, N_2 H_2 S, CO_2	Very high temperature	???
7.	Propanol , water, methanol, MEK, O_2	1-2 atm	???
8.	Benzene, water, ethanol	1-3 atm	???
9.	Benzene, water, ethanol	10-15 atm	???
10.	Water and steam	Any pressure	???

References on Property Method Selection

- Use Help in A+ to find "Guidelines for Choosing a Property Method" or press "Methods Assistant" button in the ribbon of A+.
  - Recommendations for electrolytes, non-electrolytes, and pseudocomponents
  - Decision trees

- Be sure to read the following article by Eric Carlson
  - **Don't Gamble with Your Physical Properties**, **Chemical Engineering Progress**, October 1996, pp. 35-46.





Specifying Multiple Sections and Multiple Property Methods in ASPEN PLUS

Specifying Property Methods in a Simulation

- There are 2 levels of specifying property methods in A+:
  1. Specify a single base method for the entire flowsheet (default)
     - Enter a base method in the Global sheet of Properties Specifications
  2. Specify different methods for use in individual flowsheet sections or individual unit operation blocks
     - Must first partition the flowsheet into different sections
     - Each flowsheet section may comprise one or more unit operation blocks
     - Then assign a property method to each section

Example of Multiple Flowsheet Sections and Property Methods

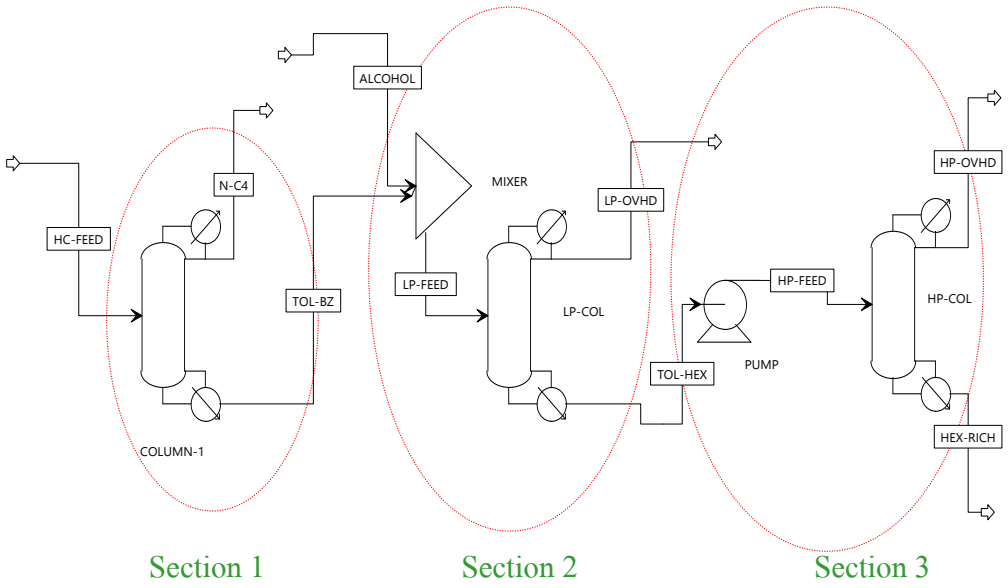
- Consider a process consisting of the following 3 sections:
  1. SECTION1: Low pressure, hydrocarbons and light gases

     Use RK-SOAVE
  2. SECTION2: Low pressure, nonideal liquid with dissolved gases

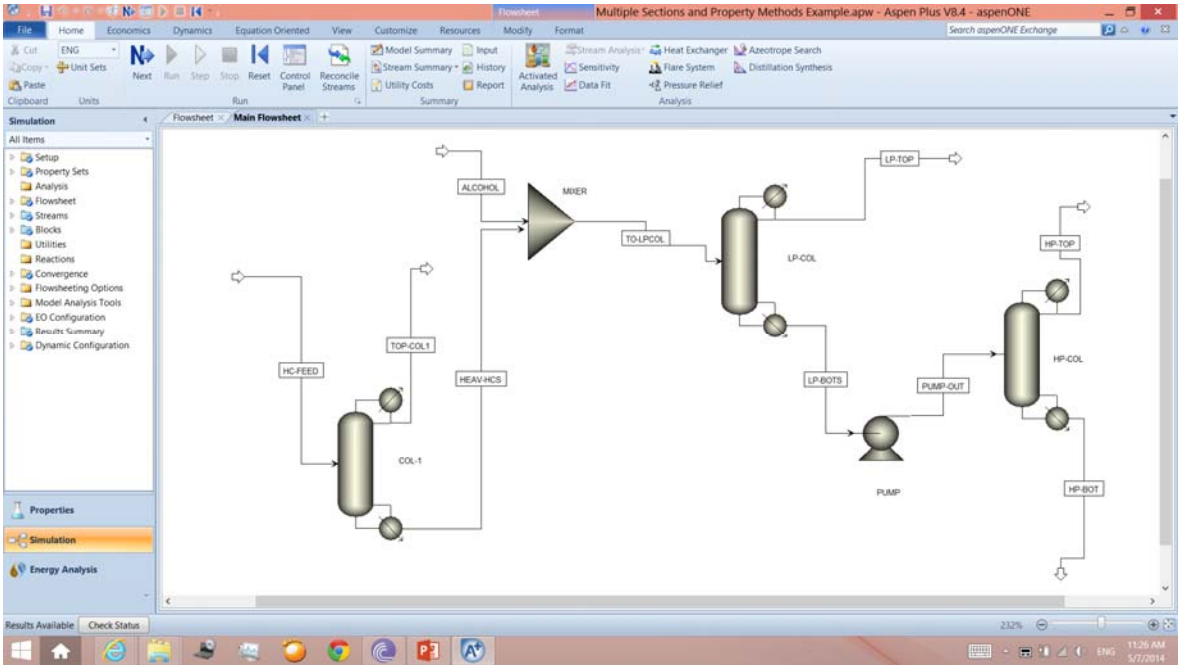
     Use NRTL-RK
  3. SECTION3: High pressure, nonideal liquid with dissolved gases

     Use SR-POLAR

Multiple Flowsheet Sections and Property Methods



Multiple Flowsheet Sections and Property Methods



Input Data for the Multiple Sections Example

- HC-FEED : Hydrocarbons feed
  - T = 100 °F , P = 20 psia
  - Benzene, toluene, and n-butane at 1000 lbmol /hr each
- ALCOHOL : feed with alcohol and light gases
  - T = 100 ° F , P = 20 psia
  - Hexanol and ethanol at 500 lbmol/hr each
  - N_2 at 50 lbmol/hr and CO_2 at 30 lbmol/hr
- COLUMN-1 : DISTIL block
  - Nstage = 10, Feed tray location = 5, RR = 2, D:F = 0.6
  - Ptop = 14.7 psia , Pbot = 16.0 psia

More Input Data

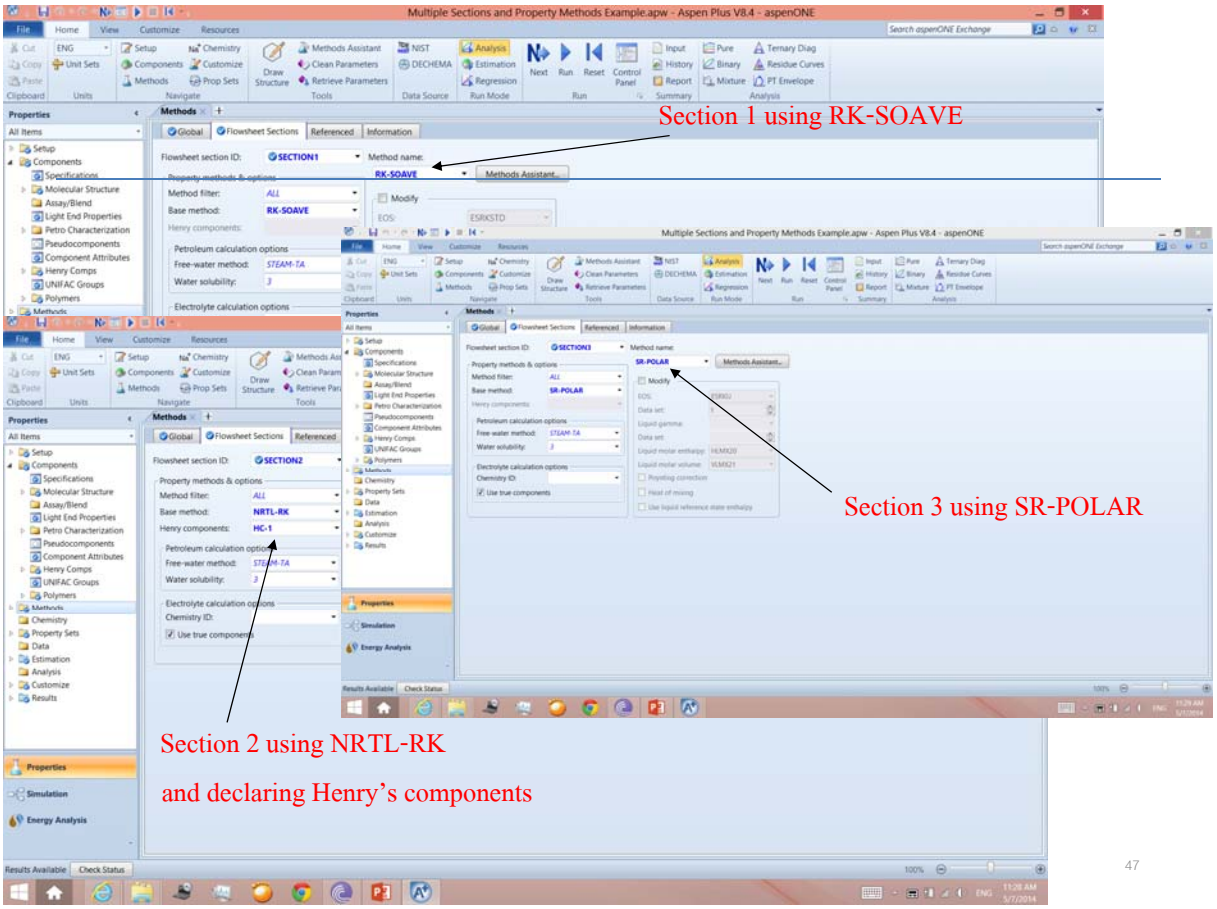
- LP-COL : Low-pressure DISTIL block
  - Nstage = 15, Feed tray location = 8, RR = 1, D:F = 0.6
  - Condenser = Partial, Ptop = 14 psia , Pbot = 15 psia
- HP-COL : High-pressure DISTIL block
  - Nstage = 20, Feed tray location = 10, RR = 2, D:F = 0.3
  - Ptop = 200 psia , Pbot = 210 psia
- PUMP
  - Discharge pressure = 220 psia

Creating Multiple Sections in a Flowsheet

- First, one must create new sections (default is one section called GLOBAL).
- Create / rename new sections in Flowsheet pulldown menu
- Then, assign each unit operation block to a section as follows:
  - Highlight a unit operation block
  - Bring up the block pop-up menu with the right mouse button
  - Choose Change Section from the pop-up menu
- Finally, assign a base property method to each section in the Flowsheet Sections tab of the Properties Specifications form

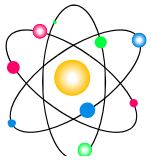
Declaring Dissolved Gases as Henry's Law Components

- Recall that in a γ method, all light gases must be treated as Henry's law components.
- Must declare CO_2 and N_2 as Henry's law in the NRTL-RK method
  - Create a Henry ID in the SECTION2 of the Flowsheet Sections tab
  - Press the Next button and A+ will bring up a form for you to declare a list of Henry's components (can also be accessed via Components-->Henry Comps from the Data Browser)



Stream Results of the Multiple Sections Example

	ALCOHOL	HC-FEED	HEAV-HCS	HP-BOT	HP-TOP	LP-BOTS	LP-TOP	PUMP-OUT	TO-LPCOL	TOP-COL1
Temperature F	100	100	225.6	432.6	384.5	250	187.9	248.3	154.3	55.8
Pressure psia	20	20	16	110	100	15	14	220	16	14.7
Vapor Frac	0	0.02	0	0	0	0	1	0	0	0
Mole Flow lbmol/hr	1080	3000	1200	638.4	273.6	912	1368	912	2280	1800
Mass Flow lb/hr	76843.768	228377.56	107613.086	63665.796	25380.804	89046.6	95410.254	89046.6	184456.854	120764.474
Volume Flow cuft/hr	1528.31	22180.891	2201.178	1884.124	687.231	1901.983	664699.74	2142.452	3672.077	2689.423
Enthalpy MMBtu/hr	-145.878	-34.18	16.453	-61.979	2.46	-69.911	-32.458	-69.798	-129.425	-47.829
Mole Flow lbmol/hr										
N-BUTANE		1000	< 0.001				< 0.001		< 0.001	1000
ETHANOL	500			trace	< 0.001	< 0.001	500	< 0.001	500	
BENZENE		1000	210.705	0.001	0.14	0.141	210.564	0.141	210.705	789.295
TOLUENE		1000	989.295	155.808	256.207	412.014	577.28	412.014	989.295	10.705
HEXANOL	500			482.591	17.253	499.844	0.156	499.844	500	
CO2	30				trace	trace	30	trace	30	
N2	50				< 0.001	< 0.001	50	< 0.001	50	



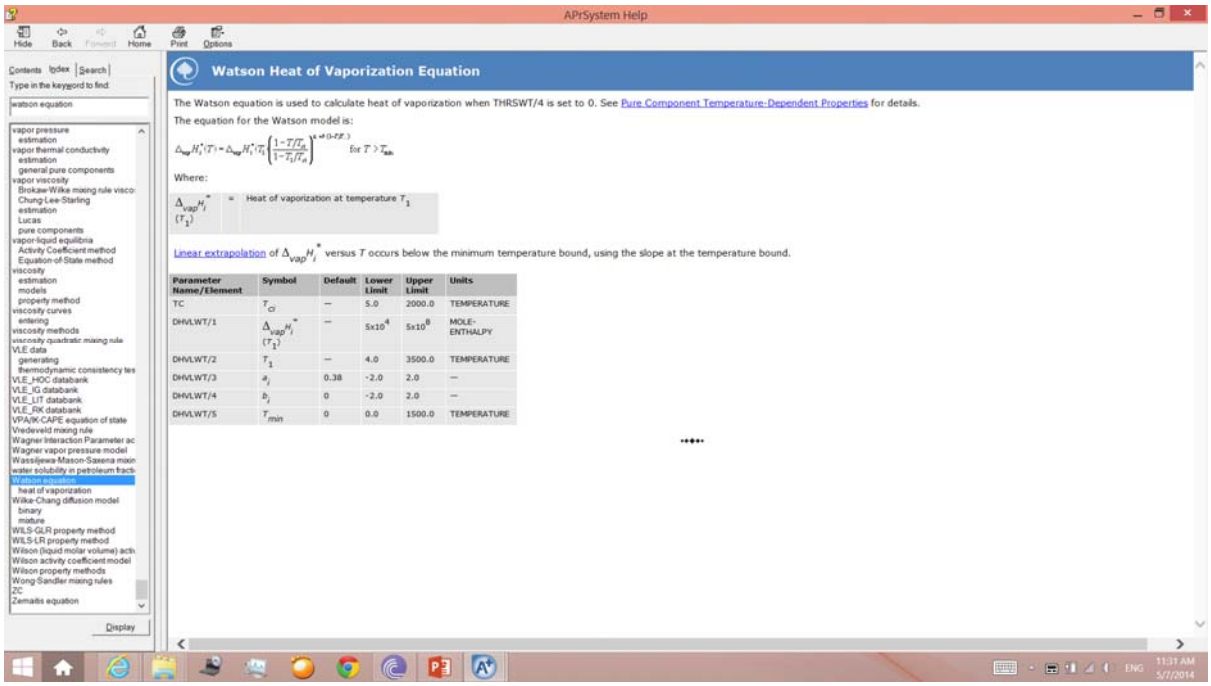
Physical Property Parameters

in

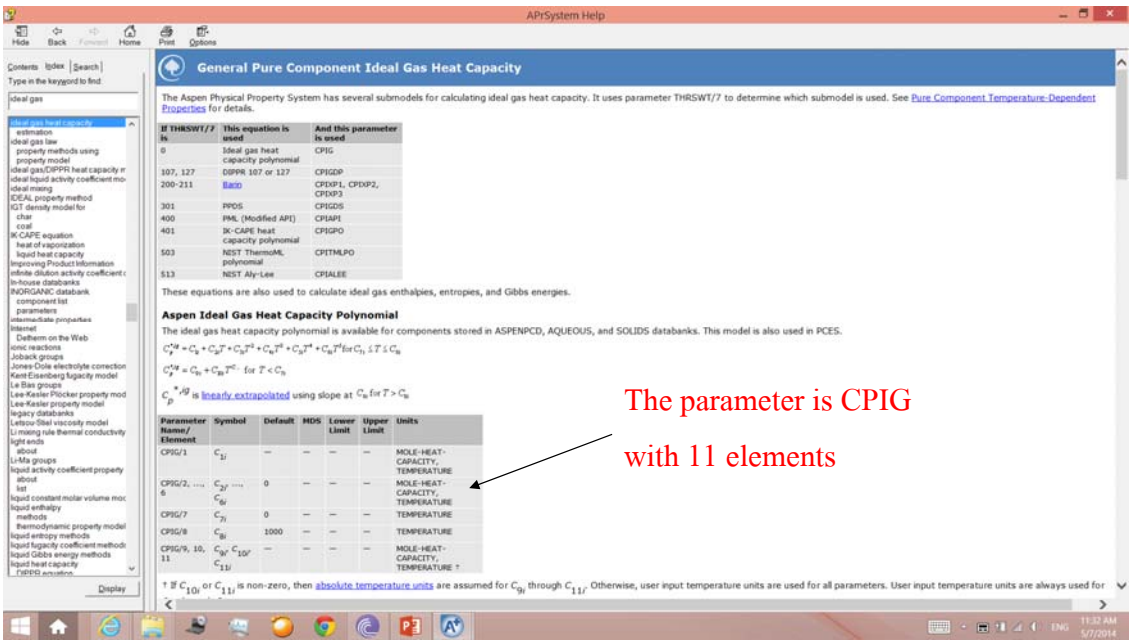
ASPEN PLUS

Physical Property Parameters

- Physical property models require parameters in order to calculate the requested physical property values.
- Example: The Watson model
  - Used to calculate the heat of vaporization of a pure component at a given temperature
  - The model contains two A+ parameters: TC and DHVLWT
  - DHVLWT in turn contains 5 elements as shown in the next slide



Another Example: The Ideal Gas Heat Capacity Model



Physical Property Parameters (Cont'd)

- In A+, property parameters can be classified in 2 different ways:
  1. Based on components
  2. Constants or correlations
- Component-based parameters
  - Unary parameters --> associated with a single component

    e.g. MW, CPIG, PLXANT, TB
  - Binary parameters --> associated with a pair of components

    e.g. HENRY, a_{ij} and b_{ij} in the γ methods, RKSKIJ, PRKIJ

Physical Property Parameters (Cont'd)

- Constants or Correlations
  - Universal constants --> not a function of temperature

    e.g. MW, TC, PC, VC, TB
  - Correlation parameters --> a function of temperature

    e.g. CPIG, PLXANT, DHVLWT
- Property parameters are stored in A+ property databanks.
- Binary databanks for various property methods are automatically invoked.
  - All RKS-based and PR-based EOS methods
  - All γ methods except Van Laar

Physical Property Databanks

- Important pure component databanks are:

1. APV84 PURE28
   - Main source of pure component parameters
   - Contains parameters for 2,114 (mostly organic) components
   - Based on the data developed by the AIChE DIPPR data compilation project (January 2012 public DIPPR release)
   - The content is continually updated, expanded, and improved

Physical Property Databanks (Cont'd)

2. APV84 AQUEOUS
   - Contain parameters for electrolyte systems (1,688 ionic species)
3. APV84 INORGANIC
   - Contains thermochemical data for about 2,477 (mostly inorganic) components used in solids and pyrometallurgical applications
4. APV84 SOLIDS
   - Contains parameters for 3,312 solid components
   - Used for solids and electrolytes applications
   - Is largely superceded by the INORGANIC databank, but is still essential for electrolytes applications.

Physical Property Parameters Requirements

- Do not assume A+ contains a complete set of property parameters for the compounds and base methods you choose for simulation.
- After choosing the chemical components and base methods, the user should:
  1. Determine what parameters are required for the property methods you chose.
  2. Determine what parameters are available in the databanks.

Parameter Requirements (Cont'd)

3. If there are missing parameters in the databanks, supply the missing values
   - from literature or experimental sources
   - from estimation (PCES)
   - from data regression

- Note: If you are not familiar with any of the parameters, be sure to use Help to examine the equation in which the parameter is used.

Exercise on Property Parameter

- Suppose you come across an A+ parameter called RKTKIJ , and you don't know what it is.
- How do we find out what it is and where it is used (i.e. what property equation contains RKTKIJ)?
- Answers:

  1. RKTKIJ is _____
  2. Property that uses RKTKIJ _____
  3. Name of the property equation that contains RKTKIJ

     _____

Steps in Checking the Property Requirements

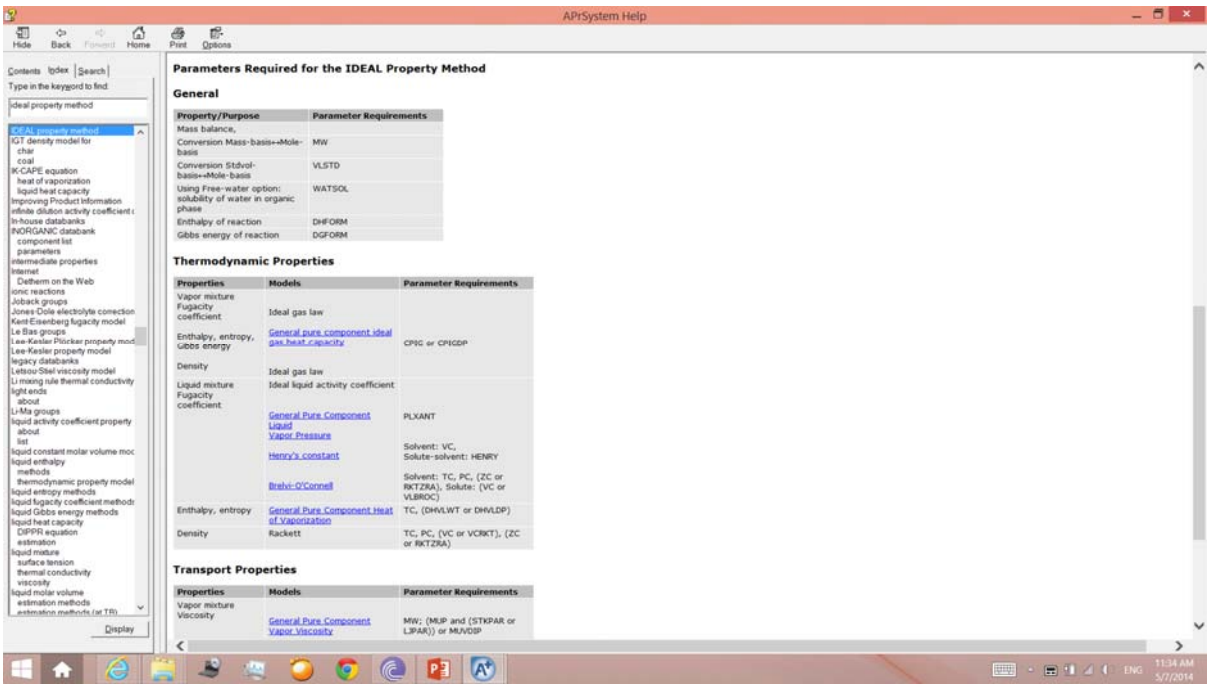
- To determine what parameters are required for a given property method, follow these three steps:

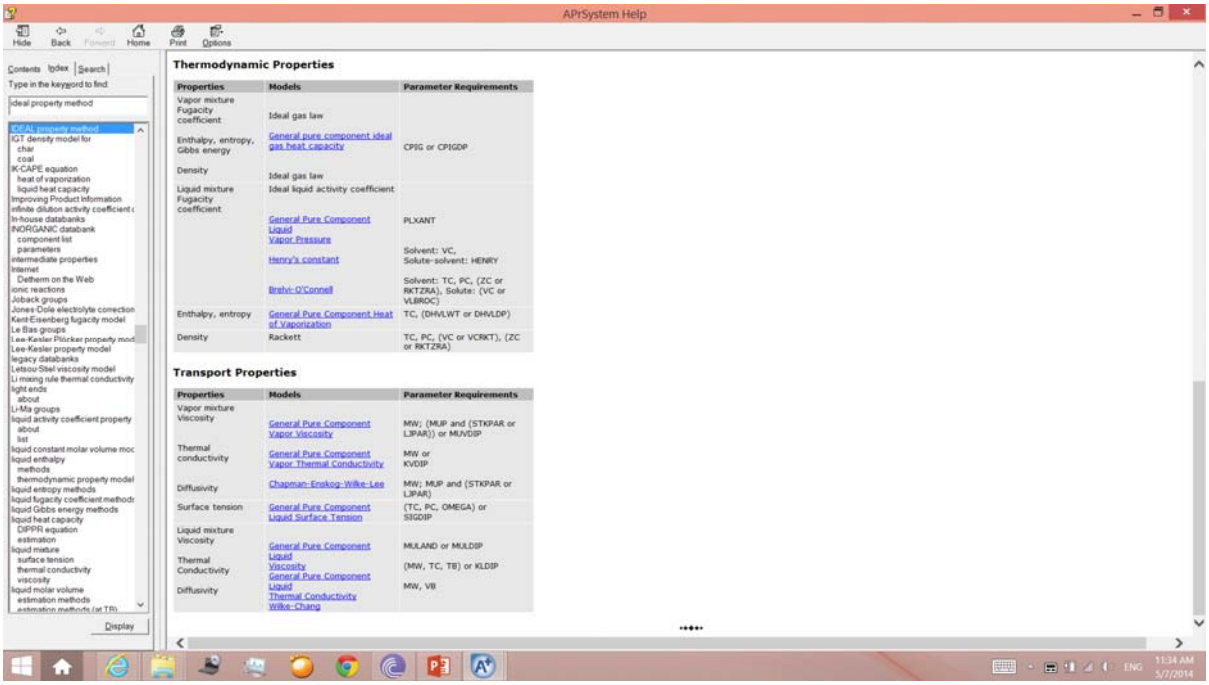
  1. Always needed: MW, CPIG (or CPIGDP), PLXANT, and DHVLWT (or DHVLDP) except for EOS models
  2. Special situations:
     - Chemical reactions: DHFORM, DGFORM (for RGIBBS model)
     - When Stdvol basis is used for feed: VLSTD
     - When Free-water calculations is requested: WATSOL
     - Declare Henry's law components: HENRY for each dissolved-gas solvent pair

Steps in Checking the Property Requirements (Cont'd)

3. Use A+ Help to find the property method and check its property requirement table
4. If transport properties are requested, check the hypertext link to Parameters Required for Common Models in each method

- Example: Find all property parameters required in the IDEAL method





Summary of Parameters Required in IDEAL

- Suppose all transport properties are requested in the simulation
  - MW, CPIG, PLXANT, DHVLWT
  - TC, PC, VC, ZC
  - MUP, STKPAR or LJPAR for vapor mixture viscosity and diffusivity
  - OMEGA for surface tension
  - MULAND for liquid mixture viscosity
  - TB for liquid mixture thermal conductivity
  - VB for liquid diffusivity

Exercise: Parameters Required in NRTL-RK

- Consider a mixture of acetone, water, ethanol, CO, O_2, and CO_2
- All light gases participate in an equilibrium reaction.
- Liquid viscosity and vapor thermal conductivity are requested.
- Determine all the required parameters if we use NRTL-RK method
  - _____
  - _____
  - _____
  - _____

Parameters Input

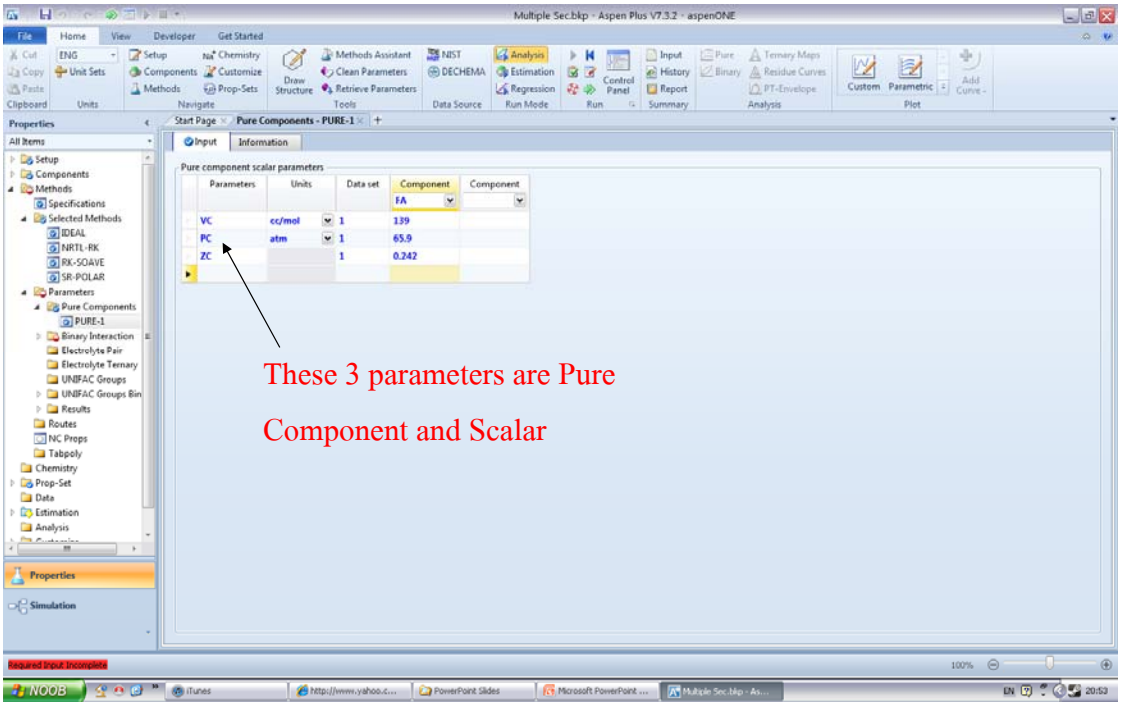
- Two reasons for entering your own values of parameters
  - The required values are missing from the A+ databanks.
  - User wants to use his/her own values, which may be more accurate.
- A+ property parameters are classified as follows
  - Pure Component
    - Scalar or T-dependent correlation
  - Binary Interaction
    - Scalar or T-dependent correlation

Parameters Input (Cont'd)

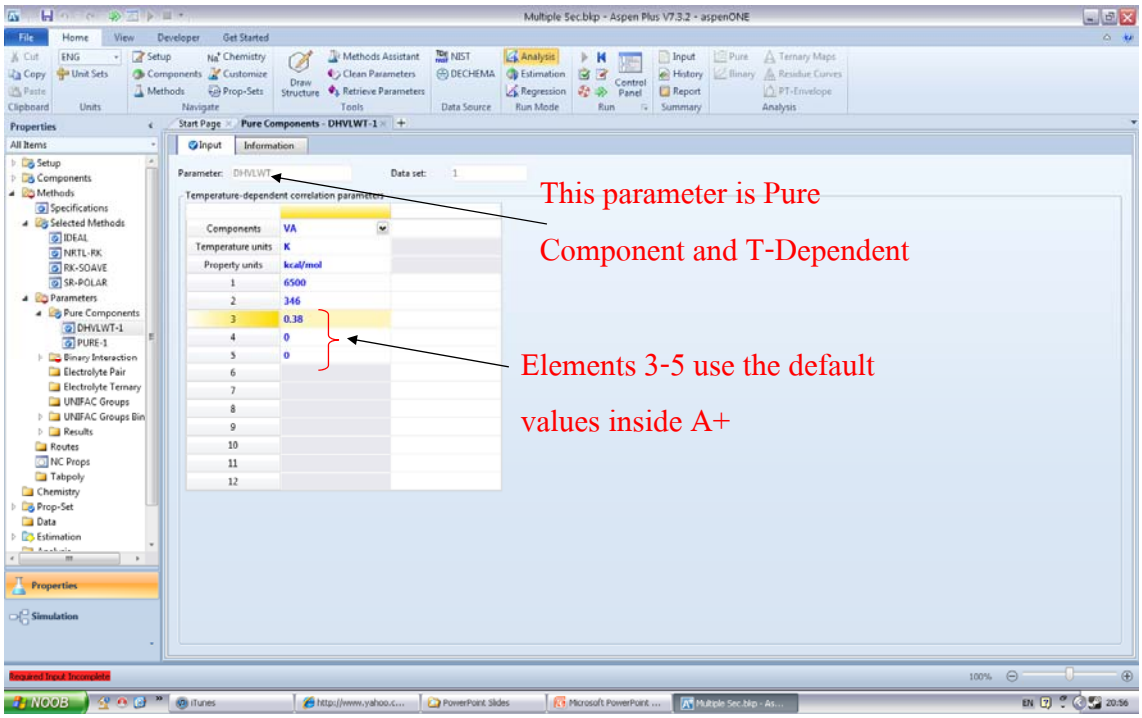
- It is very important that you know what category a parameter belongs to
- So that you can enter its value at the proper location (or form)
- Example: A mixture of 3 components, formic acid, vinyl acetate, and water
  - Formic acid: VC = 139 cc/gmol, PC = 65.9 atm, ZC = 0.242
  - Vinyl acetate: Heat of vaporization at NBP (346 K) = 6500 cal/gmol
  - Rackett k_{ij}: Formic acid - Water = 1.27

    Formic acid - Vinyl acetate = -1.54

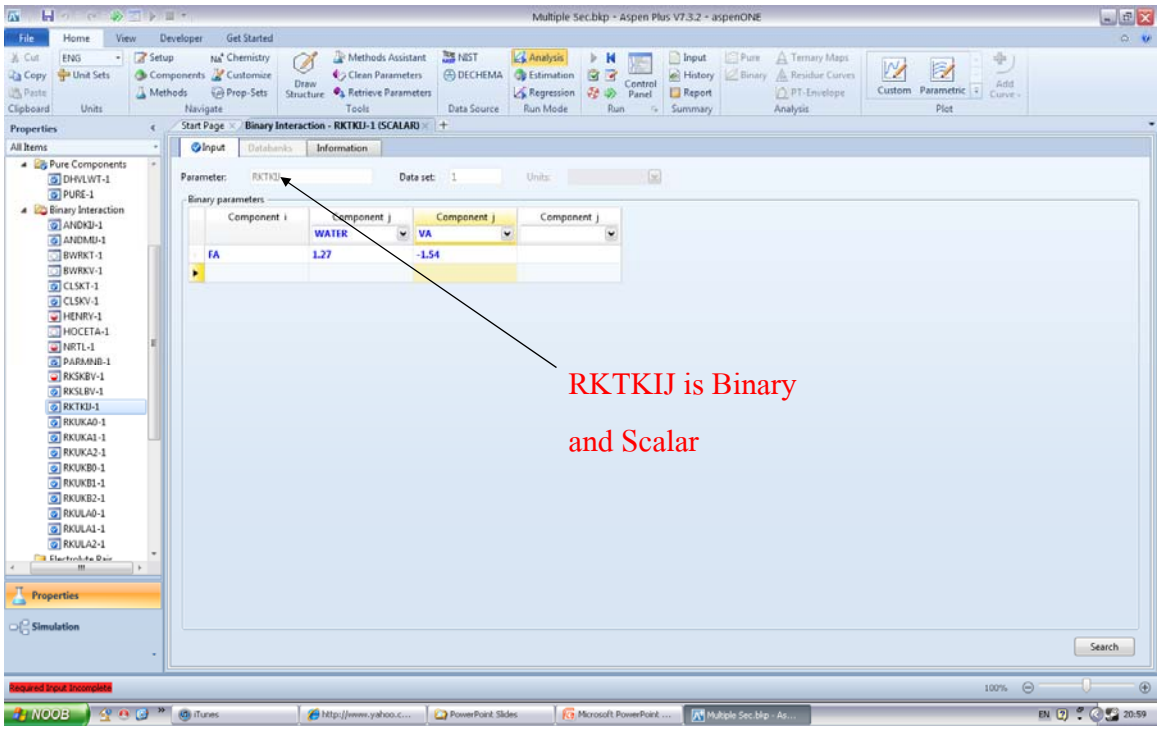
Entering Parameter Values for Formic Acid

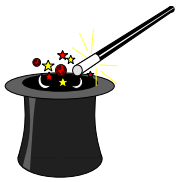


Entering Parameter Values for Vinyl Acetate



Entering the Rackett Interaction Parameter

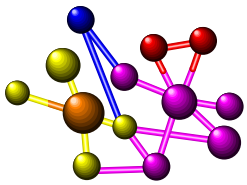




Special Topic:

Tabular and Polynomial

Physical Property Data



Entering Tabular/Polynomial Data in A+

- User may have tabular property data from experiments
  - e.g. vapor pressure vs. temperature data
- User may have polynomial property data (coefficients) that do not conform to the equations in A+
  - e.g. $C_P^{IG} = a_1 + a_2 T + a_3 /T + a_4 /T^2$
- How do we specify PLXANT with the vapor pressure vs. T data we have?
- How do we specify CPIG with the non-standard polynomial equation we have?

Entering Tabular/Polynomial Data (Cont'd)

- Answer: We cannot, unless we use the Data Regression System (DRS) in A+ to regress or fit PLXANT and CPIG from the data we have.
- Simpler Alternative:
  - Use the Tabpoly feature in A+ to enter the data directly
  - Any T-dependent property can be entered this way
  - Access Tabpoly by choosing the TabPoly folder under Properties of the Data Browser

Entering Tabular/Polynomial Data (Cont'd)

- For polynomial data in Tabpoly, you enter the coefficients of a polynomial equation of the form:

$$\left.\begin{array}{c}\text{property}\\ \text{or}\\ \ln\ (\text{property})\end{array}\right\} = \begin{array}{l}a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 / T + \\ \\ a_6 / T^2 + a_7 / T^{1/2} + a_8 \ln T\end{array}$$

- The property is either normal or logarithmic .
- Caution: A+ uses your tabular data directly, and does not fit a polynomial equation to your data. For a temperature not explicitly given, A+ uses interpolation between 2 values to determine the property.

Tabpoly Properties

Property	Model Form
Density for non-conventional components	Normal
Enthalpy for non-conventional components	Normal
Enthalpy of fusion	Normal
Enthalpy of sublimation	Normal
Enthalpy of vaporization	Normal
Henry's constant	Logarithmic
Ideal gas enthalpy	Normal
Ideal gas heat capacity	Normal
Liquid diffusion coefficient	Normal
Liquid enthalpy	Normal
Liquid enthalpy departure	Normal
Liquid entropy	Normal
Liquid entropy departure	Normal

Tabpoly Properties (Cont'd)

Property	Model Form
Liquid fugacity coefficient for a component in a mixture	Logarithmic
Liquid Gibbs free energy	Normal
Liquid Gibbs free energy departure	Normal
Liquid heat capacity	Normal
Liquid-Liquid K-value	Logarithmic
Liquid thermal conductivity	Normal
Liquid viscosity	Logarithmic
Liquid volume	Normal
Pure component liquid fugacity coefficient	Logarithmic
Pure component vapor fugacity coefficient	Logarithmic
Solid enthalpy	Normal
Solid enthalpy departure	Normal
Solid entropy	Normal
Solid entropy departure	Normal

Tabpoly Properties (Cont'd)

Property	Model Form
Solid fugacity coefficient	Logarithmic
Solid Gibbs free energy	Normal
Solid Gibbs free energy departure	Normal
Solid heat capacity	Normal
Solid thermal conductivity	Normal
Solid vapor pressure	Logarithmic
Solid volume	Normal
Surface tension	Normal
Vapor diffusion coefficient	Normal
Vapor enthalpy	Normal
Vapor enthalpy departure	Normal
Vapor entropy	Normal
Vapor entropy departure	Normal

Tabpoly Properties (Cont'd)

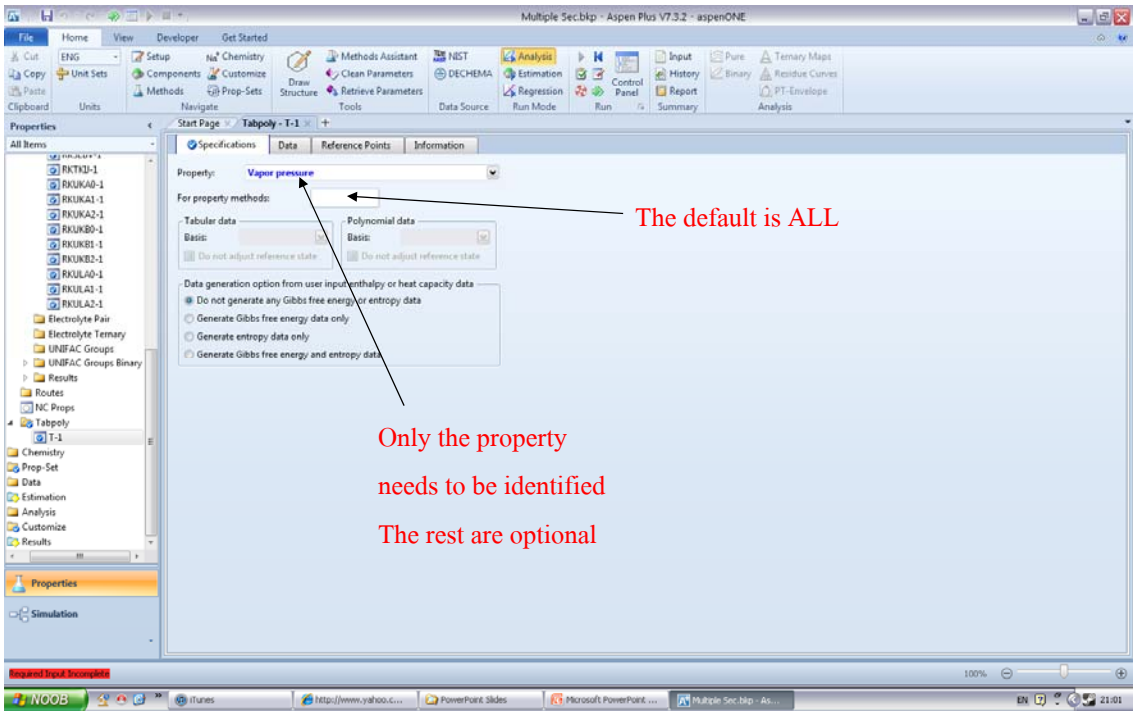
Property	Model Form
Vapor fugacity coefficient for a component in a mixture	Logarithmic
Vapor Gibbs free energy	Normal
Vapor Gibbs free energy departure	Normal
Vapor heat capacity	Normal
Vapor-Liquid K-value	Logarithmic
Vapor pressure	Logarithmic
Vapor thermal conductivity	Normal
Vapor viscosity	Normal
Vapor volume	Normal

Examples of Tabular/Polynomial Data

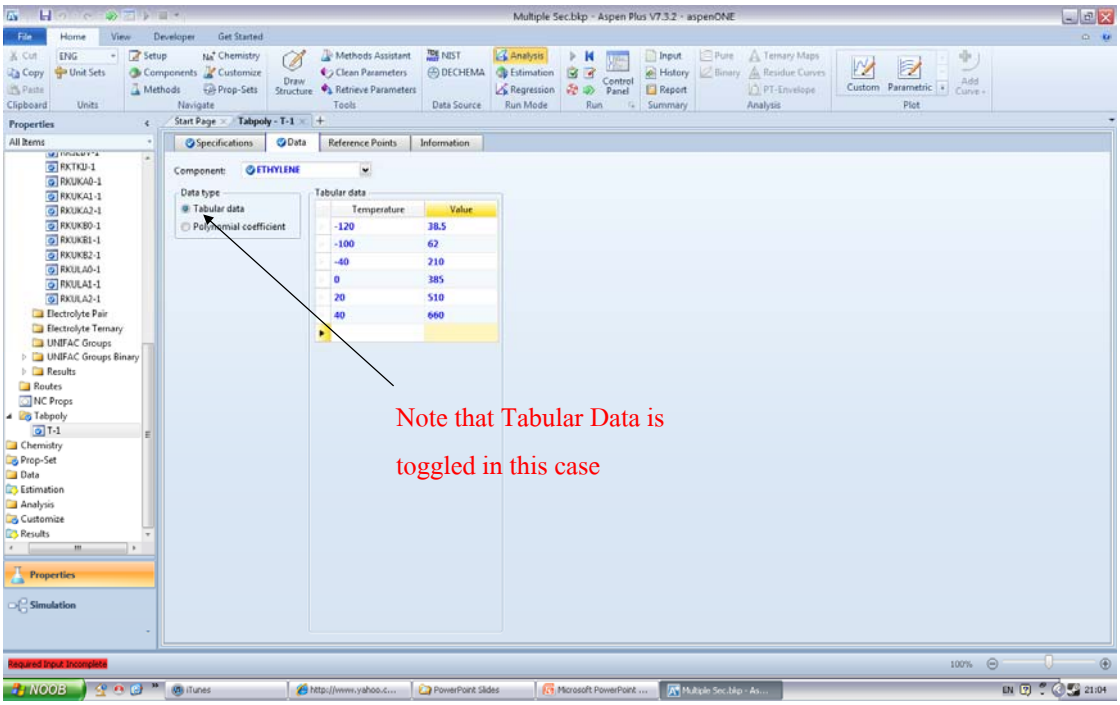
- Example 1: Enter the following tabular vapor pressure data for ethylene and propylene

Temperature (^{O}F)	Ethylene Vapor P	Propylene Vapor P
-120	38.5 psia	1.85 psia
-100	62	3.8
-40	210	20.9
0	385	48
20	510	69
40	660	97

Specification Sheet of Tabpoly



Data Sheet of Tabpoly



Examples of Tabular/Polynomial Data

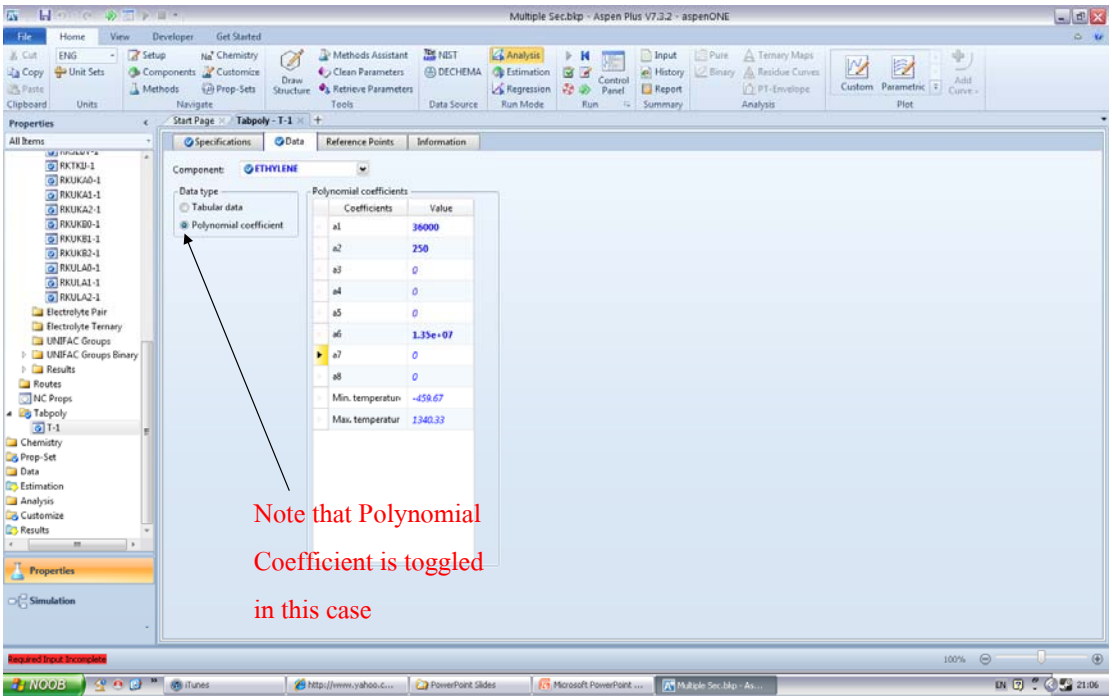
- Example 2: Enter the following equations for the heat of vaporization of ethylene

$$\Delta H^{VAP} \text{ (ethylene)} = 36{,}000 + 250T + 1.35 \times 10^{7}/T^{2}$$

Note: The use of tabular and polynomial data input decreases property parameter requirements

- For example, in the IDEAL method, if volume vs. T data are available, PC, VC, and ZC are not required for that component.

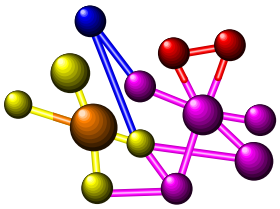
Data Sheet of Tabpoly



Workshop 4: Introducing a Non-Databank Component into the VCM Flowsheet

- Go to Course Notes Section 9 and work on Workshop 4.

Special Topic:
Property Constant
Estimation System (PCES)



Property Constant Estimation System (PCES)

- A system to estimate property parameters required by A+ including
  - Pure component physical property constants
  - Temperature-dependent pure component parameters
  - Binary interaction parameters for Wilson, NRTL, and UNIQUAC
- PCES uses the concept of group-contribution based on the molecular structure of a compound.
- Experimental data can be combined with the molecular structure to enhance the accuracy of PCES.

Two Ways to Use PCES

- On a Stand-Alone Basis
  - A+ estimates all parameters without flowsheet simulation
  - Recommended because it gives user a chance to first view estimated results
  - Invoke by choosing Properties and click Estimation in the ribbon.
- In a Simulation Run
  - A+ estimates all missing parameters that are required in a simulation run

Two Property Estimation Schemes

- Evaluate using NIST TDE (The ThermoData Engine from National Institute of Standards and Technology)
  - New in Version 7.3
  - TDE can only use molecular structure saved in an MDL file (*.mol) or specified using the drawing tool in the User Defined Component Wizard. It cannot use molecular structure specified by atom and connectivity.
- Estimate using Aspen property estimation system.
  - Can use either MDL molecular structure or molecular specified by atom and connectivity.

How to Use NIST TDE?

To run TDE:

1. Specify the component(s) on the Components | Specifications | Selection sheet.
2. On the Home tab of the ribbon, in the Data Source group, click NIST. The NIST ThermoData Engine dialog box appears. Choose Pure or Binary mixture.
3. Select the component from the list in the dialog box. For binary mixture properties select a component from the second list as well.
4. If the CAS number or molecular structure is specified for each component, then the Evaluate Now button (for pure component properties) or Retrieve Data button (for binary mixture properties) is enabled. Click it to estimate property parameters.

OR

For pure component parameters, if neither CAS number nor molecular structure is specified, click Enter Additional Data. The User Defined Component Wizard appears, allowing you to specify the molecular structure and optionally other data about the component. You will be given the option to run TDE to estimate parameters after specifying data.

How to Use NIST TDE? (Cont'd)

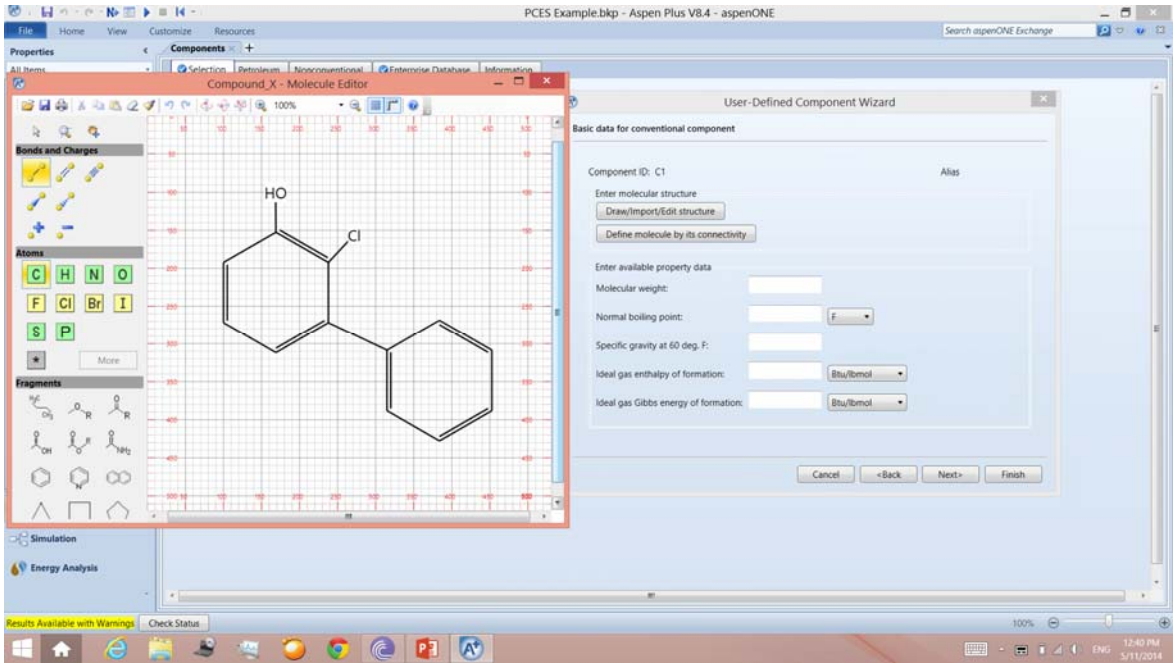
The following data can be sent to TDE:

- ❑ Vapor pressure data
- ❑ Liquid density
- ❑ Ideal gas heat capacity
- ❑ Normal boiling point
- ❑ Molecular structure (if specified using a version V2000 MDL file or using the drawing tool in the User Defined Component Wizard)

Note: TDE takes a couple minutes to run on a typical computer.

When TDE is finished, the results will appear in the TDE Pure window or the TDE Binary window

Draw Structure Tool to Specify Molecular Structure

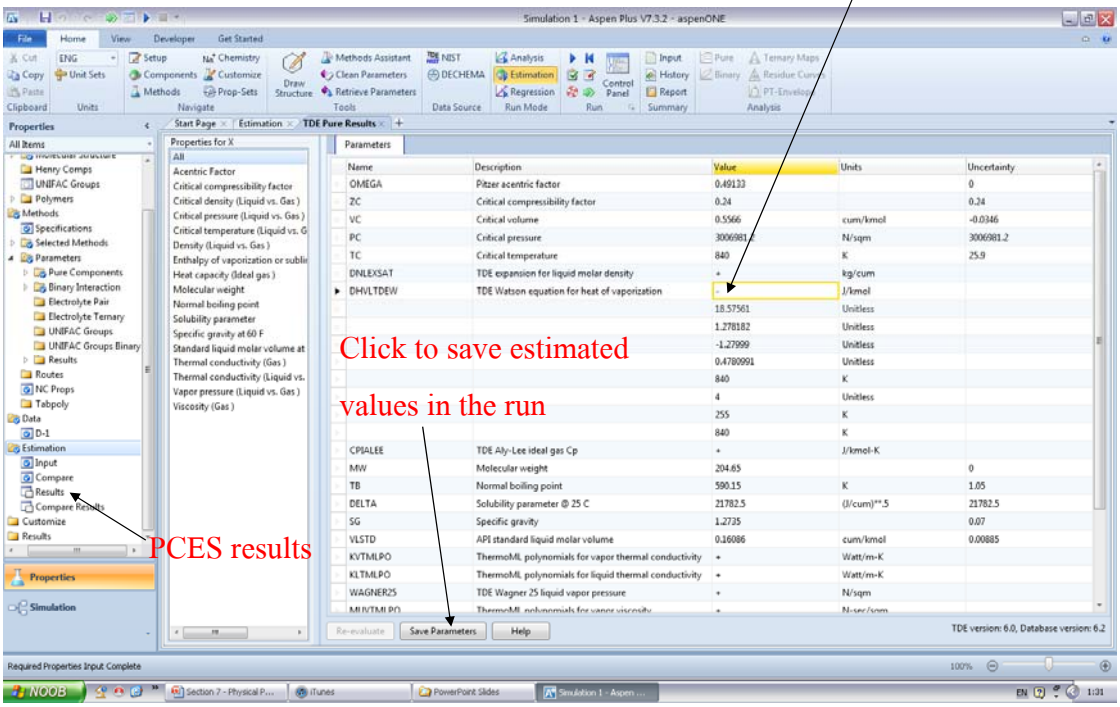


PCES Results from NIST TDE

Click to expand and see correlation

Click to save estimated values in the run

PCES results



How to Use Aspen Property Estimation System?

To run Aspen Property Estimation System:

1. Specify the component(s) on the Components | Specifications | Selection sheet.

2. On the Home tab of the ribbon, in the Run Mode group, click Estimation.

3. In the Setup sheet, choose whether you want to estimate all property parameters or just selected ones.

4. Specify the molecular structure of the component with either one of the following methods:

   (i) Draw/Import/Edit structure (Draw Structure Tool as in TDE).

   (ii) Define molecule by its connectivity.

   - Assign a unique number to each atom, except H.
   - Enter the number of an atom, one by one, and specify the type of bond between every two atoms.

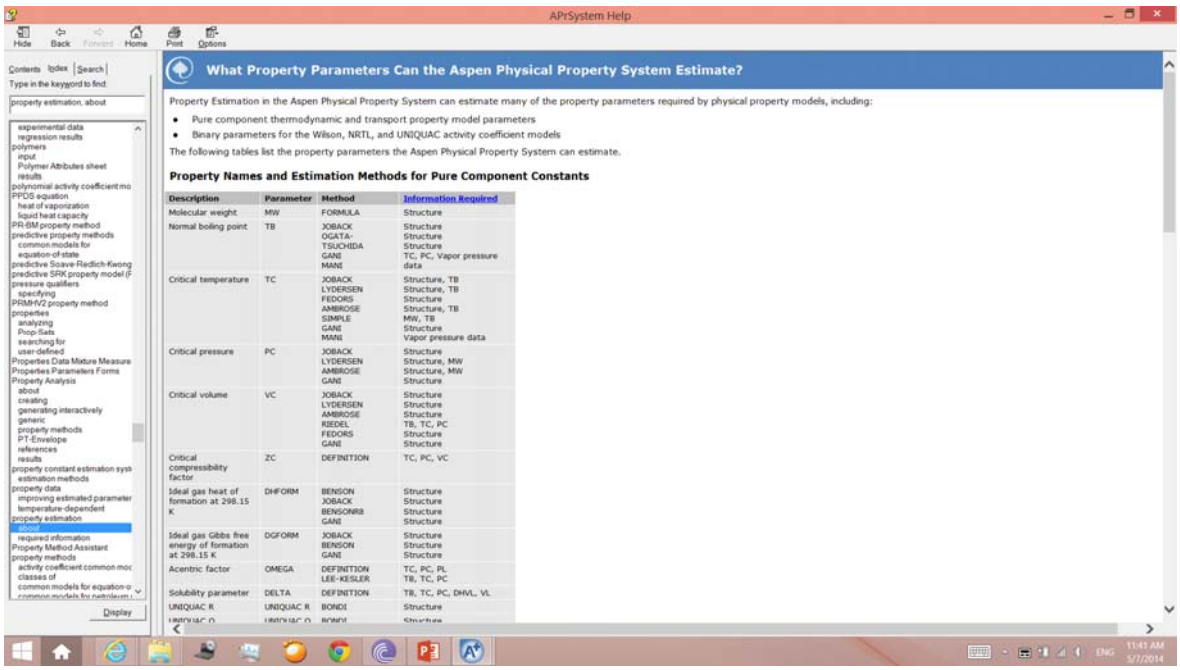
How to Aspen Property Estimation System? (Cont'd)

5. Enter any experimental data using

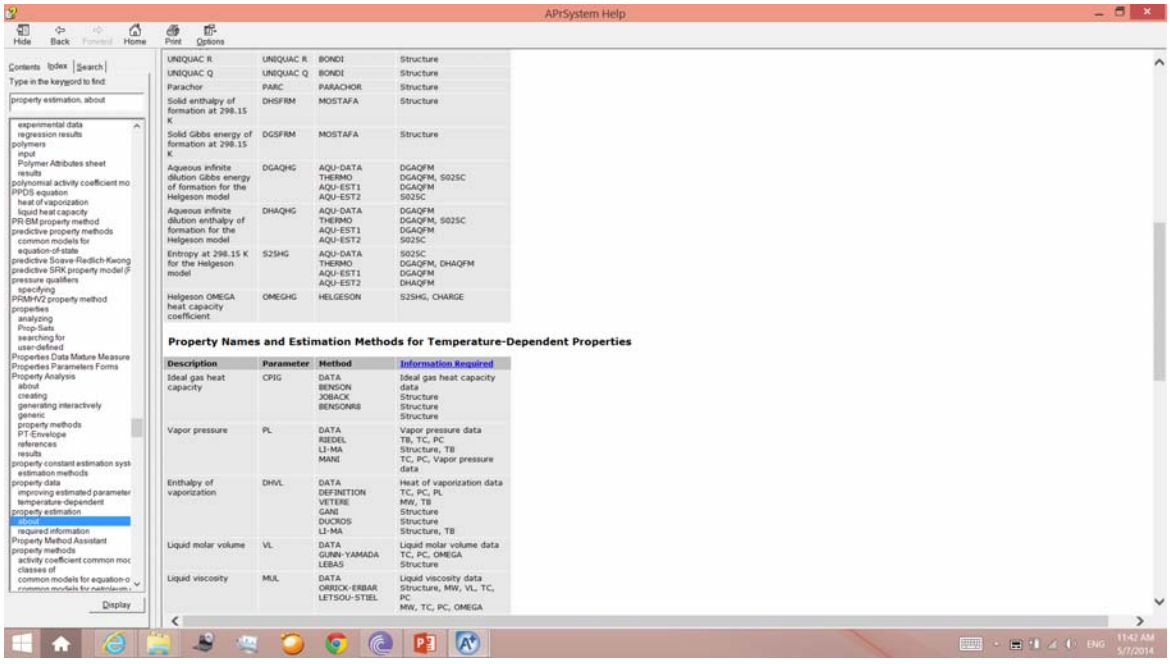
   - If TB is known, it should be entered
   - If tabular data are available, enter them via Properties Data form or Tabpoly.

     However, Data form results are more accurate since data regression will be performed by A+.
   - As much experimental data should be entered as possible in order to prevent propagation of errors.
   - Remember: experimental data should always be used in preference to estimated values.

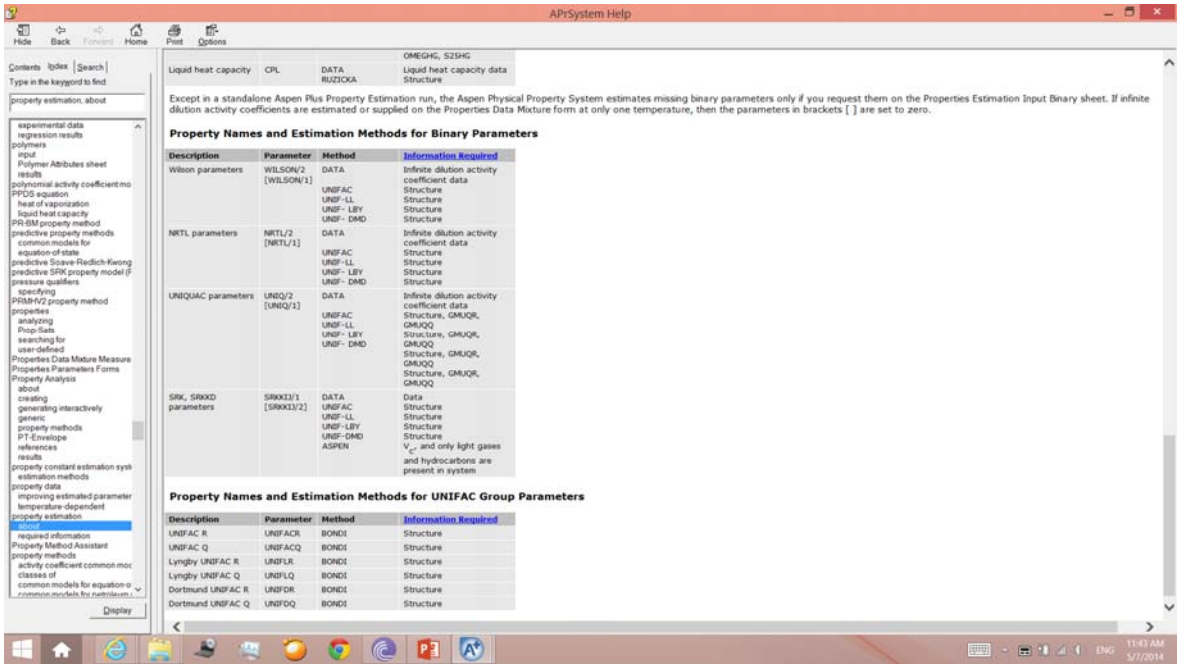
Parameters Estimated by Aspen Property Estimation System



Parameters Estimated by Aspen Property Estimation System



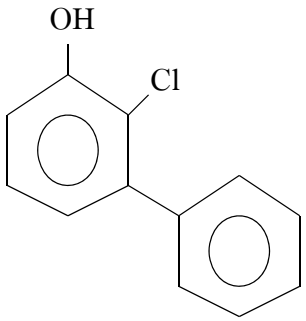
Parameters Estimated by Aspen Property Estimation System



Example of PCES

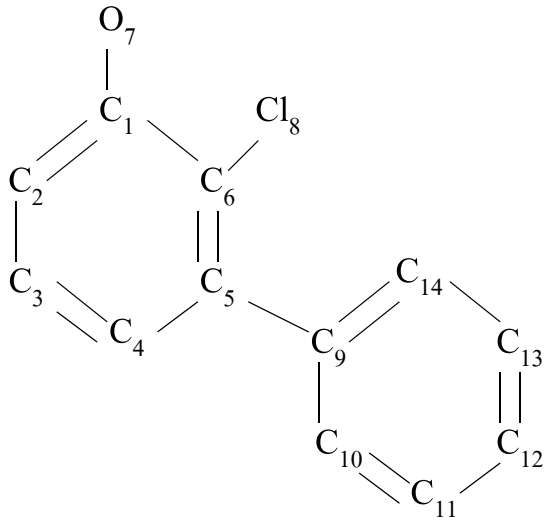
- Estimate the pure component property parameters for a compound, called “2-chloro-3-phenylphenol ” with a chemical formula of $C_{12}H_9ClO$.
- This component is not in the A+ databanks.

The structure of the compound is shown here:



Example of PCES (Cont'd)

- All atoms, except H, are numbered.

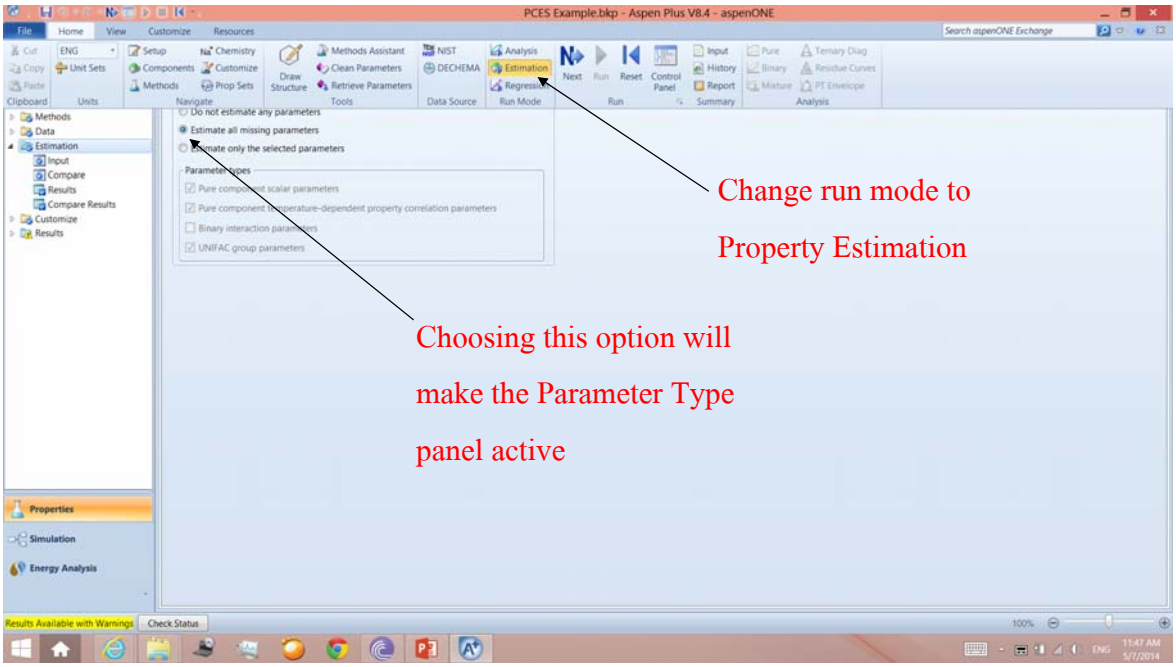


T_B = 590.15 K

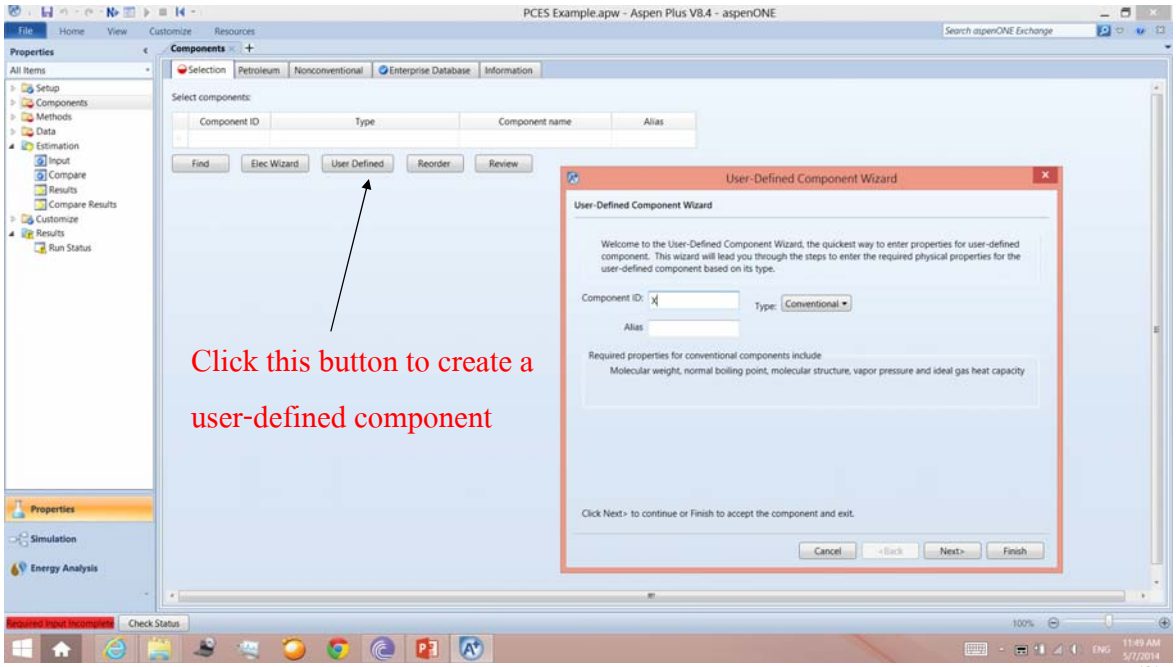
Heat of vaporization data:

Temp (K)	ΔH^{VAP} (J/kmol)
590.15	6.303×10^7
615.87	6.030×10^7
641.60	5.736×10^7
667.32	5.416×10^7
693.05	5.066×10^7
718.77	4.675×10^7
744.50	4.224×10^7

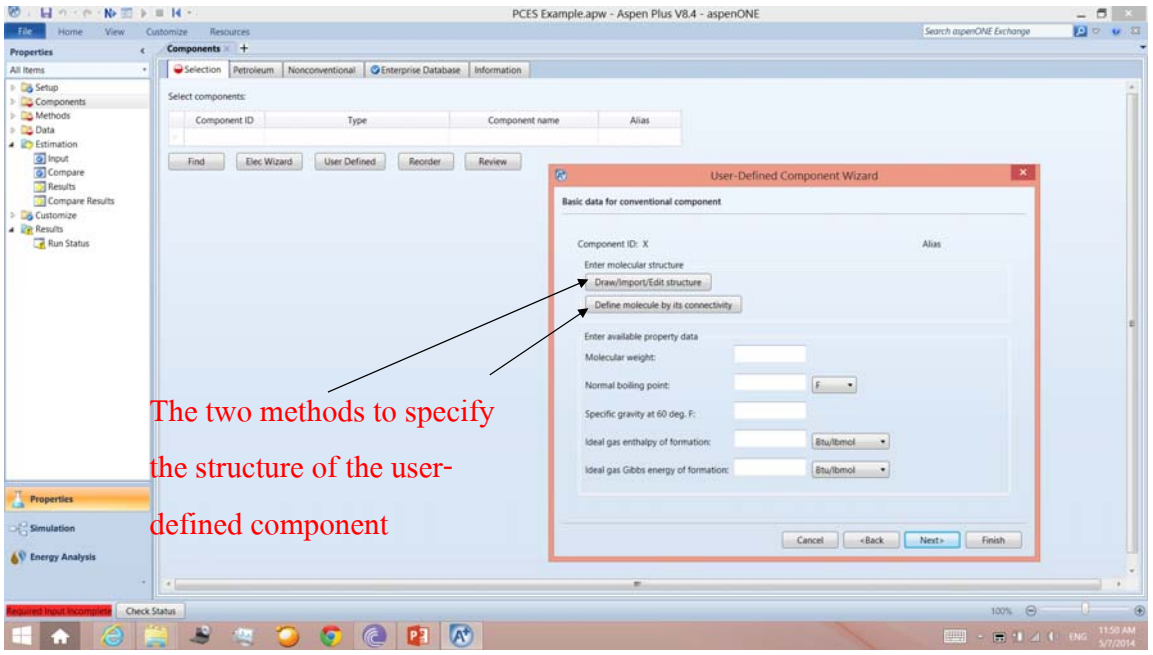
PCES Example



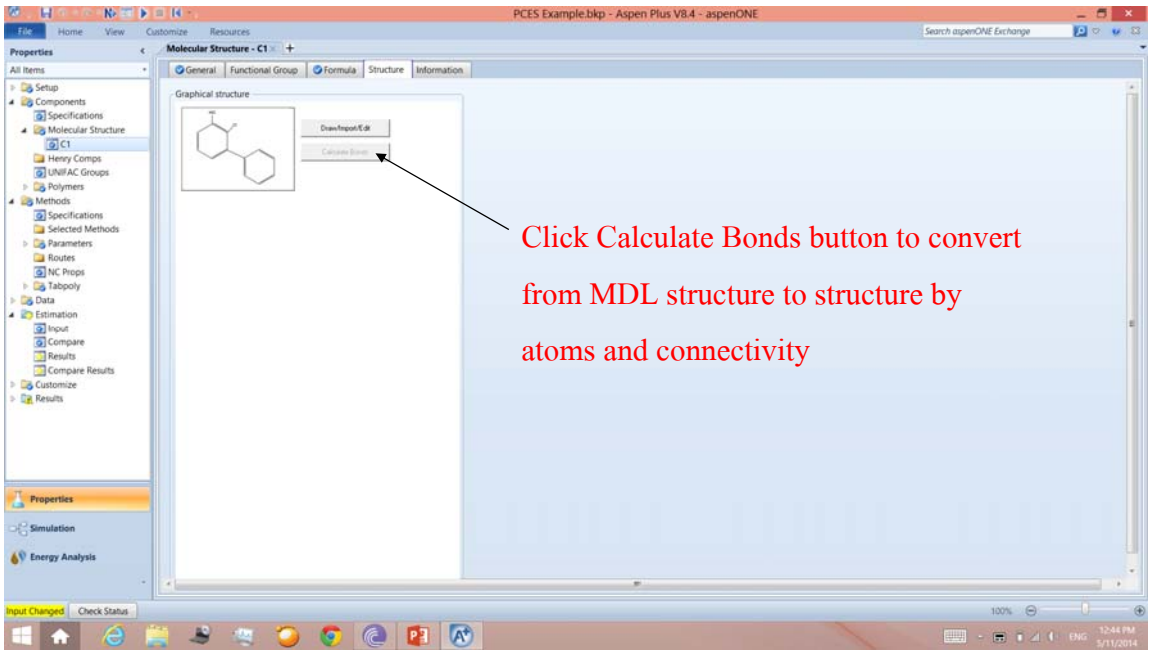
PCES Example (Cont'd)



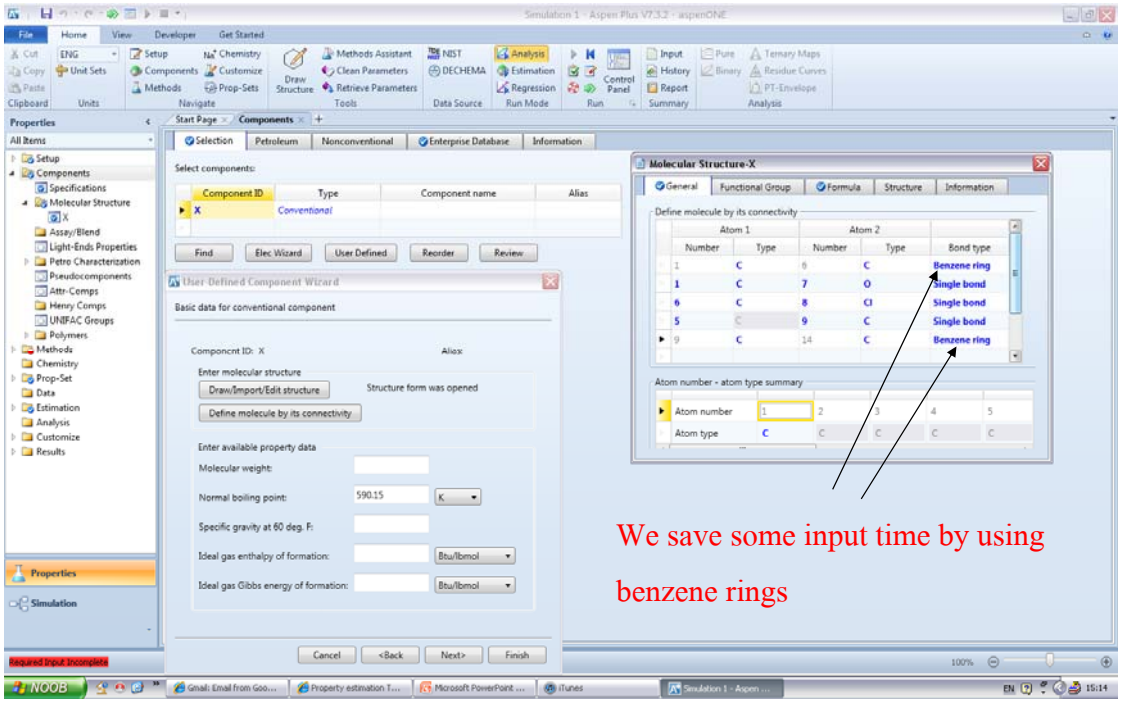
PCES Example (Cont'd)



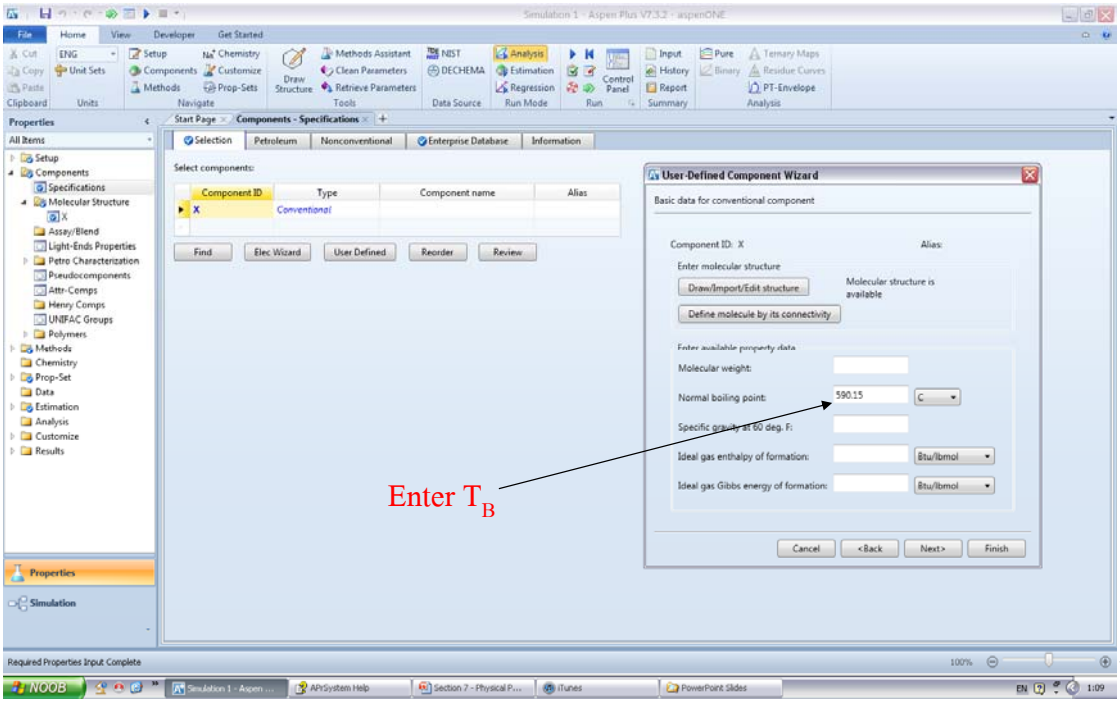
PCES Example (Cont'd)



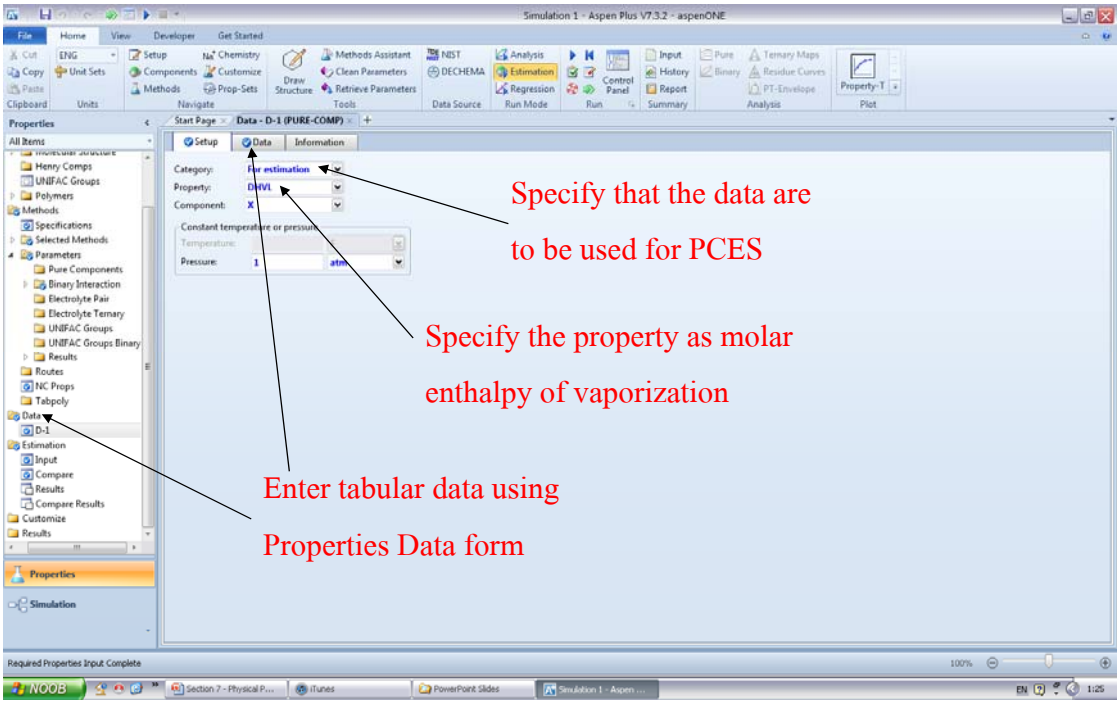
PCES Example (Cont'd)



PCES Example (Cont'd)



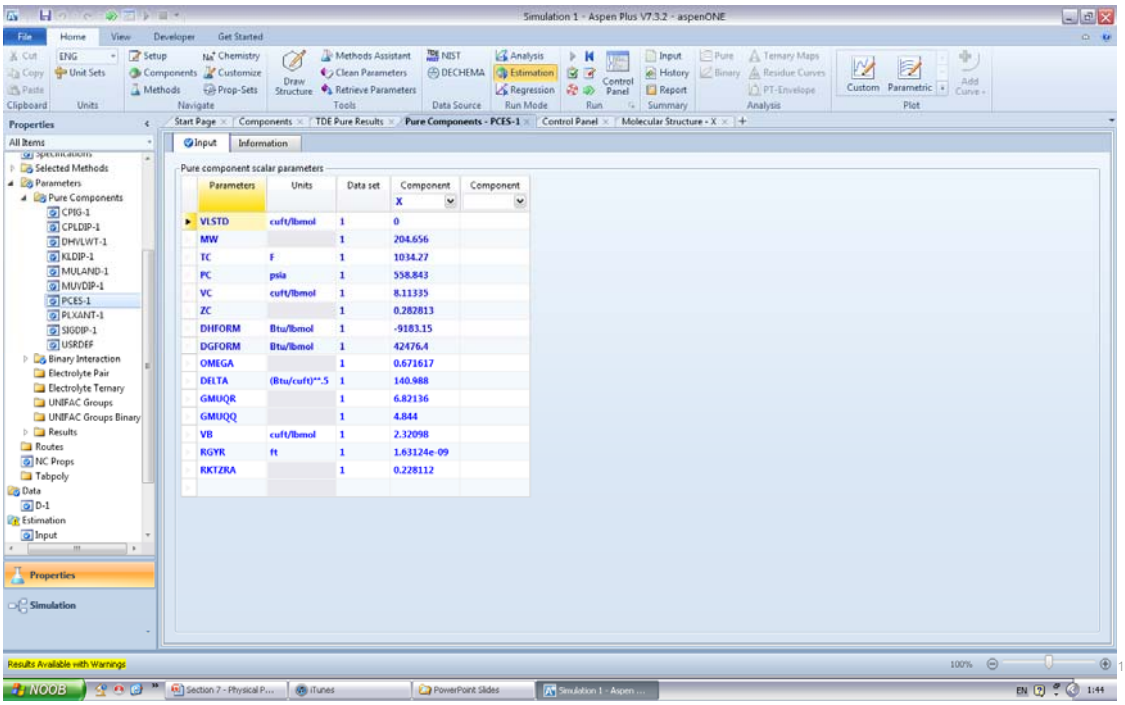
PCES Example (Cont'd)



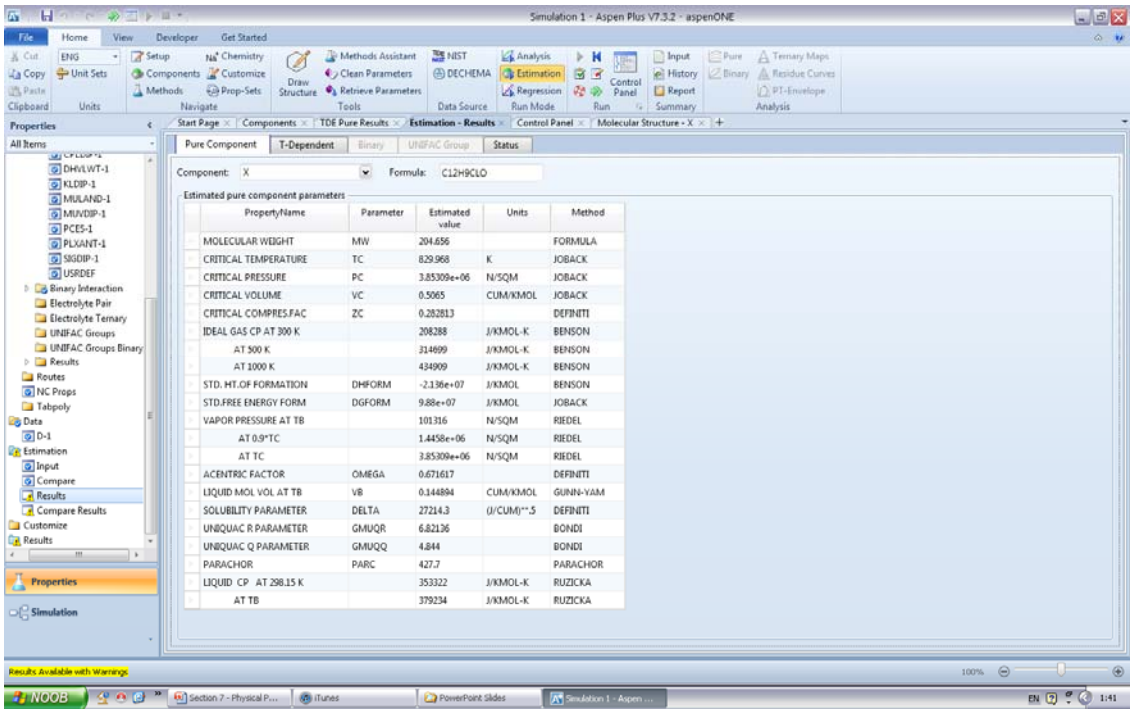
Results from A+ PCES

- Estimated property constants/parameters from PCES can be found in the Estimation folder of Properties in the Data Browser.
  - The results in the Estimation folder are divided into Pure Component and T-Dependent tabs.
  - All results are in SI units.
- A+ also automatically puts all estimated results into the Parameters folder of Properties in Data Browser.
  - By changing back to Simulation, PCES results can be immediately incorporated into a simulation run.
  - The values stored here use the same unit as specified in the Setup.
  - The values can be changed to any new desired unit.

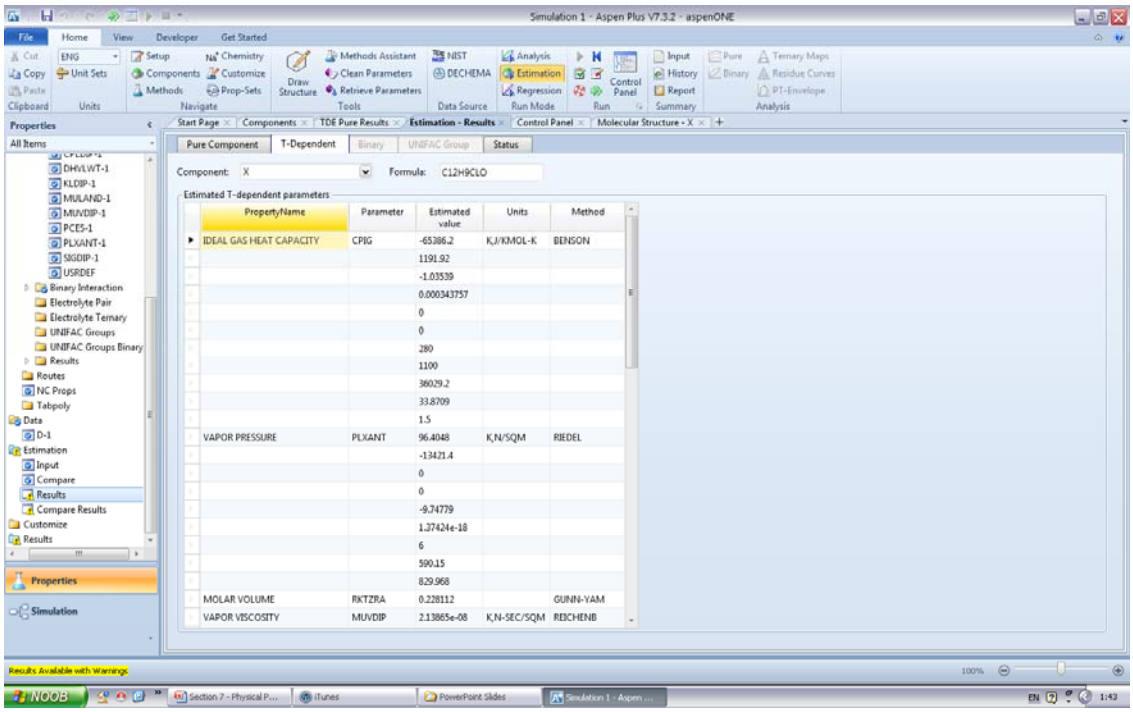
PCES Results from A+ in Parameters Folder



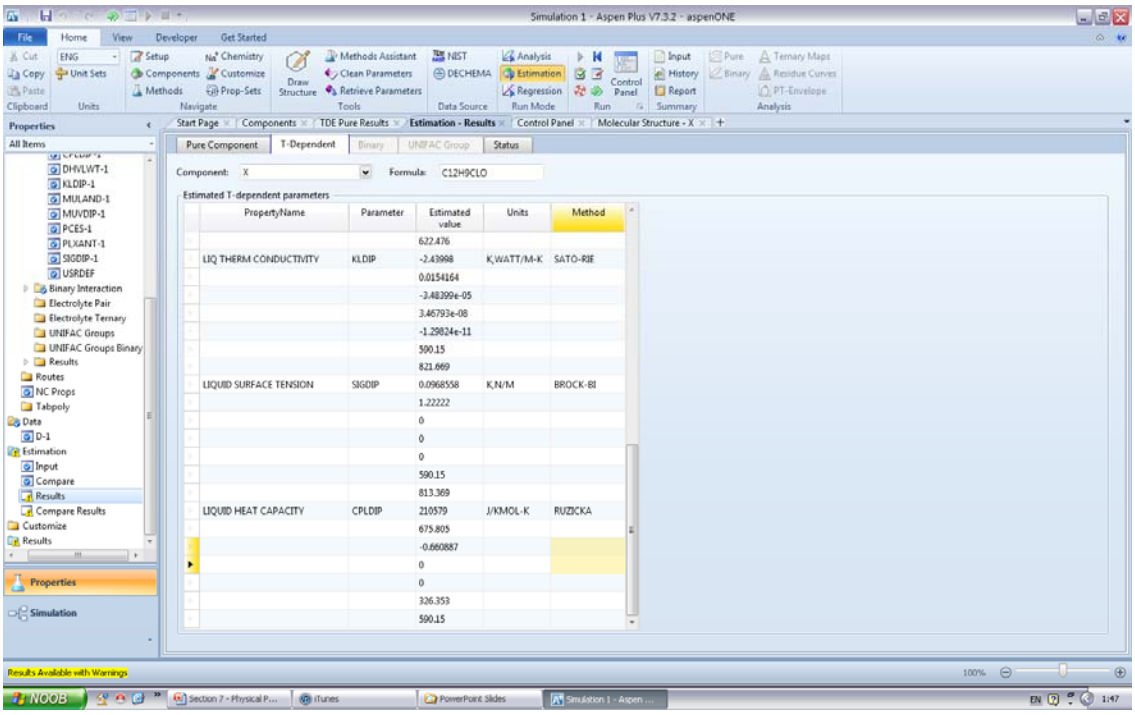
A+ PCES Results: Pure Component Constants



A+ PCES Results: T-Dependent Parameters

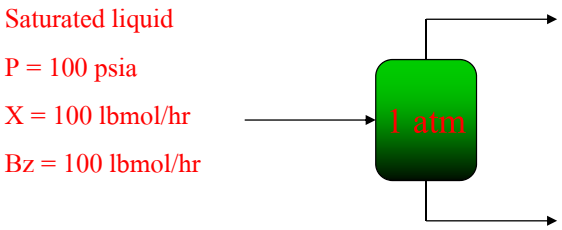


A+ Complete Results: T-Dependent Parameters (Cont'd)



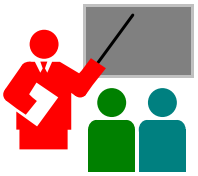
Quick Exercise on Using PCES in a Simulation

- Consider a problem of flashing a mixture of benzene and our non-databank component, 2-chloro-3-phenylphenol, as follows:



Questions:

1. How much liquid is vaporized? _____
2. Vapor and liquid compositions? _____



Property Reporting

Property Analysis

and

Property-Sets (Prop-Sets)

Property Analysis

- Allows users to quickly check the validity of the property methods chosen before starting a full simulation
- Requires a lot less input data than a flowsheet simulation
- Need only components and property method specifications
- Invoked by selecting Analysis in the ribbon

Property Analysis

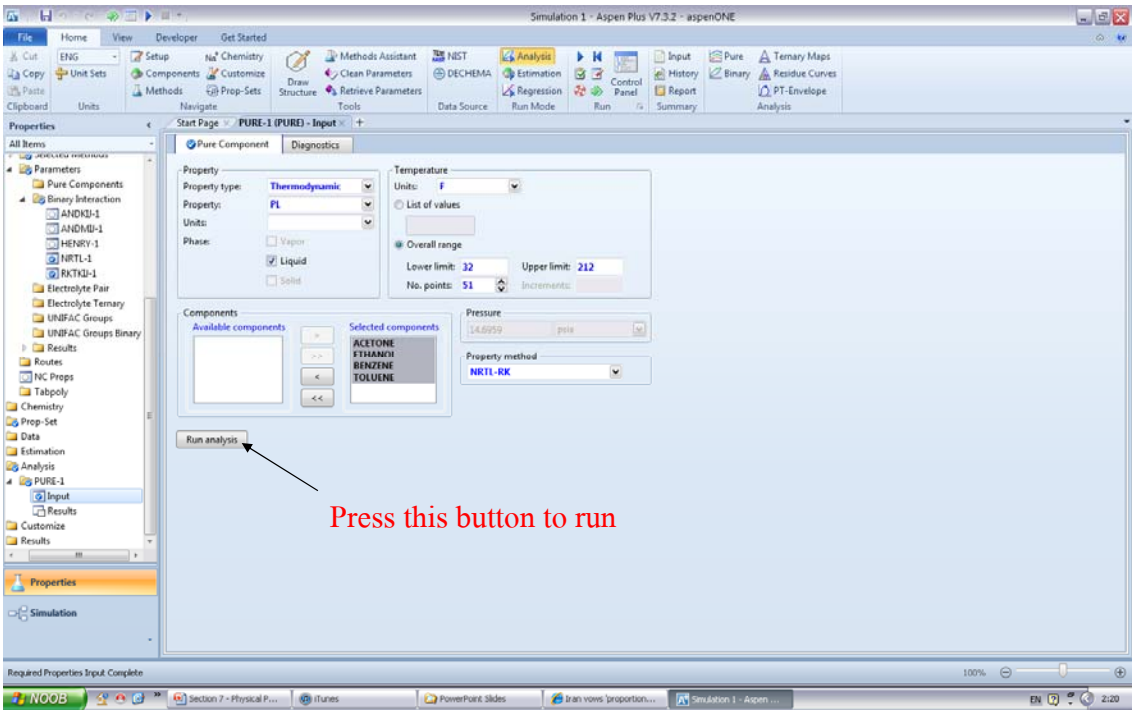
- Allows users to generate tables and plots of:
  - Pure properties
    - Thermodynamic - e.g. vapor pressure vs. **T**, density vs. **T**
    - Transport - e.g. viscosity vs. **T**
  - Binary properties, e.g. **T-xy**, **P-xy**, and **x-y** diagrams
- Required input are:
  - Components
  - Base property method
  - Browse through the Binary Interaction folder of Method Parameters in the Data Browser

Example of Property Analysis

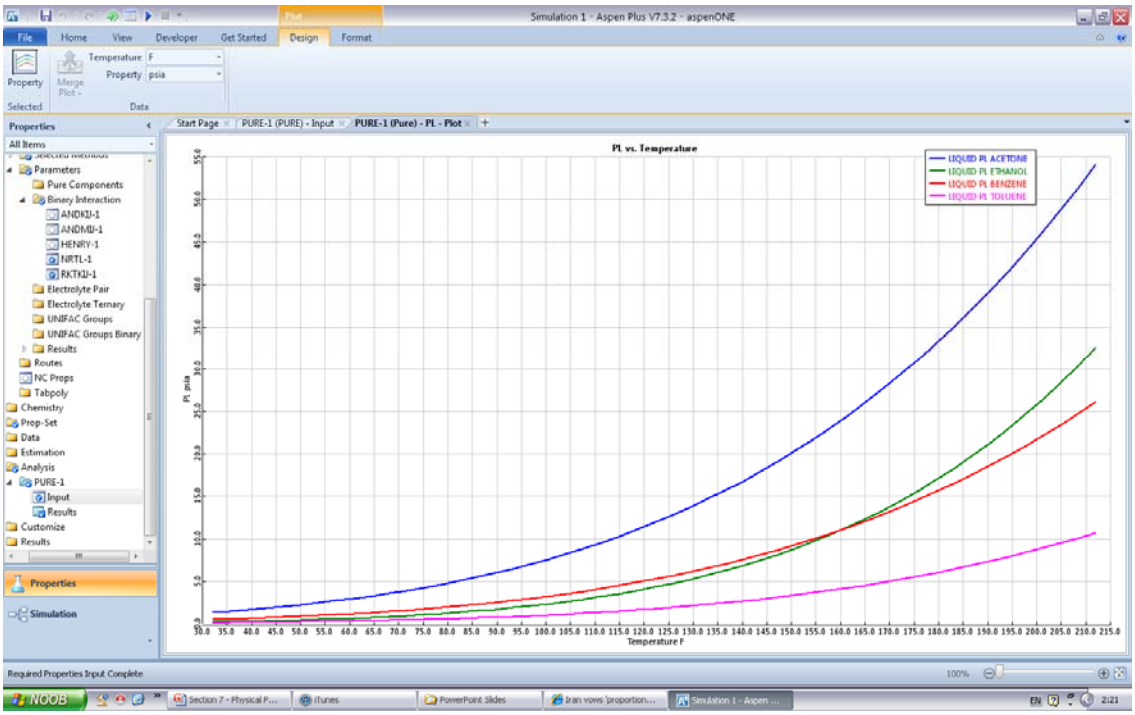
- Consider a simulation we want to make involving 4 components:
  - Acetone, Ethanol, Benzene, Toluene
- Use Property Analysis to look at the following data before making the simulation run:
  - A comparison of vapor pressure data of 4 components
    - Question: What is the relative volatility of the 4 components?
  - An **x-y** diagram of ethanol-benzene (at constant P of 1 atm)
    - Questions: Is the liquid of this binary system highly nonideal?

      Does this pair form an azeotrope?

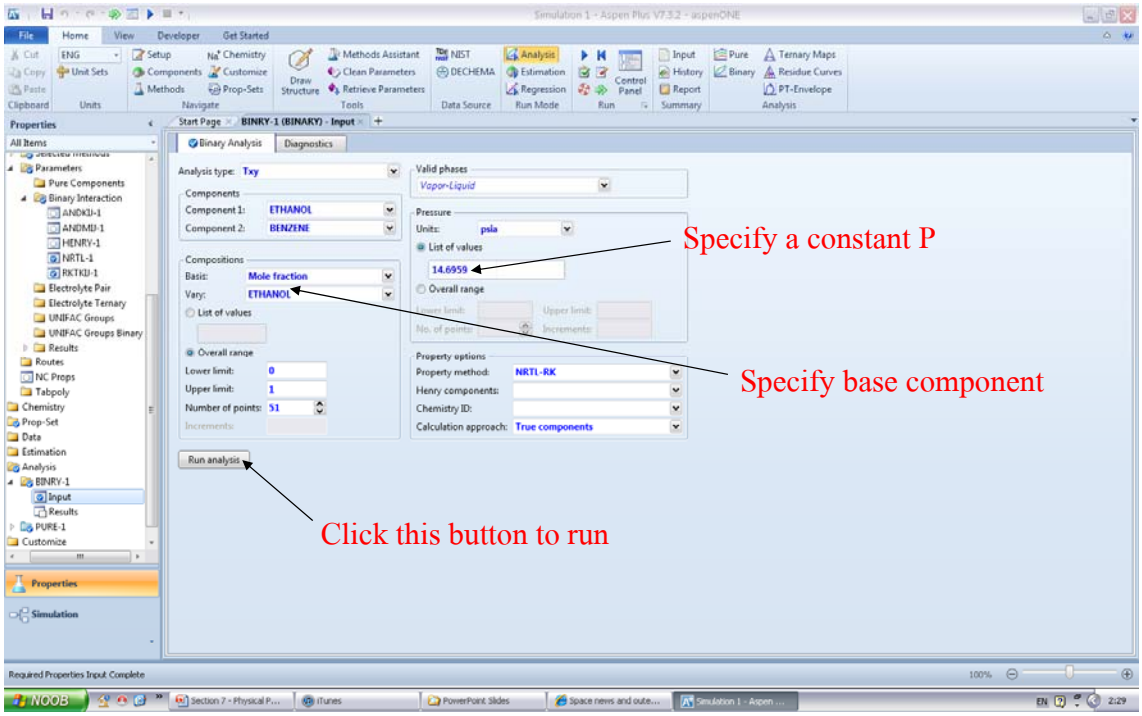
Pure Component Property Analysis - Vapor Pressure Data



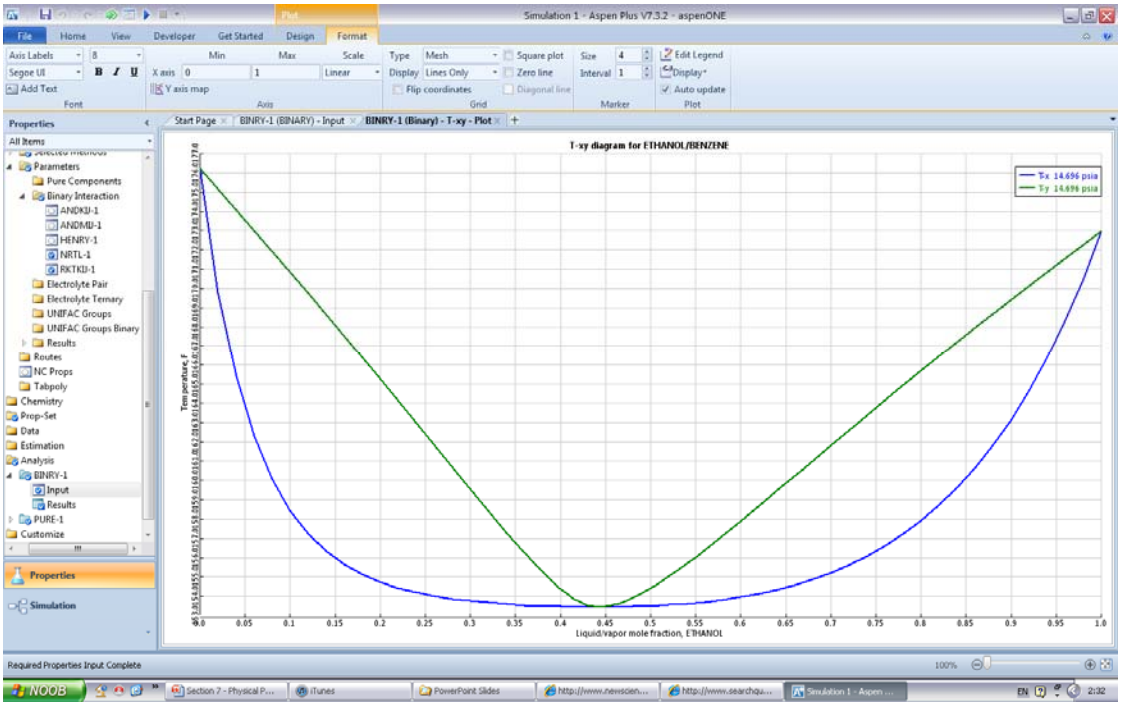
Comparison of Vapor Pressure



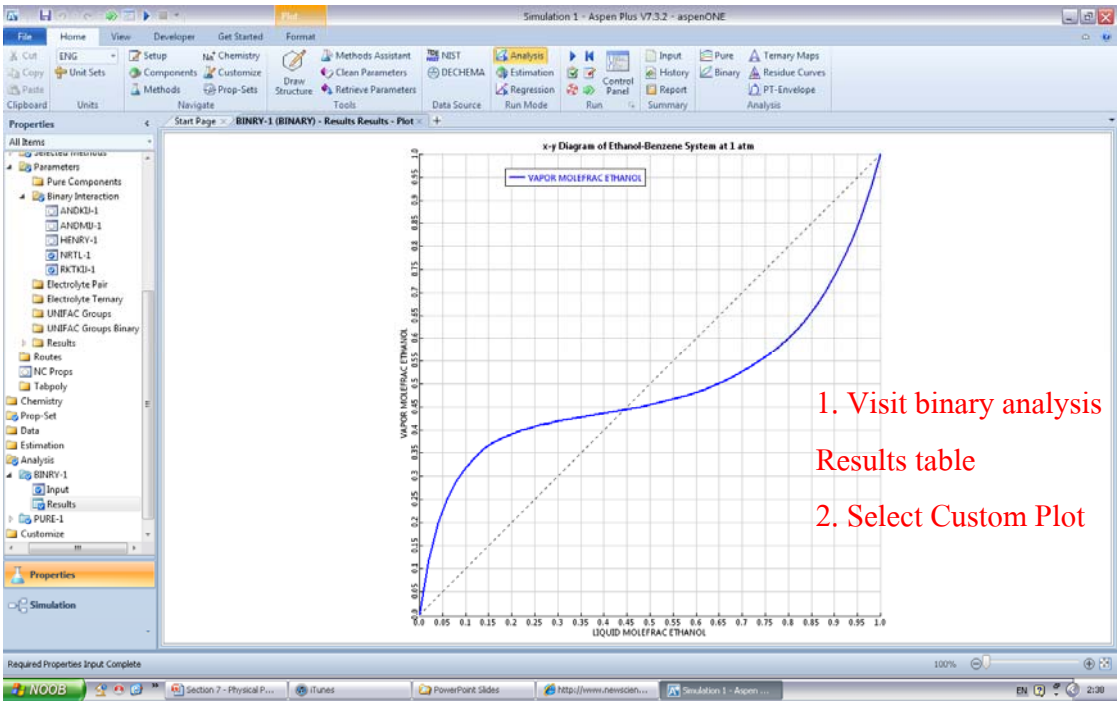
Binary Property Analysis: **T-xy** and **x-y** Diagrams



T-xy Diagram of Ethanol-Benzene System



x-y Diagram of Ethanol-Benzene System



Exercise of Quick Property Analysis

- Add a fifth component to our example, namely water.
- Use Quick Property Analysis to generate an **x-y** diagram of the benzene-water system at 1 atm.
- Questions:

1. Do you need to specify anything special in the Binary Analysis input form in order to obtain a correct plot?
2. What is this **x-y** plot telling us about the mixing of benzene and water?

Property-Sets (Prop-Sets)

- A set of properties requested by users for a pure component or a mixture
- Specified in the Prop-Sets folder of the Properties in the Data Browser
- Properties include:
  - Thermodynamic properties
    - Examples: CPMX (Constant pressure heat capacity of a mixture), GAMMA (Activity coefficient of a component in a mixture), and HIGMX (Ideal gas enthalpy of a mixture)

Prop-Sets (Cont'd)

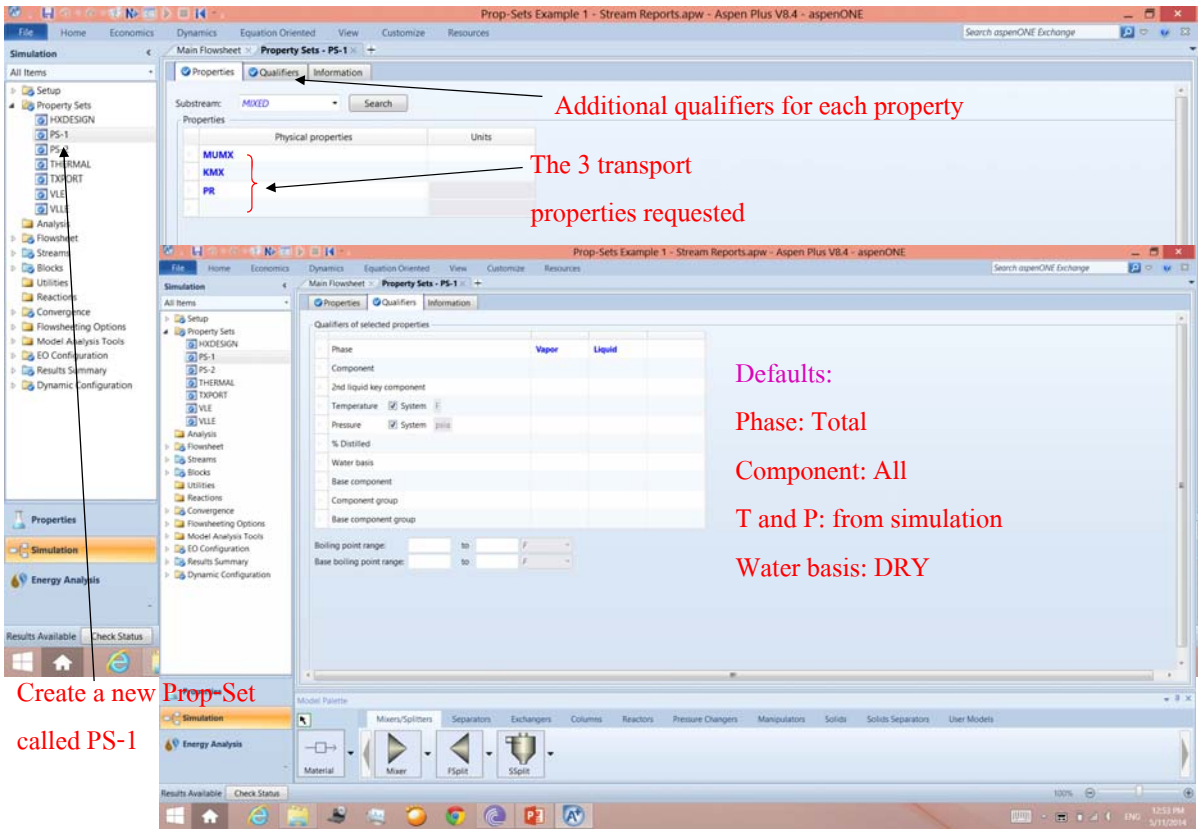
  - Transport properties
    - Examples: KMX (Thermal conductivity of a mixture), RE (Reynolds number for a mixture), and MUMX (Viscosity of a mixture)
  - Petroleum-related properties
    - Examples: API (API gravity), FLASHPT (Flash point), and D86T (ASTM D86 temperature)
  - User-defined properties via a user FORTRAN subroutine

Prop-Sets (Cont'd)

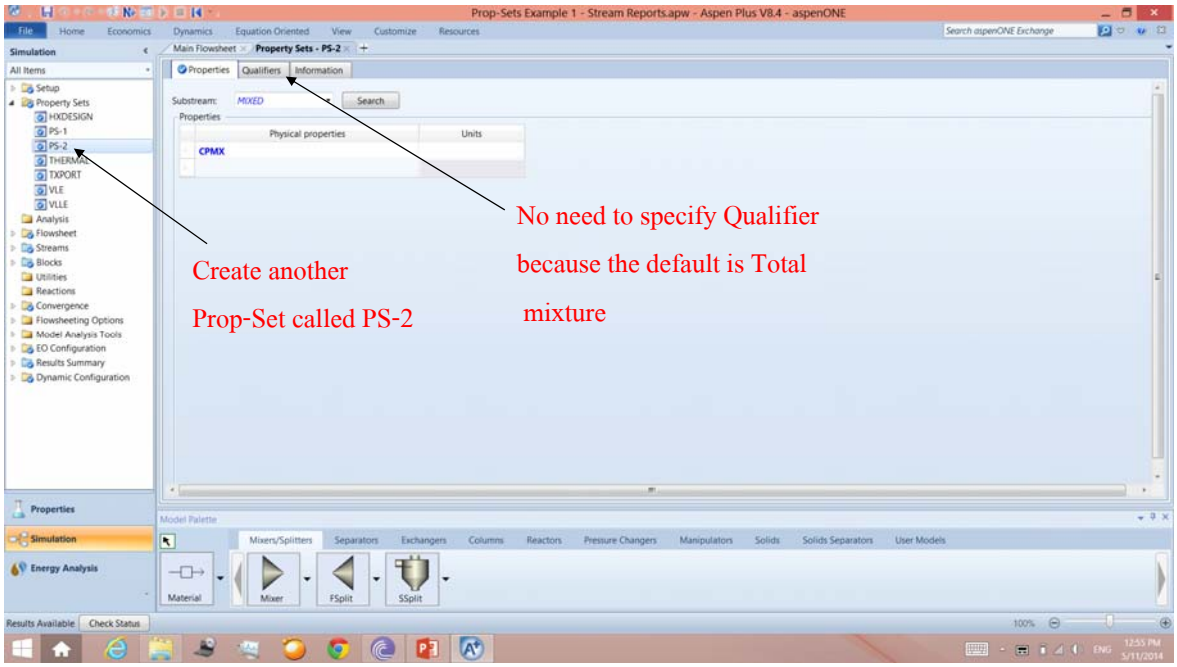
- Applications:
  - Part of the stream reports
  - Used inside a design specification or Calculator block
  - Used with property table and plot generation
  - Tray properties for distillation models
- We will see examples of the first 2 applications in a moment.

Application #1: Use Prop-Sets in Stream Reports

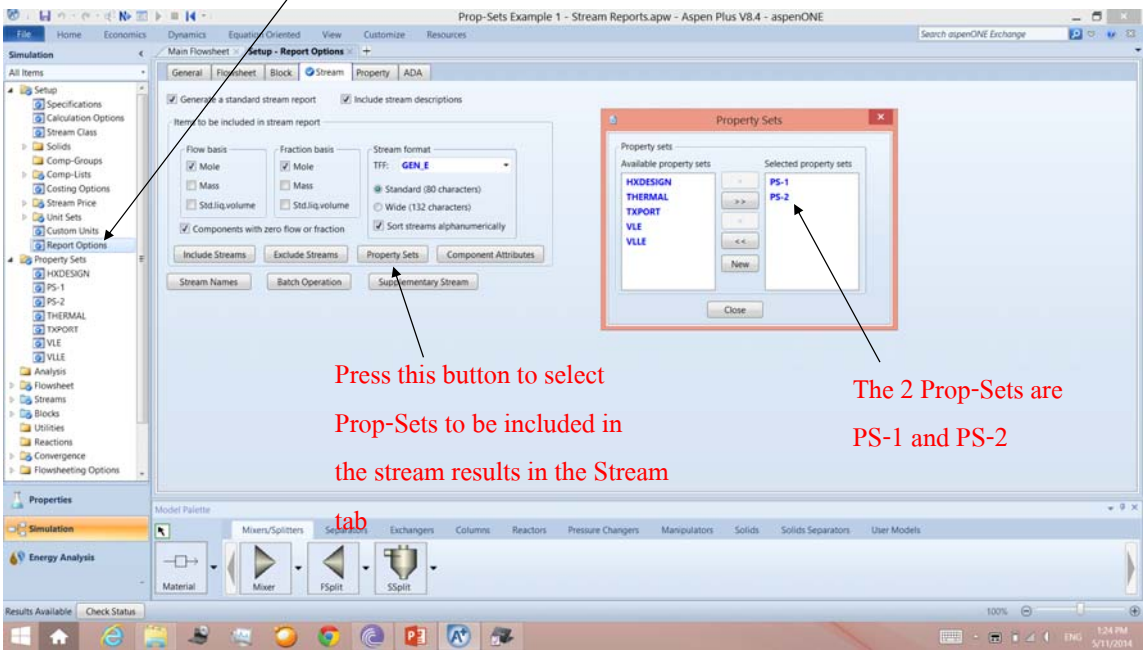
- Consider Workshop 1, Flashing of Light Hydrocarbons:
  - Request A+ to report the following properties:
    1. Viscosity, thermal conductivity, and Prandtl number of the vapor and liquid phases for all streams
    2. Constant pressure heat capacity of the total mixture for all streams
- There are 2 steps to follow:
  1. Specify the properties in the 2 Prop-Sets.
  2. Specify that these Prop-Sets be included in the stream results.



Some properties require additional qualifiers to uniquely determine the properties



Select Report Options Folder in Setup



Stream Results with Prop-Sets

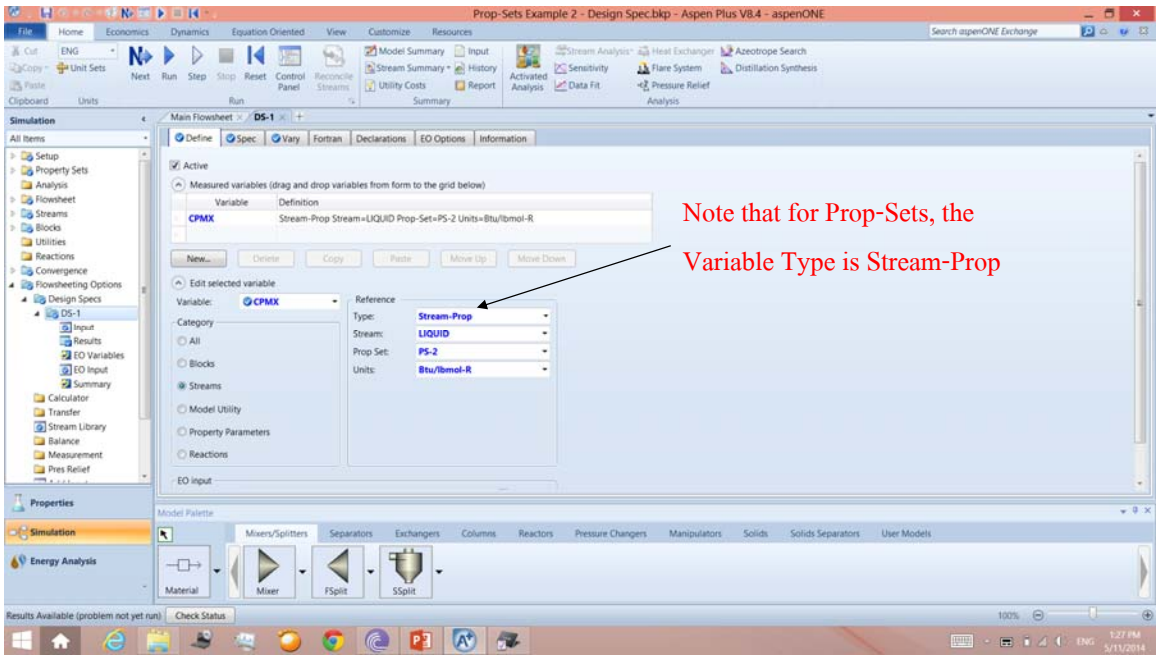
	FLASH-F	HC-FEED	LIQUID	VAPOR
Temperature F	11.1	8.8	-33.1	-33.1
Pressure psia	200	50	14.7	14.7
Vapor Frac	0	0	0	1
Mole Flow lbmol/hr	350	350	288.97	61.03
Mass Flow lb/hr	17537.814	17537.814	15173.743	2364.071
Volume Flow cuft/hr	484.896	483.687	393.81	18563.833
Enthalpy MMBtu/hr	-20.628	-20.657	-17.987	-2.641
Mole Flow lbmol/hr				
C2	50	50	18.372	31.628
C3	100	100	78.906	21.094
N-C4	200	200	191.693	8.307
Mole Frac				
C2	0.143	0.143	0.064	0.518
C3	0.286	0.286	0.273	0.346
N-C4	0.571	0.571	0.663	0.136
CPMX Btu/lbmol-R	28.507	28.561	28.12	14.19
*** VAPOR PHASE ***				
Conductivity Btu-ft/hr-sqft-R				0.007
Viscosity cP				0.007
PR				0.867
*** LIQUID PHASE ***				
Conductivity Btu-ft/hr-sqft-R	0.068	0.068	0.076	
Viscosity cP	0.166	0.168	0.24	
PR	3.368	3.401	4.11	

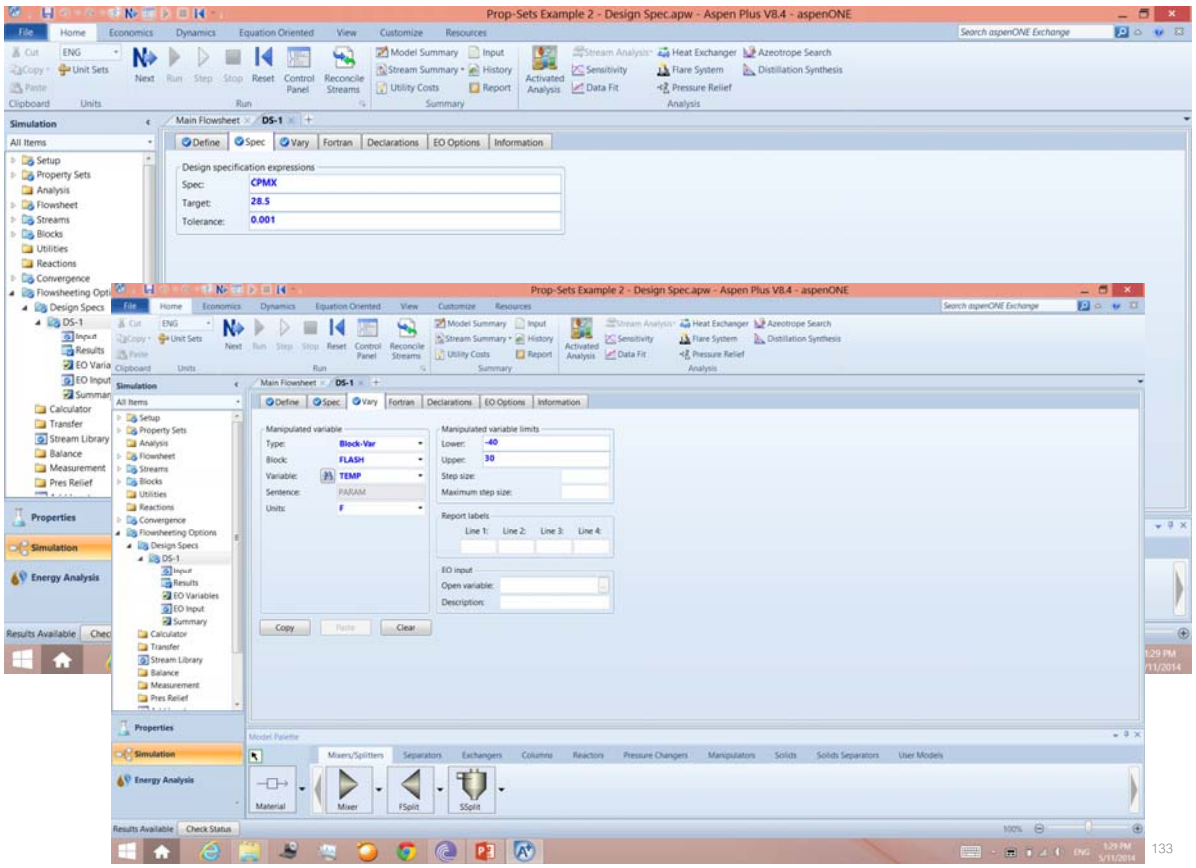
Application #2: Use Prop-Sets in a Design-Spec

- Consider again Workshop 1, Flashing of Light Hydrocarbons:
  - Replace the input pressure (1 atm) of the flash block with the calculated temperature, namely -33.3 ^{o} F.
  - The calculated CPMX of the flash liquid outlet stream is 28.12 Btu/lbmol-R.

- Suppose we want to set CPMX of the flash liquid outlet stream to be exactly 28.5 Btu/lbmol-R by varying the flash outlet temperature.

Specify a Design-Spec to Control CPMX





Stream Results with Prop-Sets in the Design-Spec

	FLASH-F	HC-FEED	LIQUID	VAPOR
Temperature F	11.1	8.8	1	1
Pressure psia	200	50	39.74	39.74
Vapor Frac	0	0	0	1
Mole Flow lbmol/hr	350	350	333.729	16.271
Mass Flow lb/hr	17537.814	17537.814	16930.168	607.647
Volume Flow cuft/hr	484.896	483.687	460.687	1924.067
Enthalpy MMBtu/hr	-20.628	-20.657	-19.946	-0.682
Mole Flow lbmol/hr				
C2	50	50	40.232	9.768
C3	100	100	95.436	4.564
N-C4	200	200	198.062	1.938
Mole Frac				
C2	0.143	0.143	0.121	0.6
C3	0.286	0.286	0.286	0.281
N-C4	0.571	0.571	0.593	0.119
CPMX Btu/lbmol-R	28.507	28.561	28.5	14.451
*** VAPOR PHASE ***				
Conductivity Btu-ft/hr-sqft-R				0.009
Viscosity cP				0.008
PR				0.851
*** LIQUID PHASE ***				
Conductivity Btu-ft/hr-sqft-R	0.068	0.068	0.07	
Viscosity cP	0.166	0.168	0.181	

In Summary

Steps in Using A+ Physical Properties

1. Determine the nature of the chemical system - petroleum mixture, hydrocarbons, ideal or non-ideal, etc. Pick an appropriate property method to use.

2. Specify all chemical components in the simulation.

3. If unsure about the suitability of the property method, use Property Analysis to check the validity of the data.

In Summary (Cont'd)

4. If there are components not found in the A+ databanks or with missing property parameters, determine what parameters need to be input for the chosen property method.

5. Supply the missing parameters from
   - the literature
   - experimental data or lab data

6. If cannot locate the missing data anywhere, use PCES to estimate the data.