Solution Thermodynamics

Module 3 · 2105603 Advanced Chemical Engineering Thermodynamics

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A partial molar property is not a property of the pure substance.

Mix one litre of ethanol with one litre of water and you get 1.93 litres.

INTRODUCTION

What this module builds

The mixture toolkit, with the rigour Module 1 applied to pure fluids: partial molar properties, fugacity in a mixture, excess properties, activity, and the constraint that ties them together.

The callback

The mixture fugacity coefficient is a **composition derivative of the same residual Helmholtz energy Module 1 built**. The equation of state is not left behind when mixtures arrive; it is differentiated once more.

Five questions

- What is a partial molar property, and why is it not a pure-component one?
- What is $\hat{f}_i$, promised at the end of Module 2?
- What is an excess property measured against?
- What constraint links γ_1 and γ_2?
- What is a model, once you see what G^E is?

PART I

Partial molar properties

Section 3.1 A composition derivative, a tangent construction, and a constraint that returns in Module 4.

The definition, and the Euler relation

The contribution one species makes to a mixture property, at fixed everything else.

$$\bar{M}_i \equiv \left(\frac{\partial (nM)}{\partial n_i} \right)_{T,P,n_{j \neq i}} \qquad nM = \sum_i n_i \bar{M}_i \qquad M = \sum_i x_i \bar{M}_i$$

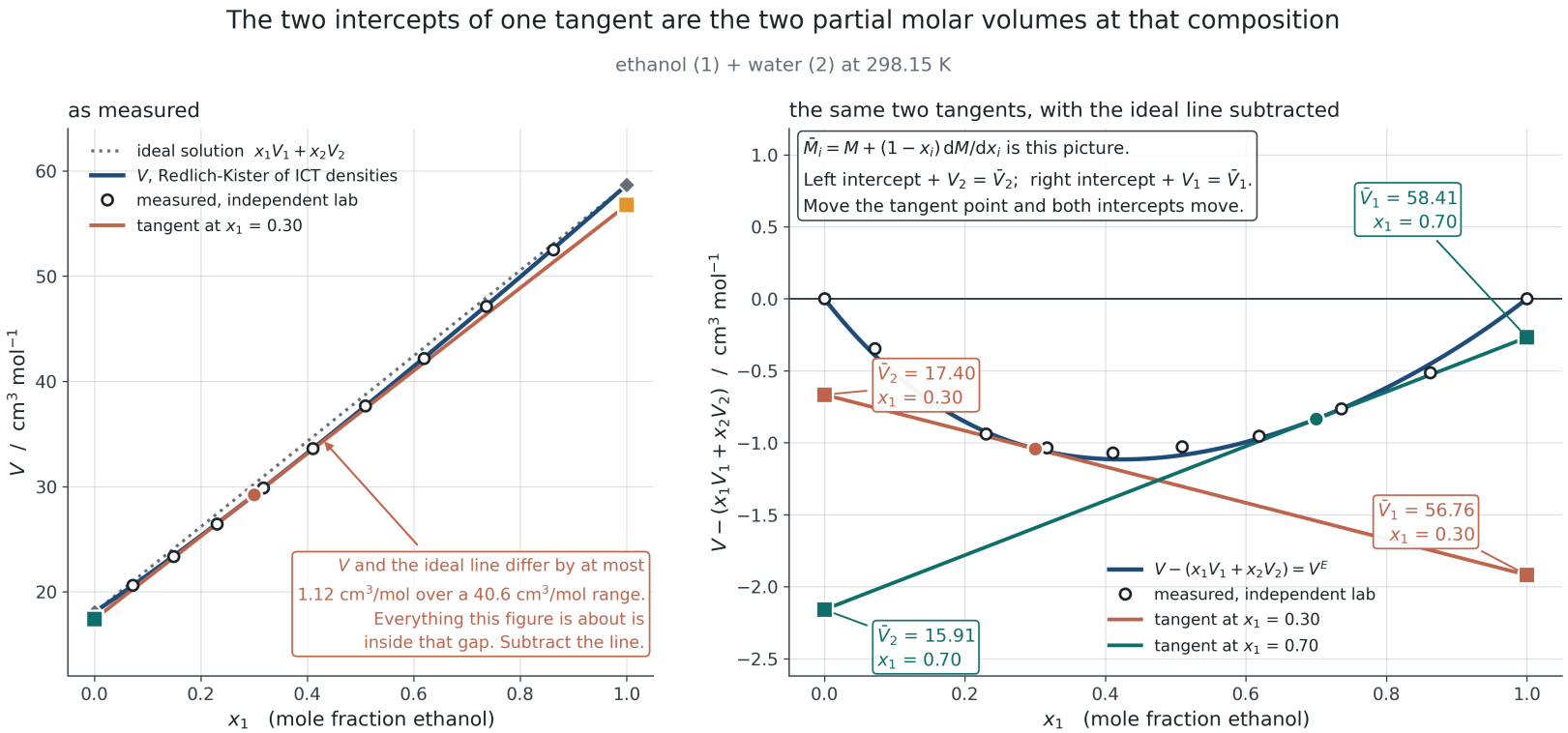
Why T, P and n_j are all fixed

Change any of them and you are measuring something else. The subscripts are not decoration: a derivative at constant T and V is a different quantity with a different value, and the two get confused constantly.

What the Euler relation says

The mixture property is exactly the mole-weighted sum of the partial molar values — with no leftover term. That is not obvious, and it is the reason the partial molar quantity is the *right* way to apportion a mixture property among its species.

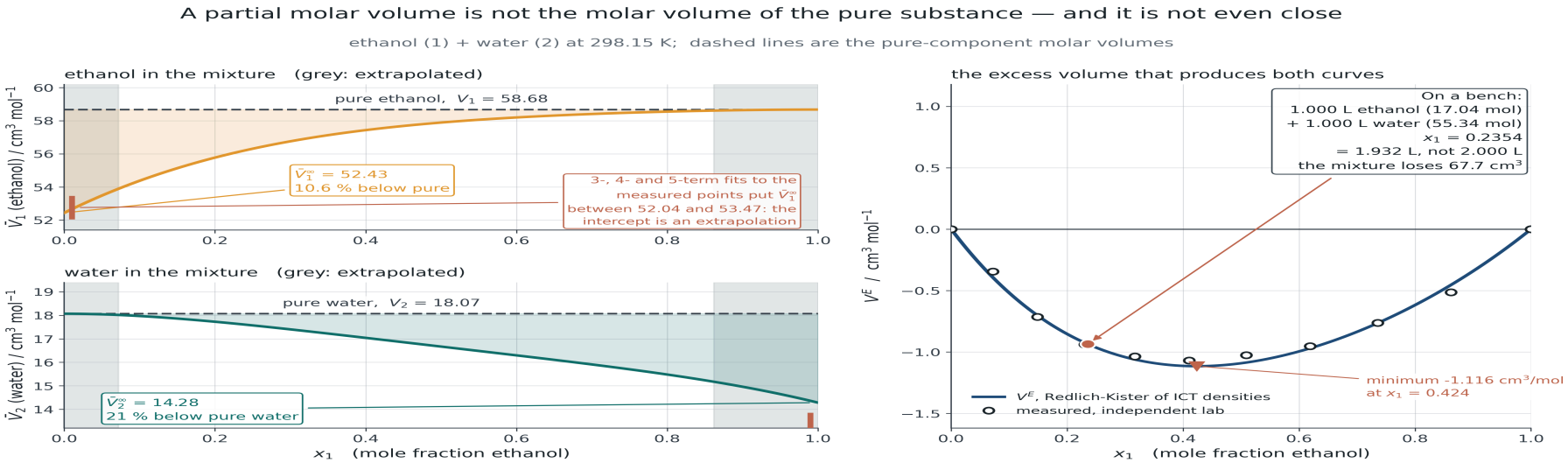
The tangent-intercept construction



MEASURED DATA, NOTHING ASSUMED OR ILLUSTRATIVE. Curve: V^E from the Redlich-Kister correlation of Danahy, Minnick & Shiflett, *Fermentation* 2018, 4(3), 72 (open access), regressed on >700 measured density-composition points from the International Critical Tables; stated validity 283.15-313.15 K, 0-100 wt% ethanol. Circles: an independent pycnometric dataset, Pawar & Aher, IJSRSET 2017, 3(6), 432-447, Table 2. The two sources agree to 0.034 cm³/mol rms; the transcribed densities reproduce that paper's own V^E column to 0.0011 cm³/mol rms. Pure V_1, V_2 from `thermo` HEOS_FIT, computed at run time.

F3.1 · Measured ethanol/water molar volume at 298.15 K. The tangent's two intercepts are the partial molar volumes.

Partial molar volume can be negative



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EXTRAPOLATED, AND LABELLED AS SUCH: no measurement exists below x_1 = 0.0719 or above x_1 = 0.8622 (shaded). Refitting the measured points with 3, 4 and 5 Redlich-Kister terms moves $\bar{V}_1^\infty$ over 1.43 cm³/mol and $\bar{V}_2^\infty$ over 1.15 cm³/mol (red bars). Pure V_1, V_2: `thermo` HEOS_FIT.

The number

At infinite dilution in water, the partial molar volume of ethanol falls about 11 % below its pure molar volume, and water's falls about 21 % below its own. Adding a mole of ethanol to a large volume of water adds *less* volume than a mole of pure ethanol occupies.

Why

Water's hydrogen-bonded network has voids. A small solute can sit in them, so the mixture takes up less room than the sum of the parts. In systems with stronger effects — an electrolyte in water — the partial molar volume of the salt is genuinely **negative**.

F3.2 · From the same measured data, differentiated. The infinite-dilution values are extrapolations and the figure marks the region where no data exist.

Gibbs-Duhem, in full

Write it with all its terms before dropping any, because the dropped ones come back in Module 4.

$$\left(\frac{\partial M}{\partial T}\right)_{P,x} \mathrm{d}T + \left(\frac{\partial M}{\partial P}\right)_{T,x} \mathrm{d}P - \sum_i x_i \,\mathrm{d}\bar{M}_i = 0$$

$$\xrightarrow[\text{constant } T,\, P]{} \qquad \sum_i x_i \,\mathrm{d}\bar{M}_i = 0$$

What it means

The partial molar properties of a mixture are **not independent functions of composition**. Specify one across the range and the other is determined. This is a constraint imposed by thermodynamics, not a modelling convenience.

The dropped terms

Constant T and P is the usual specialisation and it is the one every textbook uses. Isobaric VLE data are *not* at constant T, so the temperature term survives — as an excess enthalpy contribution that most published consistency tests quietly drop. Module 4 quantifies it.

PART II

Fugacity in a mixture

Section 3.2 The composition derivative promised at the end of Module 2.

Chemical potential is a partial molar property

Nothing mysterious. It is the partial molar Gibbs energy, and it inherits every property partial molar quantities have.

$$\mu_i \equiv \left(\frac{\partial (nG)}{\partial n_i}\right)_{T,P,n_{j\neq i}} = \bar{G}_i$$

$$\hat{f}_i \;\text{ defined by }\; \mathrm{d}\mu_i = RT\,\mathrm{d}\ln \hat{f}_i \qquad\qquad \hat{\varphi}_i = \frac{\hat{f}_i}{y_i P}$$

The pattern repeats

Module 2 defined f so that $\mathrm{d}\mu = RT\,\mathrm{d}\ln f$ held for a pure fluid. The mixture definition is the same construction applied to μ_i, with $\hat{f}_i/(y_i P) \to 1$ as $P \to 0$ fixing the constant.

Where Gibbs-Duhem bites

Because μ_i is a partial molar property, $\sum_i x_i\,\mathrm{d}\mu_i = 0$ at constant T and P — and therefore $\sum_i x_i\,\mathrm{d}\ln \hat{f}_i = 0$. The constraint is inherited, not added.

From the equation of state, again

$\ln \hat{\varphi}_i$ is the composition derivative of the residual property Module 1 built. The equation of state carries straight into mixtures.

$$\ln \hat{\varphi}_i = \frac{1}{RT} \int_{\infty}^{V} \left[\left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_j} - \frac{RT}{V} \right] \mathrm{d}V \; - \ln Z$$

For Peng-Robinson

With the van der Waals one-fluid rule $a = \sum_i \sum_j x_i x_j \sqrt{a_i a_j}(1 - k_{ij})$ and $b = \sum_i x_i b_i$, the integral closes and gives a formula of the same shape as the pure-component one plus two composition-derivative terms — $\bar{b}_i / b$ and $\sum_j x_j a_{ij} / a$.

Why this matters later

This is the $\hat{\varphi}_i$ that appears in the gamma-phi equation of Module 4, in the phi-phi route of Module 5, and in K_φ in Module 6. It is computed once and used in three later modules.

The ideal solution is a model

The Lewis-Randall rule is an assumption about behaviour, not a definition. Saying so now prevents a lot of confusion in Module 4.

$$\hat{f}_i^{\,\mathrm{id}} = x_i f_i \qquad \bar{M}_i^{\,\mathrm{id}} = M_i \ \text{ for } V \text{ and } U, \qquad \bar{G}_i^{\,\mathrm{id}} = G_i + RT \ln x_i$$

What it assumes

That a molecule of i sees the same environment in the mixture as in pure i. True when the species are chemically almost identical — benzene and toluene — and false the moment hydrogen bonding or a size disparity enters.

Why the entropy term survives

Even an ideal solution has $\bar{G}_i \neq G_i$: there is an entropy of mixing whatever the interactions are. Ideality is a statement about *energies*, not about entropy — which is why Δg_{mix} never vanishes and why Module 5's stability argument has an ideal part that always favours mixing.

PART III

Excess properties and activity

Section 3.3 Departure from an ideal solution, and the reference state that decides the number.

Excess, and why the reference is a solution

A residual property is measured against an ideal *gas*. An excess property is measured against an ideal *solution*. Different baselines, different questions.

$$M^E \equiv M - M^{\text{id}} \qquad a_i \equiv \frac{\hat{f}_i}{f_i^\circ} \qquad \gamma_i \equiv \frac{a_i}{x_i} = \frac{\hat{f}_i}{x_i f_i^\circ}$$

Why not an ideal gas

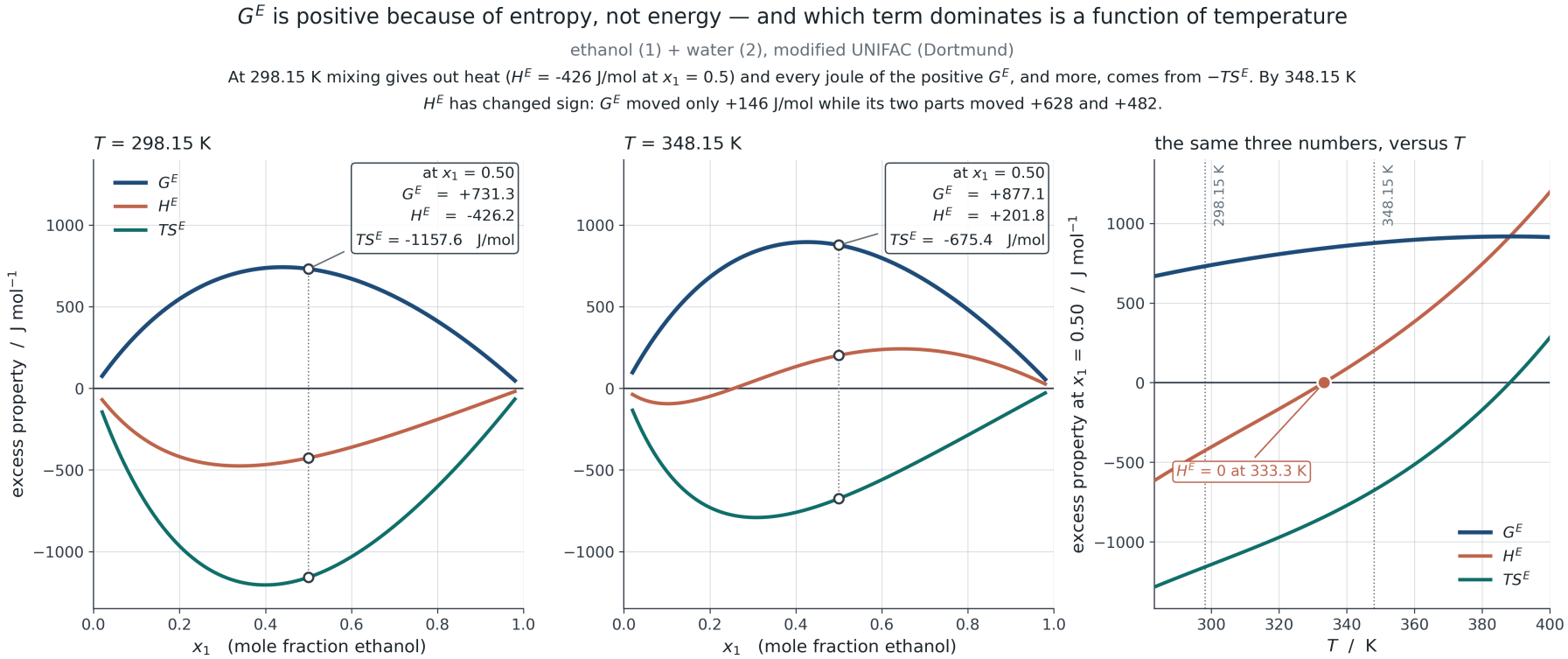
Because the departure of a liquid from an ideal gas is enormous and almost entirely uninteresting — it is dominated by condensation, which is a pure-component effect. The departure from an ideal *solution* isolates what mixing did.

The central identity

$$\frac{G^E}{RT} = \sum_i x_i \ln \gamma_i$$

and $\ln \gamma_i$ is the **partial molar quantity of G^E/RT**. Everything in Modules 4 and 5 rests on that one line.

Which terms dominate, and when



H^E IS NOT MEASURED HERE. It is obtained from the temperature dependence of the model, $H^E = -RT^2\,\partial(G^E/RT)/\partial T$. The model is modified UNIFAC (Dortmund) — `thermo.unifac.UNIFAC`, DOUFIP2006 table, DOUFSG subgroups — whose temperature-dependent group parameters were regressed simultaneously against VLE, LLE, h^E and γ^∞ data (Gmehling, Li & Schiller, *Ind. Eng. Chem. Res.* 1993, 32(1), doi:10.1021/ie00013a024), which is why its temperature derivative is worth plotting at all. `thermo`'s analytic HE() was checked against a central difference of GE() alone over 97 compositions at both temperatures: largest disagreement 3.94e-06 J/mol. No parameter here is fitted or assumed; ethanol and water enter as UNIFAC subgroups only.

F3.3 · $G^E = H^E - TS^E$ at two temperatures. H^E here is a model derivative, not a calorimeter reading — the figure says so.

Lewis-Randall against Henry

The same physical system gives different numerical γ under the two conventions. Two papers can disagree without either being wrong.

Lewis-Randall

$f_i^\circ = f_i$, the pure liquid, so $\gamma_i \to 1$ as $x_i \to 1$.

Natural for a solvent, or for components of comparable amount. The convention used throughout Modules 4 and 5.

Henry

$f_i^\circ = \mathcal{H}_i$, the Henry constant, so $\gamma_i^* \to 1$ as $x_i \to 0$.

Natural for a dissolved gas or a solute that never approaches purity — and essential when the pure liquid does not exist at those conditions.

$\gamma_i^* = \gamma_i / \gamma_i^\infty$. *The conversion is one division, and the number changes by whatever* γ_i^∞ *happens to be — often a factor of five or more.* ***A γ without its convention is not a number.***

PART IV

Gibbs-Duhem as a constraint

Section 3.4 γ_1 and γ_2 are not independent functions. Fitting them separately is not allowed.

The binary form

$$\sum_i x_i \, \mathrm{d} \ln \gamma_i = 0 \qquad \Longrightarrow \qquad x_1 \frac{\mathrm{d} \ln \gamma_1}{\mathrm{d}x_1} + x_2 \frac{\mathrm{d} \ln \gamma_2}{\mathrm{d}x_1} = 0$$

Opposite signs, fixed ratio

Wherever one curve rises the other must fall, and the slopes stand in the ratio $-x_2/x_1$. Not approximately — exactly, at every composition.

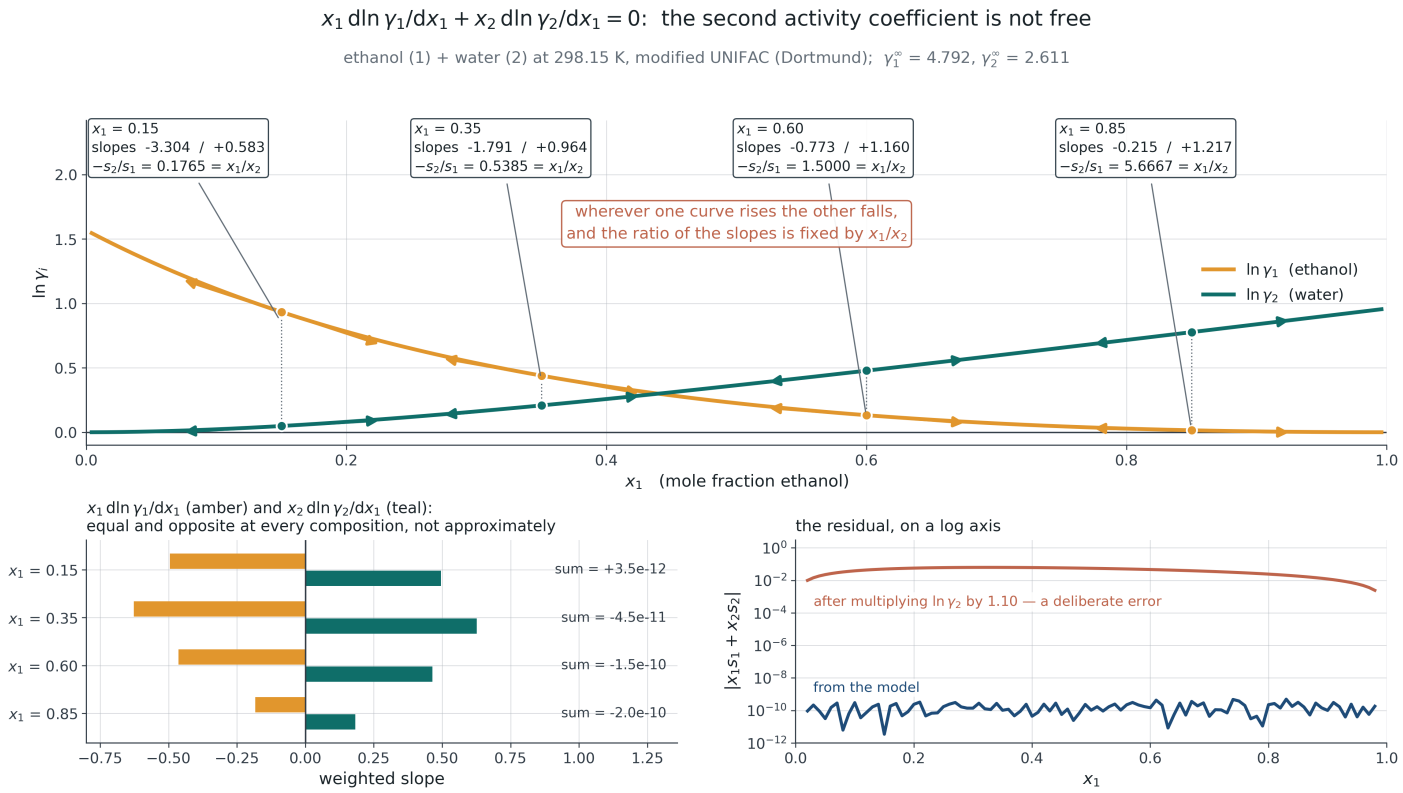
At the ends

As $x_1 \to 1$, $\mathrm{d} \ln \gamma_1 / \mathrm{d}x_1 \to 0$: the curve for the *abundant* component must flatten. A fitted γ_1 with a finite slope at $x_1 = 1$ is not admissible, whatever its residual.

The consequence

Fitting $\ln \gamma_1$ and $\ln \gamma_2$ as two independent functions produces a pair that thermodynamics forbids. Fitting one G^E and differentiating it cannot — which is the whole reason models are written as G^E.

The constraint, drawn



Activity coefficients from `thermo.unifac.UNIFAC`, DOUFIP2006 table, DOUFSG subgroups; nothing fitted, nothing assumed. Slopes by central difference, h = 1e-06. The ×1.10 curve in the right-hand panel is a DELIBERATE ARTIFICIAL ERROR introduced to show the constraint has content: it is not a property of any fluid.
Residual from the model: max 4.9e-10 over 97 compositions — the truncation error of the difference, not physics. With the 10 % error in ln γ_2: max 0.063, 1e+08 times larger.

F3.4 · Paired tangents at four compositions. The slope ratio equals $-x_2/x_1$ at every one.

PART V

Models are choices of G^E

Section 3.5 Once you see that, the list of models stops being a list to memorise.

One expansion, several special cases

Redlich-Kister is the general polynomial truncation. Margules and van Laar fall out of it.

$$\frac{G^E}{RT} = x_1 x_2 \left[A + B(x_1 - x_2) + C(x_1 - x_2)^2 + \cdots \right]$$

$B = C = 0$

Two-suffix Margules. One parameter, symmetric, and structurally unable to skew.

$C = 0$

Three-suffix Margules. Two parameters, and $\ln(\gamma_1/\gamma_2)$ becomes quadratic in $x_1 - x_2$ — which is enough to produce a **double azeotrope**, a thing often wrongly said to need three.

van Laar

Not a truncation but a ratio of polynomials. Two parameters, and its $\ln(\gamma_1/\gamma_2)$ has exactly one interior zero for same-sign parameters — so it *cannot* produce a double azeotrope, whatever the fit.

Local composition models

State the physical assumption behind each, not only the algebra.

Wilson

The composition *around* a molecule differs from the bulk composition, Boltzmann-weighted by interaction energy. Two parameters, good temperature behaviour, and **structurally incapable of liquid-liquid equilibrium**.

NRTL

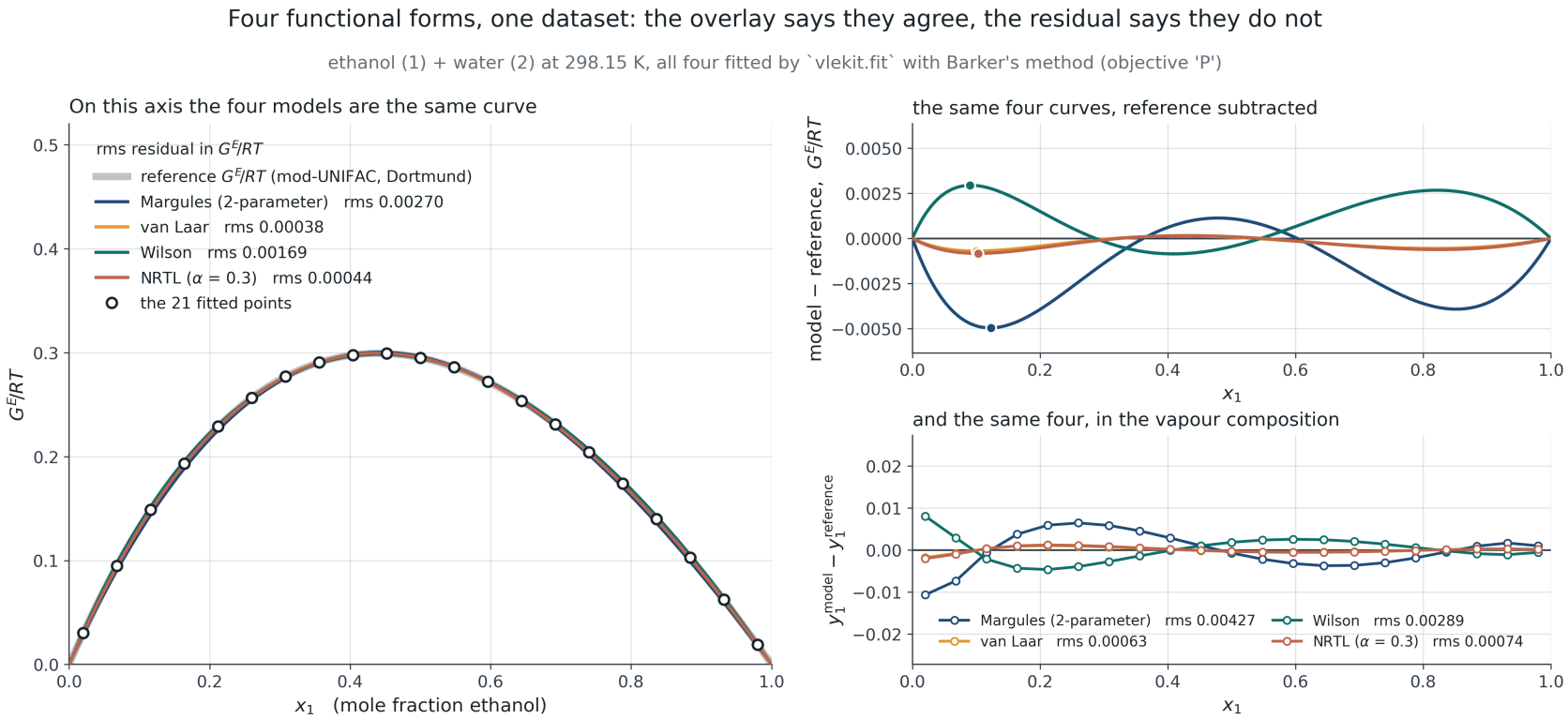
The same local-composition idea plus a non-randomness parameter α, which gives the model a second length scale. Two fitted parameters with α usually fixed at 0.3 — and it *can* produce a phase split.

UNIQUAC

Splits G^E into a combinatorial part from molecular size and shape — fixed by r and q, which are **not fitted** — and a residual part carrying the two adjustable energies. Extrapolates in composition better for that reason.

UNIFAC *is UNIQUAC with the residual parameters estimated from functional groups instead of fitted. That makes it predictive — usable with no data at all — and correspondingly less accurate than a fit to your own measurements.*

Four models, one dataset



THE DATASET IS NOT MEASURED AND CARRIES NO NOISE. It is generated by `vlekit.generate` from modified UNIFAC (Dortmund) at 298.15 K with an ideal vapour and Antoine constants from `vlekit.data.LIBRARY`, so every residual here is model-form error and nothing else; adding scatter would bury it. The rms values say how well each form can reproduce a realistic G^E, not how well it fits a particular laboratory.

Margules (2-parameter): A12=+1.4692, A21=+0.8996 | van Laar: A=+1.5496, B=+0.9532 | Wilson: L12=+0.2364, L21=+0.7949 | NRTL (α = 0.3): tau12=-0.0307, tau21=+1.5780

F3.5 · The same G^E fitted four ways. On the upper axis the curves are indistinguishable; the residual panel is where the differences live.

What each model can and cannot do

What each G^E model can do — every cell is the output of a calculation this script ran

reference system for the last two columns: ethanol (1) + water (2) at 298.15 K, γ_1^∞ = 4.792 from modified UNIFAC (Dortmund)

model	adjustable binary parameters	does G^E/RT carry its own T dependence? max|Δ|, 298 → 348 K	can it produce a liquid-liquid split? (sweep, `flash.is_stable`)	extrapolation: γ_1^∞ from a fit on $x_1 = 0.60$-0.95 only
Margules, 2 parameter $G^E/RT = x_1x_2(A_{21}x_1 + A_{12}x_2)$	2	none (0e+00)	yes — 1387 of 1600 sampled e.g. (+0.05, +2.34) splits 0.57 / 0.87	3.80 (-21 %) full-range fit: 4.35 (-9 %)
Margules, 3 parameter (Redlich-Kister, $C\,(x_1 - x_2)^2$ term)	3	none (0e+00)	yes — 1503 of 1600 sampled e.g. (+3.82, +0.59, +0.04) splits 0.05 / 0.99	4.59 (-4 %) full-range fit: 4.68 (-2 %)
van Laar $G^E/RT = ABx_1x_2/(Ax_1 + Bx_2)$	2	none (0e+00)	yes — 1287 of 1600 sampled e.g. (+0.20, +5.24) splits 0.89 / 1.00	4.55 (-5 %) full-range fit: 4.71 (-2 %)
Wilson (local composition, $\Lambda_{12}, \Lambda_{21}$)	2	none (0e+00)	NO — 0 of 14400 sampled min $d^2\Delta g/dx_1^2$ on the grid = +1.1e-05	6.92 (+44 %) full-range fit: 5.19 (+8 %)
NRTL (α fixed at 0.3, not fitted)	2	none (0e+00)	yes — 657 of 1600 sampled e.g. (-2.41, +6.56) splits 0.01 / 0.10	4.55 (-5 %) full-range fit: 4.70 (-2 %)
UNIQUAC (r, q from groups, not fitted)	2	none (0e+00)	yes — 1303 of 1600 sampled e.g. (+0.00, +2.60) splits 0.82 / 1.00	5.29 (+10 %) full-range fit: 5.01 (+5 %)
UNIFAC (original, group table) $\Psi_{mn} = \exp(-a_{mn}/T)$	0	YES (1.0e-02)	yes — n-hexane/methanol splits 0.10 / 0.91 at 298.15 K	nothing is fitted: predicts 7.62 (+59 % vs the reference)

HOW EACH COLUMN WAS OBTAINED. T dependence: gE_RT evaluated at the same parameters at 298.15 and 348.15 K over 19 compositions; the number in the cell is the largest difference. Liquid-liquid: parameter sets are swept and `vlekit.flash.is_stable` / `flash.miscibility_gap` are called on each — 40×40 grids for Margules-2, van Laar, NRTL and UNIQUAC, 1600 seeded random triples for Margules-3, and 120×120 = 14400 log-spaced pairs over $\Lambda \in [10^{-3}, 50]$ for Wilson, which is the row that matters. Not one Wilson pair is unstable and the smallest $d^2\Delta g_{mix}/dx_1^2$ found anywhere on that grid is +1.08e-05. Extrapolation: each model fitted by `vlekit.fit` (Barker) to nine points spanning x_1 = 0.60-0.95 only, then asked for γ_1^∞. The dataset is generated from the reference model with no noise, so the spread is model form alone. UNIQUAC r, q are UNIFAC group sums stored on the components, not fitted. NOT A CALCULATION: the separate UNIFAC-LLE group-interaction table is verified here only by the presence of the file in the installed `thermo` package — found: True.

F3.6 · Every claim in the table is either derivable from the functional form or verified by a sweep run for this figure.

CLOSING

What you must be able to do

The module in six statements.

1. **Define a partial molar property**
   and explain, with the ethanol/water number, why it is not a property of the pure substance.

2. **Use the tangent-intercept construction**
   and say what it is computing.

3. **Write Gibbs-Duhem in full**
   and name the term that is dropped at constant T and P — and where it returns.

4. **Get $\hat{\varphi}_i$ from an equation of state**
   and recognise it as a composition derivative of Module 1's residual property.

5. **State a reference state whenever you state a γ.**
   Lewis-Randall or Henry, and the conversion between them.

6. **Read a model as a choice of G^E**
   and say what its functional form can and cannot represent.