

Good afternoon, my name's Brian Satola.

Today I'll be discussing the development of a hybrid activity coefficient model, based on the solution of groups concept.

Fun Facts About →)ME(←



- ▣ 27 Years Young
- ▣ “To legit... To legit to quit (hey...hey...)”
- ▣ DuckTails, GI Joe, The A-Team, & MacGyver
- ▣ ...



Before I get started though, I thought it would be fun to share a few ‘fun’ facts about myself, since I haven’t had the pleasure of talking with many of you on a more personal level...

I always like to say that I’m 27 years young; the last tape deck I bought was McHammer’s “to legit to quit” single in 1991, and some of my favourite shows growing up were GI Joe and MacGyver; and like MacGyver, I even had a mullet at one point in time...

But if anyone would have asked me what I wanted to be when I grew up, a chemical engineer wouldn’t have been one of my responses, mainly because at that time I didn’t know what a chemical engineer was...

## Wie bin ich hier hergekommen?

- University of Akron, OH (USA)
  - 1999 – 2005
- Lyondell Chemicals (LyondellBasell Ind.)
  - 2005 – 2009
- University KwaZulu-Natal, Durban (South Africa)
  - Feb. 2009 - Present

And when I began school at the University of Akron in 1999, I still didn't *really* know what a Chemical Engineer was or did – but what I did know, was that you could earn a good living doing it... And in Akron, also known as the polymer valley, if you *really* wanted to make a good living then you would pursue a career in polymer science; so that is exactly what I went after...

That was until I realized in my senior year that I was not really 'excited' about where this path was leading. I had more fun in my industrial internships than I did in the research that was beginning to define my future... So I made a decision that was hard for me at the time, I scrapped everything I had worked towards and decided to go into industry after graduation, which turned out to be a good decision...

So in 2005—**CLICK**—I began my career with Lyondell Chemicals (now LyondellBasell Industries)... While working there I was fortunate enough to have many opportunities to explore different career paths...

And it was through these opportunities that I decided to go back to school, but this time for what I feel is the correct reason. To expand my knowledge of an area I find truly interesting and exciting... So it was with great delight that I've continued my education, beginning this past Febuary at the university of KwaZulu-Natal—**CLICK**— (in association with the university here in Oldenburg)...

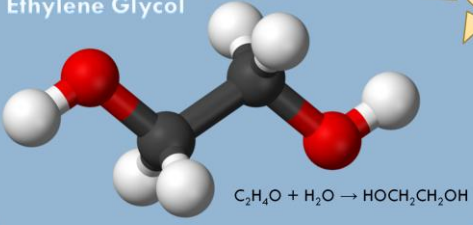
Given that I came from industry, I've been asked to give some industrial perspective... Which hopefully should be of interest to you, and also explain how and more importantly *why* I have chosen the career path I have...

Work Experience

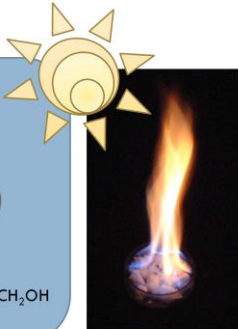
Project Support  
Process Modelling  
Phase Equilibria  
Tools Development

Project Support

Ethylene Glycol



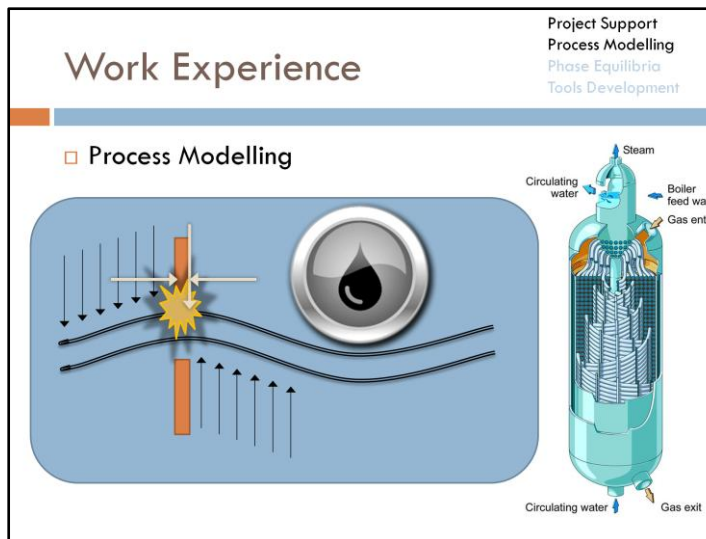
$C_2H_4O + H_2O \rightarrow HOCH_2CH_2OH$



One of my first projects was in Ethylene Glycol, which (for example) is used as a heat transfer medium in geothermal heating/cooling systems, and in pipelines to prevent the formation of gas hydrates—[CLICK...](#)

While I was providing turnaround support for the catalyst change of a glycol reactor, I found out that the reactor suffered from vibration problems. These vibrations caused “catalyst dusting” which would fall down into the lower skirt of the reactor; where the jacket of the reactor could not provide any heat transfer; causing any residual EO to auto ignite...

The plant had looked at the problem YEARS before, but had accepted the problem as the “cost of doing business.” Which I came to learn is quite common in processing environments; in cases when people know they have a problem, but don’t know how to solve it...



You see, the plant had gone through a few debottlenecking operations which pushed the capacity beyond the rates initially designed. Given that the reaction to make EG is exothermic, these rate-increases placed an additional load on the cooling of the reactor, which forced the plant to increase the oil circulating on the reactor's jacket. As the oil rates were increased, tube vibrations became a problem, which then led to the dusting of catalyst (i.e. a bottleneck)....

So I worked with a colleague on developing a reactor model, to see if we could find a cost effective solution to the problem, without resorting to buying a new BWR reactor...

Since I was relatively new out of school, this project was particularly memorable for me because it was the first time I was able to see how the dots were connected; how the engineering fundamentals I learned in school, combined with a little ingenuity, could be applied to solve real-life industrial problems... In this case we ended up building a rather sophisticated model, which allowed us to evaluate alternative options (such as running the oil in different directions, different types of heat mediums, additional baffles, vibration and flammability limit predictions, etc.)...

So, using some industry terminology, the main "take away" is that if you can accurately model your plant (and have confidence in the results it is giving you) then process models can be very useful *tools*...

In this case, this particular model was built entirely in excel, but as time went on I became more and more involved in using process simulators, such as Aspen Plus (e.g. to develop plant models... and also began to develop tools to aid co-workers in using these process simulators more effectively)...


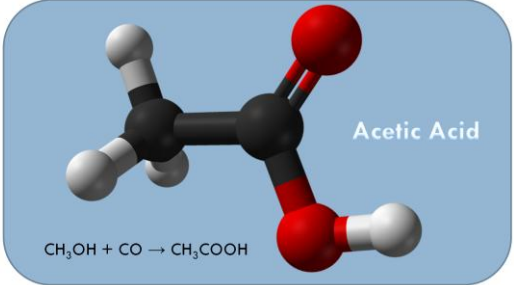
Work Experience

Project Support  
Process Modelling  
Phase Equilibria  
Tools Development

□ Project Support

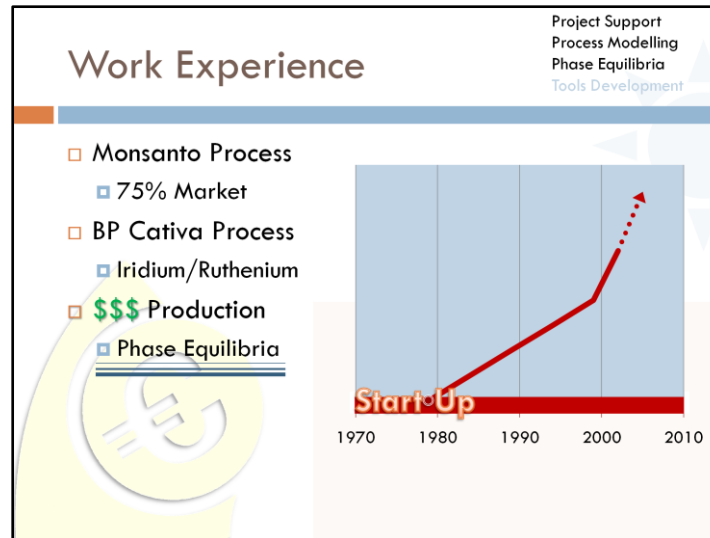
Acetic Acid

$\text{CH}_3\text{OH} + \text{CO} \rightarrow \text{CH}_3\text{COOH}$



One major application I became involved in, was in the evaluation of our Acetyl's technology, which we inherited when our company acquired Millennium Chemicals...

Here I mainly focused on AA, an intermediate in the production of items such as paints and adhesives. Given that this area was a new acquisition, the company wanted to evaluate and consolidate the technology, to see how they could maximize the production value of this newly required plant...



Which used a technology originally developed by Monsanto; (basically uses a different catalyst than BP, our biggest competitor).

Like many plants (just like the EO-reactor example I just discussed....) they went through a series of debottlenecking operations over time. In this case, you can see that after the initial start up in the late 1970's, that the plant's capacity was increased well beyond the initial design capacity...

So in building a model for a plant you would typically want to verify the initial design; since the plant was built successfully, matching the design case would give you confidence in the model that you were developing. Then you would want to use the model as a basis for matching the plant's current operating conditions.

All this diligence pays-off when you need to petition for capital \$\$\$ in order to make any process improvements, because you will be able to prove to management that you have a high degree of confidence in the *predictions* that the model is giving you...

This project really emphasised the necessity of being able to accurately describe a system's phase equilibria—**CLICK**— throughout the various operating conditions that existed in the plant; especially in this case where you seemed to have all of the cats and dogs: not just VLE but LLE, dimerization of the carboxylic acids in the vapour phase, and so forth. In order to end up with a useful model, all this has to be taken into account...

Because a process simulator will always provide you with *numbers*, but they will not always provide you with meaningful ones... The takeaway being, that process simulators are only as good as the physical properties used in their calculations...

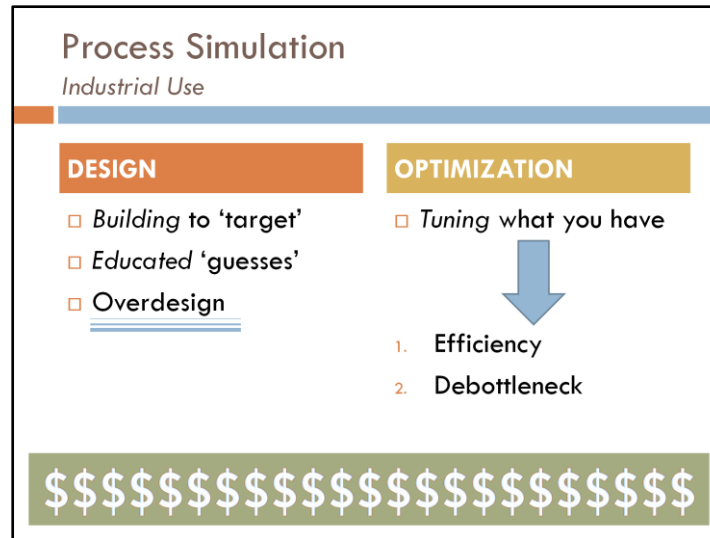
## Presentation Outline

- Industrial practice
  - ▣ Process simulators
  - ▣ Accepted models
  - ▣ Limitations
- Proposal
  - ▣ Enhancing the usability of group methods
  - ▣ Meeting industrial requirements



So for me, my experience has provided much of the driving force for wanting to come back to school; specifically into the area of applied thermodynamics: simulations can be extremely helpful, but only if the thermodynamic properties are meaningful...

As such I will briefly discuss the use of simulators by industry, and some of their limitations. This naturally leads into the proposal of a new method, which should enhance the usability of group methods such as UNIFAC, thereby further meeting industrial needs.



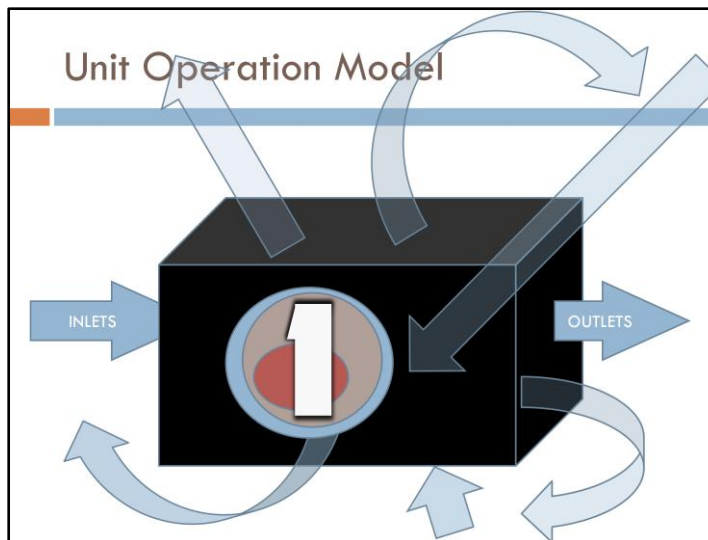
So... as per my examples, process simulators are classically used for design and optimization. Where in design, you typically build to a production 'target.'

You know where you want to go, but along the way you may not know *exactly* how to get there... So with a strong understanding of engineering fundamentals and experience (which basically is just *confidence* in being able to *connect the dots*), you will hopefully be able to make *educated* guesses to put yourself back on track – and when in doubt?

OVERDESIGN—CLICK—at least that generally seems to be the mantra...

Then once you have your plant or process built—CLICK—you will eventually have a strong driving force to optimize what you have; such as debottlenecking operations—CLICK—to meet increasing market demands (like that of EO and AA)...

In order to accomplish these tasks, process simulators are currently the industrial tools of choice...



Which essentially use what can be considered a black box approach, because you really have no control over the *details* of the calculations inside of the UnitOp (e.g. Distillation tower) —**CLICK**—all simulators are rather quite simple, and are fundamentally the same. In most cases you are performing a series of equilibrium calculations, and looping until converged...


In most cases, you typically only care about the overall mass, or energy, balance (about what is coming into, and out of the box) —**CLICK**...

Whether or not you only have one inlet and one outlet, or you have many streams —**CLICK**—entering, leaving, and recycling back to your Unit Operation...

The big limitation here is that you typically can only specify a SINGLE —**CLICK**—thermodynamic model to do the phase calculations within the box... More on this in a second...

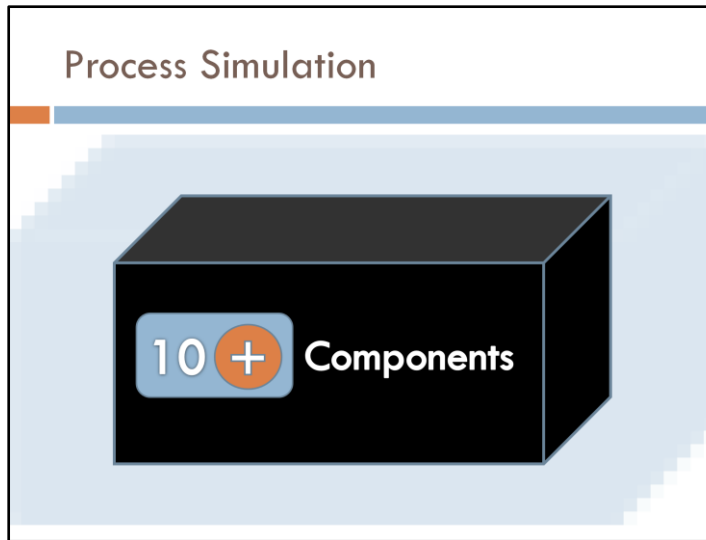
## Local Composition Models

- Wilson (1964)
  - ▣  $\Delta E_{ij}$  – Characteristic energy
- NRTL (1968)
  - ▣  $\Delta G_{ij}$  – Gibbs energy
- UNIQUAC (1975)
  - ▣  $\Delta U_{ij}$  – Internal energy



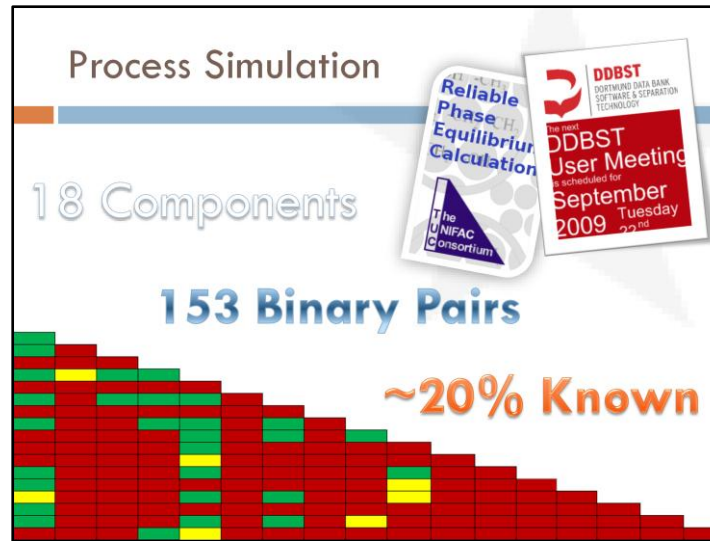
So what models does industry typically use? In my experience LC models are typically favoured in many applications. Where Wilson is usually viewed as being more academic than practical—CLICK...

The NRTL model as being the most accepted—CLICK—(and is thus usually tried first, where other models are used on an as needed basis), like UNIQUAC (which is perhaps most famous for its incorporation into group models, such as the highly successful mod. UNIFAC Do.) —CLICK...



But the problem is that in practical applications, or use of process simulators, you typically deal with 10+ components, and in order to use the generally preferred models just mentioned, would require many *many* experimental datasets to fit the 55+ binary interaction parameters... As anyone in industry can tell you, this is rarely possible.

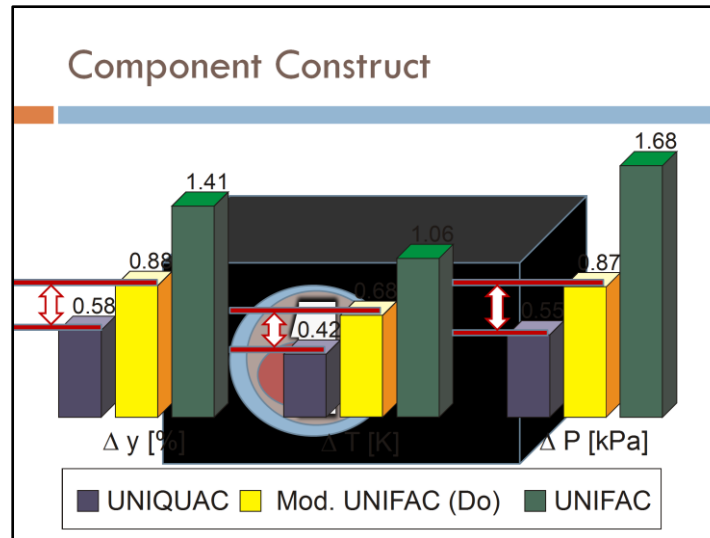
So what is typically done? To answer this, a simple example seems apt.



So as an example, this is an actual system from some of my old work files. Where I created a program that generates what I called an “equilibrium matrix”, which would visually tell you what parameter pairs existed within Aspen (the green), what parameters didn’t (the red) and what data could be obtained from open sources such as DECHEMA and KDB (yellow).

So in this case of 18 components—[CLICK](#)—you would need information for 153 binary pairs—[CLICK](#)—to use something like NRTL, and the simulator only has ~20%! —[CLICK](#)—Of the parameters you need; in my experience, this seems to be fairly typical... And to further complicate matters, that 20% that is “known” might be reduced if the base-data used for their regressions is not applicable to the operating conditions you are looking at...

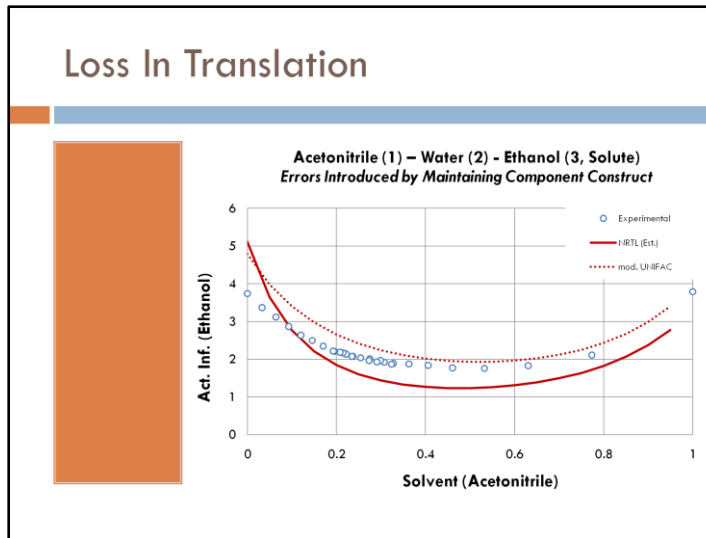
At this point you would have two options, pay for the missing data or use predictive methods such as modified UNIFAC. So it should be no wonder why there is strong industrial support for the UNIFAC consortium (to estimate these missing parameters) —[CLICK](#)—and for databases such as DDBST (to provide accurate experimental data for regressions).



As mentioned earlier, you can generally only use one thermodynamic model per Unit Operation; given this, industry is forced to use group predictions in a rather *indirect* way.

General practice is to regress missing binary parameters from group predictions, which enables practitioners to retain the 20% they *actually* know about their system, which are typically more accurate since they can be fitted directly to the experimental data—**CLICK**—as the graph clearly shows, direct fit to UNIQUAC out performs the generalities imposed by UNIFAC type methods—**CLICK**...

So in order to represent the 20% that is known as accurately as possible, practitioners are forced to stay in the component based approach (which typically uses 2 or more adjustable parameters); however in doing so, there appears to be a 'loss in translation' when going from the group construct to the component based approach...



As an example, here is a system for Acetonitrile-Water-Ethanol (solute).

When we look at the results from a 'straight-run' of mod. UNIFAC (Do) (depicted as the red-dashed line) and some experimental data for the system (depicted as blue circles), we see a fairly reasonable prediction (especially when considering that the results are, in a sense, purely predictive)...

But if we take these predicted results, and regress NRTL parameters to fit these predictions, we end up with a results that are notably worse (as can be seen by the solid red-line).

And to clarify... The NRTL parameters, in this case, were fitted to predicted results over the *entire* composition range, and not just to the predicted infinite dilution activity coefficients.

If we were to only fit the NRTL parameters to these anchor points, like the simulator Aspen Plus does by default, then we would obtain a much worse fit with NRTL; especially given that the anchor points are not always predicted accurately by UNIFAC. By fitting over the entire composition range, you are much less acceptable for introducing additional error into your simulation. For more information on this issue, and a solution, it is worthy to have a look at the DDBST's website (<http://www.ddbst.de/new/Default.htm>)...

So to recap on the slide: The 'straight-run' estimation using mod. UNIFAC (Do) is reasonable, but current practice requires translating this estimation into a component-based approach (such as NRTL) in order to retain greater accuracy in the 20% of the systems that are known experimentally; in so doing, there appears to be a loss in translation...

Correlation Results for Binary Isothermal VLE-Data Using UNIFAC and UNIQUAC		
<small>Source: J. Gmehling, R. Raouyan, An. Freiburger, Ind. Eng. Chem. Process Des. Dev. 21, 118-127 (1982)</small>		
System	Temperature [K]	Ratio of the Deviations* UNIFAC / UNIQUAC
Ethanol + Octane	348	0.27
Propanol + Decane	363	0.85
Diethylamine + Heptane	328	1.09
Acetone + Cyclohexane	328	0.89
Acetone + Decane	318	0.94
3-Pentanone + Heptane	363	0.78
1-Octene + Cyclohexane	313	0.94

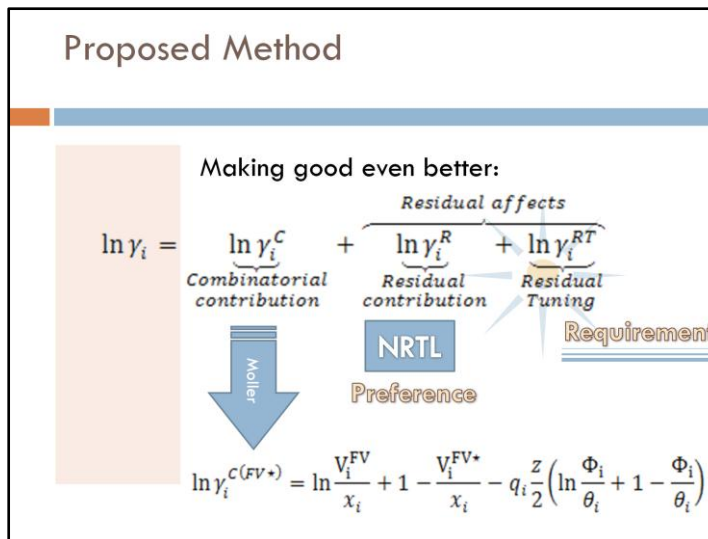
$$\text{*Deviation} = \sum \left[ \left( \frac{x_{1,\text{ber}} - x_{1,\text{exp}}}{\sigma_x} \right)^2 + \left( \frac{y_{1,\text{ber}} - y_{1,\text{exp}}}{\sigma_y} \right)^2 + \left( \frac{T_{1,\text{ber}} - T_{1,\text{exp}}}{\sigma_T} \right)^2 + \left( \frac{P_{1,\text{ber}} - P_{1,\text{exp}}}{\sigma_P} \right)^2 \right]$$

Using following variances:  $\sigma_x = \sigma_y = 0.005$ ;  $\sigma_T = 0.1 \text{ K}$ ;  $\sigma_P = 1.0 \text{ mmHg}$

This is a shame though, especially when considering that it has been observed that group parameters regressed directly to experimental data on a case-by-case basis often perform better than other local composition models fitted to the same data...

Where it has been argued that this is due to the better localization of interactions to the structural groups instead of the smearing of interactions over the whole molecule, which is characteristic of component interaction models (such as NRTL).

But in order to realize this potential benefit, industry requires control in matching what experimental data is available, which is one thing group contribution models currently do not provide.



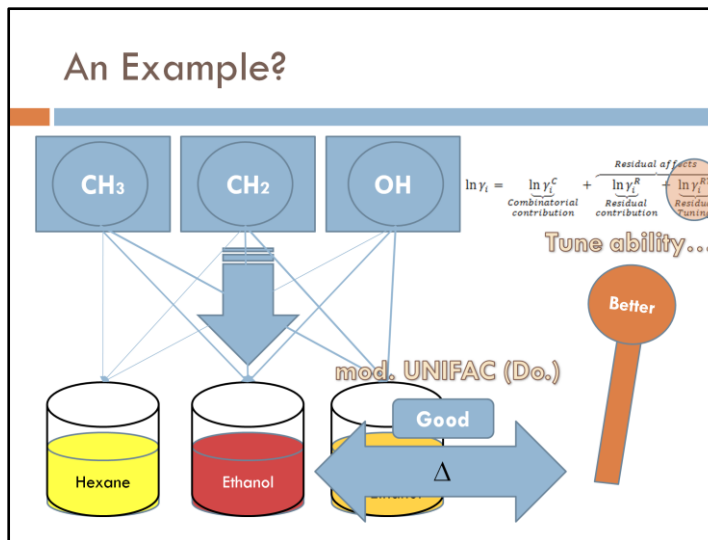
**So is there a way to enhance the usability of UNIFAC; to make the good even better?**

As shown by Bruce Moller last week, we saw that the combinatorial used by modified UNIFAC does quite well for components of similar sizes, and for small solutes in large solvents, but may benefit from a FV modification to better describe large solutes in small solvents—[CLICK](#).

Since the empirical modification proposed by Bruce seems to give similar results to the mod. UNIFAC for similar sizes, and for small in large, this expression can be introduced without a loss for the systems that are already well described by mod. UNIFAC. So we propose that this modification should be included in this work.

Also since industry seems to prefer NRTL over UNIQUAC, it seems natural to develop a group method that uses NRTL instead of UNIQUAC—[CLICK](#)—speaking from an industrial perspective, I believe that this would be well received – the use would just be more intuitive to practitioners, because they have much more experience with using NRTL than they due using UNIQUAC... But although there are certainly arguments for this approach, the extra work that would be required to regress new group parameters is not justified, especially given that mod. UNIFAC already provides good predictions; so is there a way we can transfer the knowledge base of mod. UNIFAC to the proposed method?—that has yet to be seen, but is one of the objectives of this work...

Also, industry requires control, or tune ability, in the models used for process simulation. By adding a tuning portion to the model, practitioners would then be able to use the group method throughout their simulations, thereby eliminating the loss of translation and possibly enabling more accurate representation of the 20% that’s known experimentally—and is an



So as an example... If we wanted to predict the activities of a mixture of Hexane and Ethanol using the group approach.

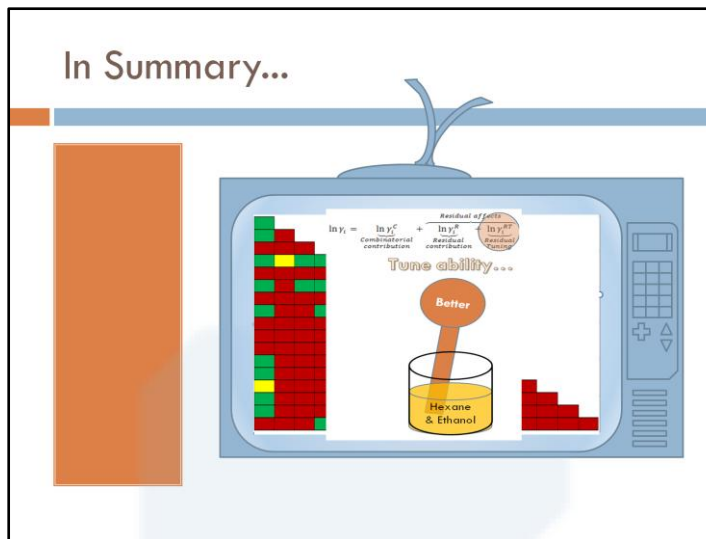
We could think of CH<sub>3</sub>, CH<sub>2</sub>, and OH molecules as the building-blocks (or in this case groups) of Hexane and Ethanol—[CLICK](#).

So with these blocks, we would be able to form a solution of pure Hexane—[CLICK](#), and of pure Ethanol—[CLICK](#).

And if we imagine mixing these two pure substances, we would have a mixture of Hexane and Ethanol, which is also comprised of the same groups—[CLICK](#).

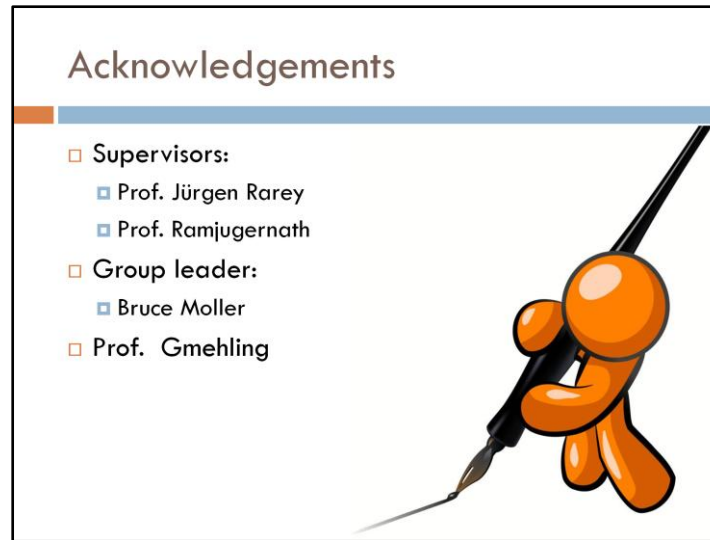
The solution of groups in the pure components and in the mixture, give us the necessary information to determine the activity of the mixture—[CLICK](#)—[CLICK](#)—all predictive methods use these calculation steps, and methods such as mod. UNIFAC often provide good results—[CLICK](#).

And basically what this work proposes to do, is to introduce a tune ability portion to the residual term in an effort to make Good predictions → Better—[CLICK](#)—by enabling practitioners to tune the predictions to any experimental data that may exist.



So to summarize:

1. **CLICK** Industrial applications typically deal with 10+ components
2. **CLICK** But as we have seen the experimental *knowledge* of these systems is usually quite small; for this reason, methods such have mod. UNIFAC have gained wide acceptance in industry.
3. **CLICK** But the direct use of these group predictions is limited, due to the limitation imposed by process simulators (where typically only one thermodynamic model can be used for any one Unit Operation).
4. **CLICK** In order to retain the knowledge you *do know* about your system, predictive methods have to be translated into the component approach...
5. **CLICK** But there seems to be a “loss in translation” when this is done; however, there is currently no tuneable group model available to practitioners.
6. **CLICK** This is a shame, because it has also been observed that the group approach can provide better results than some of the currently accepted models, if the group parameters are regressed directly to experimental data on a case-by-case basis.
7. **CLICK** So in this work we propose to use the mod. UNIFAC (Do.) model as the basis for a new model that should expand the usability of the group-based approach...



I would like to thank my supervisors, Prof. Rarey and Prof. Ramjugernath for their continuing support, encouragement, and never ending energy and enthusiasm.

I would also like to thank my group leader, Bruce Moller. For his understanding, good set of ears, and help.

And last, but not least, Prof. Gmehling for the rewarding partnership that exists between Durban and his group here in Oldenburg.



And with that... I will now open the floor up for any questions?