

# Reading Gibbs energy graphs

Week 3 review · Calculate, compare, explain

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24 October 2026

# Start with these two documents

**Open:** the [four-page calculation and Lab guide](#) and [Lab 04: Liquid stability](#) in another tab.

Use a calculator with **natural logarithms, ln**. No spreadsheet or code is needed.

| Follow this route                         | Write in the guide | Suggested time |
|-------------------------------------------|--------------------|----------------|
| Read the graph and calculate one case     | A–B, pages 1–2     | 20 min         |
| Reproduce it in Lab 04; change the feed   | C, page 3          | 15 min         |
| Solve a new case and check your reasoning | D, page 4          | 10 min         |

This optional review supports your original Week 3 worksheet. Use the parts you need; no additional attendance or exit-ticket submission is required.

# Keep two questions separate

## **Lab 03: Are the data compatible with a thermodynamic constraint?**

Applicable consistency tests assess relationships such as Gibbs–Duhem, with assumptions about the data and their path.

## **Lab 04: Which allowed state has the lowest total Gibbs energy?**

A liquid model can satisfy Gibbs–Duhem and still predict separation into two liquids.

**Your action:** On guide page 1, A1, write which question a common tangent helps answer. This review concerns a binary liquid at fixed  $T$  and  $P$ ; vapor and solid phases are excluded.

# Read the axes before the curve

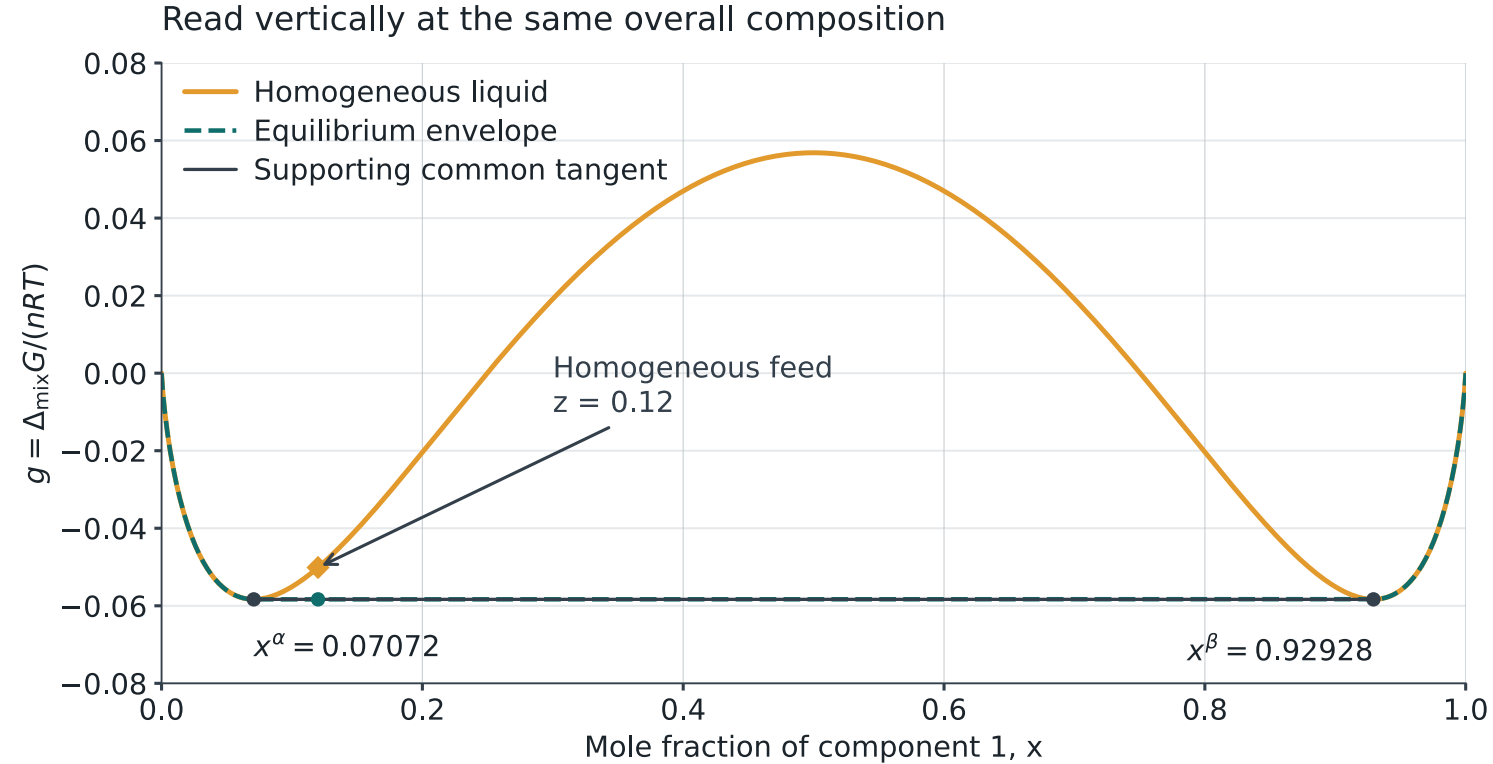
$$g(x) = \frac{\Delta g_{\text{mix}}(x)}{RT}, \quad x = x_1, \quad x_2 = 1 - x.$$

- **Horizontal:** composition of a possible homogeneous liquid, from pure component 2 to pure component 1.
- **Vertical:** molar Gibbs energy of mixing divided by  $RT$ , dimensionless. Lower means lower mixing energy at the same composition.
- **Feed:**  $z = z_1$  is the overall composition. A single liquid has  $x = z$ ; two liquids can have  $x^\alpha \neq z \neq x^\beta$ .

The pure-liquid reference is an affine function of composition. It cancels when states have the same total amounts of both components, so this graph can compare their total Gibbs energies.

**Your action:** Guide A2: mark  $z = 0.12$  and distinguish it from the two phase compositions.

# Compare states at the same overall composition



Dimensionless Gibbs mixing energy for symmetric Margules  $A=3$ , with a globally supporting common tangent and feed  $z=0.12$ .

The curve at  $z$  represents **one homogeneous liquid**. The line segment between the two tangent contacts represents a **two-liquid mixture**, with amounts chosen to give that same  $z$ .

**Your action:** Guide A2: at  $z = 0.12$ , which state is lower? A negative value of  $g$  alone does not answer this comparison.

# One model for every calculation

For the synthetic, symmetric one-parameter Margules liquid, use **A = 3**:

$$g(x) = x \ln x + (1 - x) \ln(1 - x) + 3x(1 - x).$$

$$g'(x) = \ln \frac{x}{1 - x} + 3(1 - 2x), \quad g''(x) = \frac{1}{x} + \frac{1}{1 - x} - 6.$$

All quantities here, including A, are dimensionless. At pure endpoints, use the limit  $x \ln x \rightarrow 0$ .

**Your action:** Guide B1, page 2: enter  $z = 0.12$ . Use  $\ln$ , not  $\log_{10}$ . Keep A fixed when changing the feed later.

# Step 1: test local curvature

At the homogeneous feed composition  $z = 0.12$ :

$$\begin{aligned} g''(0.12) &= \frac{1}{0.12} + \frac{1}{0.88} - 6 \\ &= 8.333333 + 1.136364 - 6 = \boxed{3.469697 > 0}. \end{aligned}$$

This state resists sufficiently small composition fluctuations: it is **locally stable**. A distant pair of compositions may still lower the total Gibbs energy.

At  $z = 0.50$ ,  $g'' = 2 + 2 - 6 = -2$ : the homogeneous liquid is **locally unstable**.

**Your action:** Record both curvatures in B1. Do not write “globally stable” from a positive curvature alone.

## Step 2: find the two tangent contacts

A common tangent must satisfy

$$g'(x^\alpha) = g'(x^\beta) = \frac{g(x^\beta) - g(x^\alpha)}{x^\beta - x^\alpha}.$$

Symmetry makes this particular tangent horizontal:  $x^\beta = 1 - x^\alpha$  and  $g'(x^\alpha) = 0$ .

$$\ln \frac{x^\alpha}{1 - x^\alpha} + 3(1 - 2x^\alpha) = 0.$$

The low-composition root lies between **0.0707 and 0.0708**. Refinement gives

$$x^\alpha = 0.07072018, \quad x^\beta = 0.92927982.$$

**Your action:** Guide B2: substitute  $x^\alpha$  in  $g'$ . The root at 0.50 is a maximum here, not a second liquid phase. A horizontal tangent is specific to this symmetric case.

## Step 3: calculate the phase amounts

Use a basis of **1 mol of total feed**. Let  $f^\alpha + f^\beta = 1$ .

$$z = f^\alpha x^\alpha + f^\beta x^\beta \quad \Longrightarrow \quad f^\beta = \frac{z - x^\alpha}{x^\beta - x^\alpha}.$$

At  $z = 0.12$ :

$$f^\beta = \frac{0.12000000 - 0.07072018}{0.92927982 - 0.07072018} = \boxed{0.057398}.$$

$$f^\alpha = 1 - f^\beta = \boxed{0.942602}.$$

**Your action:** Guide B3: write the amounts as 0.942602 mol  $\alpha$  and 0.057398 mol  $\beta$  per mol of feed.

These are liquid phase fractions; no vapor fraction is involved.

## Step 4: check the component balance

$$0.942602 + 0.057398 = 1.000000$$

$$0.942602(0.07072018) + 0.057398(0.92927982) \approx \boxed{0.120000}.$$

For component 2, the same amounts give  $1 - z = 0.88$ .

The result satisfies the amount and composition constraints. **A closed balance alone does not prove that the state minimizes Gibbs energy.**

**Your action:** Guide B3: check this sum on your calculator. If a phase fraction is outside 0–1, that proposed split cannot represent this feed.

## Step 5: calculate the homogeneous energy

$$g(0.12) = 0.12 \ln(0.12) + 0.88 \ln(0.88) + 3(0.12)(0.88)$$

| Term                                      | Value              |
|-------------------------------------------|--------------------|
| $0.12 \ln(0.12)$                          | -0.25443162        |
| $0.88 \ln(0.88)$                          | -0.11249337        |
| $3(0.12)(0.88)$                           | +0.31680000        |
| <b>Sum: homogeneous <math>g(z)</math></b> | <b>-0.05012499</b> |

**Your action:** Guide B4: reproduce the sum. This is  $\Delta G_{\text{mix}}/(nRT)$  for the homogeneous feed, not an energy in joules.

## Step 6: compare with the split

Both endpoints have  $g(x^\alpha) = g(x^\beta) = -0.05834135$ .

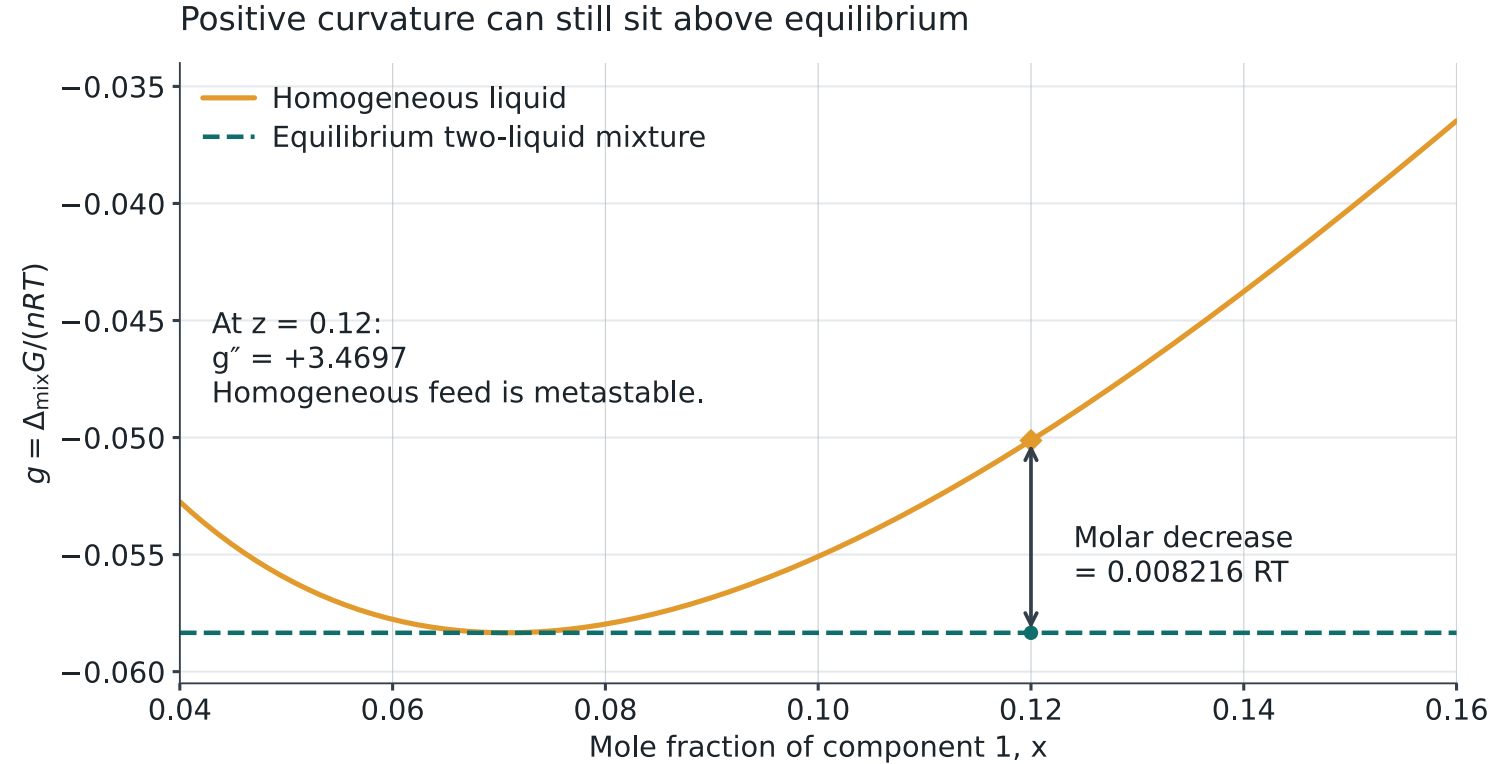
$$g_{\text{split}} = f^\alpha g(x^\alpha) + f^\beta g(x^\beta) = -0.05834135.$$

$$\text{Energy decrease} = g(z) - g_{\text{split}} = \boxed{0.00821636 > 0}.$$

The split is lower even though  $g''(0.12) > 0$ . The original homogeneous feed is **metastable**; the equilibrium state is two liquids.

**Your action:** Guide B4: circle the lower energy. To obtain an actual total energy decrease, multiply 0.00821636 by  $nRT$  using consistent units.

# See the same comparison on the graph



Close view of the homogeneous feed and the lower two-liquid energy at  $z=0.12$ .

Read the **vertical** separation at the same  $z$ . It equals  $g(z) - g_{\text{split}}$ , not a distance between the two phase compositions.

**Your action:** Return to B4: label the upper point “homogeneous” and the lower point “equilibrium split.”

# Step 7: check global support

For a candidate line  $\ell(x)$ , examine the whole allowed interval:

$$d(x) = g(x) - \ell(x) \geq 0 \quad \text{for all } 0 \leq x \leq 1.$$

Here  $\ell(x) = -0.05834135$ . The two contacts are the global minima: checking the stationary points and endpoints verifies that no part of this curve lies below the line.

- Equal chemical potentials identify a **candidate** pair.
- The material balance checks whether its amounts are feasible.
- Global support establishes the lowest energy within this binary liquid model.

**Your action:** Guide B5: explain why testing only the two contacts is insufficient. A finite plotted grid can miss a narrow dip; the Lab also searches stationary points and uses a numerical tolerance.

# Verify support for this model

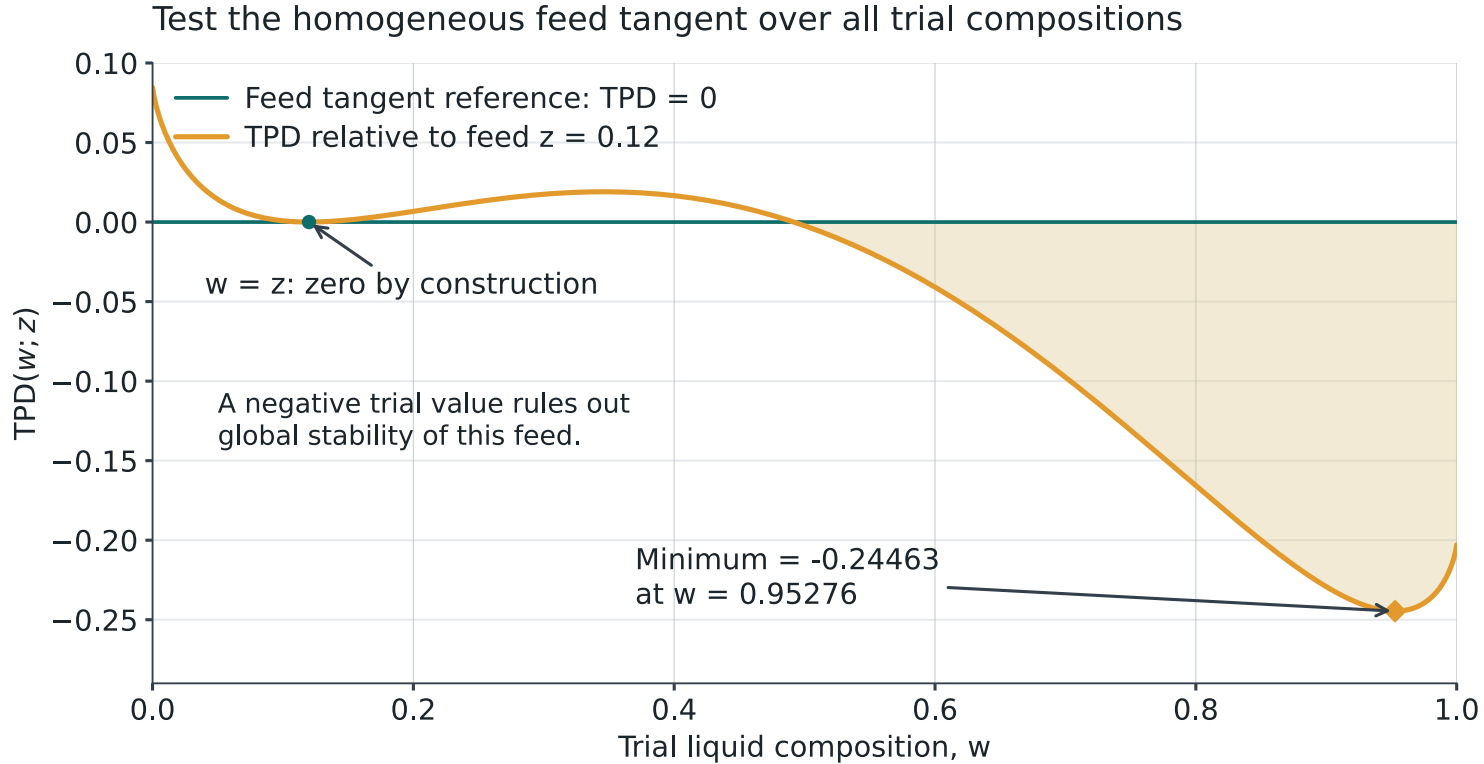
For  $A = 3$ , the stationary points are  $x^\alpha$ , 0.50 and  $x^\beta$ . Add both pure endpoints to cover the candidates for the lowest value of  $d(x) = g(x) - \ell(x)$ .

| Candidate composition    | $d(x)$                                        |
|--------------------------|-----------------------------------------------|
| 0 and 1                  | $0 - (-0.05834135) = 0.05834135$              |
| $x^\alpha$ and $x^\beta$ | 0                                             |
| 0.50                     | $(0.75 - \ln 2) - (-0.05834135) = 0.11519417$ |

All candidate values are nonnegative, so the line supports this entire curve. The contacts give its lowest value.

**Your action:** Guide B5: reproduce the middle-composition value. This exhaustive stationary-point check applies to the stated  $A = 3$  model; checking a few arbitrary plotted points would not be equivalent.

# A different tangent tests the homogeneous feed



Tangent-plane distance relative to the homogeneous  $z=0.12$  liquid, showing a negative value at a trial composition.

$$\text{TPD}(w) = g(w) - [g(z) + g'(z)(w - z)].$$

A negative value rejects global stability of the **homogeneous feed**. This feed tangent differs from the **coexistence common tangent**. The trial minimizer  $w$  is not automatically a binodal endpoint.

**Your action:** Guide C1, page 3: keep these two reference lines distinct when switching Lab views.

# Open Lab 04 and reproduce the calculation

**Open:** [Lab 04: Liquid stability](#). Keep guide **C1** beside it.

1. Under **Explore a state**, choose **Metastable** • **A = 3**,  **$z_1 = 0.12$** .
2. Confirm **Liquid model = Margules** • **1 parameter**, **A = 3**, and **Feed mole fraction  $z_1 = 0.12$** .
3. Click **Find equilibrium** →. Select **View** → **Gibbs energy & common tangent**.
4. Open **Verify the equilibrium**. Compare the homogeneous and equilibrium energies and the component balance residual with your hand calculation.

**Your action:** Record the values before revealing the comparison on the next slide. If the Lab opens at a different state, use the preset above; opening the page alone does not set this case.

# Compare the outputs, then change the view

| Quantity                                    | Hand calculation / expected Lab value |
|---------------------------------------------|---------------------------------------|
| Coexisting compositions $x^\alpha, x^\beta$ | 0.070720, 0.929280                    |
| Phase fractions $f^\alpha, f^\beta$         | 0.942602, 0.057398                    |
| Local curvature of feed                     | +3.469697                             |
| Homogeneous $g(z)$ / equilibrium $g(z)$     | -0.050125 / -0.058341                 |
| Energy decrease                             | 0.008216 (dimensionless)              |

**Your action:** Guide C1: switch to **Local curvature**, then **Tangent-plane distance • feed stability**.

Positive local curvature and negative minimum feed TPD are compatible here.

Allow for display rounding. Small residuals check the numerical solution; assess global support separately.

# Predict before changing the feed

Keep the same model and **A = 3**. On guide **C2**, predict these two cases before running them:

| Feed       | Questions to answer                                                                 |
|------------|-------------------------------------------------------------------------------------|
| $z = 0.02$ | Does this feed lie between the binodal endpoints? Is the lever-rule split feasible? |
| $z = 0.50$ | What is the sign of $g''$ ? What amounts does symmetry suggest?                     |

Then select the matching **Stable** and **Unstable** presets and click **Find equilibrium** → for each case.

**Pause for 5 minutes.** Record your prediction, Lab result and one reason for any correction. Continue only after both cases.

# Three feed states, two equilibrium outcomes

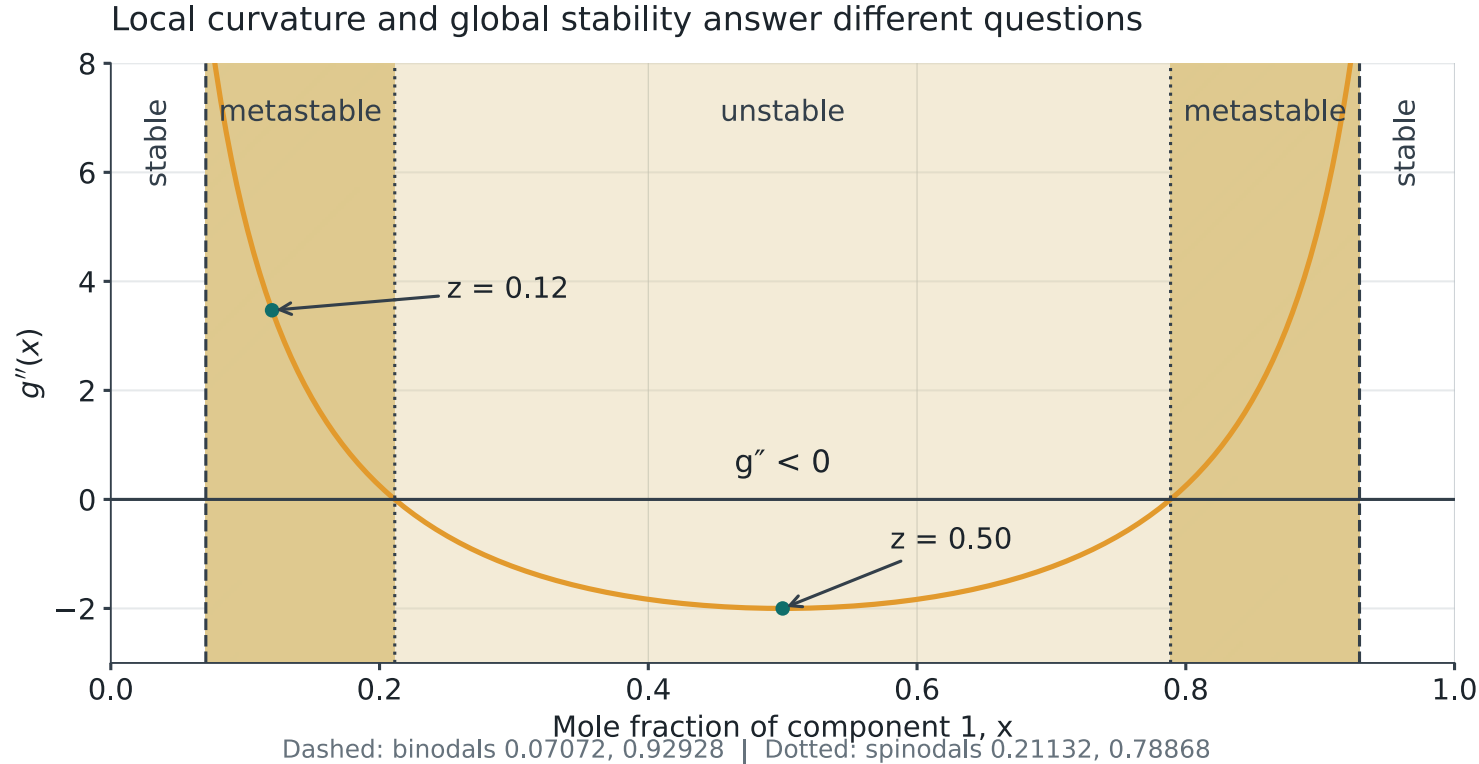
| Feed $z$ | $g''(z)$   | Homogeneous feed | Equilibrium                             |
|----------|------------|------------------|-----------------------------------------|
| 0.02     | +45.020408 | Stable           | One liquid, $x = z$                     |
| 0.12     | +3.469697  | Metastable       | Two liquids; $f^\beta = 0.057398$       |
| 0.50     | -2.000000  | Unstable         | Two liquids; $f^\alpha = f^\beta = 0.5$ |

For  $A = 3$ , the spinodals are **0.211325** and **0.788675**. They mark the change in local curvature, not the coexistence compositions.

At  $z = 0.02$ , the proposed binodal split gives  $f^\beta < 0$ . Do not use a line extended outside its contacts as a feasible two-phase mixture.

**Your action:** Guide C2: distinguish “classification of the initial homogeneous feed” from “stable equilibrium after allowing separation.”

# Locate the three regions on the same curve



Classification of homogeneous feeds for symmetric Margules  $A=3$ , with separate binodal and spinodal boundaries.

Between a binodal and its neighboring spinodal, a homogeneous feed is metastable. Inside the spinodals, it is locally unstable. Allowing separation gives two-liquid equilibrium throughout the binodal interval.

**Your action:** On guide C2, locate 0.02, 0.12 and 0.50. These labels classify the homogeneous feed; the lower common-tangent segment describes its equilibrium when separation is allowed.

# Your turn: solve a new feed

**Guide D1, page 4. Keep  $A = 3$  and set  $z = 0.35$ .**

1. Calculate  $g''(z)$  and classify the homogeneous feed locally.
2. Use the same endpoints to calculate  $f^\alpha$  and  $f^\beta$ .
3. Check  $f^\alpha x^\alpha + f^\beta x^\beta = z$ .
4. Calculate  $g(z)$  and  $g(z) - g_{\text{split}}$ .
5. In Lab 04, enter **Feed mole fraction  $z_1 = 0.35$**  and click **Find equilibrium** →. Explain any difference from your calculation.

**Pause for 8 minutes before the next slide.** The endpoints depend on the model and fixed conditions, not on the feed's position inside this tie line.

# Check your new-feed calculation

$$g''(0.35) = \frac{1}{0.35} + \frac{1}{0.65} - 6 = -1.604396.$$

$$f^{\beta} = \frac{0.35 - 0.07072018}{0.85855964} = 0.325289, \quad f^{\alpha} = 0.674711.$$

$$0.674711(0.07072018) + 0.325289(0.92927982) \approx 0.350000.$$

$$g(0.35) = 0.35 \ln(0.35) + 0.65 \ln(0.65) + 3(0.35)(0.65) = 0.03505336.$$

$$g(0.35) - g_{\text{split}} = \boxed{0.09339471}.$$

**Your action:** Correct D1 in a different color. The feed is locally unstable and its stable liquid equilibrium is the same pair of compositions, with different amounts.

# Save a result you can explain

**Guide C3, page 3.** At the case you want to keep:

1. In **Your explanation**, state A, z, the feed classification and the equilibrium phase amounts. Include one balance or energy comparison.
2. Click **Export study JSON** and keep the downloaded file with your worksheet.
3. To reopen it, expand **Study workspace • reopen and compare cases** near the top. Use **Load studies or a comparison JSON**, then **Restore** beside your case.
4. Click **Find equilibrium** → to recompute from restored inputs.

**If something differs:** check model, A and z first; then the selected view, rounding and whether you recalculated. Keep a screenshot and the study JSON when asking for help. No manual JSON editing is needed.

# Check the reasoning without the Lab

**Guide D2, page 4. Answer before opening the next slide.**

1. Can  $g''(z) > 0$  alone establish global stability?
2. What is fixed, and what changes, when  $z$  moves inside this tie line at fixed  $T$ ,  $P$  and  $A$ ?
3. Why does equality of chemical potentials alone not finish the stability test?
4. The common tangent lies below  $g(0.02)$  when extended left. Why is its binodal split not the equilibrium for this feed?

Use one short sentence for each. Keep these corrections with the original Week 3 worksheet; this review adds no form submission.

# Answers and reading

1. **No.** Positive curvature establishes local stability. A feasible distant split can still lower total Gibbs energy.
2. **Fixed:**  $x^\alpha$  and  $x^\beta$ . **Changing:** phase amounts according to the material balance.
3. It identifies a candidate. Check feasible amounts and a common tangent that supports the whole allowed Gibbs curve.
4. Since  $0.02 < x^\alpha$ , reproducing this feed with those endpoints would require a negative phase amount.

**Read further:** [MIT OpenCourseWare, Lecture 21: phase coexistence and stability](#). Our numerical values come from the stated synthetic Margules model, not a real-fluid dataset.

**Next:** Return to the [Week 3 study route](#). Use the [Lab 04 demonstration in the Week 3 video](#) if you need another screen walkthrough.