

Lab 03: use one controlled change

Guide page 1 | Use during practice D1-D4, minutes 50-80. No Excel upload or Lab 08 JSON is needed.

[Open the Consistency Tests Lab](#)

1. Establish the reference and record it

Set **Data set** → **Synthetic · isothermal, 350 K**; **Controlled perturbation** → **Consistent reference**; **Sampling resolution** → **41 points**. The page default is 81 points, so explicitly change it. Leave the synthetic H^E checkbox as supplied; the thermal correction is zero on this isothermal path.

Read the scorecards. Under **Inspect**, choose **Log-activity ratio & integrated area**, then **Local Gibbs-Duhem residual**. Copy D, the local score and the status into practice D1. These generated data are independent of the Lab 08 demo dataset.

Do not run the model yet. Compare the two controlled defects next; return to the clean reference for the single required model fit in D4. For numeric detail, expand **Inspect data & numerical results**.

2. Insert canceling errors

Change **Controlled perturbation** → **Canceling errors · zero net area**. Set the **Amplitude** slider to **0.25**; check its displayed number. Keep the dataset and 41 points unchanged. The charts and scores update automatically. Record D2. Explain the difference between the integrated and local evidence.

3. Insert a narrow local defect

Change only **Controlled perturbation** → **Localized defect near $x_1 = 0.35$** . Keep amplitude 0.25 and 41 points. Record D3. Inspect the **Local Gibbs-Duhem residual** plot near 0.35. An averaged score can meet its threshold while a narrow peak remains visible.

Optional within the same 30-minute block: change **Sampling resolution** to **161 points**, note changes, then return to 41 before comparing with the reference answers. Resolution changes both sampling and numerical derivatives; it does not add experimental evidence.

4. Return to the reference for the modeling test

At minutes 74-80, return **Controlled perturbation** → **Consistent reference**. Keep 350 K and 41 points. Click **Run modeling test** → once. Wait for “Converged,” then record Δp and Δy in D4. If the fit fails, record no modeling verdict. Explain why Herington is not applicable to this path.

For each case, type the settings and interpretation in **Your conclusion**, then click **Export all results**. The download is **thermodynamic-consistency-study.json**. Rename each copy to include clean, canceling or localized. A screenshot of the local chart is also useful. Changing settings clears a previous fit, so record or export it first.

The JSON contains the settings, synthetic set, area and differential outputs, modeling result if run, and your explanation. Exporting saves locally; it is not a submission. Complete E1-E2 at minutes 80-90, then take the 10-minute break.

Lab 03: what the four methods mean

Guide page 2 | Read with the slides at minutes 15-35; revisit during D4 and E. The core practice is area plus local diagnostics.

Area: a global integral

$L = \ln(\gamma_1/\gamma_2)$; A is area above zero and B is the positive magnitude below zero. $D = 100|A-B|/(A+B)$. This lab uses piecewise-linear integration, and the isothermal criterion is **D < 5%**, with the excess-volume pressure term neglected. Small signed area may conceal opposing local errors. Near ideality the normalization can be undefined. Missing endpoints mean no full-range verdict unless an explicit extrapolation is assumed.

Differential: a local relationship

With $g = g^E/(RT) = x \ln \gamma_1 + (1-x) \ln \gamma_2$, the lab uses

$$r = dg/dx - \ln(\gamma_1/\gamma_2) + h^E/(RT^2) dT/dx$$

The local score is **100 mean |r|**, with a teaching threshold of **5**. Three-point finite differences use interior points and actual composition spacing. This is **not** the fitted Padé/Kojima point test in NIST TDE. Derivatives amplify noise; inspect the plot, not just the averaged score. Isothermal data have no temperature term. For real isobaric data without independent h^E , the raw residual has no consistency verdict.

Herington: empirical allowance for an isobaric path

$J = 150(T_{\max} - T_{\min})/T_{\min}$, with temperatures in kelvin. This lab uses **D-J < 10**. J is a boiling-range allowance, not measured h^E . It is **not applicable** to the required isothermal runs. Endpoint extrapolation yields a conditional result, not new measurements. The full NIST near-ideal decision tree is not implemented.

Van Ness-type: reproduction by a selected model

Clicking **Run modeling test** → fits NRTL jointly to P and y. Isothermal fits use two constant τ values with $\alpha = 0.47$ fixed. $\Delta p = \text{mean}[100|P_{\text{calc}} - P_{\text{obs}}|/P_{\text{obs}}]$; $\Delta y = \text{mean}[100|y_{\text{calc}} - y_{\text{obs}}|]$. Criteria are **$\Delta p < 1\%$** and **$\Delta y < 1$ percentage point**. This is a teaching parameterization, not NIST TDE's five-parameter model. A bound hit is flagged. Small error shows reproduction; failure can reflect model flexibility, property approximations or data error.

Use the status literally

Not applicable: the method does not match the path. **Not assessed:** required information is missing or disabled.

Meets criterion: this particular numerical criterion is met under its assumptions. None is a blanket certificate of data quality or prediction.

Sources: [NIST Herington](#) | [NIST point test](#) | [NIST Van Ness](#). Inspect Lab 03 “Sources & scope” for implementation and original data provenance.

Lab 04: separate equilibrium from amounts

Guide page 3 | Use during practice G1-G4, minutes 120-165. Complete F by hand first.

[Open Liquid Stability & LLE](#)

1. Predict, then fix a reproducible state

At **For symmetric Margules with $A > 2$, a feed near $x_1 = 0.5$** ..., choose your prediction. Set **Liquid model** → **Margules** · **1 parameter**, **Interaction parameter A** → **3** and **Feed mole fraction z_1** → **0.50**. Click **Find equilibrium** →. Typing alone is not enough; this button applies typed values. Sliders update immediately.

Alternatively, **Explore a state** → **Unstable** · **$A = 3$** , **$z_1 = 0.50$** selects this example. Check all values before recording. These are hypothetical model parameters at fixed conditions, not a fitted chemical mixture. There are no T or P input boxes in this lab.

2. Read the actual common-tangent result

Choose **View** → **Gibbs energy & common tangent**. Record **Coexisting composition x_1^α** , **Coexisting composition x_1^β** , and **Fraction of β liquid**. β is the component-1-rich liquid. Inspect **Homogeneous feed**, the phase label, and **Gibbs energy decrease / RT**. The feed classification describes the hypothetical single liquid; the equilibrium state may be two liquids.

Expand **Verify the equilibrium**. Check material balance, chemical potentials and tangent evidence. A common tangent must support the admitted curve from below. Positive local curvature alone cannot prove global stability; a metastable liquid can still lower its Gibbs energy by a finite split.

3. Change only the overall composition

Keep the model and $A=3$. Change **Feed mole fraction z_1** → **0.35**, then click **Find equilibrium** →. Record G2. Calculate $f\beta = (z_1 - x_1^\alpha) / (x_1^\beta - x_1^\alpha)$, then independently check $f\alpha x_1^\alpha + f\beta x_1^\beta = z_1$ for G3. Use the lab endpoints, **not** the illustrative 0.20 and 0.80 from F2.

For G4, explain why endpoints stay fixed at the same model conditions while phase fractions change. State why the lower Gibbs energy supports two liquids. A consistent activity model can still predict a nonconvex Gibbs curve and liquid separation.

4. Save, self-check, submit the reflection

Type your explanation in **Your explanation**, then click **Export study JSON**. The download is **liquid-stability-study.json**. Rename copies with z050 and z035. Save the practice record. Do H1-H4 before opening the solutions, then use practice page 4 for the Session 3 exit ticket and feedback.

Stop after the required comparison. NRTL, two-parameter Margules, LLE fitting, VLLE and additional feed states are optional later investigations. They are not additional tasks for this 180-minute holiday lesson.