



Practical Thermodynamics Used in Simulations

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- Basic thermodynamics
- Selecting a [decent] VLE model
- Validating a model selection

The basics of Thermo Models will be reviewed to put us all on the same page

Choice of Thermo models can be the difference between useful results and non-sense

So How do we know a Thermo model is appropriate?

How can we improve the usefulness of our simulations.

- Use of process simulators by engineers has greatly expanded
- Simulation programs include many VLE models
- Computers are great at calculating, poor at giving advice
- Many simulator problems can be traced to improper thermodynamic choices

Where do we stand today

Before PC's and Simulation software, Flash Calcs Tedious

So Engineers carefully selected model before warming up

slide rule. Engineers from that era have told us that 40% of the project time was invested in validating Thermo before the process design was undertaken

Today everyone has dozens of equations which are selected by a mouse-click. Abbreviations Acronyms Initials are Intimidating

Choice is a “professional” decision not a computation

The wrong choice will give you the wrong answer - but it could LOOK FINE AT LEAST IN A SNAPSHOT MODE



Impact of Thermodynamics on Process Simulation

- A simulator calculates mass and energy balances around equipment.
- Pure component properties...
 - what's the boiling point? Viscosity? Heat capacity? Critical points?
- Phase equilibria
 - how much alcohol stays in the whiskey liquid?
- Enthalpy balance
 - how much energy to heat, to burn, or to mix it?

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Thermodynamics is the principal theory behind process simulation

In order to calculate Mass and energy balances.

The simulation program needs some fundamental information

Volatility

Heat Capacities

Equilibrium Equations

Heats of vaporization, formation etc.

- Mathematical models which describe the composition of the vapor and/or liquid phases of a mixture
- Models can be based on physical effects, thermodynamic constraints, or fit to empirical data
- K Values: $K_i = y_i/x_i$

The equilibrium equations are where confusion often starts.

Dr. Gibbs tells us “At any Temperature and pressure If we know analysis of feed...

We can calculate quantity and analysis of Vapor & Liquid”

BUT Does Calculation agree with reality?!?

Many different equations have been developed to calculate K_i



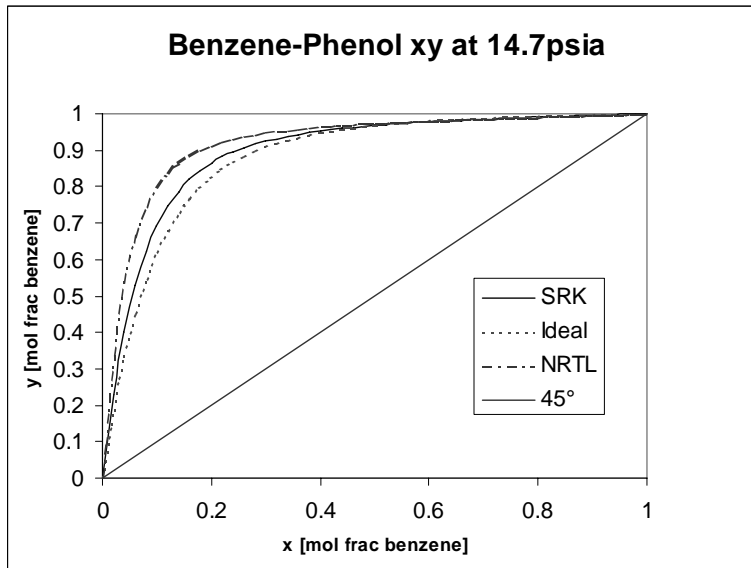
Why there are different thermodynamic models

- No [precise and accurate] universal model exists.
- Different systems have different dominating effects.
- While some systems are well understood, many are not.

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Water and hexane are not the same

We have great data on properties of pure water. We don't have such extensive data on most chemicals.



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How do we know which is right?

Pick a model which of the equation class that is appropriate for the chemicals in the process

You will note however at very high and very low benzene levels everyone gets the same answer

So there is a chance that a Bad choice will look good

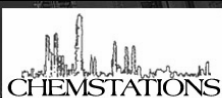
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Perfect (Ideal) Gas Behavior

- Ideal gases are point masses with no attractive or repulsive force
- No energy is exchanged during collisions

$$P_1V_1/T_1 = P_2V_2/T_2 \quad \sim \quad PV = nRT$$

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Boyle observed that PV~constant

Becomes closer to being true as Temperature increases

- Real gases have volume
- Real gases have attractive / repulsive forces between particles
- Ideal gas law must be corrected to account for the interactions and volume

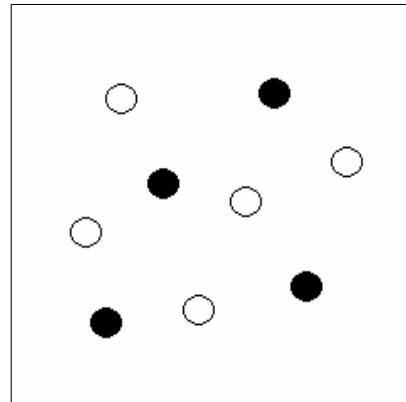
$$\left(P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT$$

n^2a/V^2 term is correcting for the interactions of these particles. The value of a is a constant, and must be experimentally determined for each gas.

Since real gas particles have real volume, the nb term is correcting for the excluded volume.

Vapor fugacity comes into effect...vapors don't mix the way we would expect them to

- Particles are distributed randomly
- All interactions are (on average) the same
- Described by Raoult's law
 - $y_i P = x_i p_i^{\text{sat}}$



Most Thermodynamic Vapor Liquid Equilibrium models are driven by the behavior of the molecules in the liquid phase

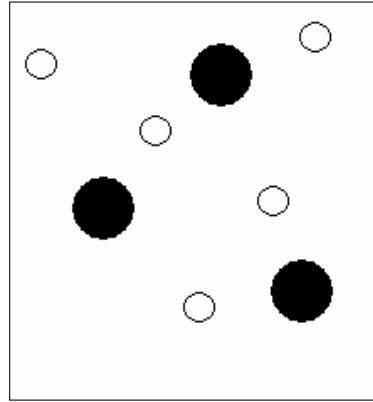
Mostly true for gas mixtures at high pressure

Partial molar volumes are nearly the same. They mix evenly (1+1=2)

Random distribution means no clumps (azeotropes, LLE, extreme GE from packing...)

Not much is really ideal

- Particles are distributed randomly
- Interactions are not the same
 - Physical collisions are affected by size differences
 - (weak) Intermolecular forces exist
- Sizes are only moderately different

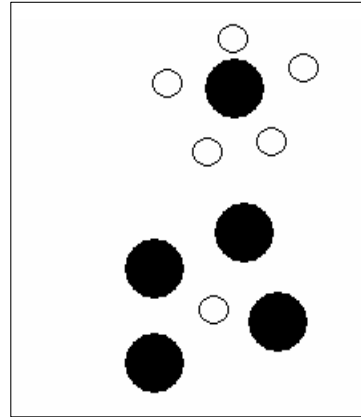


Regular liquid solutions are much more common in chemical processing

Entropy of mixing is zero, heat of mixing may be nonzero

liquid is not ideal. Raoult's law doesn't apply for the mixtures, because of differences in liquid.

- Particles are not distributed randomly
- Intermolecular forces of attraction or repulsion dominate
- Hydrogen bonding can be significant
- Azeotropes may occur



Because of the pervasiveness of water in most of our processes ..

Modeling Polar non-ideal liquids is required

Water and

- Electrolytes -- dissociation is a reaction
- Dissolved gases in a solute
- Reactive systems
- Polymers
- Solids

Examples of chemical systems that require specialized calculations

In these systems it is difficult to derive an equation from thermodynamic models unsupported by other data.



Categories of Thermo Models

- Equations of State
- Activity coefficient methods
 - Correlated
 - Predictive
- Combined models
- Special purpose / empirical
- Advanced models (SAFT, ESD, SPEAD, COSMO, etc)

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Combined model eg PSRK accounts for vapor phase non-idealities modest improvement over Poynting factor



Thermodynamic Methods

- Activity Coefficient Models
 - UNIFAC (LLE, VLE)
 - UNIFAC (Polymers)
 - UNIQUAC,
 - NRTL Van Laar
 - Wilson, Wilson Salt,
 - T.K. Wilson
 - Margules, Hiranuma, GMAC
 - Regular Solution
- Equations of State
 - Peng-Robinson
 - Grayson Streed
 - SRK, API SRK, TSRK,
 - MSRK, PSRK, BWRS
- Other
 - Sour Water
 - TEG Dehydration
 - Amines
 - ESSO

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Some examples of Thermo Methods

- Basic thermodynamics
- Selecting a [decent] VLE model
- Validating a model selection

So How can we make and intelligent selection from this wealth of possible mistakes?

•



Use an Equation of State

- Equations of state are based on PVT relations
- Real gases and regular solutions are well modeled by equations of state
- Molecules should be moderately similar size
- Calculates compressibility effect; pressure effect on enthalpy
- Well suited for hydrocarbon mixtures
- These models need pure component properties: critical properties and acentric factor
- Mixing terms allow fine tuning for regular solutions

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Here are some general guidelines on the selection of a category of thermodynamic models to use.

EOS = Equation of State



Activity Coefficient Models

- Activity models are based on thermodynamic constraints on the liquid ($\Delta G = RT \ln \gamma$)
- Assume ideal gas (corrections can be made)
- Use for non-ideal solutions
- Molecules may have drastically different size
- Binary parameter models are fit to data
- Predictive models based on structure
- Can predict LLE
- Extended versions can handle electrolytes, polymers
- Interaction parameters are important

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Polar Solutions are best modeled with Activity Coefficient models



Effects of phase equilibria model selection

- How easy is it to separate two components?
Different models give you different results
(TPxy plots...)
- What comes out the top?
- How much heat from the reactor?
- The wrong model will not describe the
physical process
 - Qualitatively
 - Quantitatively

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Plotting TPxy diagrams will give an indication of the ease of separating two components by distillation

If low boiling azeotropes exist, a mixture will be the top product

The energy to be provide to or extracted from the reaction device is critical to safety and yield

If a simulation is to be useful it must first be qualitatively correct

(If you increase feed rate in sim it moves in same direction as plant)

Better yet it is quantatively correct the actual numbers will agree

- Equations of state – SRK and Peng Robinson
- Activity Coefficient models—NRTL and Wilson
- Predictive Activity – UNIFAC, UNIQUAC
- Associating – SAFT, ESD

Predictive: Not regressed BIP's

Depends on functional group estimations

These are general rules for selecting Thermo models based on the chemicals processed. While these might not be the best choices they are normally not bad choices.

Dr. Schad's article offers a decision tree with more detailed recommendations



Special Systems

- Top tier simulators have electrolytes methods
- Most simulators have amines and sour water treatment empirical models

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Electrolytes are special because the dis-association reaction is beyond the scope of the simple Gibbs excess energy model.

Amine sweetening models try to match industrial data and are empirical

eg. Mixed Amines depend on differing rates of absorption/combination to model take up of H₂S vs. CO₂



How conditions affect selection

- Single phase?
- Moderate to high pressure over nonideal liquid
- Dissolved supercritical gases
- Immiscibles?

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It's not sufficient to consider the chemicals and then choose a system. You should also consider the conditions in the system you're going to model.

For example:

If you expect the system to be single phase, VLE model becomes less important.

If you have a very high pressure, an activity coefficient becomes less accurate for the vapor over a nonideal liquid (pressure begins to have significant effect on such a system at 3-10 atm, generally)

If light gases are all dissolved in water, you shouldn't use an equation of state.

If you have two separate liquid phases...you need to pick a model which can describe the phenomena.



Environmental Problems

- At very low concentrations, precision becomes important
- Equations of state have inherent error in the model
- Activity coefficient models can't extrapolate to infinite dilution without data
 - Gamma data
- Predictive models may also be capable

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All simulation programs are trial & error till “close enough”

So how precise is “Close enough” when ppm or jail is criteria

EPA has published gamma data that can be regressed to BIP'

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Having chosen a model or a family of models how can we zero in on better choices (or at a minimum eliminate invalid choices)



Validating your model selection

- Verify property data is appropriate
- Inspect the results from a model
- Compare to external data
- Compare to similar models and predictive models
- Compare to similar systems

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You should take several steps and employ multiple checks to confirm the model you are working with is valid.



Verify property data available

- For EOS, need good T_c , P_c , Acentric Factor
- For activity methods, need binary interaction parameters and saturated pressures
- For subgroup methods...need subgroups
 - Vacuum Processing Caveat

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In order for the Thermo Method you have chosen to have a fighting chance you need to assure that appropriate pure component information is available - at least for the major or important compounds.

Subgroup values have been regressed from temperature above the normal boiling point and so if you are considering subgroup contributions in vacuum distillations you are dealing with extrapolations



Inspecting your results

- Check TPxy plots for key component pairs
- Check residue curve maps for azeotropes
- Check binodal plots for LLE
- Perform simple flash separations to confirm expectations

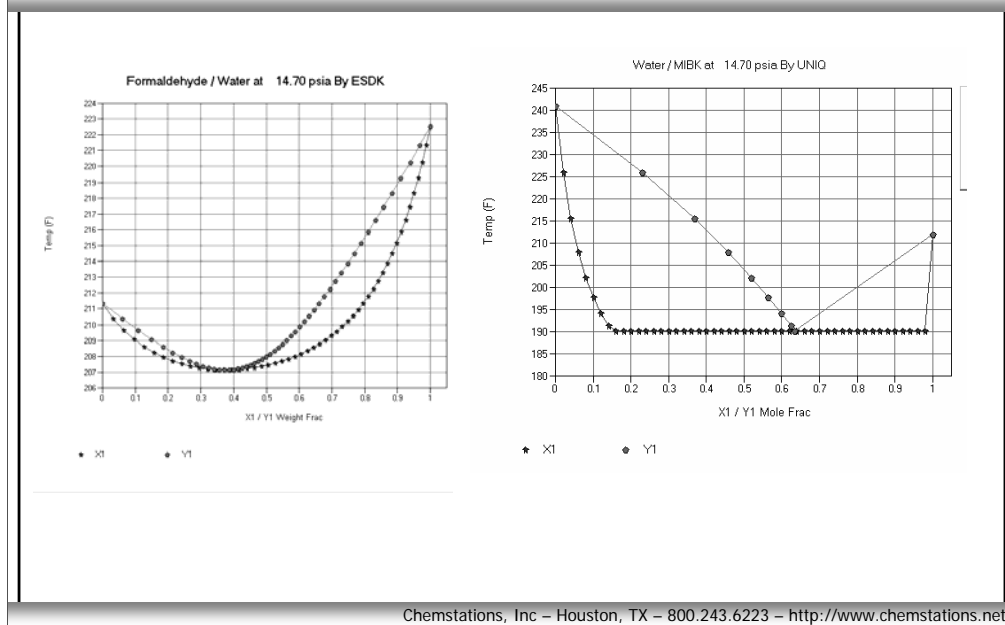
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There are several “quick” steps that can give you encouragement or warning flags.

These should almost always be run even in the absence of real world data to develop a feel for how the process may finally lay out



TPxy plots show the binary separation



If you know you have an azeotrope or two liquid phases, look for this type of tpxy in chemcad!

If you see this type of tpxy...you probably have an azeotrope!

Two azeotropes

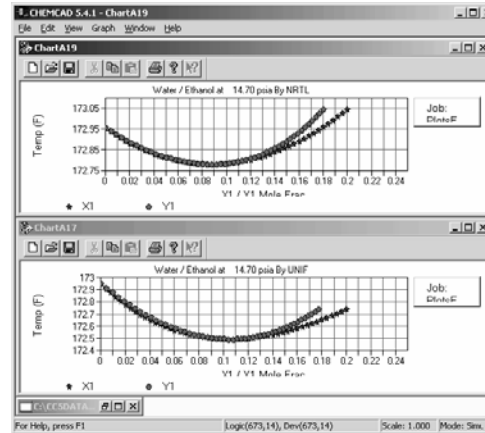
Both Minimum Boiling

Formaldehyde & water are a single phase Homogeneous

Water MIBK form two liquid phases over much of the composition range (FLAT LINE) with the two phase analyses represented by the extreme points of the flat portion and the proportions of the phases by the reverse lever arm rule

Note that you should verify that this is the correct prediction of azeotrope!

- Predictive methods often 'come close' to the right answer



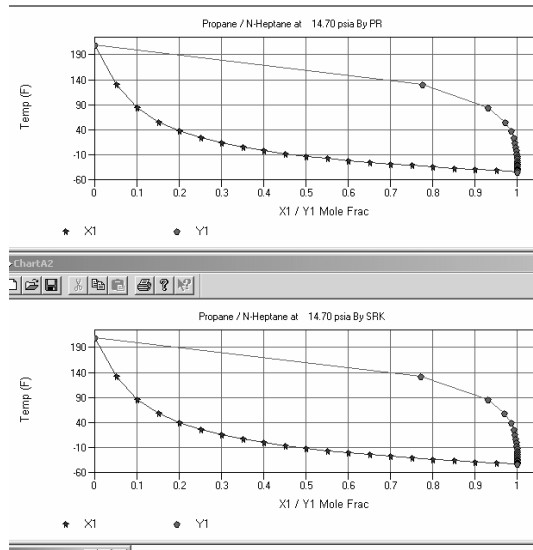
NRTL depends on regressed BIP's

UNIFAC is predictive

If a predictive model comes close to a bip activity model...be encouraged that the model probably isn't bad (which doesn't necessarily mean good).

If a predictive model and bip model disagree sharply...you need to do more validation to determine which is correct.

- Models with similar basis should have similar results
- If models disagree... investigate why



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Two Equations of State separating alkanes

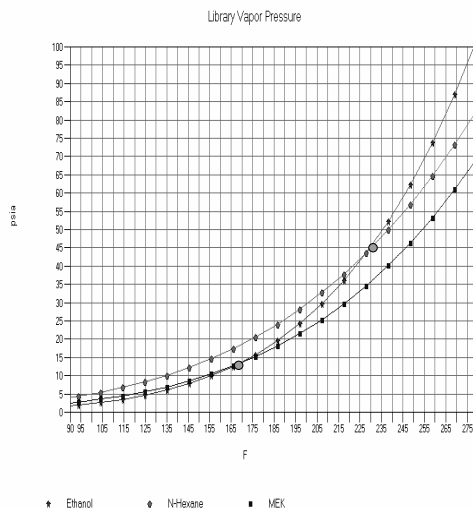
Models which are developed from the same concepts, but with mathematical variances, should behave similarly. For example:

PR, SRK

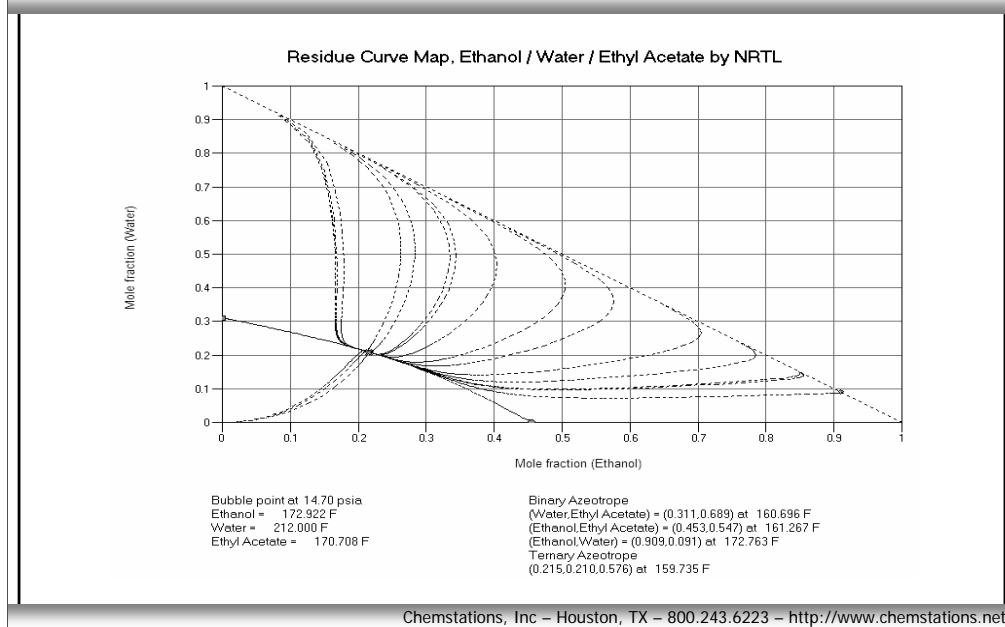
Unifac, Uniquac, Modified Unifac

Wilson, Van laar, NRTL

- Plot VP vs T for all compounds in Flowsheet
- Bancroft Points are crossings. Often predict azeotropes.
- When Bancroft lower than "ambient"; Raise Pressure.
- When Bancroft higher than ambient; decrease Pressure.



Bancroft point plots can be an early indication that azeotropes are likely



Residue Curve Maps can find ternary azeotropes (and in the case above 3 binary azeotropes)

looking for azeotropes isn't always simple. Use residue curve map to determine where they are predicted by your selected model.



Confirming Thermo

For the system Ethanol, Ethyl Acetate, Water three Binary Azeotropes exist as well as a ternary azeotropes. NRTL predicts the azeotropes below:

Bubble point at 14.70 psia
Ethanol = 172.922 F
Water = 212.000 F
Ethyl Acetate = 170.708 F

Binary Azeotrope
(Water,Ethyl Acetate) = (0.311,0.689) at 160.696 F
(Ethanol,Ethyl Acetate) = (0.453,0.547) at 161.267 F
(Ethanol,Water) = (0.909,0.091) at 172.763 F
Ternary Azeotrope
(0.215,0.210,0.576) at 159.735 F

UNIFAC predicts the azeotropes tabulated below

Bubble point at 14.70 psia
Ethanol = 172.922 F
Water = 212.000 F
Ethyl Acetate = 170.708 F

Binary Azeotrope
(Water,Ethyl Acetate) = (0.314,0.686) at 159.297 F
(Ethanol,Ethyl Acetate) = (0.466,0.534) at 159.816 F
(Ethanol,Water) = (0.893,0.107) at 172.467 F
Ternary Azeotrope
(0.099,0.301,0.600) at 158.510 F

The significant difference between NRTL and UNIFAC with respect to Ethanol and Ethyl Acetate ternary azeotropes composition needs to be confirmed by experimental data.

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For the previous system two activity coefficient methods predicted the binary azeotropes but deviate in the analysis of the Ternary



Get Data to Validate Choice

- Even a few data points valuable
 - Regress Physical Properties
 - Get best match between Reality and model
- “Good” Data
 - Plant scale trumps Pilot Plant
 - Pilot Plant trumps bench work
 - Bench measurements better than Literature
 - Literature values better than estimates

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Definitive validation: actual data

Find data to compare the model to

Even a few data points can help validate the model

Data can be used to select between models giving similar results

If you don't compare to 'real' data, you don't know the 'real' answer

Modeling existing operations gives access to best data.

Pilot Plants may be somewhat idealized

There are mistakes in literature! Is you design victim of one?

Measurements are generally better than unsupported estimates.



Sources of data

- Books and journals
 - DECHEMA, Fluid Phase Eq., J.Che.Eng.D., JANAF tables, Int'l Critical. Tables,
- Data companies
 - AIChE\DIPPR, DECHEMA/DETERM, Knovel.com, PPDS
- Predictive packages
 - don't use them blindly! Read about the model before applying it
 - Vacuum Processing Caveat



Sources of new experimental data

- Lab data
 - internal chemist
 - corporate chemist
- A handful of companies like Wiltec do custom labwork
- Labs of large corporations becoming available for contract
- Few universities run analytical labs



Absent any Valid Data...

- The known unknowns...things we don't know that we know we don't know
- Homologue plots
- Qualitative behavior and expectations

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For example, maybe we suspect know the basis for our property estimation is questionable or that a trace component has an impact far out of proportion to its concentration.

If we know properties of monomethyl chickenwire and dimethyl chickenwire it is easier to extrapolate trimethy...

The processing performance of like compounds should be similar and should fall into a familiar pattern and a simulation should qualitatively match the real world response.

Even absent data the engineer has experience which can rough out expected behavior of the undocumented component



Some Important Caveats

- Can't do ppm with models that have error
- H for EOS is not from the Cp
- EOS for a nonregular pure component can give funny results
- EOS is dependent on T_b, T_c, P_c , acentric
- Activity methods depend on P_{sat} , bips
- Pure components don't have a phase envelope

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Gamma data at infinite dilution + tight convergence

Enthalpy accounting vulnerable to calculation of enthalpy departure function

Checking TPxy with EOS: funny phase diagrams mean Thermo is not reliable. Using Act Coeff failing to choose 2 liquids when they are present likewise

Remember what you must have to use EOS &/or Activity for some /most components



Some Reading

- Poling, Bruce E. Prausnitz, John M. O'Connell, John P. The Properties of Gases and Liquids 5th. Edition McGraw-Hill ISBN: 0070116822
- Carlson, Eric C. Don't Gamble with Physical Properties For Simulations *Chemical Engineering Progress* October 1996 Pages 35-46 *Has Thermo choice decision trees*
- Kister, Henry Z. Can We Believe Simulation Results *Chemical Engineering Progress* October 2002 Pg.52-6 *Be careful of these key issues that may generate differences between a distillation-tower simulation and its actual performance.*
- Barnicki, Scott D. How Good Are Your Data? *Chemical Engineering Progress* June 2002 Pg 58 67 *Some thoughts on the measurement and interpretation of vapor-liquid equilibrium*



Thank You

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