Fugacity, Chemical Potential and the Equilibrium Criterion

Module 2 · 2105603 Advanced Chemical Engineering Thermodynamics

Soorathep Kheawhom

9 August 2026

Fugacity is not corrected pressure.

It is the quantity constructed so that the ideal-gas equation
stays valid for a real fluid.

INTRODUCTION

What this module establishes

Chemical potential is the true driving force, it is unusable in raw form, and fugacity is what makes it usable. Then a result you were handed in Module 1 is proved.

The callback

Module 1 presented the Maxwell equal-area construction as a geometric recipe and asked you to accept it.

This module ends by deriving it from equality of fugacity. You were owed that proof.

Four questions

- Why is pressure not the driving force?
- How do you get φ out of an equation of state?
- What is the fugacity of a liquid?
- What follows from $f^L = f^V$?

PART I

Why pressure is not the driving force

Section 2.1 Three equalities at equilibrium, and the one that does the work.

Three equalities

Two of them are familiar. The third is the one this course is about.

$$T^{\alpha} = T^{\beta} \qquad P^{\alpha} = P^{\beta} \qquad \mu_i^{\alpha} = \mu_i^{\beta}$$

Thermal

Equal temperature. Otherwise heat flows, and the state is not equilibrium.

Mechanical

Equal pressure — for a flat interface. Otherwise the interface accelerates. **This holds for a real fluid exactly as it does for an ideal one.**

Chemical

Equal chemical potential. Otherwise matter flows from high μ to low μ, and that is the transfer every separation process exists to control.

Read the middle card again. Nothing in this module says the pressure is unequal in a real fluid. What is lost is the simple link between pressure and chemical potential — not the mechanical equality itself.

The ideal gas is a special case

For an ideal gas, pressure measures the chemical driving force directly. That is why it feels like a driving force — and why the feeling misleads.

$$\left(\frac{\partial \mu}{\partial P}\right)_T = v = \frac{RT}{P} \qquad \Longrightarrow \qquad \mathrm{d}\mu = RT\,\mathrm{d}\ln P$$

$$\mu = \mu^\circ + RT \ln \frac{P}{P^\circ}$$

Why it fails

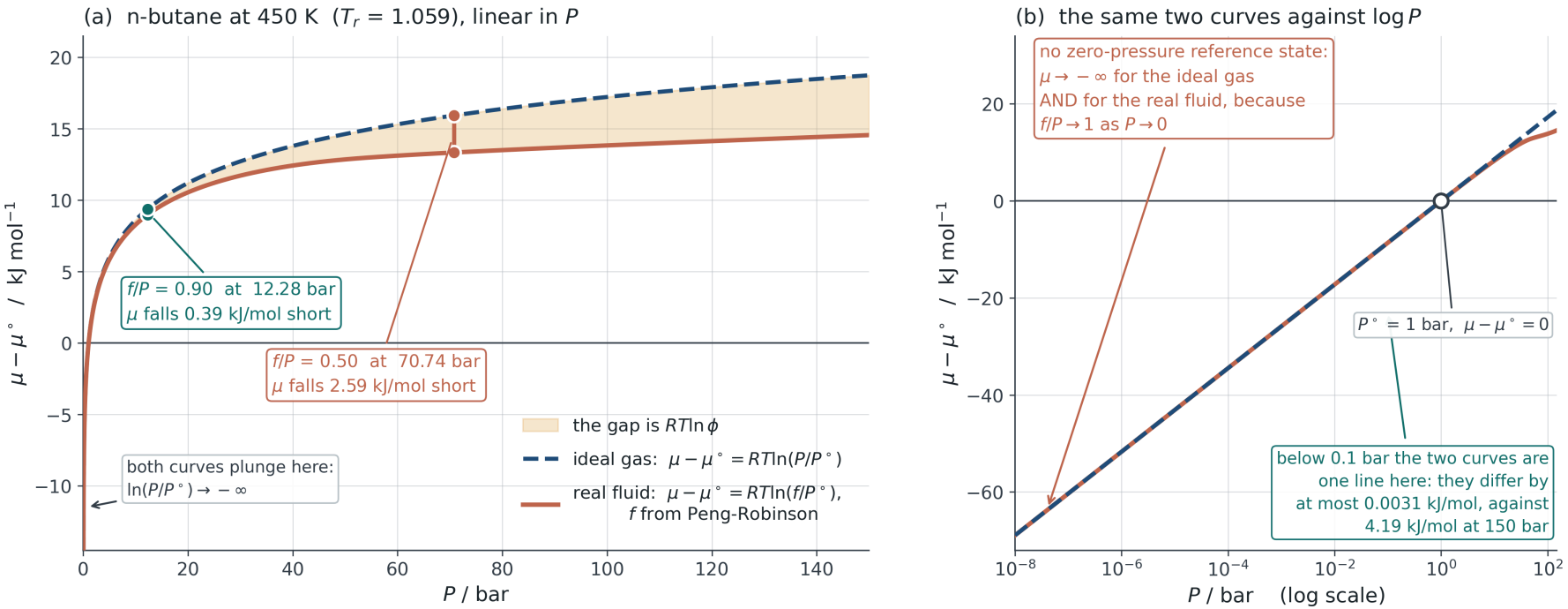
For a real fluid $v \neq RT/P$, so $\mathrm{d}\mu = v\,\mathrm{d}P$ no longer collapses to a logarithm in P. The relation between the measurable quantity and the driving force is broken.

And a second problem

$\mu \to -\infty$ as $P \to 0$, for **every** fluid, ideal or not. A zero-pressure reference state is therefore impossible — which is why the definition on the next slide is written as a *ratio* from the start.

Both curves diverge

The logarithm is the whole difficulty: it separates the two curves at high P and it destroys both of them at $P = 0$



n-butane, T_c = 425.12 K, P_c = 37.96 bar, ω = 0.2 [Yaws, log10(mmHg), T in C; Tc/Pc/omega Poling et al.].
Fugacity from `vlekit.cubic.PengRobinson.phi`, 1976 α function, root chosen by lower G; at T_r = 1.059 there is only one root, so no phase choice arises.
ASSUMED (a definition, not a measurement): P° = 100 kPa and the standard state is the ideal gas at P°. RT = 3.7415 kJ/mol at 450 K.
At 150 bar, f/P = 0.3267, so μ falls 4.19 kJ/mol short of the ideal-gas value.

F2.1 · Ideal and real chemical potential on one axis. Both fall without bound as $P \to 0$; they separate at high pressure.

The definition

Define the quantity that keeps the logarithmic form true. Everything else follows.

$$\mathrm{d}\mu \equiv RT\,\mathrm{d}\ln f \qquad \text{with} \qquad \frac{f}{P} \to 1 \;\text{ as }\; P \to 0 \qquad \Longrightarrow \qquad \mu = \mu^\circ + RT\ln\frac{f}{f^\circ}$$

What it is

A *definition*, not a derivation. f is whatever it has to be for the middle equation to hold. The second condition fixes the arbitrary constant by anchoring f to P in the limit where they must agree.

Always a ratio

Write $\mu - \mu^\circ = RT\ln(f/f^\circ)$ from the first slide and never write anything else. Absolute μ and absolute f are not measurable; only ratios against a stated reference are.

The trap ahead

The reference state f° is what students get wrong in Modules 3, 4 and 6 — Lewis-Randall against Henry, gas against liquid against solute. Fix the habit of naming it now.

PART II

The fugacity coefficient

Section 2.2 Where the equation of state finally does something other than plot an isotherm.

From the equation of state

$\varphi = f/P$, and it comes out of the same residual property integral you already met.

$$\ln\varphi = \int_0^P (Z-1)\,\frac{\mathrm{d}P}{P} \qquad\qquad \ln\varphi = \frac{1}{RT}\int_\infty^V \left[\frac{RT}{V} - P\right]\mathrm{d}V - \ln Z + (Z-1)$$

Which form, and why

The left form needs Z as a function of P. A cubic equation of state is **pressure-explicit** — it gives $P(V)$, not $V(P)$ — so evaluating it would mean solving the cubic at every integration point.

The right form integrates over volume instead, and a cubic can be integrated analytically. That is why every implementation uses it.

The connection back

This is the same integral that produced the residual enthalpy and entropy in Module 1. Nothing new has been introduced — the departure-function machinery is being asked a different question.

Peng-Robinson in closed form

Derive it rather than quote it. The integral is elementary and the result is used in every remaining module.

$$\ln\varphi = Z - 1 - \ln(Z - B) - \frac{A}{2\sqrt{2}\,B}\,\ln\left[\frac{Z + (1+\sqrt{2})B}{Z + (1-\sqrt{2})B}\right]$$

$$A = \frac{aP}{R^2T^2}, \qquad B = \frac{bP}{RT}$$

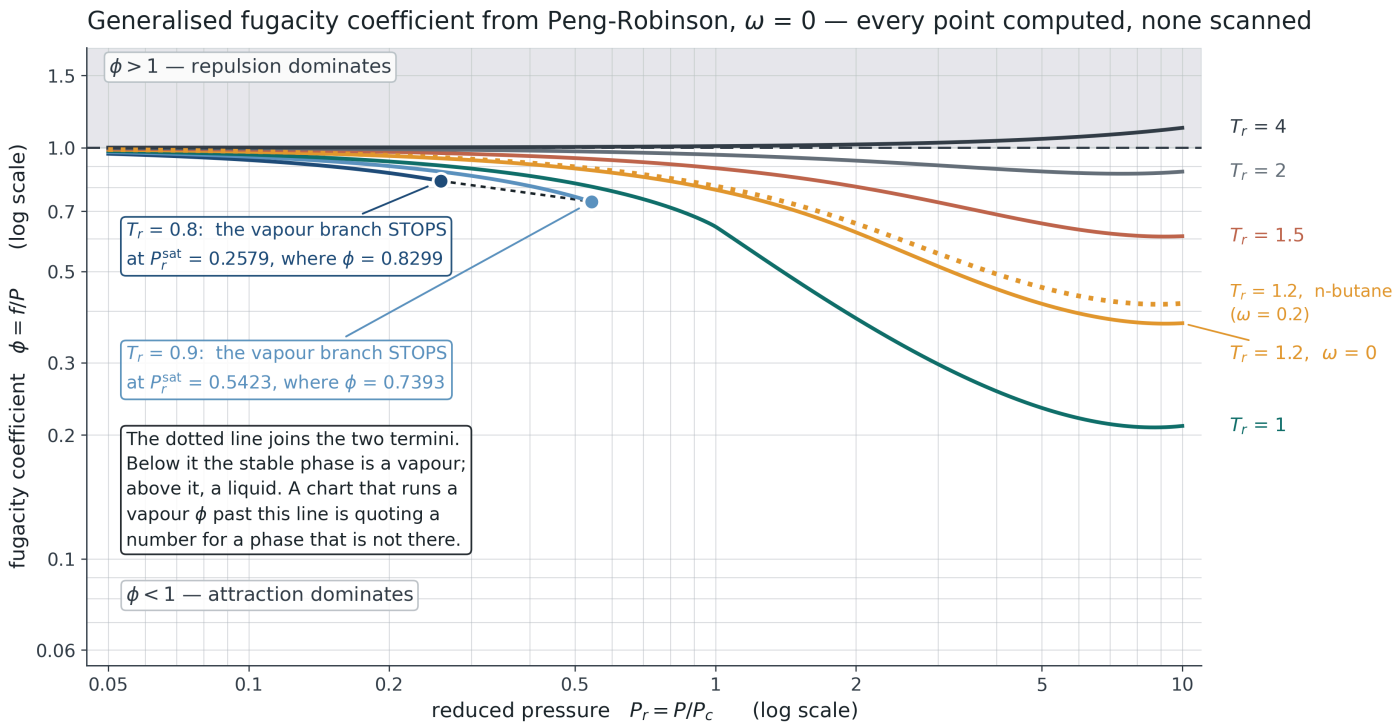
Where each term comes from

$Z - 1 - \ln(Z - B)$ is the repulsive part — the excluded volume. The logarithm with the $\sqrt{2}$ is the attractive part, and the $\sqrt{2}$ is there only because Peng-Robinson put b in two places in the denominator.

The root question

Below the critical temperature the cubic has three roots. The largest is the vapour, the smallest the liquid, and the middle one is mechanically unstable and meaningless. Choosing between the two outer roots by the lower φ — equivalently the lower Gibbs energy — is how a code decides which phase it is looking at.

The whole pressure range at once



ϕ from `vlekit.cubic.PengRobinson.ln_phi` (1976 α, vapour root); the saturation termini from `vlekit.cubic.psat`, which solves $g^L = g^V$ on the same equation of state.
T_c = 300 K and P_c = 5000 kPa carry the reduced variables and then cancel out of $\phi(T_r, P_r)$: this is not a chart of any substance.
ONE ACENTRIC FACTOR, ASSUMED: $\omega = 0$ on every solid curve. That single choice is what "generalised" means here, and it is the chart's only real assumption.
The dotted curve is n-butane at the same $T_r = 1.2$ with its library $\omega = 0.200$: at $P_r = 10$ it reads 0.4181 against 0.3742, a departure of 11.7 %, and the departure grows with ω. Read the solid curves as a first estimate, never as the answer.

F2.2 · Generalised chart computed from Peng-Robinson at $\omega = 0$, not scanned from a textbook. The subcritical curves stop at saturation.

PART III

The fugacity of a liquid

Section 2.3 Anchor it at saturation, then carry it to any pressure.

At saturation, and away from it

The liquid has no low-pressure limit to be anchored to, so it is anchored to the vapour it is in equilibrium with.

$$f^{L}(T, P^{\mathrm{sat}}) = f^{V}(T, P^{\mathrm{sat}}) = \varphi^{\mathrm{sat}} P^{\mathrm{sat}}$$

$$f^{L}(T, P) = \varphi^{\mathrm{sat}} P^{\mathrm{sat}} \underbrace{\exp\left[\frac{v^{L}(P - P^{\mathrm{sat}})}{RT}\right]}_{\text{Poynting factor}}$$

Why this works

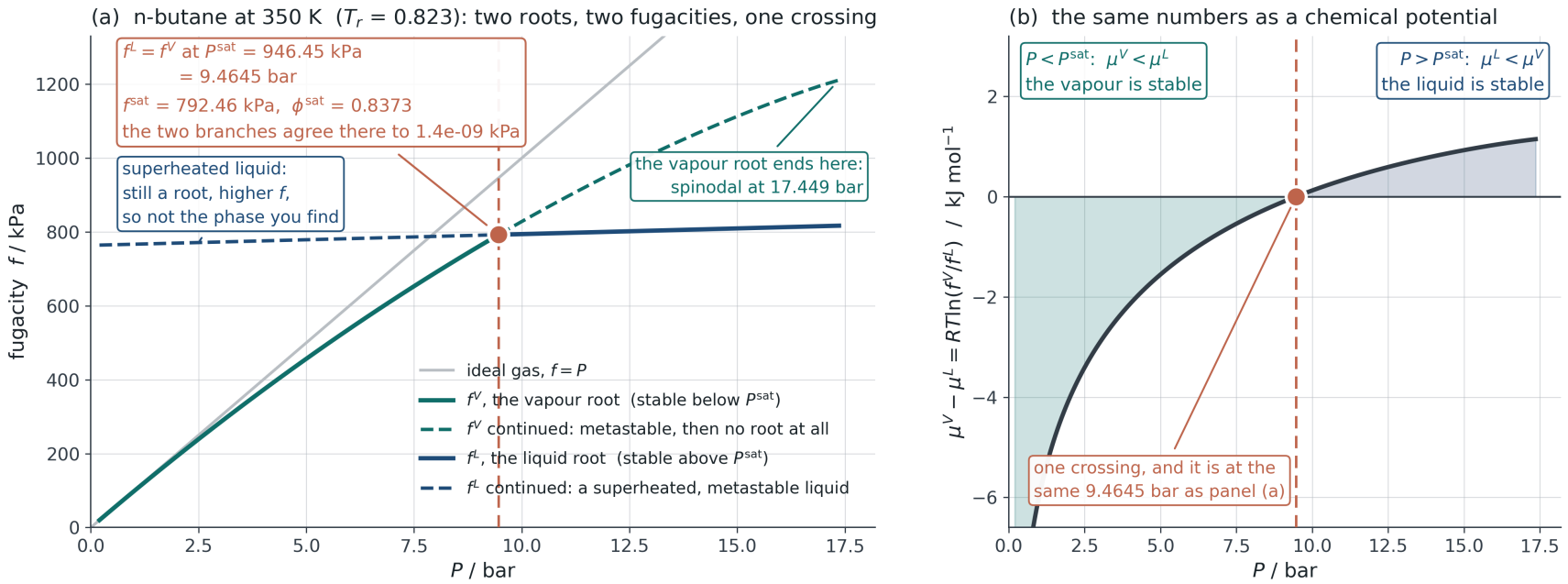
The liquid is nearly incompressible, so v^{L} can be taken outside the integral $\int v \, \mathrm{d}P$. Everything hard about the liquid has been pushed into P^{sat} and φ^{sat}, both of which are properties of the saturated state and both of which are measurable.

The hypothetical liquid

Above the critical temperature there is no P^{sat} and no liquid to anchor to. The reference becomes a *hypothetical* subcooled or superheated liquid, and the resulting arbitrariness reappears in Module 4 as the Lewis-Randall reference for a component that cannot exist pure at those conditions.

Fugacity across the saturation line

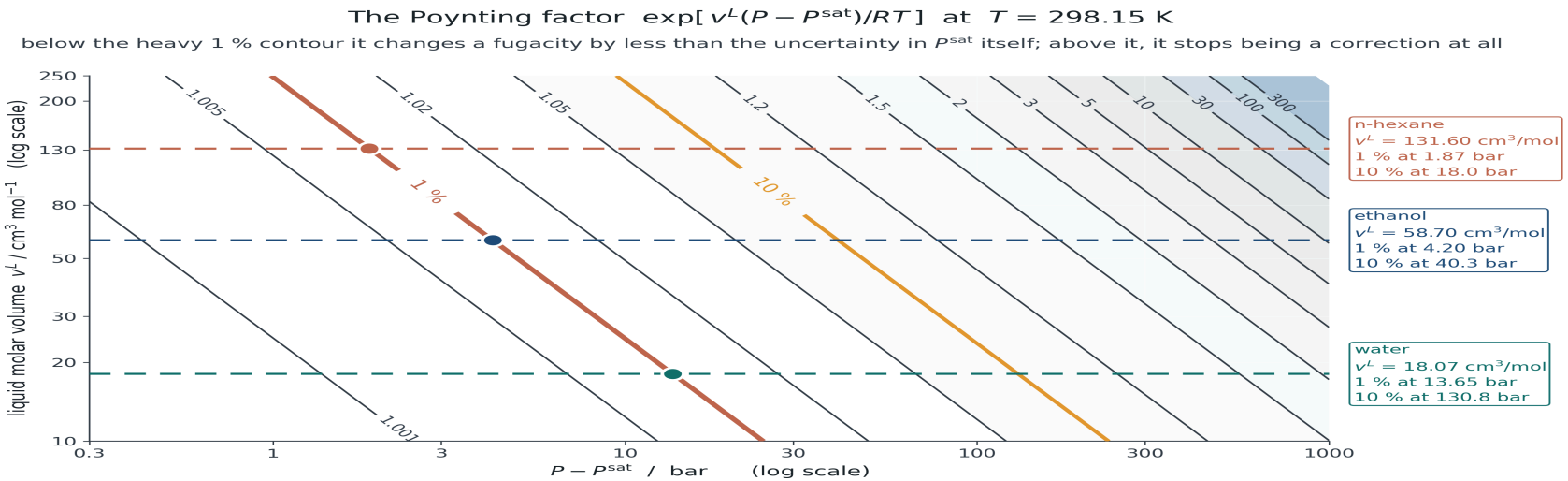
The equation of state offers two answers at every pressure; the equilibrium criterion picks one, and they are equal only at P^{sat}



n-butane: T_c = 425.12 K, P_c = 37.96 bar, ω = 0.2 [Yaws, log10(mmHg), T in C; Tc/Pc/omega Poling et al.].
Fugacities from `vlekit.cubic.PengRobinson.ln_phi` with the root forced to 'liquid' and to 'vapour'; P^{sat} from `vlekit.cubic.psat`;
the spinodals from $(\partial P/\partial v)_T = 0$ on the same isotherm. ASSUMED: nothing beyond the library constants above and the 1976 α function.
Peng-Robinson puts P^{sat} at 946.45 kPa; the library Antoine correlation puts it at 932.97 kPa, 1.4 % lower.
The figure uses the equation of state throughout so that both branches come from one model — the discrepancy is the cubic's, and it is stated rather than patched.
The liquid root survives down to the liquid spinodal at -60.65 bar, which is negative, so it exists everywhere on this axis; the vapour root dies at 17.449 bar.

F2.3 · The two branches meet at P^{sat}. The dashed continuations are the metastable and unstable extensions of each.

When the Poynting factor matters



ASSUMED: $T = 298.15$ K. RT enters only as a scale factor, so every contour slides to the right in proportion to T.
ASSUMED: v^L constant, independent of pressure — that is what the Poynting factor is. A real liquid at 1000 bar is denser, so the true $\int v^L\,dP$ is smaller than the exponential drawn here. v^L values are `vlekit.data.LIBRARY`, one number per component with no temperature attached to it.
The contours are exactly straight because $v^L(P - P^{sat})$ is constant along each one; the marked pressures follow from $P - P^{sat} = RT\ln(1.01)/v^L$ and nothing else.
P^{sat}(298.15 K) from the library Antoine constants is 3.19 kPa for water, 7.90 kPa for ethanol, 20.20 kPa for n-hexane — all far below 1 bar, so here $P - P^{sat}$ and P are the same number.

Quantified, not asserted

“Usually negligible” is not a statement anyone can act on. At 298 K the correction reaches one per cent at about 14 bar for water, 4 bar for ethanol and under 2 bar for n-hexane — because the exponent scales with v^L, and a bulky molecule has three times the molar volume of water.

The rule that follows

Drop it deliberately, with the pressure and the molar volume in front of you, and record that you dropped it. Never drop it because a textbook said it was small for a system it was not describing.

F2.4 · The one per cent contour, with three real liquids marked.

PART IV

The criterion, and a proof

Section 2.4 One criterion, two classical results — and the answer to a question asked three weeks ago.

Equality of fugacity

Equal chemical potential becomes equal fugacity the moment the definition is substituted.

$$\mu^L = \mu^V \quad \text{and} \quad \mu = \mu^\circ + RT \ln \frac{f}{f^\circ} \qquad \Longrightarrow \qquad \boxed{f^L = f^V}$$

Why this is the useful form

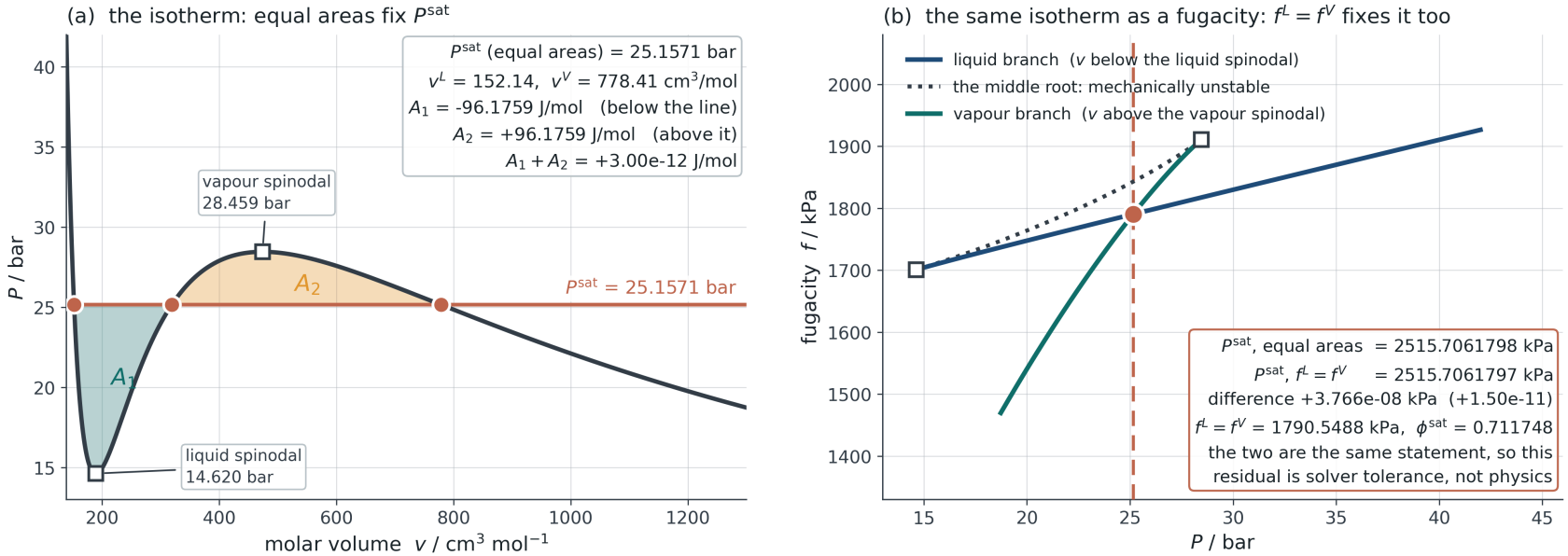
μ is not measurable and not computable without a reference. f has the units of pressure, tends to P in a limit everyone agrees on, and comes out of an equation of state in closed form. The criterion has been made *arithmetic*.

How a simulator uses it

Locating P^{sat} is a one-dimensional root find on $\ln f^L - \ln f^V = 0$, with both fugacities from the same cubic. That is exactly what `cubic.psat` in the course toolkit does, and exactly what a commercial package does.

The equal-area construction, proved

Equal areas and equal fugacities are one statement: $\int_{v^L}^{v^V} v\,\mathrm{d}P = g^V - g^L = RT\ln(f^V/f^L) = 0$



n-butane at 400 K (T_r = 0.941), Peng-Robinson with T_c = 425.12 K, P_c = 37.96 bar, ω = 0.2 [Yaws, log10(mmHg), T in C; Tc/Pc/omega Poling et al.], 1976 α.
LEFT: P^{sat} from Brent on $F(v^V) - F(v^L) - P^{sat}(v^V - v^L)$, with F the closed-form antiderivative of $P(v)$;
the two areas are then re-integrated numerically with `scipy.integrate.quad` as an independent check.
RIGHT: $\ln\phi = G^{res}/RT$ from `PengRobinson.gres_RT` at $Z = Pv/RT$ along the same isotherm — that is what puts the unstable middle branch on the figure;
P^{sat} from `vlekit.cubic.psat`. Open squares are the spinodals, where a branch runs out of roots.
ASSUMED: only the constants above and the choice of 400 K, picked because both spinodal pressures are positive there so the construction fits on one linear axis.
Quadrature check: $A_1 + A_2$ = +3.00e-12 J/mol against the closed form's -5.68e-14 J/mol.

F2.5 · The Module 1 construction and the fugacity criterion, on the same isotherm. Agreement: 4×10^{-8} *kPa out of 2515.7.*

The Clapeyron equation, from the same place

One criterion, differentiated along the saturation line, gives the second classical result.

$$f^{\,L}(T, P^{\mathrm{sat}}) = f^{\,V}(T, P^{\mathrm{sat}}) \ \text{ for all } T \qquad \Longrightarrow \qquad \frac{\mathrm{d}P^{\mathrm{sat}}}{\mathrm{d}T} = \frac{\Delta h^{\mathrm{vap}}}{T\,\Delta v^{\mathrm{vap}}}$$

The step

Differentiate the equality along the coexistence curve. The Gibbs energies stay equal, so $\mathrm{d}g^{\,L} = \mathrm{d}g^{\,V}$, and with $\mathrm{d}g = -s\,\mathrm{d}T + v\,\mathrm{d}P$ the result falls out in two lines.

Why it matters here

Two results that arrive in most courses as separate facts — an equal-area recipe and a slope formula — are consequences of one statement. That is what it means for a subject to have a structure rather than a syllabus.

Where this goes next

Everything so far has been a pure substance. Mixtures need one more idea, and it arrives in Module 3.

The preview

In a mixture each species has its own fugacity in the mixture, $\hat{f}_i$, and its own coefficient $\hat{\varphi}_i = \hat{f}_i/(y_i P)$. The equilibrium criterion becomes $\hat{f}_i^{\,L} = \hat{f}_i^{\,V}$ for **every** species.

What is missing

$\hat{f}_i$ is a *partial molar* quantity — a composition derivative — and the machinery for those is Module 3. Until then the symbol is a promise, not a definition.

*The spine: an equation of state gives P-V-T → **fugacity gives chemical potential a usable form** → an equation of state lets you compute fugacity → equality of fugacity predicts phase equilibrium. You are at the second step.*

CLOSING

What you must be able to do

The module in six statements.

1. **Name the three equalities**
   and say which one drives mass transfer — and that pressure is still equal in a real fluid.

2. **Say why fugacity was invented.**
   To keep the ideal-gas logarithmic form valid, and because μ diverges at zero pressure.

3. **Get φ from an equation of state.**
   Including why the volume-explicit form is the one a cubic can use.

4. **Compute the fugacity of a liquid**
   from P^{sat}, φ^{sat} and Poynting — and say when the last term matters.

5. **Derive the equal-area construction and Clapeyron**
   from $f^L = f^V$, and say why they are the same statement rather than two.

6. **Always name the reference state.**
   Every fugacity is a ratio against something.