

A-C. Retrieve, qualify, integrate

Use after attempting the questions. All numerical data in these exercises are synthetic teaching data.

A. VLE and the meaning of a fit

A1. x_1 is liquid mole fraction; y_1 is vapor mole fraction; z_1 is overall mole fraction. γ_1 is the dimensionless liquid activity coefficient for the chosen pure-liquid standard state. Activity is $a_1 = \gamma_1 x_1$, not γ_1 alone.

A2. $\gamma_1 = (0.704857144627 \times 158.707198211) / (0.5 \times 150) = \mathbf{1.49154537}$. $\exp(0.399813) \approx \mathbf{1.49154575}$; the difference is rounding. This inference assumes ideal vapor and negligible Poynting correction, with applicable saturation pressure data.

A3. A small fitted residual shows reproduction by the selected model under its property assumptions. It does not establish thermodynamic consistency of all observations or accuracy on independent data.

B. A constraint with a thermodynamic path

B1. $x_1 d \ln \gamma_1 + (1-x_1) d \ln \gamma_2 = 0$ at fixed **T** and **P**. Activity coefficients from one excess Gibbs-energy function cannot vary independently.

B2. More generally, $\sum x_i d \ln \gamma_i = -h^E / (RT^2) dT + v^E / (RT) dP$, with molar excess properties. Isothermal VLE can have variable **P**; our model neglects the excess-volume pressure term. For an isobaric local diagnostic, independently supplied h^E is needed for the temperature correction. Synthetic h^E in Lab 03 is generator information, not experimental calorimetry.

B3. No. “Not applicable” means the selected path is outside that method. “Not assessed” means required information is missing or disabled. Neither is a successful test.

C. Trapezoidal signed area is not normalized D

Interval	Baseline trapezoid	After adding 0.20
0 to 0.25	$0.25(2+1)/2 = 0.375$	0.425
0.25 to 0.50	$0.25(1+0)/2 = 0.125$	0.175
0.50 to 0.75	$0.25(0-1)/2 = -0.125$	-0.075
0.75 to 1	$0.25(-1-2)/2 = -0.375$	-0.325
Signed sum S	0	0.200

C1. Positive area = 0.5; signed negative area = -0.5; $S = 0$. **C2.** Adding a constant 0.20 over a unit composition interval adds 0.20 to S . **C3.** The endpoint limits were provided analytically. Real interior observations do not determine missing endpoint intervals. Opposing local errors can cancel in the integral.

The lab reports $D = 100|A-B|/(A+B)$, where A and B are nonnegative area magnitudes. D is undefined when its denominator is essentially zero. Do not label the signed S above as D .

D-E. Scores and charts must be read together

Reference engine values: isothermal 350 K; 41 points; perturbation amplitude +0.25. Small last-digit differences are numerical.

Case	Area D (%)	Local score	Interpretation
Consistent reference	0.078692	0.117763	Both meet teaching criteria
Canceling errors	0.073552	15.598698	Area meets; local outside
Localized defect	2.013463	1.671839	Both meet; visible local peak

Isothermal area criterion: $D < 5\%$. Local teaching criterion: **100 mean $|r| < 5$** . The local score is a scaled mean residual, not a probability, confidence level or percentage of bad observations. Finite integration/differentiation explains why the clean numerical values are small rather than exactly zero.

D1-D4. What each result permits

D1. The clean reference uses an independent Lab 03 generator, not the Lab 08 example parameter set. The clean modeling result is $\Delta p \approx 1.12 \times 10^{-6}\%$ and $\Delta y \approx 6.48 \times 10^{-7}$ **percentage points**. Near-zero reproduction is expected because the generating model is in the fit family.

D2. With $f(x)=0.25 \cos(2\pi x)$, the added log-ratio has zero full-range integral. It still violates the local relationship. Thus a small integrated error can conceal substantial structured local errors.

D3. The localized perturbation is narrow, centered near $x_1=0.35$. Its residual plot shows a peak, but averaging over the composition range dilutes it. At these exact settings **both aggregate criteria are met**. Do not report a failed averaged score merely because a defect was deliberately inserted.

D4. Herington is an empirical isobaric criterion, so it is not applicable to this isothermal dataset. The Van Ness-type run shows reproduction by the chosen NRTL model and property approximation. It does not prove consistency or prediction. Changing inputs clears the previous model fit; rerun if a new model result is required.

E1-E2. A defensible conclusion

The perturbation adds $(1-x)f$ to $\ln \gamma_1$ and $-xf$ to $\ln \gamma_2$. Their weighted sum $g^E/(RT)$ is unchanged, while $\ln(\gamma_1/\gamma_2)$ increases by f . The exact local residual therefore changes by $-f$, apart from numerical differentiation error. Zero integral of f does not mean f is zero at every composition.

Example conclusion: “For the synthetic isothermal 41-point canceling-error case at amplitude 0.25, $D=0.07355\%$ meets the area criterion, while the local score 15.5987 exceeds 5 and the plot shows an oscillating residual. The integral misses canceling local discrepancies. This conclusion is conditional on the ideal-vapor, negligible-Poynting and negligible excess-volume pressure assumptions; the derivative score also depends on sampling.”

A real-data failure may arise from measurements, vapor-pressure correlations, omitted phase corrections, endpoint assumptions, model flexibility or numerical differentiation. It does not identify a unique cause.

F-I. A stable tie line, then phase amounts

Keep the supplied hand example separate from the actual Margules model calculation.

F1-F3. Hand calculation and stability

F1 / F3. Equal chemical potentials give an equilibrium candidate. Stable equilibrium minimizes total Gibbs energy over the admitted states at fixed T and P. A valid stable common tangent supports the whole admitted molar curve from below. Merely finding a stationary point or equal slopes is insufficient.

F2. For supplied $x^a=0.20$ and $x^b=0.80$: at $z_1=0.50$, $f\beta=(0.50-0.20)/0.60=\mathbf{0.50}$; at $z_1=0.35$, $f\beta=0.15/0.60=\mathbf{0.25}$ and $f\alpha=\mathbf{0.75}$. The balance is $0.75(0.20)+0.25(0.80)=\mathbf{0.35}$.

G1-G4. Actual Lab 04: symmetric Margules A = 3

z_1	x_1^a	x_1^b	$f\alpha$	$f\beta$
0.50	0.07072018	0.92927982	0.50000000	0.50000000
0.35	0.07072018	0.92927982	0.67471122	0.32528878

At $z_1=0.35$, $f\beta=(0.35-0.07072018)/(0.92927982-0.07072018)=\mathbf{0.32528878}$. Check $0.67471122(0.07072018)+0.32528878(0.92927982) \approx \mathbf{0.35000000}$. Full-precision engine balance residual is near zero; rounded entries may leave a small residual.

Both hypothetical homogeneous feeds are **unstable**; equilibrium has **two liquids**. The Gibbs-energy decrease per RT is about **0.11519417** at $z_1=0.50$ and **0.09339471** at $z_1=0.35$. At fixed model and conditions, the coexisting compositions stay fixed while the phase fractions change.

A Gibbs-Duhem-consistent model may have a nonconvex mixing-Gibbs curve and predict phase separation. Consistency constrains derivatives; stability compares total Gibbs energies. A consistent model does not require a stable single liquid.

H1-H4. Brief self-check

H1: No; local errors can cancel. **H2:** Check the thermodynamic path, excess-property correction, phase/property assumptions and differentiation resolution/noise before blaming measurements. **H3:** No; fitting-data reproduction is not independent predictive validation. **H4:** $f\beta=0.25$ and $0.75(0.20)+0.25(0.80)=0.35$, provided the tangent supports the full admitted curve.

I. Finish with your own evidence

In Session 3, answer the existing LLE concept question from G; use the evidence field to explain D2 versus the clean reference. Complete feedback and save local files. There is no additional required task after the 180-minute lesson.

Method background: [NIST area / Herington](#); [NIST point test](#); [NIST Van Ness](#). Lab 03 uses teaching variants, not the complete NIST TDE implementations. Exact reference values were computed from the shipped Lab 03 and Lab 04 engines.