

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, $\gamma_1^\infty = 4.792$ from modified UNIFAC (Dortmund)

model	adjustable binary parameters	does G^E/RT carry its own T dependence? max $ \Delta $, 298 $\rightarrow$ 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 $d^2\Delta g_{\text{mix}}/dx_1^2$ 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.