Physical Properties estimation using Aspen Plus

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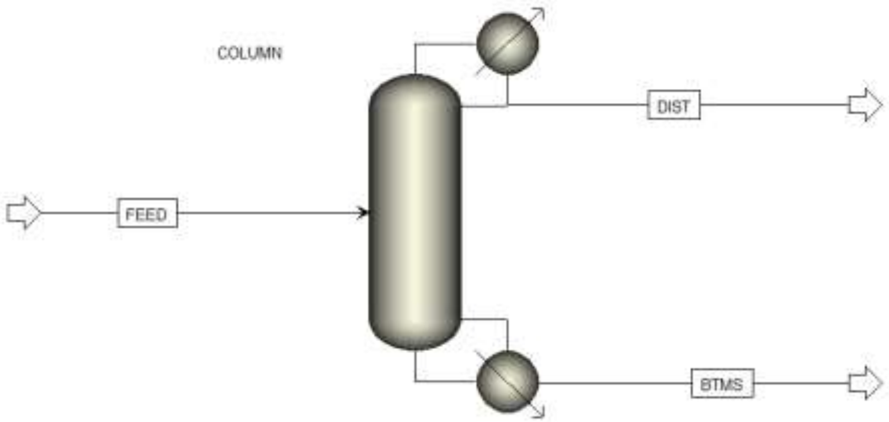
Agenda

- Physical properties estimation with ASPEN+
  - Property methods: selection guidelines
  - Property analysis
  - Property sets
  - Data regression

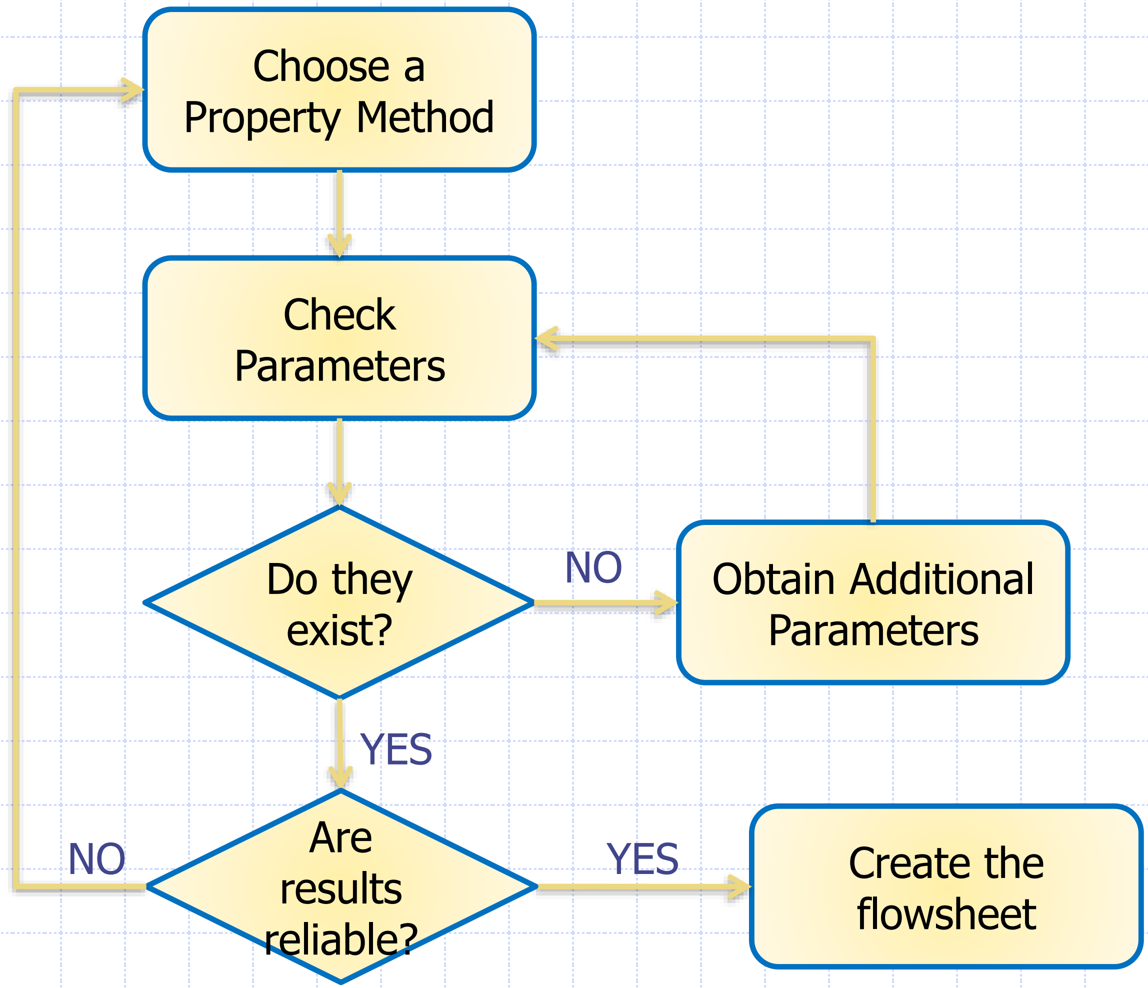
Ooops... the results are different!



Specification:
- 30 stages
- Distillate rate 500 kmol/hr
- Reflux ratio 1.3

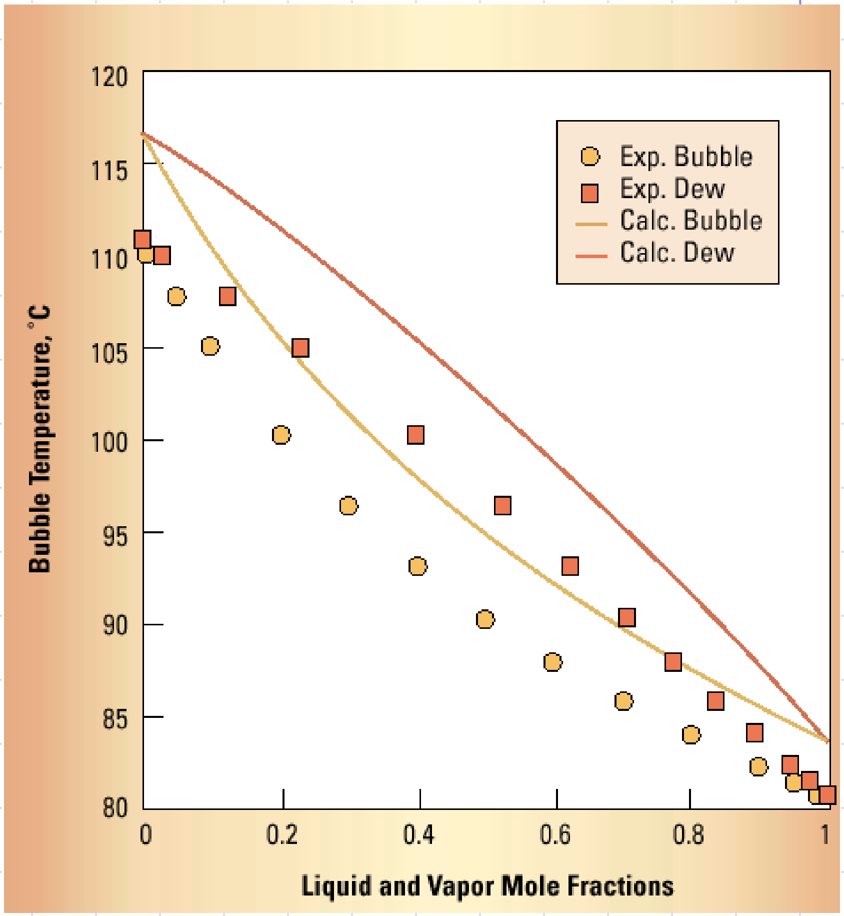
	Units	FEED	BTMS (IDEAL)	DIST (IDEAL)	BTMS (NRTL)	DIST (NRTL)	BTMS (PENG-ROBINSON)	DIST (PENG-ROBINSON)
− Mole Flows	**kmol/hr**	**2328.31**	**1828.31**	**500**	**1828.31**	**500**	**1828.31**	**500**
WATER	kmol/hr	1754.07	1691.96	62.1051	1753.92	0.147487	1754.05	0.0143418
METHANOL	kmol/hr	574.243	136.349	437.895	74.3909	499.853	74.2578	499.986
− Mole Fractions								
WATER		0.753365	0.925424	0.12421	0.959312	0.000294974	0.959384	2.86836e-05
METHANOL		0.246635	0.0745763	0.87579	0.0406884	0.999705	0.0406155	0.999971

How to establish Physical Properties



Vapor pressure is the king

- Simple EOS do not use Antoine constants
  - Do nor play around with w (entalpy is affected…)
- More complex EOS may or may not use vapor pressure
  - Always check vapor pressure
- Do not get careless if the problem is simple
  - Low pressure
  - Ideal system
  - Vapor pressure and vapor phase correction becomes important
- Use simple models to your advantage
  - Playing with vapor pressure
  - Playing with simple gamma models



Points of attention in using process simulators

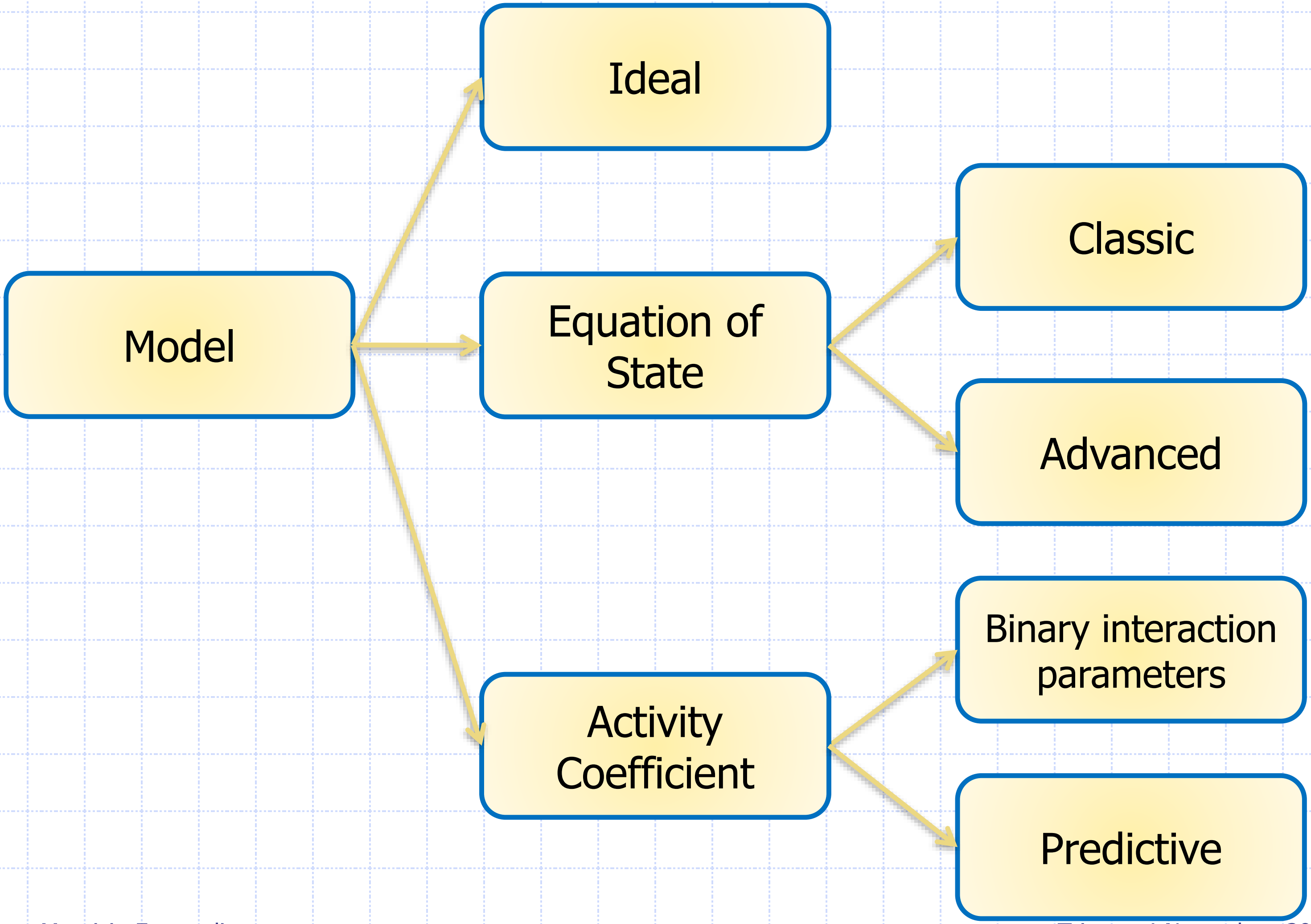
- Extrapolation and documentation
  - Simulation models tend to live longer than their creator ….
- Check your model also versus the 'less attractive area'
  - Density, entropy, enthalpy, viscosity, …
  - Find some data and check the models
- Accuracy vs. precision
  - Remember that Process Simulators are precise
  - Process simulators may NOT be accurate
  - Use error analysis
  - Consider the significant digits
- Henry's law is used to determine the amount of a supercritical component or light gas in the liquid phase
  - Declare any supercritical component or light gas (CO2, N2, etc) as Henry's component in the Properties Environment.
  - Remember to specify Henry's components ID in the thermodynamic method!

Ten Golden Rules

1. Check vapor pressure
2. Check pure and mixture densities – for aqueous mixtures excess volumes are important
3. Check pure and mixture enthalpy and heat capacities
4. Check transport properties (for heat exchangers and trays)
5. Check surface tension if you design trays
6. Azeotropes: check if they are present
7. Check trace components behavior versus infinite dilution activity coefficients
8. Talk to people, interact with chemists (new processes), talk to process simulators vendors
9. Beware of estimation methods for screening alternatives
10. Check the simulation results versus the reality, talk to the plant personnel, consider the reality (air leaks,…)

Models

The choice of model depends on degree of non-ideality, model parameters availability and operating conditions



Equation of state vs Activity coefficient

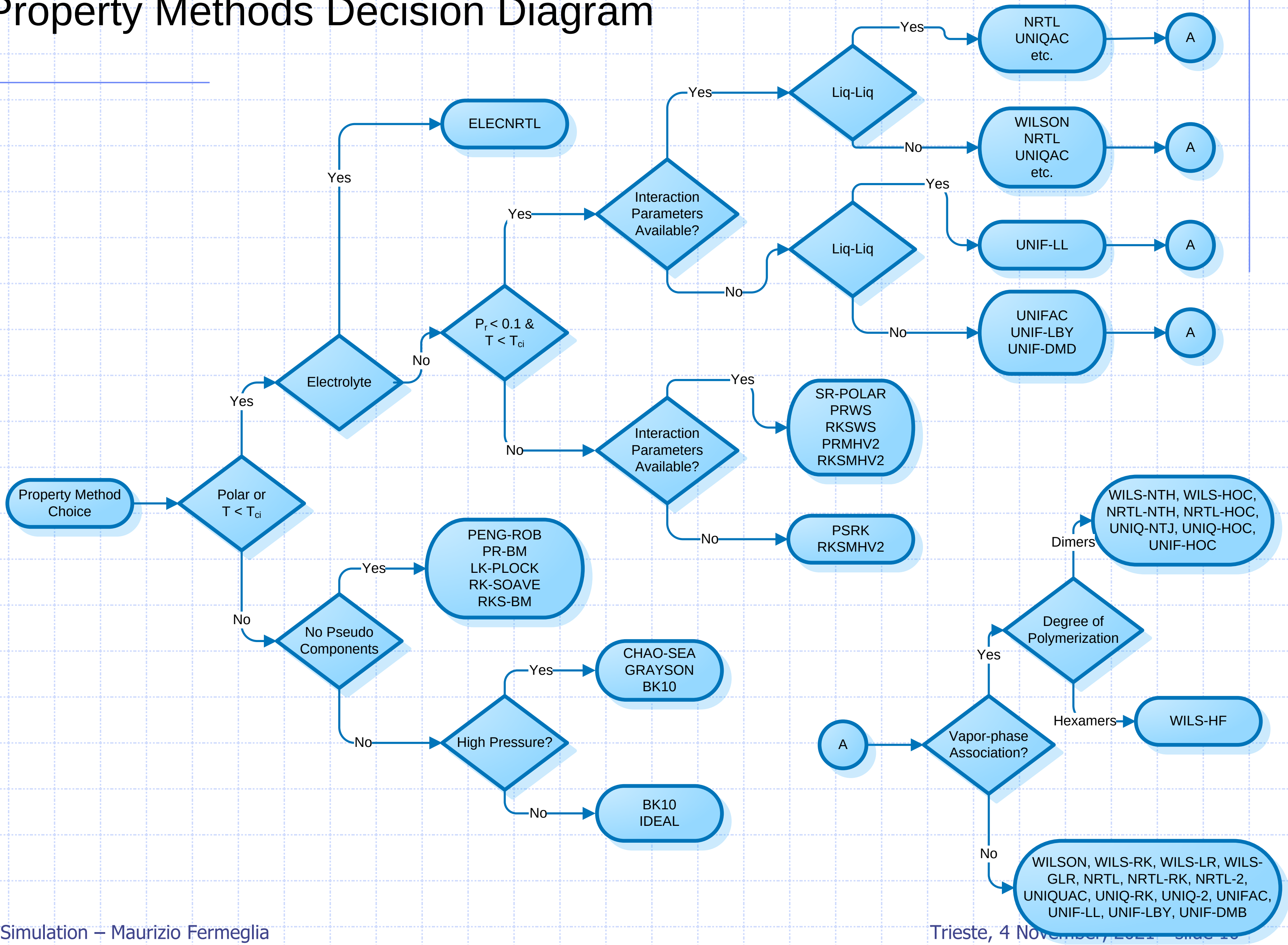
Equation of state

- Good for vapor phase modeling and liquids of low polarity
- Fewer binary parameters required
- Parameters extrapolated reasonably with temperature
- Consistent in critical region
- Typically limited in ability to represent non-ideal liquids
- Examples:
  - PENG-ROB
  - RK-SOAVE
  - PC-SAFT
  - PSRK

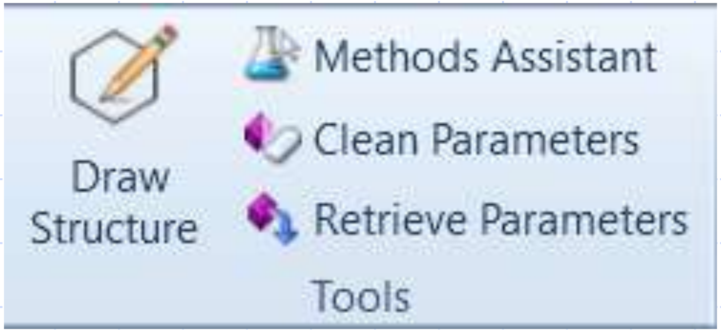
Activity coefficient

- Good for liquid phase modeling only
- Many binary parameters required
- Binary parameters are highly temperature dependent
- Inconsistent in critical region
- Can represent highly non-ideal liquids
- Examples:
  - NRTL
  - UNIQUAC
  - WILSON
  - UNIFAC

Property Methods Decision Diagram

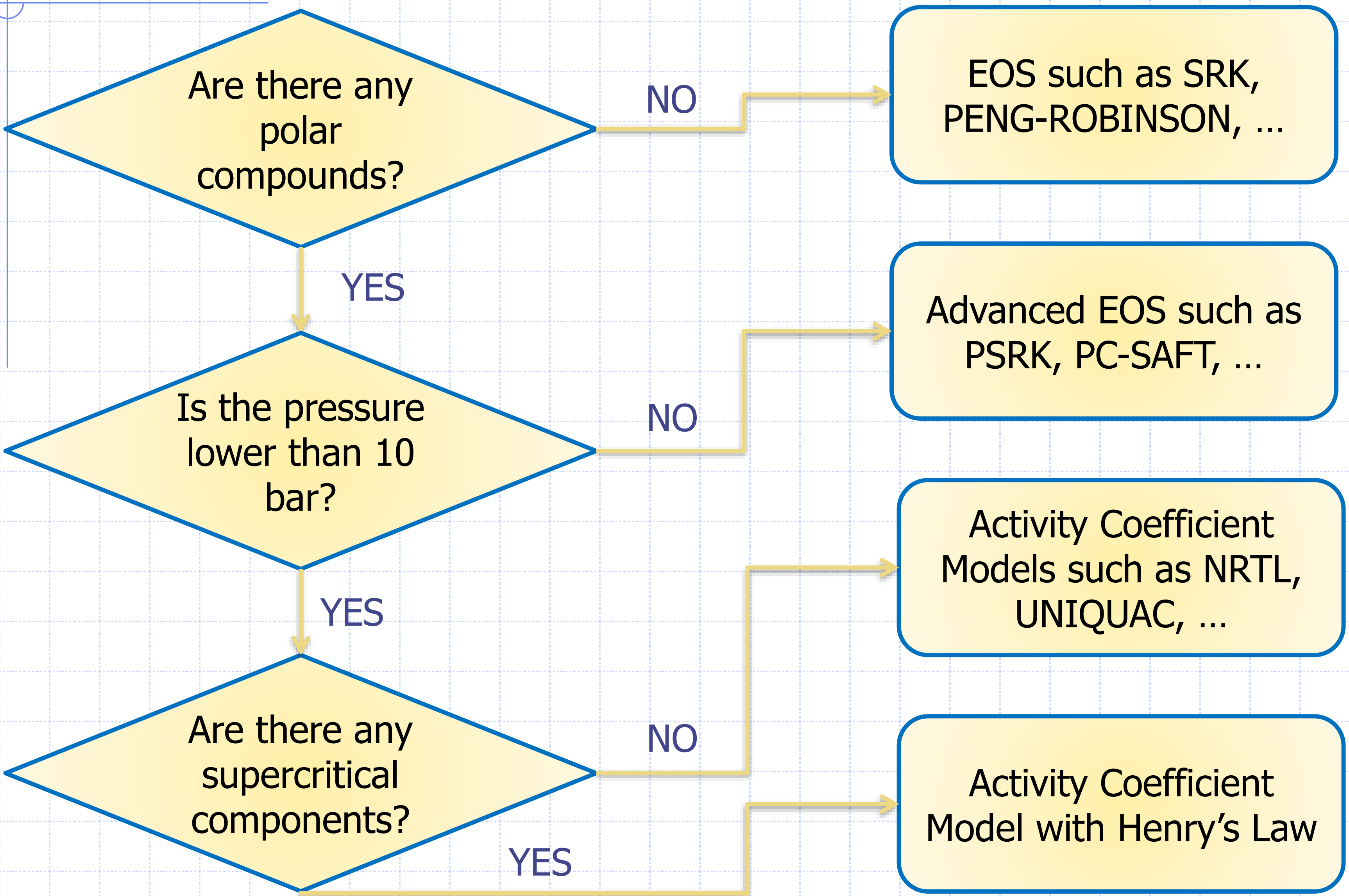


Property Method Selection Assistant



- The assistant will help you select the most appropriate property method by guiding you through a series of questions
- Search by components or process types
- At the end, the help topics for the recommended property methods are linked
- A report is also available that can be saved or printed

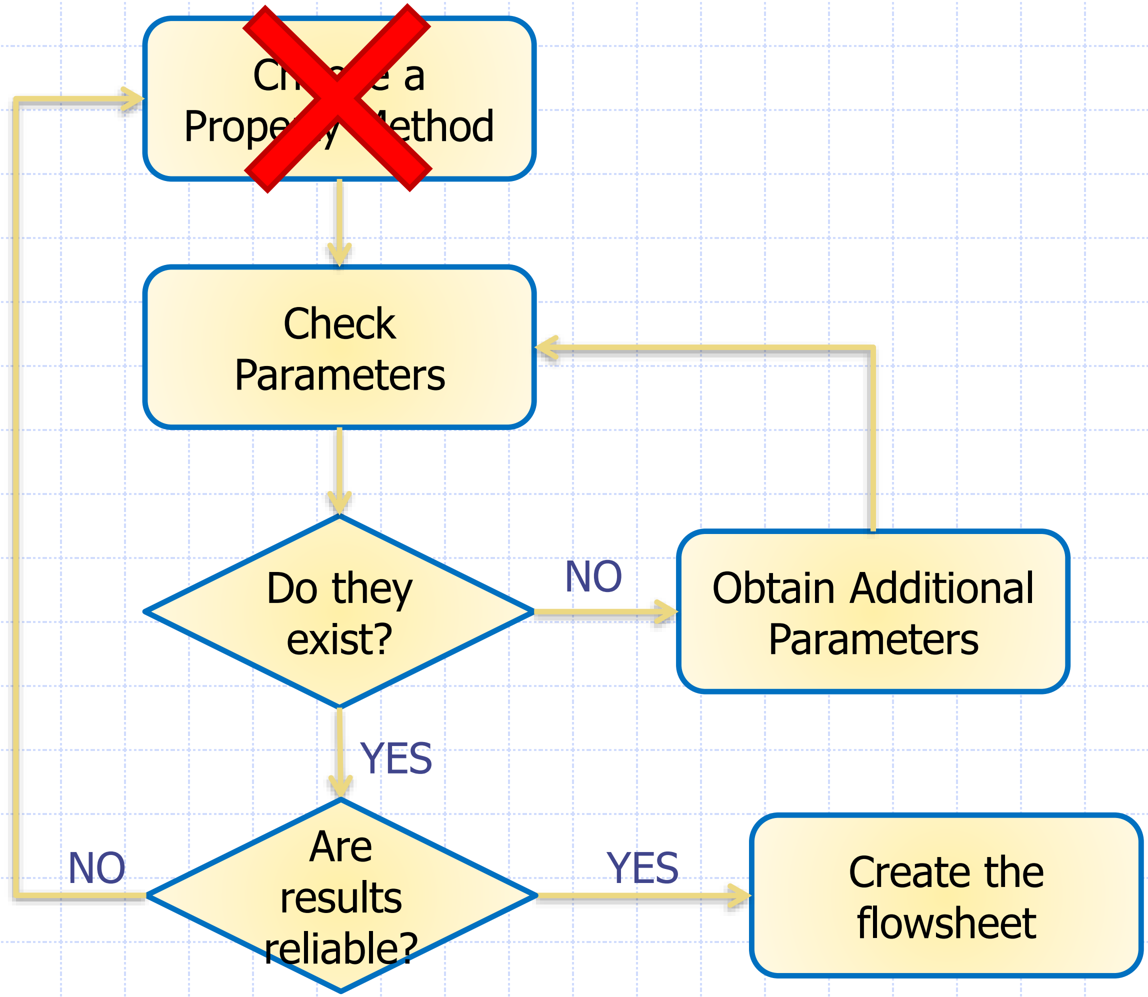
Choosing a Property Method



Choosing a Property Method - Examples

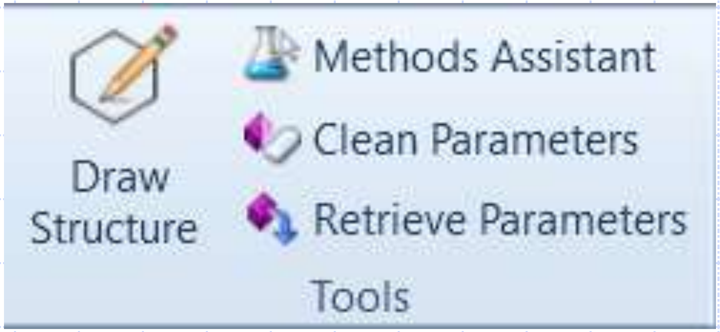
System @ 1 atm	Property Method
Propane, Ethane, Butane	EOS (SRK, PENG-ROB…)
Benzene, Water	AC (UNIQUAC, NRTL-RK, …)
Acetone, Water	AC (NRTL, WILSON, …)
Ethanol, Water	AC (NRTL,UNIFAC…)
Benzene, Toluene	EOS
Acetone, Water, Carbon Dioxide	AC+Henry
Ethane, Propanol	AC

How to establish Physical Properties



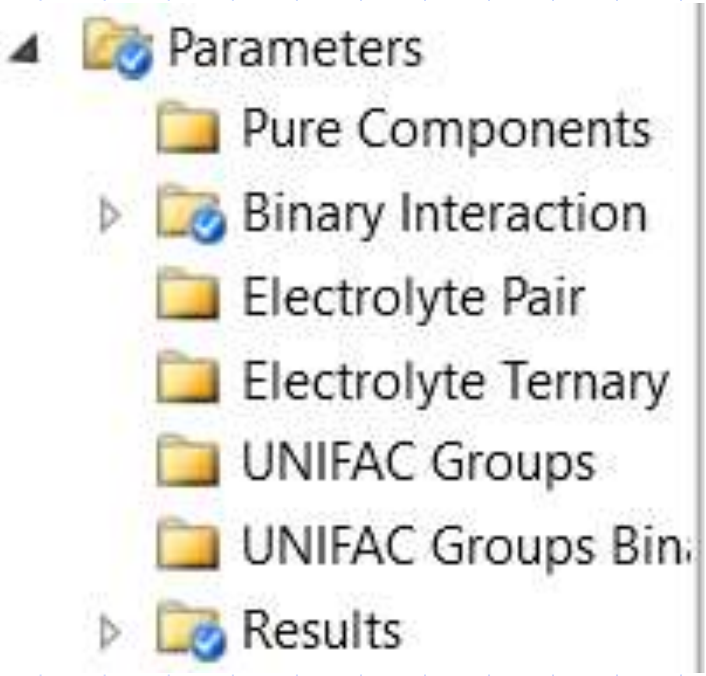
Pure components parameters

- Represent attributes of a single component
- Stored in databanks such as (PURE, AQUEOUS, SOLIDS, ...)
- Scalar: MW, ACENTRIC FACTOR, ...
- Temperature-dependent: PLXANT for parameters in the extended Antoine vapor pressure model



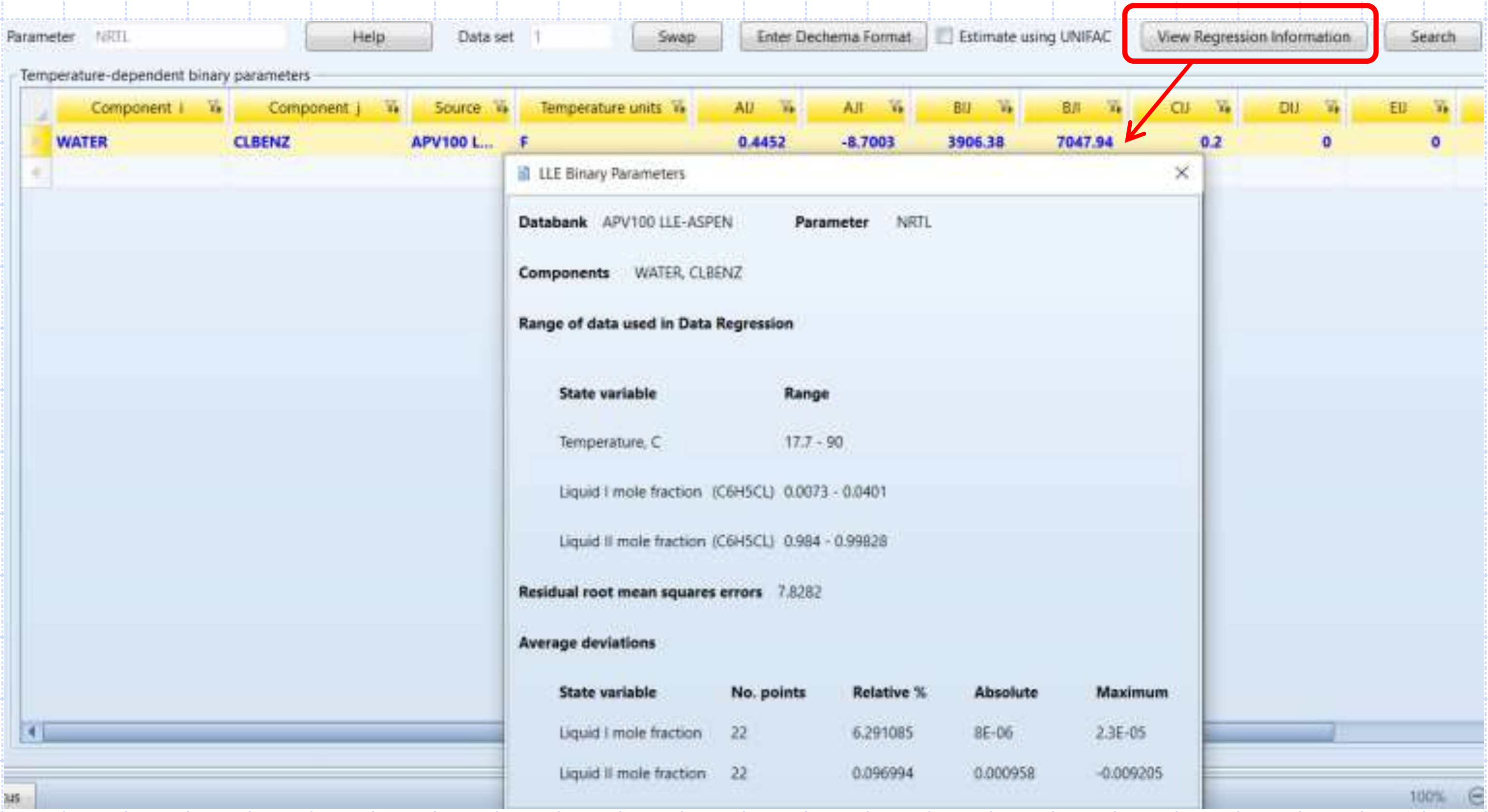
Binary Interaction parameters

- Used to describe interactions between two compounds
- Stored in binary databanks such as APV VLE-IG, APV LLE-ASPEN
- Parameters values from the databanks are visible automatically through the graphical user interface
- Examples:
  - Scalar: RKTKIJ-1 for Rackett model
  - Temperature-dependent: NRTL-1 for parameters in NRTL model

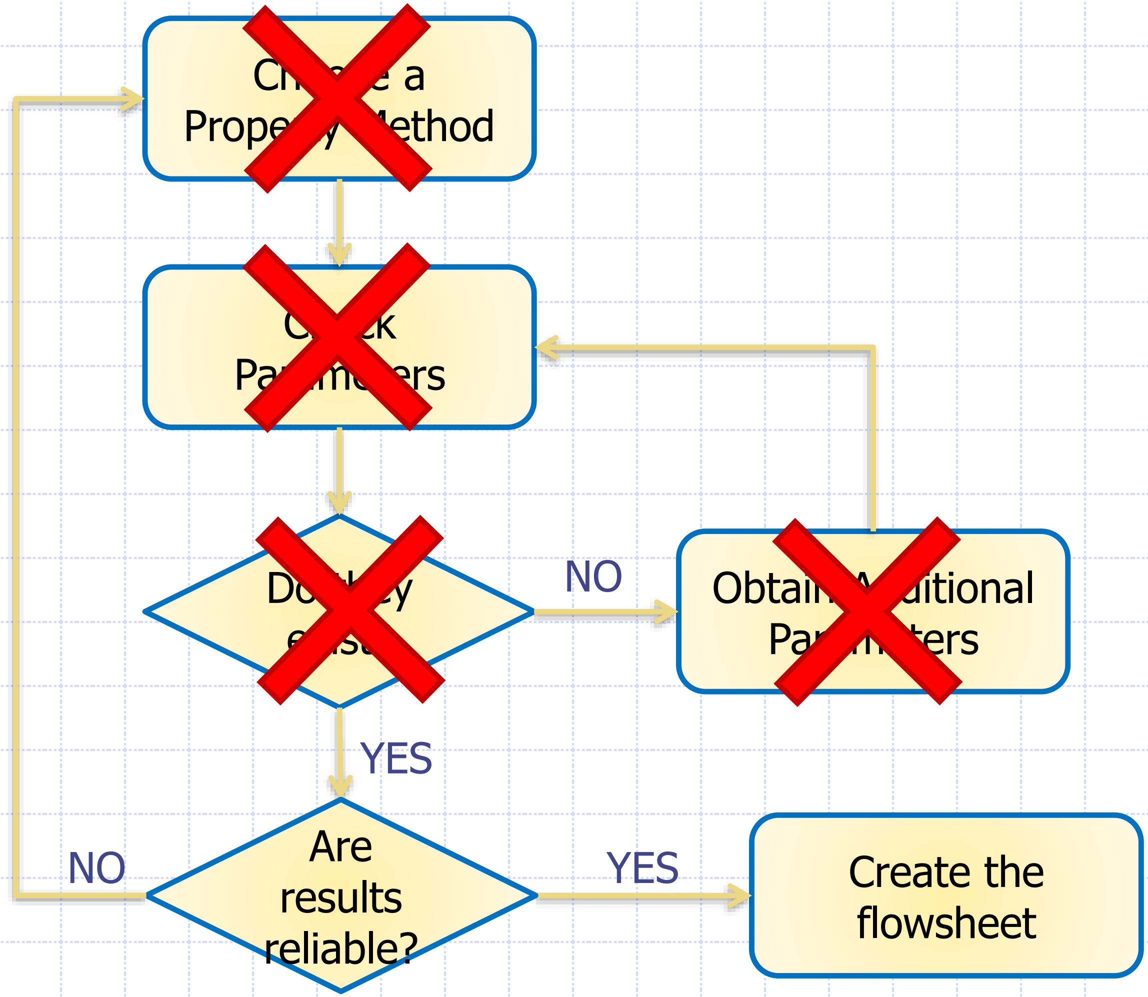


Binary Interaction parameters

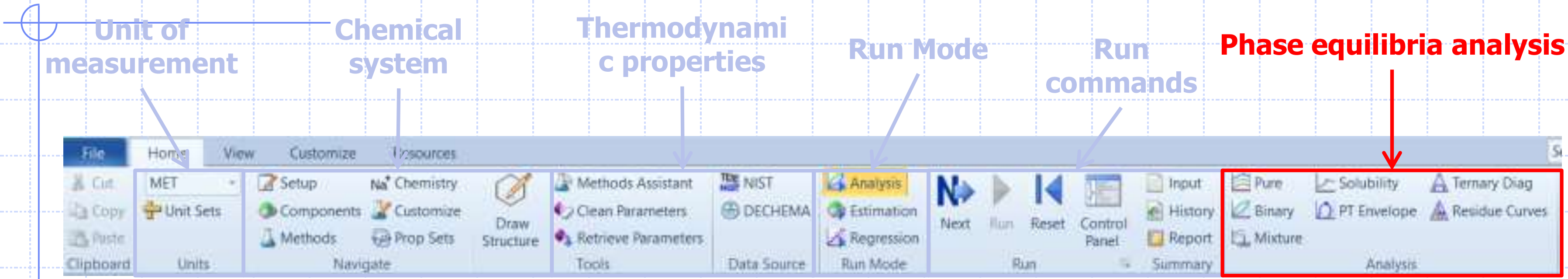
- Properties Parameters Binary Interaction NRTL-1 Form
  - Press the Regression Info button to display the regression data for each component pair



How to establish Physical Properties



Property Analysis



- Used to generate simple property diagrams to validate physical property models and data
- Diagram types:
  - Pure component, i.e. vapor pressure vs temperature
  - Binary, i.e. Txy, Pxy
  - Mixture
  - Ternary Residue Maps
  - Ternary Phase diagrams
  - PT envelope

Property Analysis - Review

1. Choose property method, based on:
   - Components present in simulation
   - Operating conditions in simulation
   - Available data or parameters for components
2. Check parameters:
   - Determine availability of parameters in Aspen Plus databanks, obtain additional parameters if necessary
3. Confirm Results:
   - Verify choice of Property Method and physical property data using Property Analysis plotting tool

Property Analysis – Hands on A+

Create binary XY diagram for mixtures:

- Methanol – Propanol
- Water - Ethanol
- Ethanol – Toluene
- Toluene – Water

For each binary create Txy, XY graph

Compare ideal with NRTL model

Compare with experimental data at P= 1 bar

Property Analysis - Exercise

- Objective: simulate a two-liquid phase settling tank and investigate the physical properties of the system

- A chemical plant has a settling tank that they use to decant off the water from a mixture of water and chlorobenzene; the inlet stream to the tank also contains some carbon-dioxide and nitrogen; the tank and feed are at ambient conditions (25 °C, 1 atm) and have the following flow rates:
  - Water: 230 kg/hr
  - Chlorobenzene: 2000 kg/hr
  - CO_2: 340 kg/hr
  - N_2: 20 kg/hr

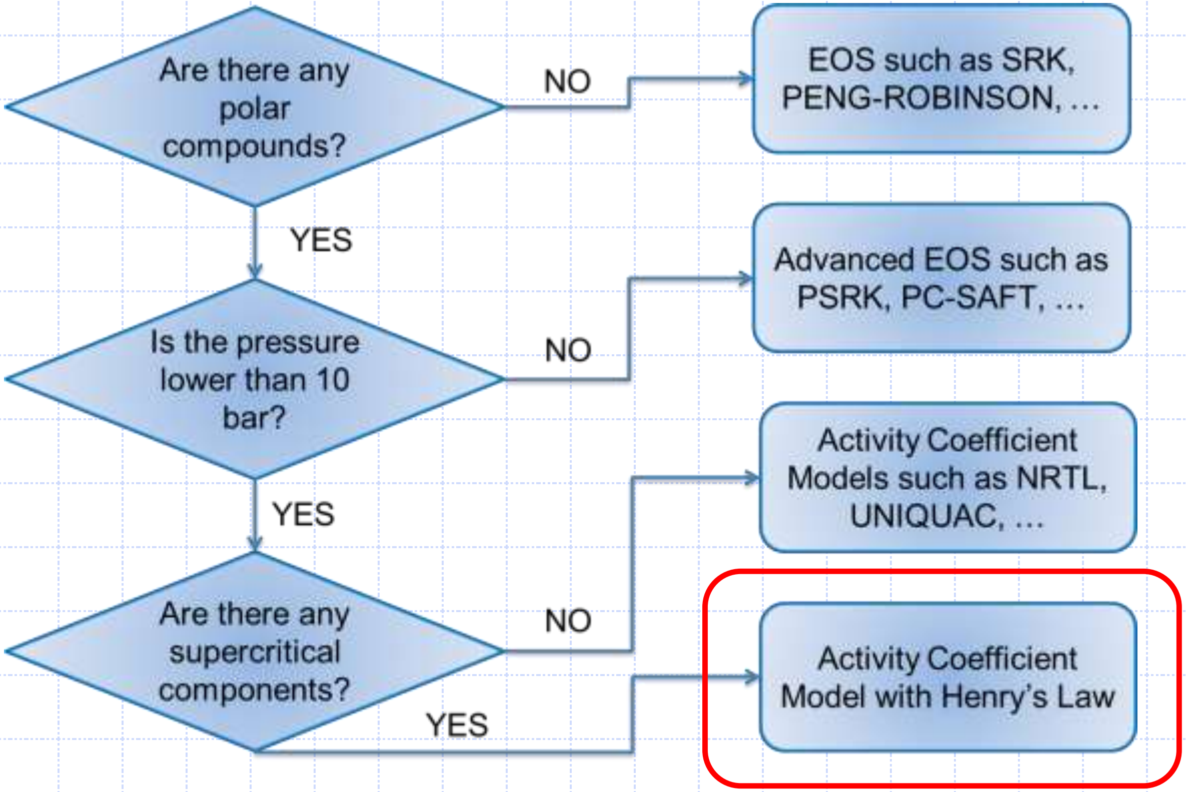
Water and Chlorobenzene form two-liquid phases under the conditions in the tank

Property Analysis - Exercise

1. Choose an appropriate Property Method to represent the system. Parameters available?
2. Retrieve the T_c for CO2 and water
3. Use the binary isotherm analysis to investigate the phase equilibrium of the liquid mixture @ 1 atm
4. Set up the flowsheet to model the settling tank using a flash drum

Property Analysis - Exercise

1. Choose an appropriate Property Method to represent the system.

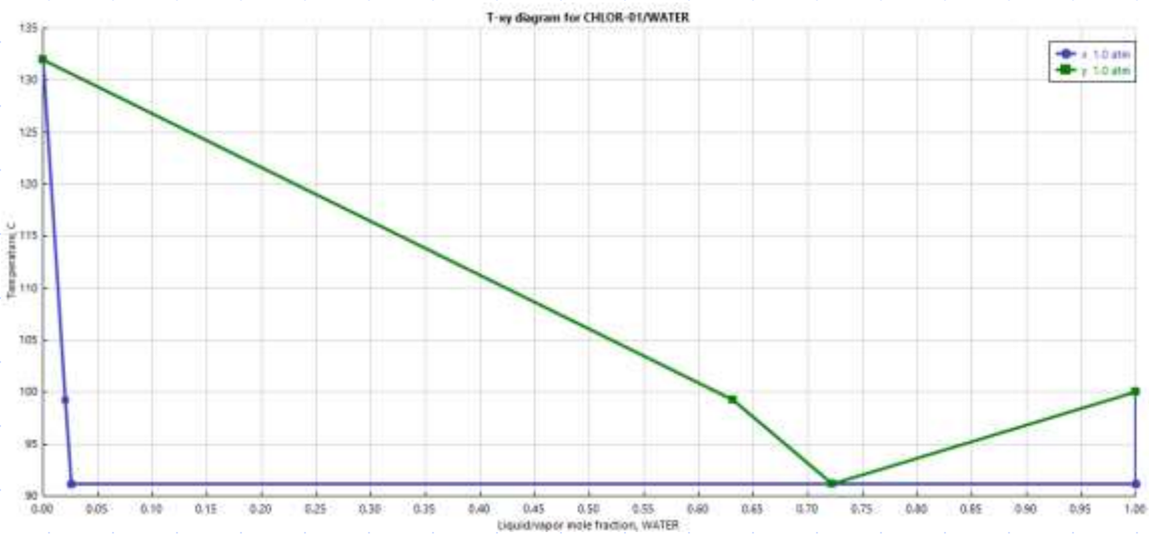


Property Analysis - Exercise

1. Choose an appropriate Property Method to represent the system.
   NRTL, UNIQUAC with Henry's components
2. Retrieve the Tc for CO_2 and water

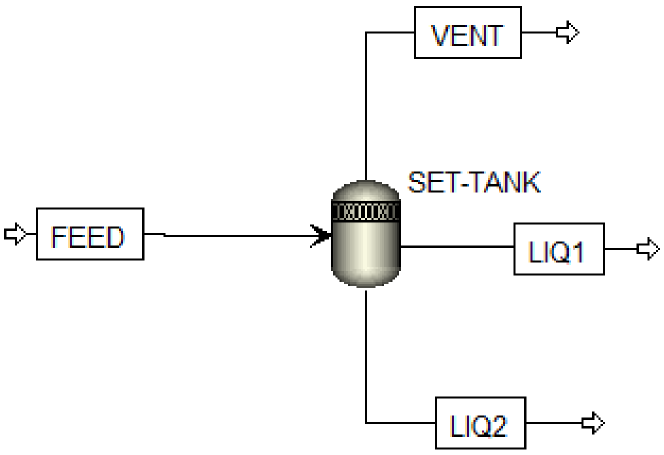
Parameters	Units	Data set	Component WATER	Component CLBENZ	Component CO2
TC	C	1	373.946	359.2	31.06

3. Use the binary isotherm analysis to investigate the phase equilibrium of the liquid mixture @ 1 atm



Property Analysis - Exercise

1. Set up the flowsheet to model the settling tank using a flash drum



2. Modify the stream report to include the constant pressure heat capacity (CPMX) for each phase (Vapor, Liquid 1 and Liquid 2), and the fraction of L1 to total liquid for a mixture (BETA)
3. Display Total stream mass density as Global Data on the Flowsheet

Property sets

- A property set is a way of accessing a collection, or set, of properties as an object with a user-given name; only the name of the property set is referenced when using the properties in an application.
- Use property sets to report thermodynamic, transport and other property values.
- Current prop-set include:
  - Design specifications, Calculator Blocks, Sensitivity Analysis
  - Stream reports
  - Physical property tables (Property Analysis)
  - Tray Properties (RadFrac, MultiFrac, etc.)
  - Heating/cooling curves (Flash2, HeatX, etc.)

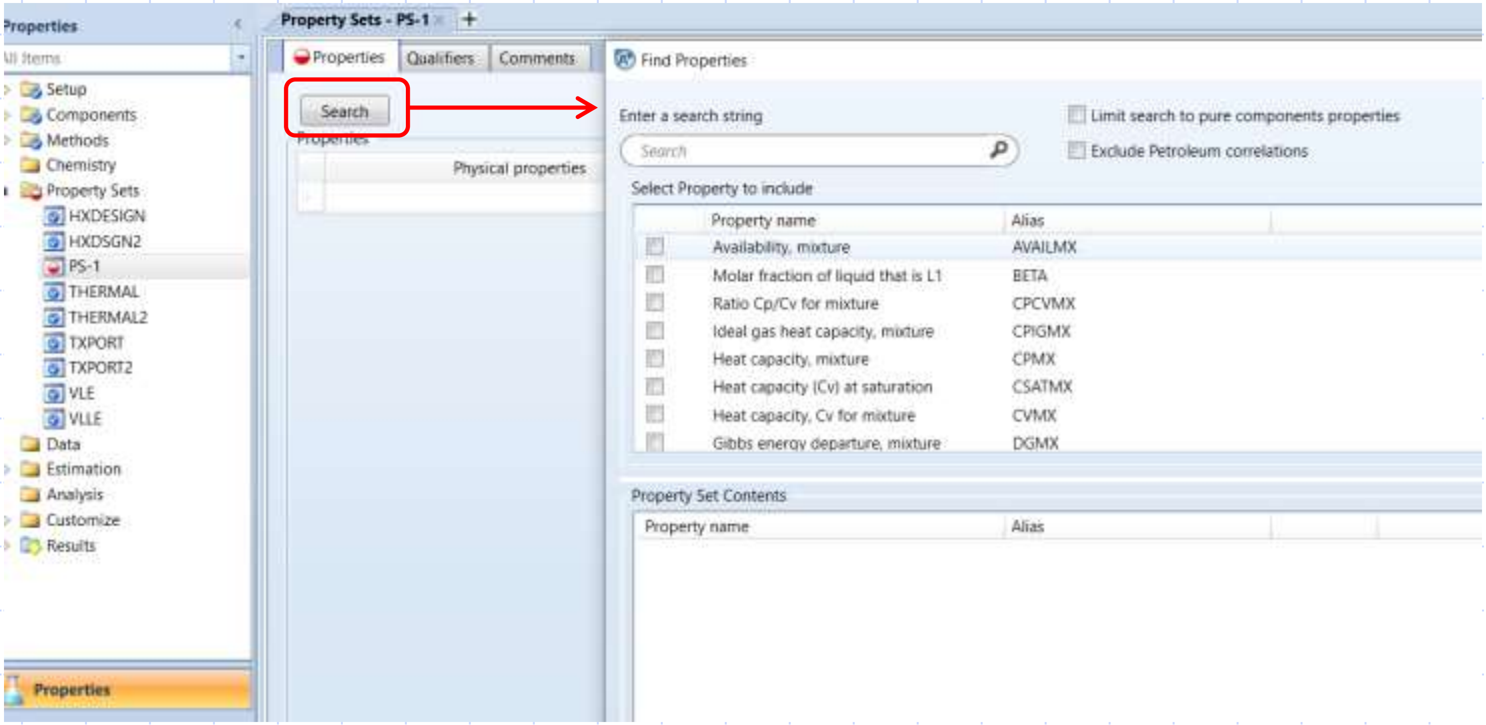
Default Prop-sets

- Some templates contain predefined property sets

Property Set	Types of Properties
HXDESIGN	Heat Exchanger Design
HSDSGN2	Heat Exchanger Design (SI Units)
THERMAL	Mixture Thermal (HMX, CPMX, KMX)
THERMAL2	Mixture Thermal (HMX, CPMX, KMX) (SI Units)
TXPORT	Transport Properties
TXPORT2	Transport Properties (SI Units)
VLE	Vapor-Liquid Equilibrium (PHIMX, GAMMA, PL)
VLLE	Vapor-Liquid-Liquid Equilibrium

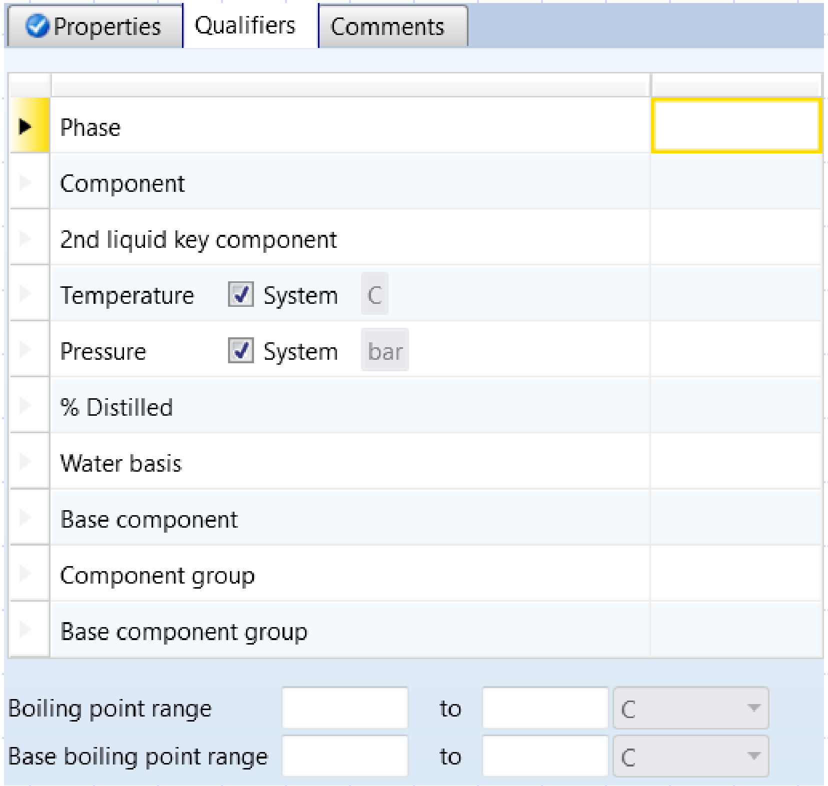
Specifying new Prop-sets

- Select properties for a property set using the Methods Prop-Sets form
- "Search" button can be used to search for a property
- If "Units" are not specified, Global Units will be used



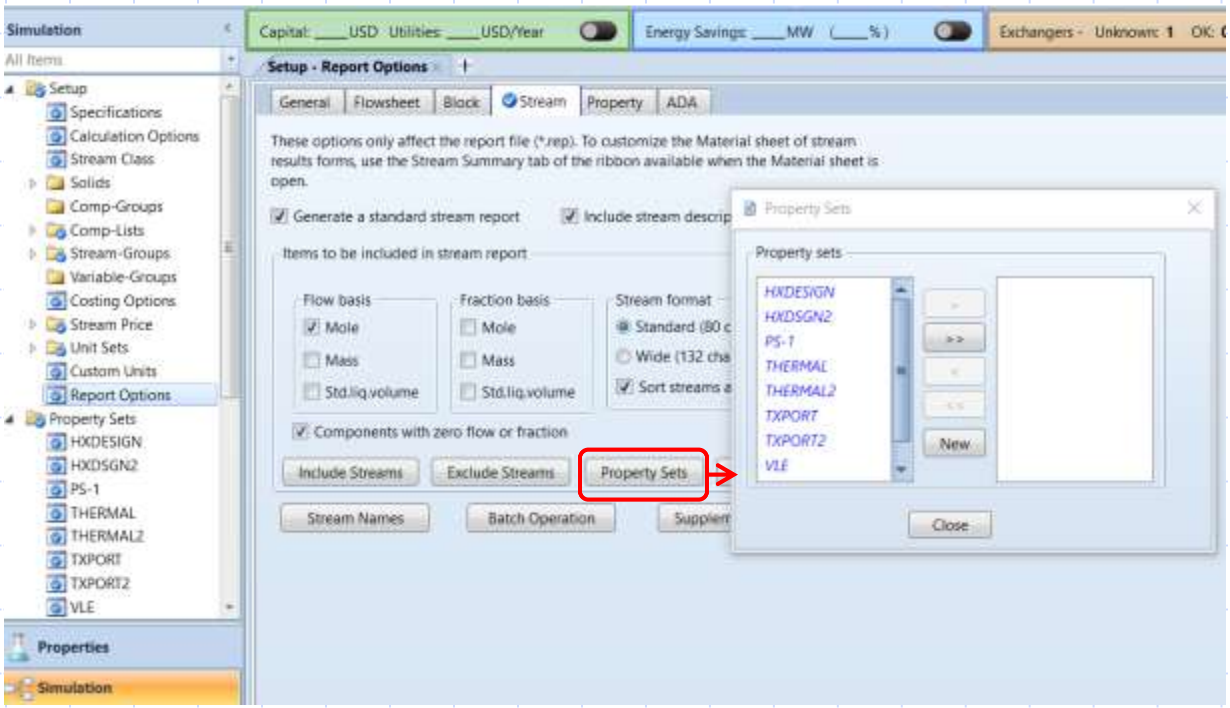
Specifying new Prop-sets

- Each specified qualifiers apply to each selected property, where applicable



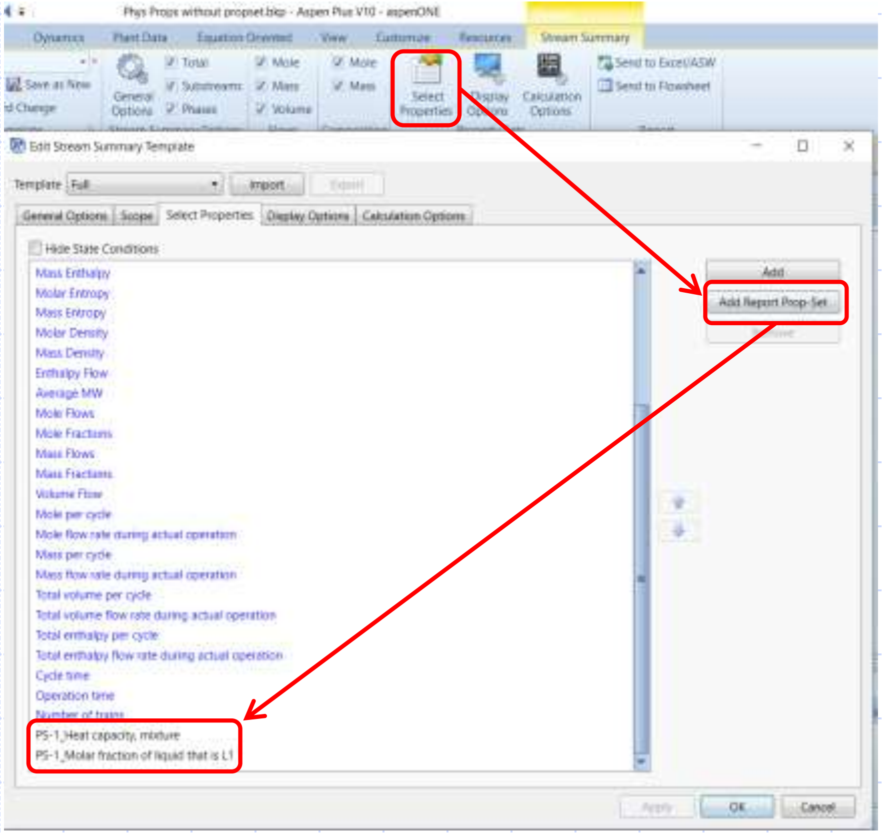
Report Prop-sets

- In the Simulation Environment, go to Setup | Report Options | Stream sheet click on Property Sets and move the desired Prop-Set from available to selected area



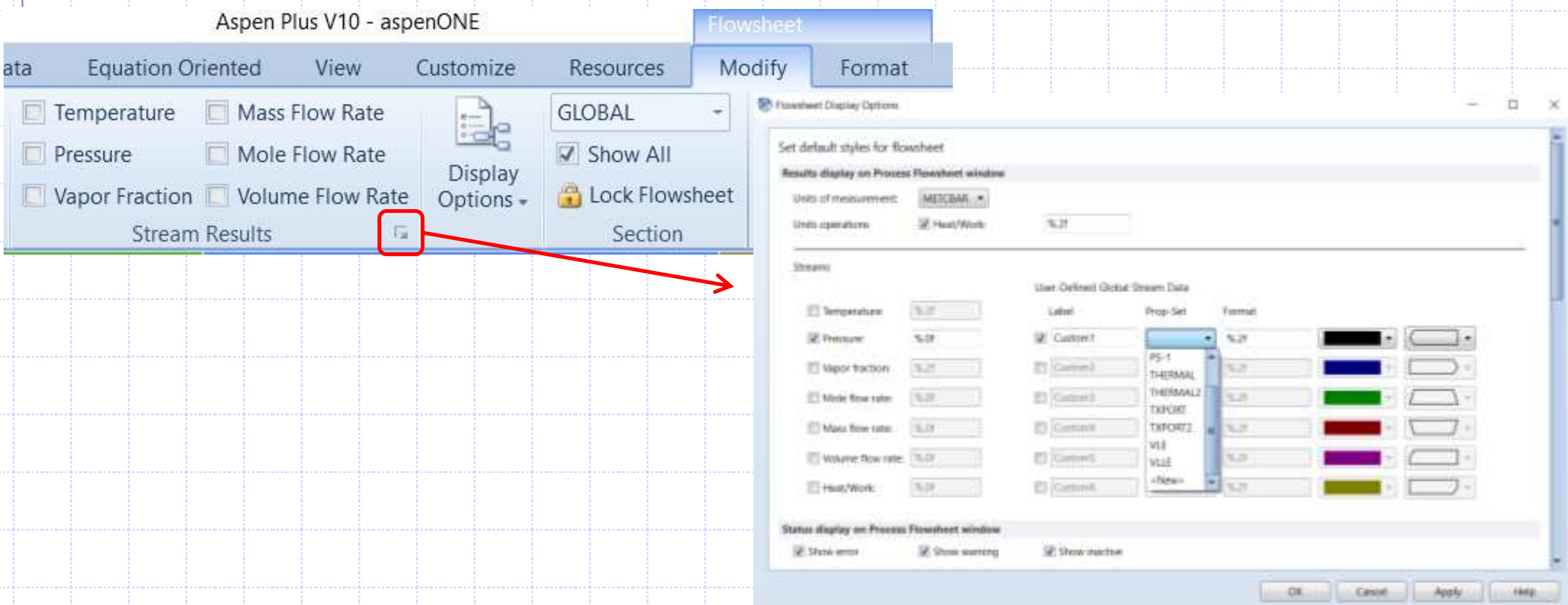
Add property to Stream Results

- To view the calculated properties on the Stream report, in the Stream Summery Ribbon, click "Select Properties", then "Add report Prop Set"



Add variable to flowsheet

- Global Variables can be added to Aspen Plus flowsheet:
  - Temperature, Pressure, Flow rates, Vapor frac, etc…
  - Up to six additional variables, via Property Sets, can be included with regularly available variables



Additional Property Data Source

- When physical property data is unavailable, it may be obtained through alternate sources, including:
  - Literature data
  - NIST TDE or DECHEMA DETHERM databank
  - Estimation of pure, binary, and UNIFAC parameters based on limited input data using Property Estimation run mode
  - Regression of pure and binary parameters based upon experimental data using Data Regression run mode

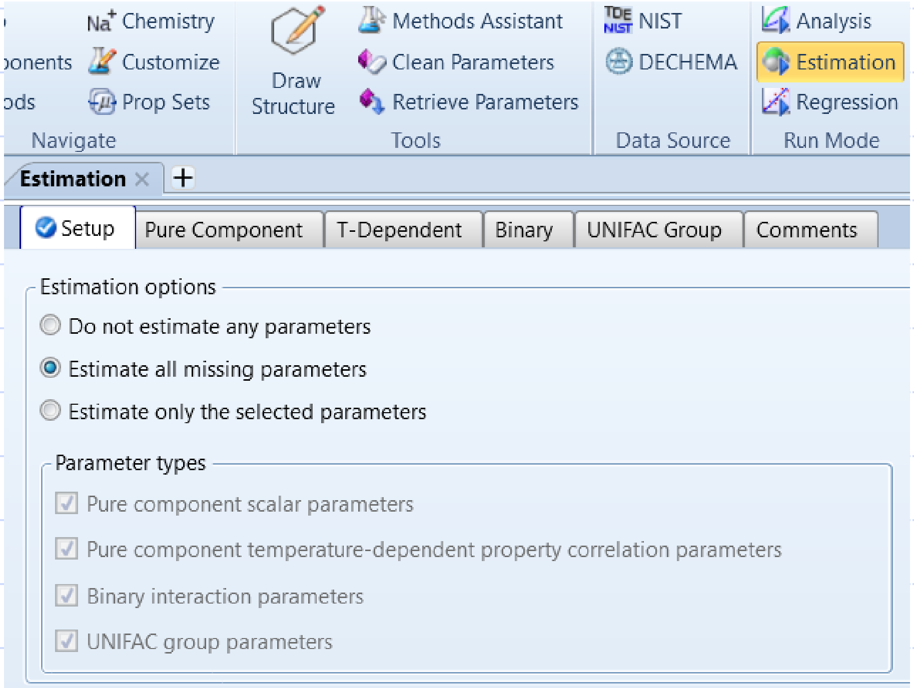
Property Database

- NIST Source Database
  - Over 4 million experimental data points
  - Includes data for over 24000 pure components and 30000 binary mixtures
  - Tools to evaluate and regress data included in A+
  - Updates available quarterly

- DECHEMA DETHERM Database
  - Link to DECHEMA web site
  - Well established comprehensive property database
  - Download data to A+ for data regression
  - Requires a subscription or pay-per-dataset online purchase

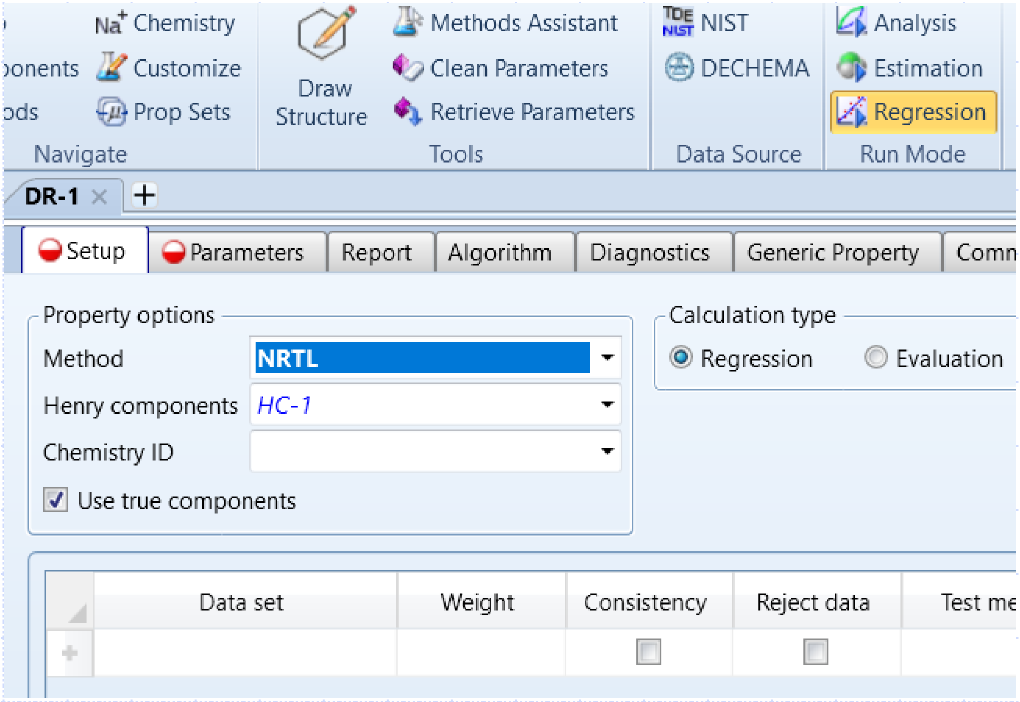
Property Estimation

- Estimate physical property parameters for components not present in A+ databanks or for components whose properties were regressed under different thermal conditions. It can estimate:
  - Pure component physical property constants
  - Parameters for Temperature-dependent models
  - Binary interaction parameters for Wilson, NRTL and UNIQUAC activity coefficient models
  - Group parameters for UNIFAC
- Estimation via mol file



Data Regression

- Estimate Processes raw data to determine the parameters pf physical property models required by Aspen Plus to measure pure component, VLE, LLE, and other mixture data, such as:
  - Properties of components in a mixture
  - Pure component properties
  - Electrolyte properties
- Regresses parameters to multiple data types simultaneously
- Data Regression can contain property estimation and property analysis calculations



Data Regression Demo

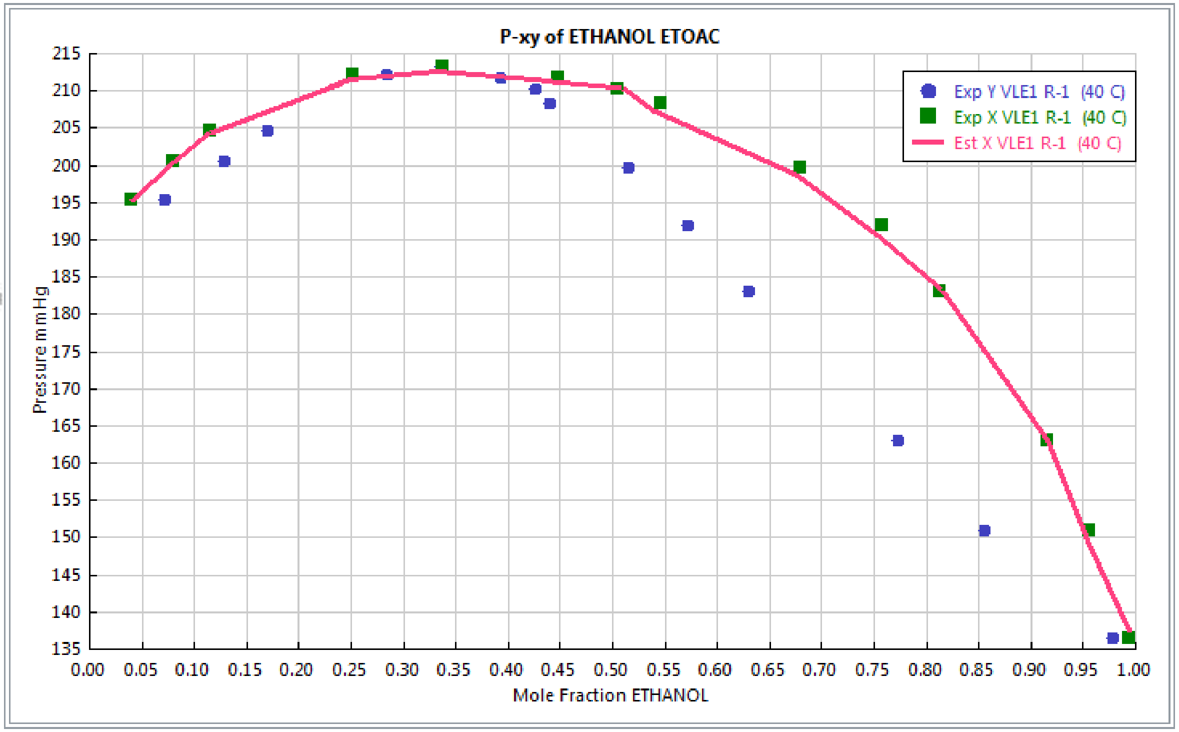
- Using a set of data provided, produce the regression curve plot for the phase equilibrium of the binary mixture ethyl-acetate/ethanol.

40C and 70C data of Martl, *Collect.Czech. Chem. Commun.* 37,266 (1972):

T=40C			T=70C		
P MMHG	X ETOAC	Y ETOAC	P MMHG	X ETOAC	Y ETOAC
136.600	0.00600	0.02200	548.600	0.00650	0.01750
150.900	0.04400	0.14400	559.400	0.01800	0.04600
163.100	0.08400	0.22700	633.600	0.13100	0.23700
183.000	0.18700	0.37000	664.600	0.21000	0.32100
191.900	0.24200	0.42800	680.400	0.26300	0.36700
199.700	0.32000	0.48400	703.800	0.38700	0.45400
208.300	0.45400	0.56000	710.000	0.45200	0.49300
210.200	0.49500	0.57400	712.200	0.48800	0.51700
211.800	0.55200	0.60700	711.200	0.62500	0.59700
213.200	0.66300	0.66400	706.400	0.69100	0.64100
212.100	0.74900	0.71600	697.800	0.75500	0.68100
204.600	0.88500	0.82900	679.200	0.82200	0.74700
200.600	0.92000	0.87100	651.600	0.90300	0.83900
195.300	0.96000	0.92800	635.400	0.93200	0.88800
			615.600	0.97500	0.94800

Atmospheric data of Ortega J. and Pena J.A., *J. Chem. Eng.Data* 3

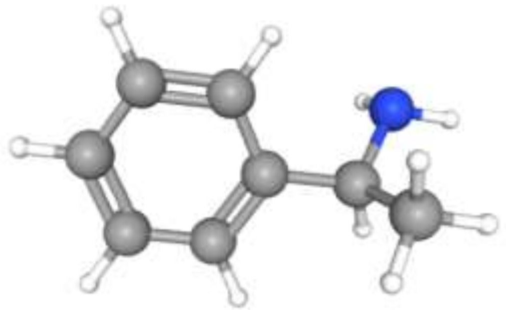
T C	X ETOAC	Y ETOAC	T C	X ETOAC	Y ETOAC
78.450	0.00000	0.00000	71.850	0.44700	0.48700
77.400	0.02480	0.05770	71.800	0.46510	0.49340
77.200	0.03080	0.07060	71.750	0.47550	0.49950
76.800	0.04680	0.10070	71.700	0.51000	0.51090
76.600	0.05350	0.11140	71.700	0.56690	0.53120
76.400	0.06150	0.12450	71.750	0.59650	0.54520
76.200	0.06910	0.13910	71.800	0.62110	0.56520
76.100	0.07340	0.14470	71.900	0.64250	0.58310
75.900	0.08480	0.16330	72.000	0.66950	0.60400
75.600	0.10050	0.18680	72.100	0.68540	0.61690
75.400	0.10930	0.19710	72.300	0.71920	0.64750
75.100	0.12160	0.21380	72.500	0.74510	0.67250
75.000	0.12910	0.22340	72.800	0.77670	0.70200
74.800	0.14370	0.24020	73.000	0.79730	0.72270
74.700	0.14680	0.24470	73.200	0.81940	0.74490
74.500	0.16060	0.26200	73.500	0.83980	0.76610
74.300	0.16880	0.27120	73.700	0.85030	0.77730
74.200	0.17410	0.27800	73.900	0.86340	0.79140
74.100	0.17960	0.28360	74.100	0.87900	0.80740
74.000	0.19920	0.30360	74.300	0.89160	0.82160
73.800	0.20980	0.31430	74.700	0.91540	0.85040
73.700	0.21880	0.32340	75.100	0.93670	0.87980
73.300	0.24970	0.35170	75.300	0.94450	0.89190
73.000	0.27860	0.37810	75.500	0.95260	0.90380
72.700	0.30860	0.40020	75.700	0.96340	0.92080
72.400	0.33770	0.42210	76.000	0.97480	0.93480
72.300	0.35540	0.43310	76.200	0.98430	0.95260
72.000	0.40190	0.46110	76.400	0.99030	0.96860
71.950	0.41840	0.46910	77.150	1.00000	1.00000
71.900	0.42440	0.47300			

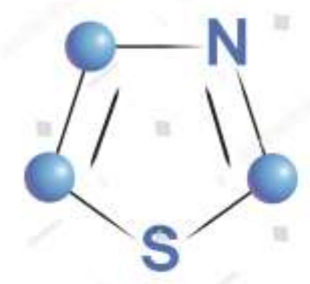


Exercises on thermodynamic modeling

Property constant estimation system

- Estimate the property of Phenyl ethyl amine.
  - Estimate all the pure component properties
  - Compare with TB = 477.85
- Estimate the properties of Thiazole
  - Estimate all the pure component properties
  - Compare with TB = 116.8
- Check Acetone – chloroform properties
  - Acetone TB = 56 C
  - Chloroform TB = 61 C
  - Azeotrope = 64.5 C





Thermodynamic analysis

- Prepare a graph of the phase envelope and a complete table of all the thermodynamic properties of the following system:
  - methane 0.3
  - Ethane 0.3
  - N-pentane 0.3
  - N-decane 0.1
- Consider the system water acetonitrile and show if a miscibility gap will appear by changing temperature
  - Try with an EOS and with a Ge model
- Data regression system
  - Methyl cyclohexane – n-butanol (regression 1 data set)
  - Ethanol – ethyl acetate (regression 3 data sets)
  - Benzene – cyclohexane

Data regression system

- Perform an evaluation and a regression for the folowing systems
  - Heptane – n-butanol
  - Water – 1,4 dioxane – 50 C
  - Water – 1,4 dioxane – 50 C
  - Water – 1,4 dioxane – 70 C
  - Acetone – Water – 100 C
  - Acetone – Water – 35 C