

Section 2.2

Activity Coefficient models

In the previous section, we discussed the ideal gas model, which is appropriate to use for gaseous species at low pressures. However, it is unable to model the liquid phase and, as a result, phase equilibria.

Nevertheless, there is one other idealised model which can give us some insight on the liquid phase: the ideal solution model. An ideal solution, by definition, obeys Raoult's law:

$$y_i p = x_i p_{\text{sat},i}$$

To get a physical understanding of what this equation actually means. Let us say that we have a pure fluid at its boiling point. The rate of condensation and evaporation have to be the same:

$$R_{\text{cond.}} = R_{\text{evap.}}$$

We can imagine that the rate of evaporation is proportional to the number of particles at the surface of the liquid:

$$R_{\text{evap.}} = k_{\text{evap.}} n$$

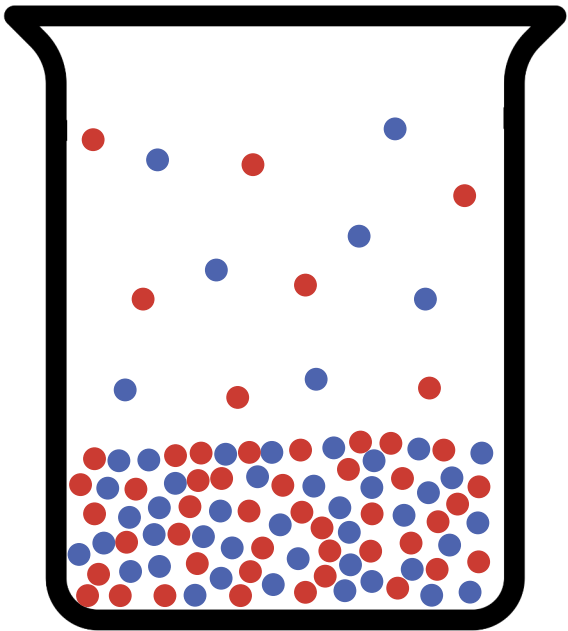
Similarly, the rate of condensation is proportional to the pressure of the gas (in this case, the saturation pressure):

$$R_{\text{cond.}} = k_{\text{cond.}} p_{\text{sat}}$$

This gives:

$$k_{\text{cond.}} p_{\text{sat}} = k_{\text{evap.}} n$$

Let us now consider a mixture of fluids A and B at their bubble point:



If we assume everything about them is the same (size, interactions, etc.) except for the saturation pressure, then, for fluid A, the rate of evaporation is:

$$R_{A,\text{evap.}} = k_{A,\text{evap.}} n x_A$$

And the rate of condensation is (the gas obeys Dalton's law):

$$R_{A,\text{cond.}} = k_{A,\text{cond.}} p y_A$$

Giving:

$$k_{A,\text{cond.}} p y_A = k_{A,\text{evap.}} n x_A$$

If we re-arrange this expression and the expression for the pure, we find:

$$\frac{k_{A,\text{cond.}}}{k_{A,\text{evap.}} n} = \frac{x_A}{y p} = \frac{1}{p_{A,\text{sat.}}}$$

Re-arranging:

$$y_i p = x_i p_{\text{sat},i}$$

This gives us Raoult's law. A by-product of this expression is that the chemical potential of a pure-liquid, i , can be written as:

$$\mu_{i,\text{vap.}} = \mu_{i,\text{liq.}}$$

$$\mu_i^0 + RT \ln (p_i/p^0) = \mu_i^0 + RT \ln (x_i p_{i,\text{sat}}/p^0)$$

$$\mu_{i,\text{liq.}} = \mu_i^* + RT \ln x_i$$

The Gibbs free energy of mixing can be obtained as:

$$\Delta G^{\text{mix}} = \sum_i x_i (\mu_i - \mu_i^*) = RT \sum_i x_i \ln x_i$$

Where, despite now being in the liquid phase, the Gibbs free energy of mixing matches that obtained from an ideal gas. Although some fluids do conform to the ideal solution model (such as alkane mixtures), many do not. We measure deviations from ideal solution using the excess Gibbs free energy:

$$\Delta G^{\text{E}} = \Delta G^{\text{mix}} - \Delta G^{\text{mix,ideal}}$$

Typically, the excess Gibbs free energy is written as:

$$\Delta G^E = RT \sum_i x_i \ln \gamma_i$$

where γ_i is the activity coefficient of species i . We can also modify Raoult's law to account for these deviations:

$$y_i p = x_i \gamma_i p_{\text{sat},i}$$

Based on the magnitude of γ_i , we can determine if the mixture is ideal ($\gamma_i = 1$), has favourable interactions ($\gamma_i < 1$) or unfavourable interactions ($\gamma_i > 1$). The next models discussed will provide ways to estimate the activity coefficient for a fluid in solution.

Pros and Cons of Activity Coefficient Models

The objective of activity coefficient models is to obtain γ_i as a function of composition and temperature:

$$\gamma_i = f(\mathbf{x}, T)$$

The elimination of the volume dependence simplifies calculations immensely. Furthermore, the fact that we can obtain activity coefficients directly means we can solve for complex properties quite easily. For example, the bubble pressure at a certain temperature and composition can simply be obtained using:

$$p_{\text{bub.}}(\mathbf{x}, T) = \sum_i x_i \gamma_i(\mathbf{x}, T) p_{\text{sat},i}(T)$$

A similar operation can be performed for the dew pressure. The bubble temperature is a bit more complex as the temperature now needs to be solved for iteratively:

$$p = \sum_i x_i \gamma_i(\mathbf{x}, T_{\text{bub.}}) p_{\text{sat},i}(T_{\text{bub.}})$$

Nevertheless, as will be shown in the third part of this course, this is by far one of the easiest (and computationally cheaper) methods to obtain equilibrium properties. However, the above equations hint at one limitation. Firstly, as we rely on Raoult's law, we need to have a function for the saturation pressure at a given temperature. This limits us to sub-critical properties only. For example, we could not model a carbon dioxide+water system at temperatures above the critical temperature of carbon dioxide (304 K). This heavily limits the number of systems we can model.

Furthermore, as activity coefficient models can only obtain (unsurprisingly) activity coefficients; we can't obtain the saturation pressure or any other pure-component property. Inherently, activity coefficient models cannot be used on their own. Typically, they are combined with other equations of state (such as cubics), for example:

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• m = UNIQUAC(["water", "ethanol"]; puremodel=PR);
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Nevertheless, activity coefficient models are still some of the most-commonly used approaches for modelling in industry due to their simplicity in modelling otherwise complex systems.

Section 2.2.1

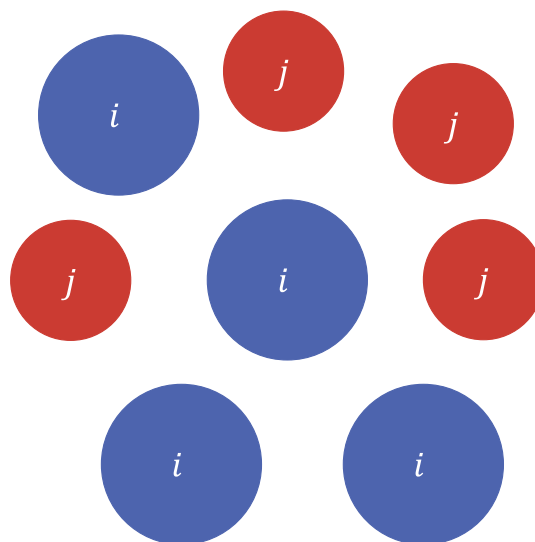
Wilson Equation

While the concept of activity coefficients had been around for many years, the only approaches which could be used to model them were purely correlative. This includes equations such as the van-Laar equation where:

$$\ln \gamma_1 = A_{12}x_2^2$$

$$\ln \gamma_2 = A_{21}x_1^2$$

This approach is limited to just binary mixtures (without the introduction of a ternary parameter). Furthermore, the coefficients A_{ij} don't really carry much physical meaning. It wasn't until Wilson presented his equation in 1964 that activity coefficient approach start becoming useable. The insight Wilson gave was that the composition of a species i around itself was not equal to the composition of the bulk (these approaches are also known as local composition models). Visually:



Thus, the Gibbs free energy of mixing should actually be written as:

$$\Delta G^{\text{mix}} = RT \sum_i x_i \ln \xi_i$$

where ξ_i is the local volume fraction of species i which can be obtained from:

$$\xi_i = \frac{x_{ii}v_i}{\sum_j x_{ji}v_j}$$

where x_{ji} is the local composition of species j around species i and v_i is the molar volume of a pure species i . Unsurprisingly, it is not possible to obtain the x_{ji} experimentally. As such, Wilson made the following assumption:

$$\frac{x_{ji}}{x_{ii}} = \frac{x_j}{x_i} \exp(-\Delta\lambda_{ij}/(RT))$$

where $\Delta\lambda_{ij}$ is an interaction energy parameter, quantifying how favourable interactions between species i and j are relative to the interaction of species i with itself. Substituting this into our expression for ξ_i and re-arranging for the excess Gibbs free energy gives:

$$\Delta G^E = RT \sum_i x_i \ln \sum_j x_j \Lambda_{ij}$$

where:

$$\Lambda_{ij} = \frac{v_j}{v_i} \exp(-\Delta\lambda_{ij}/(RT))$$

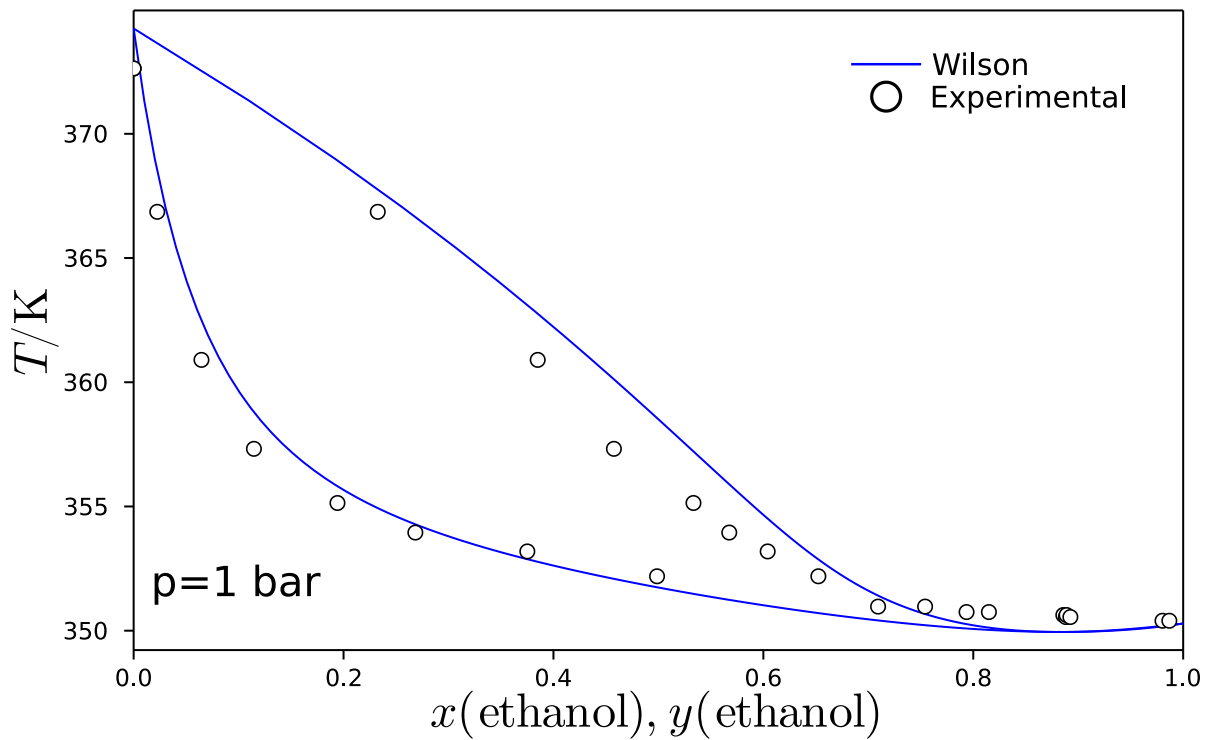
Where Λ_{ij} is known as Wilson's parameter. One can notice that two effects have been accounted for in this single factor: the relative size of the two species using the ratio of the volumes, and the favourability of the interactions using the exponential. These two effects appear in all activity coefficient models we will discuss.

Nevertheless, although the volumes of the two species can be obtained experimentally (typically a correlation for the saturated liquid densities is used), the interaction parameter $\Delta\lambda_{ij}$ needs to be fitted to experimental data. However, the key benefit of the Wilson equation, in contrast to previous approaches like van Laar is that the binary interaction parameters can be used for multicomponent (3+) mixtures.

The Wilson equation also proved to be very effective when modelling complex mixtures involving hydrogen-bonding, such as the infamous water+ethanol system:

```
• model=Wilson(["ethanol","water"]);
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Txy diagram of ethanol+water



Unfortunately, despite its substantial improvements to activity coefficient modelling, the Wilson equation does have a few failings. The most notable of which is its inability to model liquid-liquid equilibrium (or immiscibility between liquids). This does limit the range of systems one can model using the Wilson equation. However, at the time, it was a big step forward for thermodynamic modelling of complex systems.

Section 2.2.2

Non-Random Two-Liquid (NRTL) model

Taking a similar approach to the Wilson equation, the non-random two-liquid model (NRTL) also assumes the local composition around species is different from the bulk and uses a similar equation to the one used by Wilson:

$$\frac{x_{ji}}{x_{ii}} = \frac{x_j}{x_i} \exp(-\alpha_{ij} \Delta g_{ij} / (RT))$$

where a new parameter, α_{ij} is introduced, named the non-randomness factor. Unlike Δg_{ij} (which is the Gibbs free energy change for moving a species i from a pure system to being surrounded by species j), this parameter is symmetric ($\alpha_{ij} = \alpha_{ji}$) and is meant to account for 'order' in the fluid ($\alpha_{ij} = 0$ is equivalent to a completely random fluid).

Rather than using the approach used by Wilson, in NRTL, the excess Gibbs free energy is given by:

$$\Delta G^E = \sum_i x_i \sum_j x_{ij} \Delta g_{ij}$$

Substituting our definition for x_{ij} :

$$\Delta G^E = RT \sum_i x_i \frac{\sum_j x_j \tau_{ji} G_{ji}}{\sum_k x_k G_{ki}}$$

where:

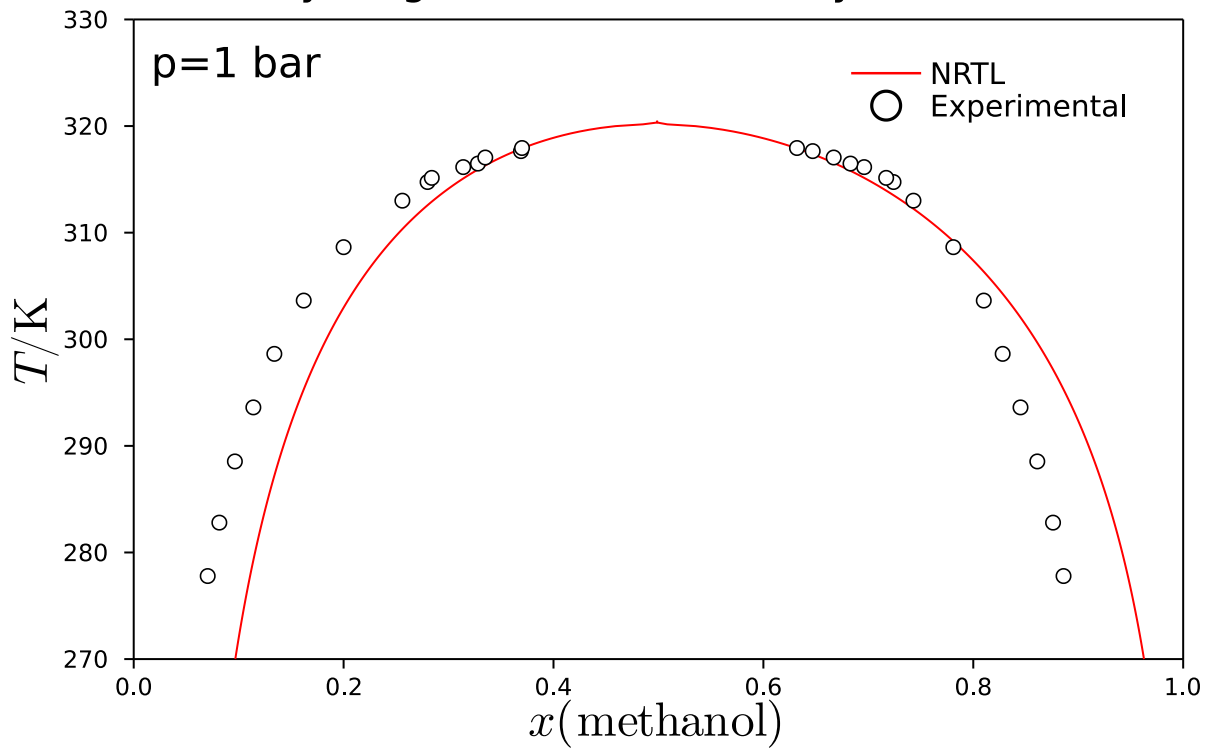
$$\tau_{ij} = \Delta g_{ij} / (RT)$$

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij})$$

In contrast to the Wilson equation, the NRTL model models the excess Gibbs free energy purely by accounting for the interactions between species, without accounting for size differences between species.

Nevertheless, one key benefit of NRTL over the Wilson equation is its ability to model immiscibility between two fluids:

Txy diagram of methanol+cyclohexane



Section 2.2.3

UNIversal QUasichemical Activity Coefficient (UNIQUAC) model

While NRTL is able to model a greater range of equilibria, Abrams and Prausnitz returned to the approach used by Wilson where, instead of using the volumes of the species to determine the local composition, the surface area is used instead:

$$\Lambda_{ij} = \frac{q_i}{q_j} \exp(-a_{ij}/(RT))$$

where q_i is proportional to the surface area of species i . However, rather than using the exact equation as Wilson, Abrams and Prausnitz divide the excess Gibbs free energy into two terms:

$$\Delta G^E = \Delta G_{\text{comb.}}^E + \Delta G_{\text{res.}}^E$$

The first term is known as the combinatorial term and can be thought of as an entropic term to account for size asymmetry between species. The term is referred to as Staverman-Guggenheim term:

$$\Delta G_{\text{comb.}}^E = RT \sum_i (x_i \ln(\Phi_i/x_i) + 5q_i \ln(\theta_i/\Phi_i))$$

where Φ_i is the surface fraction of species i and θ_i is the volume fraction of species i . The second term is the residual term which accounts for the enthalpic interactions between species:

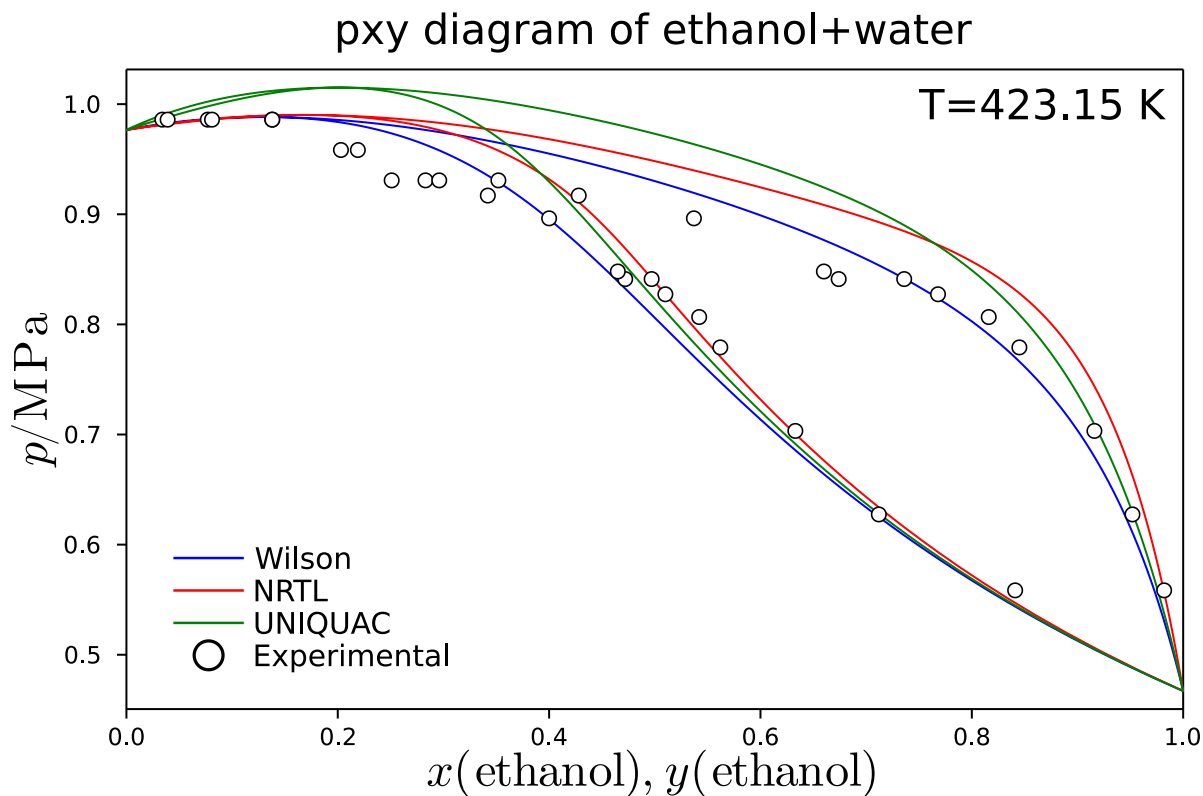
$$\Delta G_{\text{res.}}^E = RT \sum_i \left(x_i q_i \ln \left(\sum_j \theta_j \tau_{ij} \right) \right)$$

where τ_{ij} is:

$$\tau_{ij} = \exp(-a_{ij}/(RT))$$

This results in the UNIQUAC approach and, unlike the NRTL approach, UNIQUAC requires both species-specific and binary interaction parameters (parameters that involve two species).

The Wilson equation, NRTL and UNIQUAC represent the industry standards for activity coefficient models and, whilst the Wilson equation is limited to just vapour-liquid equilibrium, they all have very similar performance:



As with most thermodynamic models, it is important to verify how accurate a given model is for a particular system and the conditions of interest.

Section 2.2.4

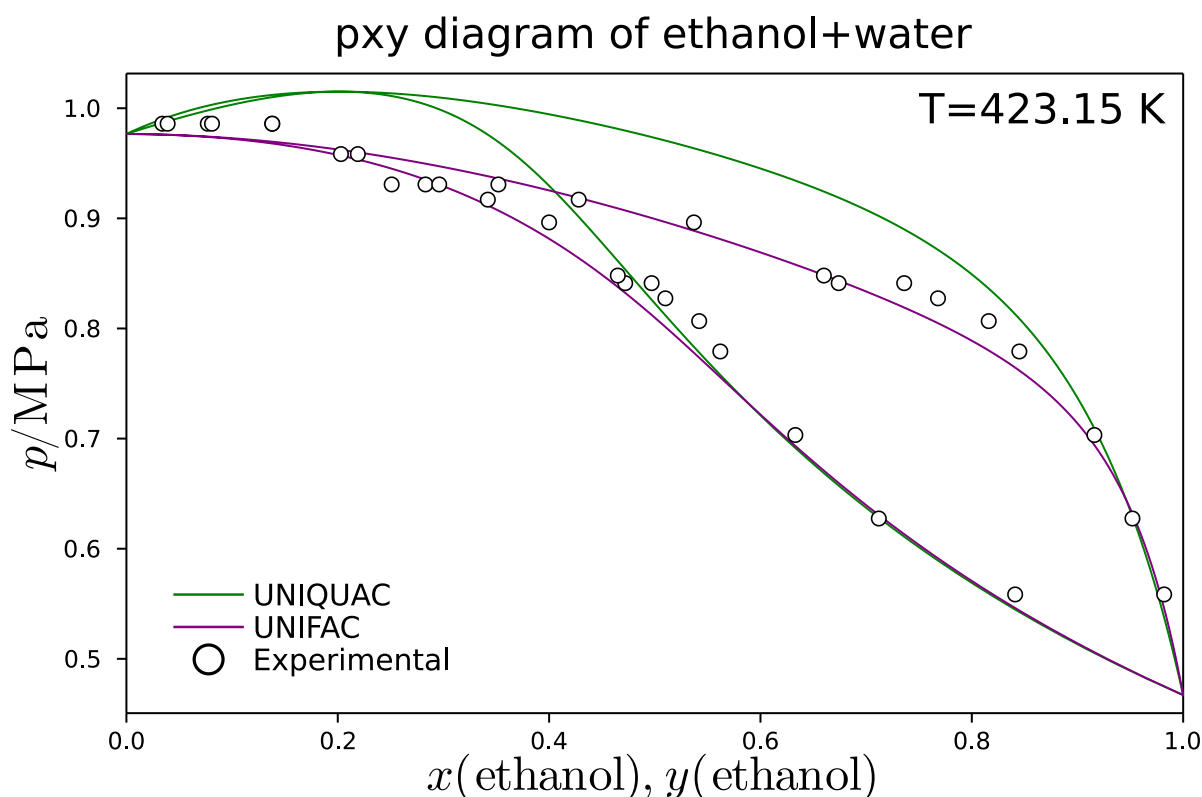
UNIQUAC Functional-group Activity Coefficients (UNIFAC)

The last activity coefficient model we will consider is an extension of UNIQUAC. One of the limitations of the Wilson equation, NRTL and UNIQUAC is that they are species-specific approaches meaning they cannot be extended to new systems without fitting additional parameters.

As we showed with the ideal equations, one way to work around this is through group-contribution methods where species are split into smaller groups which can be re-assembled into new species. The UNIQUAC Functional-group Activity Coefficients model (UNIFAC) is one such approach. The equations used to define UNIQUAC are essentially unchanged where, the only thing that has changed is that, rather than discussion interactions between species or the local composition around species, this is done from the point of view of the groups.

While this approach grants users a great deal of flexibility, unfortunately, as it was for the ideal equations, it is bound to be slightly less accurate than the species-specific approaches:

```
• mix = UNIFAC(["water","ethanol"]);
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One important thing to bear in mind when using UNIFAC, particularly when looking at literature, is that many variants do exist. As a matter of fact, when people refer to UNIFAC, they usually are not referring to the original version published in 1979. They usually mean the Dortmund modification in 1987 (used above) which improved over many of the original failings of UNIFAC where, as shown above, it can perform better than even a species-specific approach. One of these improvements came from replacing the a_{ij} parameter in the expression for τ_{ij} with a temperature-dependent correlation:

$$a_{kl} = A_{kl} + B_{kl}T + C_{kl}T^2$$

where we've changed the indices from ij to kl to denote the switch from species-specific parameters to group-specific parameters.

This UNIFAC model also has many more groups (over 200), meaning it is by far the most-extensible version available. Unfortunately, there are also versions of UNIFAC designed for specific applications (e.g. UNIFAC-FV for polymer systems) which need to be used carefully.

Nevertheless, UNIFAC represents the industry standard for group-contribution based approaches for mixture systems.

