

Read the graph before using the Lab

Open: [Gibbs review slides](#) and [Lab 04: Liquid stability](#). Keep this guide and a calculator with **ln** beside them. No spreadsheet or code is needed.

Allow about **45 minutes**: read and calculate (20), compare in the Lab (15), then practice and check (10). Use only the parts you need to support your original Week 3 worksheet. This review adds no attendance or exit-ticket submission.

A1. Identify the question

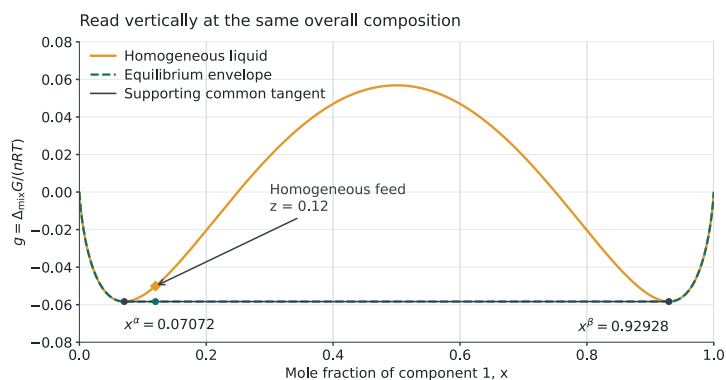
Consistency: Are data compatible with an applicable thermodynamic constraint? **Stability:** Which feasible state has the lowest total Gibbs energy at fixed T , P and total amounts?

A common tangent answers the question of: _____

A2. Read the axes and the state

We plot $g(x) = \Delta g_{\text{mix}}(x)/(RT)$, a dimensionless molar mixing energy. The horizontal variable $x = x_1$ describes a possible homogeneous liquid. The overall feed composition is $z = z_1$.

At a given z , the curve represents one homogeneous liquid. A feasible mixture of two compositions lies on the line segment joining their energies. Compare states at the **same** z . The affine pure-liquid reference cancels because the total amounts of both components are the same.



At $z = 0.12$: Mark the homogeneous point, the lower two-liquid point, and the two tangent contacts on the graph. Which state has lower energy? _____

A3. Keep the two tests separate

Test	What it establishes
Local curvature $g''(z)$	Positive: stable to sufficiently small composition fluctuations. Negative: locally unstable.
Global energy/support test	Compares all allowed states. A supporting common tangent lies on or below the whole curve.

Positive curvature does not rule out a lower-energy distant split. A negative mixing energy does not prove stability against two mixed liquids. All calculations here use a hypothetical binary liquid model; vapor and solids are excluded.

B. Work one case: $A = 3, z = 0.12$

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

$$g'(x) = \ln[x/(1 - x)] + 3(1 - 2x)$$

$$g''(x) = 1/x + 1/(1 - x) - 6$$

B1. Check local curvature

$$g''(0.12) = 8.333333 + 1.136364 - 6 = +3.469697.$$

This is locally stable; the global question is still open.

B2. Locate the common-tangent contacts

The general tangent condition is $g'(x^a) = g'(x^b) = [g(x^b) - g(x^a)]/(x^b - x^a)$. In this symmetric case the tangent is horizontal, so $x^b = 1 - x^a$ and $g'(x^a) = 0$.

The low-composition root is between 0.0707 and 0.0708. Refining it gives $x^a = 0.07072018$ and $x^b = 0.92927982$. Substitute x^a into g' to check a value near zero. The stationary point 0.50 has negative curvature and is not a binodal endpoint.

B3. Calculate amounts and check the balance

Use a basis of 1 mol of total feed. The mole-based phase fractions describe amounts of liquid phases, not compositions or vapor fractions.

$$f^b = (z - x^a)/(x^b - x^a)$$

$$= (0.12 - 0.07072018)/0.85855964 = 0.057398$$

$$f^a = 1 - f^b = 0.942602$$

$$0.942602(0.07072018) + 0.057398(0.92927982) \approx 0.120000$$

B4. Compare the energies at the same feed composition

Homogeneous calculation	Value
$0.12 \ln 0.12$	-0.25443162
$0.88 \ln 0.88$	-0.11249337
$3(0.12)(0.88)$	+0.31680000
Sum $g(z)$	-0.05012499

Both tangent contacts have $g = -0.05834135$. Thus $g_{\text{split}} = f^a g(x^a) + f^b g(x^b) = -0.05834135$. The decrease is $g(z) - g_{\text{split}} = 0.00821636$. Multiply by nRT for a total energy in joules when R is in $\text{J mol}^{-1} \text{K}^{-1}$.

B5. Complete the global test

Check $g(x) - \ell(x) \geq 0$ across the whole interval, where $\ell(x) = -0.05834135$. The candidate minima are the endpoints and stationary points: $d(0) = d(1) = 0.05834135$; $d(0.50) = 0.11519417$; $d(x^a) = d(x^b) = 0$. All are nonnegative. A coarse plot alone can miss a dip. **Conclusion:** the homogeneous $z = 0.12$ liquid is metastable; equilibrium is two liquids.

C. Reproduce, compare, save

C1. Reproduce the worked case in Lab 04

1. Open [Lab 04](#). Under **Explore a state**, choose **Metastable · A = 3, z₁ = 0.12**.
2. Confirm **Margules · 1 parameter, A = 3** and **Feed mole fraction z₁ = 0.12**. Click **Find equilibrium** →.
3. Set **View** → **Gibbs energy & common tangent**. Compare both contacts and the two energies with page 2. Open **Verify the equilibrium** to inspect the component balance residual.
4. Switch to **Local curvature**, then **Tangent-plane distance · feed stability**. Observe positive g'' but a negative minimum feed TPD.

Feed TPD uses the tangent at the **homogeneous feed**: $TPD(w) = g(w) - [g(z) + g'(z)(w - z)]$. Negative TPD rejects global stability of that feed. The trial minimizing w is not automatically an equilibrium endpoint. Do not confuse this tangent with the coexistence common tangent.

Record from the Lab	Your result	Expected
f^{α}, f^{β}		0.942602, 0.057398
Homogeneous / equilibrium g		-0.050125 / -0.058341
$g''(z)$ / sign of minimum TPD		+3.469697 / negative

C2. Predict, then run two other feeds

Keep $A = 3$. First predict without the output, then select the matching **Stable** or **Unstable** preset and click **Find equilibrium** →. Allow 5 minutes.

Feed	Your prediction	Observed equilibrium and reason
$z = 0.02$		
$z = 0.50$		

Checks after your attempt: at 0.02, one liquid and $g'' = +45.020408$; the proposed binodal split needs a negative fraction. At 0.50, the homogeneous liquid has $g'' = -2$ and equilibrium has equal amounts of two liquids. Spinodals 0.211325 and 0.788675 are local-curvature boundaries, not the binodal endpoints.

C3. Save evidence and reopen it

Write the settings, classification and one balance or energy comparison in **Your explanation**. Click **Export study JSON**. To reopen, expand **Study workspace · reopen and compare cases**, choose **Load studies or a comparison JSON**, select **Restore** beside the case, then click **Find equilibrium** →.

If results differ: check model, A , z , selected view and recalculation first. Keep the JSON and a screenshot when asking for help. You do not need to edit JSON manually.

D. Explain a new case yourself

D1. A = 3, z = 0.35: attempt before checking

Keep the same two endpoints. Allow about 8 minutes. Calculate by hand first, then enter **Feed mole fraction $z_1 = 0.35$** in Lab 04 and click **Find equilibrium** →.

Calculation	Your hand result	Lab comparison
$g''(0.35)$ and local classification		
f^α and f^β		
$f^\alpha_{X^\alpha} + f^\beta_{X^\beta}$		
Homogeneous $g(0.35)$		
$g(0.35) - g_{\text{split}}$		

D2. Check the reasoning without the verification panel

1. Why does positive curvature not finish a global stability test?

.....

2. What stays fixed when z changes inside a supported tie line?

.....

3. What must be checked after equal chemical potentials are found?

.....

4. Why is the binodal split infeasible for $z = 0.02$?

.....

Answers: uncover after your attempt

D1: $g'' = -1.604396$; locally unstable. $f^\alpha = 0.674711$, $f^\beta = 0.325289$. The balance gives 0.350000. $g(0.35) = 0.03505336$; $g_{\text{split}} = -0.05834135$; decrease = 0.09339471. The same two compositions coexist, with new amounts.

D2: (1) A distant feasible split may still lower total Gibbs energy. (2) Phase compositions stay fixed; amounts change. (3) Check feasible amounts/material balance and global support, not only equality. (4) The feed lies outside the endpoints, so a negative phase amount would be required.

Reading: [MIT OpenCourseWare, 3.020 Lecture 21](#). Return to the [Week 3 route](#) or the [Lab 04 screen demonstration](#). Keep corrections with the original worksheet; no repeat submission is required.