Worked Examples

Evolution of Equations of State: A Physics-Driven Perspective

Every numerical value below is reproduced by the accompanying Python script `worked_examples.py`.

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Chapter 1

Worked examples

This chapter works ten problems in full. They are ordered so that each uses the result of the previous one: a compressibility factor, then the cubic that produces it, then the selection of the correct root, then the comparison of models, then the temperature dependence that separates them, then the fugacity coefficient, then the saturation pressure, then the mixture, then the departure functions, and finally the corresponding-states framework in which all of it sits.

Three conventions apply throughout. First, all critical constants and acentric factors are taken from §8 of the design specification, and the gas constant is $R = 8.314\,\mathrm{J\,mol^{-1}\,K^{-1}} = 83.14\,\mathrm{bar\,cm^3\,mol^{-1}\,K^{-1}}$; the second form is used wherever pressures are in bar and volumes in $\mathrm{cm^3\,mol^{-1}}$, and the two are the same constant because $1\,\mathrm{bar\,cm^3} = 0.1\,\mathrm{J}$. Second, every numerical value printed below is produced by `code/worked_examples.py`; nothing is estimated. Third, results are quoted to four significant figures, which is well beyond the accuracy of the models but is necessary if a reader is to reproduce the arithmetic exactly.

Example 1: Compressibility factor and its engineering consequence

Problem. Methane is stored and transported at $T = 300\,\mathrm{K}$ and $P = 100\,\mathrm{bar}$. Using $T_c = 190.6\,\mathrm{K}$, $P_c = 45.99\,\mathrm{bar}$ and $\omega = 0.012$, compute the compressibility factor and molar volume from the ideal gas law and from the Peng–Robinson equation. Convert the difference into (i) the error in the mass of methane held in a $50\,\mathrm{m^3}$ vessel at that condition, taking the molar mass as $16.043\,\mathrm{g\,mol^{-1}}$, and (ii) the error in the volumetric flow that a compressor handling $100\,\mathrm{kmol\,h^{-1}}$ must accept.

Strategy. The ideal gas law gives $Z = 1$ directly. The Peng–Robinson equation is solved in the dimensionless form $Z^3 - (1-B)Z^2 + (A - 2B - 3B^2)Z - (AB - B^2 - B^3) = 0$ with $A = a(T)P/(RT)^2$ and $B = bP/(RT)$. Because $Z = PV/(RT)$ is exactly the ratio of the real to the ideal molar volume, every volumetric quantity scales with Z and every quantity inversely proportional to volume scales with $1/Z$; the two engineering consequences are therefore obtained without further modelling.

Solution.

1. Reduced state: $T_r = T/T_c = 300/190.6 = 1.574$ and $P_r = P/P_c = 100/45.99 = 2.174$. The fluid is supercritical and strongly compressed.
2. Ideal gas: $V^{ig} = RT/P = (83.14)(300)/100 = 249.4\,\mathrm{cm^3\,mol^{-1}}$ with $Z = 1$ by definition.
3. Peng–Robinson constants: $\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 = 0.3931$, $\alpha = [1 + \kappa(1 - \sqrt{T_r})]^2 = 0.8099$, $a(T) = 0.45724\,R^2T_c^2\alpha/P_c = 2.022 \times 10^6\,\mathrm{bar\,cm^6\,mol^{-2}}$ and $b = 0.07780\,RT_c/P_c = 26.81\,\mathrm{cm^3\,mol^{-1}}$.
4. Dimensionless groups: $A = aP/(RT)^2 = 0.3250$ and $B = bP/(RT) = 0.1075$, so the cubic reads

$$Z^3 - 0.8925\,Z^2 + 0.07540\,Z - 0.02214 = 0.$$

   It has one real root, $Z = 0.8339$, and one complex conjugate pair.
5. Molar volume: $V = ZRT/P = (0.8339)(83.14)(300)/100 = 208.0\,\mathrm{cm^3\,mol^{-1}}$, smaller than the ideal-gas value by $41.42\,\mathrm{cm^3\,mol^{-1}}$.
6. Vessel inventory: $n = V_{\mathrm{vessel}}/V$. The ideal gas law gives $n^{ig} = 50\,\mathrm{m^3}/V^{ig} = 200.5\,\mathrm{kmol}$ and $m^{ig} = 3216\,\mathrm{kg}$, whereas Peng–Robinson gives $n = 240.4\,\mathrm{kmol}$ and $m = 3856\,\mathrm{kg}$. The ideal gas law understates the inventory by $640.4\,\mathrm{kg}$, that is by $1 - Z = 16.61\,\%$.
7. Compressor suction: $\dot{Q} = \dot{n}V$. The ideal gas law gives $\dot{Q}^{ig} = 24.94\,\mathrm{m^3\,h^{-1}}$ against the real $20.80\,\mathrm{m^3\,h^{-1}}$, so a machine sized on the ideal gas law is oversized by $1/Z - 1 = 19.91\,\%$.
8. Summary of the two routes:

quantity	ideal gas	Peng–Robinson	error of the ideal gas law
Z	1	0.8339	+0.1661
V / cm^3 mol^{-1}	249.4	208.0	19.91 %
inventory in 50 m^3 / kg	3216	3856	−16.61 %
suction volume / m^3 h^{-1}	24.94	20.80	19.91 %

The two percentages differ because one is referred to the real state and the other to the ideal state; the underlying error is the same single factor Z.

Check. Back-substituting $V = 208.0\,\mathrm{cm^3\,mol^{-1}}$ into the pressure-explicit form of the equation returns 100.0000 bar, so the root is exact. As an independent route, the second virial coefficient implied by the Peng–Robinson equation is $B_2 = b - a/(RT) = -54.26\,\mathrm{cm^3\,mol^{-1}}$, and the two-term virial expansion gives $Z = 1 + B_2P/(RT) = 0.7825$. This has the correct sign and the correct order of magnitude but is 0.0515 too low, which is the expected behaviour of a density expansion truncated after one term at $P_\mathrm{r} = 2.174$.

Engineering comment. A single number, $Z = 0.8339$, moves the vessel inventory by 640 kg and the compressor suction volume by one fifth. In custody transfer the first figure is a direct financial error repeated on every transaction; in machine selection the second is a capital error frozen at the purchase order. Neither can be recovered by tuning downstream, which is why the volumetric closure is chosen before any unit operation is sized.

Example 2: van der Waals parameters and the cubic in V

Problem. For carbon dioxide at $T = 300\,\mathrm{K}$ and $P = 60\,\mathrm{bar}$, with $T_\mathrm{c} = 304.2\,\mathrm{K}$ and $P_\mathrm{c} = 73.83\,\mathrm{bar}$, obtain the van der Waals constants a and b from the critical constants, write the resulting cubic in molar volume, find all its real roots, and select the physically correct one by an explicit criterion. Compare the van der Waals critical compressibility factor with the measured value, taking $V_\mathrm{c} = 94.0\,\mathrm{cm^3\,mol^{-1}}$ from the literature.

Strategy. Imposing $(\partial P/\partial V)_T = (\partial^2 P/\partial V^2)_T = 0$ at the critical point gives $a = 27R^2T_\mathrm{c}^2/(64P_\mathrm{c})$ and $b = RT_\mathrm{c}/(8P_\mathrm{c})$. Multiplying $P = RT/(V-b) - a/V^2$ by $V^2(V-b)$ produces a cubic in V that is solved numerically. Root selection uses three tests in order: physical admissibility $V > b$, mechanical stability $(\partial P/\partial V)_T < 0$, and, if two roots survive, the lower molar Gibbs energy, which because $G - G^{ig} = RT\ln\varphi$ at fixed T and P is the smaller $\ln\varphi$.

Solution.

1. Constants: $a = 27(83.14)^2(304.2)^2/[64(73.83)] = 3.655 \times 10^6\,\mathrm{bar\,cm^6\,mol^{-2}}$ and $b = (83.14)(304.2)/[8(73.83)] = 42.82\,\mathrm{cm^3\,mol^{-1}}$.
2. Reduced state: $T_\mathrm{r} = 0.9862$, $P_\mathrm{r} = 0.8127$. The state is subcritical and close to the critical point.
3. The cubic. With $RT/P = 415.7\,\mathrm{cm^3\,mol^{-1}}$,
$$V^3 - \left(b + \frac{RT}{P}\right)V^2 + \frac{a}{P}V - \frac{ab}{P} = 0 \implies V^3 - 458.5\,V^2 + 6.092\times10^4\,V - 2.608\times10^6 = 0,$$
with V in $\mathrm{cm^3\,mol^{-1}}$.
4. Roots: one real root $V = 266.9\,\mathrm{cm^3\,mol^{-1}}$ and one complex conjugate pair $95.81 \pm 24.36\,i$, which has no physical meaning. Hence $Z = PV/(RT) = 0.6420$, $\ln\varphi = -0.2890$ and $\varphi = 0.7490$.
5. Selection. The single real root satisfies $V > b$ and $(\partial P/\partial V)_T = -0.1123\,\mathrm{bar\,mol\,cm^{-3}}$, so it is admissible and mechanically stable; with only one root the choice is forced. The van der Waals saturation pressure at this temperature, obtained from the isofugacity condition, is 69.82 bar, so $P = 60\,\mathrm{bar}$ lies below it and the fluid is a vapour, consistent with the single vapour-like root. For comparison the Peng–Robinson equation gives $P^{sat} = 67.22\,\mathrm{bar}$ at the same temperature, and at the specified state it gives $Z = 0.5663$ and $V = 235.4\,\mathrm{cm^3\,mol^{-1}}$, so the van der Waals molar volume is high by 13.38 % even in the vapour.

6. The criterion exercised. At 70 bar and the same temperature the same cubic has three real roots, so the selection rule has work to do:

branch	Z	V / cm^3 mol^{-1}	$\ln\varphi$
liquid	0.2882	102.7	−0.355182
middle	0.3766	134.2	−0.354537
vapour	0.4554	162.3	−0.354739

   The middle root is discarded on mechanical stability grounds, and $G^V - G^L = RT(\ln\varphi^V - \ln\varphi^L) = 1.104\,\mathrm{J\,mol^{-1}} > 0$ selects the liquid, consistent with $P > P^{sat}$. The three fugacity coefficients agree to three decimal places because 70 bar is only 0.18 bar above the saturation pressure of the model at this temperature; the discrimination between phases becomes numerically delicate near saturation, and more so near the critical point, which is one reason flash algorithms are written in terms of $\ln\varphi$ rather than φ.

7. Critical compressibility: van der Waals predicts $Z_c = 3/8 = 0.3750$, whereas $P_c V_c/(RT_c) = (73.83)(94.0)/[(83.14)(304.2)] = 0.2744$. The model overpredicts Z_c, and equivalently $V_c = 3b = 128.5\,\mathrm{cm^3\,mol^{-1}}$ against $94.0\,\mathrm{cm^3\,mol^{-1}}$, by 36.66 %.

Check. Evaluating the cubic in Z at the critical point using the same constants returns $Z = 0.374997$ against the analytic $3/8 = 0.375000$, so the parameter set is internally consistent and the residual is the accuracy attainable at a triple root. The units check as well: a has the dimensions of pressure times volume squared, so a/P has those of $(\mathrm{cm^3\,mol^{-1}})^2$ and ab/P those of $(\mathrm{cm^3\,mol^{-1}})^3$, which are exactly the dimensions required of the coefficients of V and of V^0 in a cubic whose leading term is V^3.
Engineering comment. The van der Waals equation places the fluid on the correct side of the saturation curve and returns a vapour volume of the right order, but its critical volume is too large by more than a third. Since V_c sets the scale of the entire liquid branch, any liquid density taken from this equation is unusable for sizing, inventory or pump calculations. That single defect, and not the vapour-phase behaviour, is what drove the developments of Chapters 8 to 10.

Example 3: Three real roots and the selection of the stable branch

Problem. *n*-butane at $T = 350\,\mathrm{K}$ and $P = 10\,\mathrm{bar}$, with $T_c = 425.1\,\mathrm{K}$, $P_c = 37.96\,\mathrm{bar}$ and $\omega = 0.200$, is described by the Peng–Robinson equation. Obtain all three real roots of the cubic in Z, identify the vapour, unstable and liquid branches, and decide which phase is thermodynamically stable by comparing $\ln\varphi$, equivalently the molar Gibbs energy.
Strategy. At $T_r = 0.8233$ the isotherm is subcritical, so the cubic may have three real roots. The smallest and largest are the liquid and vapour branches; the middle root lies on the segment where $(\partial P/\partial V)_T > 0$ and is mechanically unstable, hence never physical. Between the two admissible roots the stable phase is the one with the lower molar Gibbs energy, and since both are evaluated at the same T and P, comparing $G - G^{ig} = RT\ln\varphi$ is equivalent to comparing G itself.
Solution.

1. Parameters: $\kappa = 0.6723$, $\alpha = 1.1284$, $a(T) = 1.698\times10^7\,\mathrm{bar\,cm^6\,mol^{-2}}$ and $b = 72.44\,\mathrm{cm^3\,mol^{-1}}$, hence $A = 0.2005$ and $B = 0.02489$.
2. The cubic: $Z^3 - 0.9751\,Z^2 + 0.1489\,Z - 0.004356 = 0$, with the three real roots listed below.
3. Branch properties, with $V = ZRT/P$ and $\ln\varphi$ from the Peng–Robinson expression of Chapter 10:

branch	Z	V / cm^3 mol^{-1}	$\ln\varphi$	φ	$(\partial P/\partial V)_T$ / bar mol cm^{-3}
liquid	0.03867	112.5	−0.2301	0.7944	−6.942
middle (unstable)	0.1418	412.5	+0.06694	1.069	+0.07460
vapour	0.7947	2312	−0.1885	0.8282	−0.003287

   The middle root is eliminated at once: its $(\partial P/\partial V)_T$ is positive, so a fluctuation that compresses it

lowers its pressure and the compression runs away.

4. Stability test between the survivors:

$$G^V - G^L = RT\left(\ln\varphi^V - \ln\varphi^L\right) = (8.314)(350)\left[-0.1885-(-0.2301)\right] = 121.2\,\mathrm{J\,mol^{-1}} > 0,$$

so the liquid has the lower molar Gibbs energy and is the stable phase.

Check. Solving the isofugacity condition independently gives $P^{sat}(350\,\mathrm{K}) = 9.469\,\mathrm{bar}$ for this model. The state pressure 10 bar exceeds it, so the fluid must be a subcooled liquid; this is exactly what the Gibbs comparison returned, by a different route.

Engineering comment. Selecting the vapour root here would put $V = 2312\,\mathrm{cm^3\,mol^{-1}}$ in place of $112.5\,\mathrm{cm^3\,mol^{-1}}$, a factor of 20.55 in molar volume and therefore in density. A $50\,\mathrm{m^3}$ drum would be reported as holding 1.257 t instead of 25.83 t. This is the single most common practical error in equation-of-state work, and it is not an error of the model but of its use: the cubic returns three mathematically valid numbers and the code must decide. Any implementation that simply takes the largest root, or the root closest to the previous iterate, will silently produce this failure somewhere near the saturation curve, which is precisely where process equipment operates.

Example 4: Redlich–Kwong, Soave and Peng–Robinson at one state point

Problem. Propane at $T = 350\,\mathrm{K}$ and $P = 15\,\mathrm{bar}$, with $T_c = 369.8\,\mathrm{K}$, $P_c = 42.48\,\mathrm{bar}$ and $\omega = 0.152$. Tabulate $a(T)$, b, A, B, Z, V and φ from the Redlich–Kwong, Soave–Redlich–Kwong and Peng–Robinson equations, and account physically for the ordering of the results.

Strategy. All three models share the form $P = RT/(V-b) - a(T)/[(V+\delta_1 b)(V+\delta_2 b)]$ with $(\delta_1,\delta_2) = (1,0)$ for the first two and $(1+\sqrt{2}, 1-\sqrt{2})$ for the third, so one cubic solver and one fugacity expression serve all three. The models differ in two independent places: the temperature dependence of the attraction, which is $T_r^{-1/2}$ for Redlich–Kwong and a fitted $\alpha(T_r,\omega)$ for the other two, and the volume dependence of the attraction, which Peng and Robinson alone modified. At $T_r = 0.9465$ the model saturation pressure is 29.71 bar, so the state is a superheated vapour and each cubic has a single real root.

Solution.

1. Alpha functions at $T_r = 0.9465$: $\alpha^{RK} = T_r^{-1/2} = 1.0279$, $\alpha^{SRK} = 1.0392$ with $m = 0.7152$, and $\alpha^{PR} = 1.0330$ with $\kappa = 0.6028$.
2. Dimensionless groups and roots, with $A = a(T)P/(RT)^2$, $B = bP/(RT)$ and $V = ZRT/P$:

Model	$a(T)$ / bar cm^6 mol^{-2}	b / cm^3 mol^{-1}	A	B	Z	V / cm^3 mol^{-1}	φ
RK	9.778×10^6	62.71	0.1732	0.03232	0.8418	1633	0.8618
SRK	9.885×10^6	62.71	0.1751	0.03232	0.8391	1628	0.8599
PR	1.051×10^7	56.31	0.1862	0.02903	0.8255	1601	0.8479

3. Comparison with the ideal gas, for which $V^{ig} = 1939.9\,\mathrm{cm^3\,mol^{-1}}$: the three models place $Z-1$ at -0.1582, -0.1609 and -0.1745 respectively, so all three agree that attraction dominates, and they differ among themselves by 0.01631 in Z, that is 1.975 % of the Peng–Robinson value, and by 1.638 % in φ.
4. Physical ordering. Redlich–Kwong and Soave share the same b, because both use $\Omega_b = 0.08664$, and differ only through α; at $T_r = 0.9465$ the Soave alpha is 1.1 % larger, its attraction term is correspondingly larger and its Z smaller. Peng–Robinson uses $\Omega_b = 0.07780$, so its co-volume is smaller by the factor $0.07780/0.08664 = 0.8980$, and its larger $\Omega_a = 0.45724$ raises $a(T)$ by roughly six percent; both changes act in the same direction, weakening repulsion and strengthening attraction, and Z falls furthest. The fugacity coefficients follow Z monotonically, which they must, since $\ln\varphi = \int_0^P (Z-1)\,\mathrm{d}P/P$ and the three isotherms do not cross below 15 bar.

Check. For each model $\ln\varphi$ was computed twice, once from the closed-form expression and once

by numerically integrating $(Z-1)\,\mathrm{d}P/P$ from zero pressure along the isotherm. The results are -0.1487397, -0.1509628 and -0.1649880 by both routes, agreeing to better than 1×10^{-15}, which confirms both the algebra of the fugacity expressions and the root selection at every pressure on the integration path.

Engineering comment. The three models disagree by 0.01631 in Z and 1.638 % in the vapour-phase fugacity coefficient, which for a distillation or absorption calculation is immaterial, since equilibrium depends on ratios of fugacities and the discrepancy largely cancels between the components. The reason to prefer Peng–Robinson is not visible at this state point at all: it appears on the liquid branch, where the smaller $b = 56.31\,\mathrm{cm^3\,mol^{-1}}$ against $62.71\,\mathrm{cm^3\,mol^{-1}}$ and the modified volume dependence displace the saturated liquid molar volume by roughly twelve percent, as recorded in Chapter 10. Choosing between cubics on vapour-phase evidence is therefore a common and misleading exercise, and a comparison table of this kind should always be read with the question of which branch is being tested kept in view.

Example 5: The alpha function and the sensitivity to ω

Problem. For propane ($T_c = 369.8\,\mathrm{K}$, $P_c = 42.48\,\mathrm{bar}$, $\omega = 0.152$) compute α and $a(T)$ at $T_r = 0.6$, 0.8, 1.0 and 1.3 for the Redlich–Kwong, Soave–Redlich–Kwong and Peng–Robinson equations. Then quantify how a 5 % error in ω propagates into the saturation pressure predicted by the Peng–Robinson equation between $T_r = 0.6$ and 0.95.

Strategy. The attraction parameter factorizes as $a(T) = a_c\alpha$, where a_c depends only on the critical constants and α carries all the temperature dependence. Redlich–Kwong uses $\alpha = T_r^{-1/2}$, a universal function with no adjustable content; Soave and Peng–Robinson use $\alpha = [1 + m(1-\sqrt{T_r})]^2$ with m a fitted function of ω. The saturation pressure is then obtained from the isofugacity condition $\varphi^L = \varphi^V$ for the nominal and the perturbed acentric factor, and the ratio of fractional changes is reported as an amplification factor.

Solution.

1. Reference constants: $a_c = 0.42748\,R^2T_c^2/P_c = 9.512\times10^6\,\mathrm{bar\,cm^6\,mol^{-2}}$ for Redlich–Kwong and Soave, $a_c = 0.45724\,R^2T_c^2/P_c = 1.017\times10^7\,\mathrm{bar\,cm^6\,mol^{-2}}$ for Peng–Robinson; $m = 0.480 + 1.574\omega - 0.176\omega^2 = 0.7152$ and $\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 = 0.6028$.
2. Alpha functions and $a(T)$, with $a(T)$ in $10^6\,\mathrm{bar\,cm^6\,mol^{-2}}$:

T_r	T / K	α^{RK}	α^{SRK}	α^{PR}	a^{RK}	a^{SRK}	a^{PR}
0.6	221.88	1.2910	1.3484	1.2902	12.28	12.83	13.13
0.8	295.84	1.1180	1.1567	1.1313	10.64	11.00	11.51
1.0	369.80	1.0000	1.0000	1.0000	9.512	9.512	10.17
1.3	480.74	0.8771	0.8095	0.8381	8.343	7.701	8.528

   All three coincide at $T_r = 1$ by construction. Below the critical temperature the three-parameter forms rise faster than $T_r^{-1/2}$, and above it they fall faster; at $T_r = 1.3$ the Soave alpha is 7.7 % below the Redlich–Kwong value, which is the entire content of Soave's correction expressed as a number.
3. Perturbing the acentric factor by 5 %, $\omega' = 1.05\omega = 0.1596$, moves κ from 0.6028 to 0.6139, an increase of 1.838 %: the correlation is already strongly damping.
4. Propagation into the saturation pressure:

T_r	T / K	$P^{sat}(\omega)$ / bar	$P^{sat}(\omega')$ / bar	change / %	$\lvert\Delta P^{sat}/P^{sat}\rvert/\lvert\Delta\omega/\omega\rvert$
0.60	221.88	0.6703	0.6505	−2.955	0.5910
0.70	258.86	2.987	2.934	−1.760	0.3519
0.80	295.84	8.978	8.891	−0.9713	0.1943
0.90	332.82	21.14	21.05	−0.4177	0.08353
0.95	351.31	30.45	30.39	−0.1962	0.03924

The sensitivity is largest at low reduced temperature and decays monotonically toward the critical point.

Check. At $T_\mathrm{r}=1$ the alpha function equals unity for every ω, so $a(T_\mathrm{c})$ must be independent of the acentric factor; the computation returns $1.017\,451\,1\times10^{7}\,\mathrm{bar\,cm^{6}\,mol^{-2}}$ for both ω and ω'. The saturation pressure at T_c is P_c for both, so the sensitivity is required to vanish as $T_\mathrm{r}\to1$, and the tabulated amplification does fall monotonically from 0.5910 to 0.03924 across the range. This is a limiting-case verification of the whole table.

Engineering comment. A 5 % error in ω produces at most a 3 % error in the predicted vapour pressure, so the acentric factor is a robust input: tabulated values differing in the third decimal place between sources are of no consequence. The result also shows why Soave's correlation mattered. The quantity being predicted, the vapour pressure, varies by a factor of 45.43 between $T_\mathrm{r}=0.60$ and 0.95, and the two-parameter Redlich–Kwong alpha cannot follow it for a non-spherical molecule at all; introducing ω into α converts a qualitative curve into a quantitative one, at the cost of one tabulated number per compound whose accuracy barely matters.

Example 6: Fugacity coefficient from the Peng–Robinson equation

Problem. State the Peng–Robinson fugacity coefficient in full, evaluate it for carbon dioxide at $T=320\,\mathrm{K}$ and $P=70\,\mathrm{bar}$ with $T_\mathrm{c}=304.2\,\mathrm{K}$, $P_\mathrm{c}=73.83\,\mathrm{bar}$ and $\omega=0.224$, and verify the result independently by integrating $\ln\varphi=\int_0^P(Z-1)\,\mathrm{d}P/P$ numerically along the isotherm.

Strategy. Integrating $(Z-1)\,\mathrm{d}P/P$ analytically for a cubic with denominator $(V+\delta_1 b)(V+\delta_2 b)$ gives a closed form; with $\delta_1-\delta_2=2\sqrt{2}$ it reads

$$\ln\varphi = Z-1-\ln(Z-B)-\frac{A}{2\sqrt{2}\,B}\ln\left(\frac{Z+\left(1+\sqrt{2}\right)B}{Z+\left(1-\sqrt{2}\right)B}\right),\qquad A=\frac{a(T)P}{R^2T^2},\quad B=\frac{bP}{RT}. \tag{1.1}$$

The state is supercritical ($T_\mathrm{r}=1.052$), so a single root exists at every pressure between zero and 70 bar and the integration path is unambiguous. The integrand is finite at the lower limit, where $(Z-1)/P\to B_2/(RT)$ with $B_2=b-a/(RT)$ the second virial coefficient of the model.

Solution.

1. Parameters: $\kappa=0.7066$, $\alpha=0.9641$, $a(T)=3.819\times10^{6}\,\mathrm{bar\,cm^{6}\,mol^{-2}}$, $b=26.65\,\mathrm{cm^{3}\,mol^{-1}}$, hence $A=0.3777$ and $B=0.07012$.
2. Root: $Z=0.6298$, so $V=ZRT/P=239.3\,\mathrm{cm^{3}\,mol^{-1}}$. The state is $T_\mathrm{r}=1.052$, $P_\mathrm{r}=0.9481$, just above the critical point, where the fluid is dense but single phase.
3. Term by term in Equation (1.1), with $A/(2\sqrt{2}B)=1.904357$ and the logarithm argument $[Z+(1+\sqrt{2})B]/[Z+(1-\sqrt{2})B]=1.330168$, whose natural logarithm is 0.2853054:

$$\underbrace{Z-1}_{-0.3702461}\quad\underbrace{-\ln(Z-B)}_{+0.5804760}\quad\underbrace{-\frac{A}{2\sqrt{2}B}\ln(\cdot)}_{-0.5433233}\;=\;\ln\varphi=-0.3330935.$$

4. Hence $\varphi=\exp(-0.3330935)=0.7167$, and the fugacity is $f=\varphi P=(0.7167)(70)=50.17\,\mathrm{bar}$. The three terms of Equation (1.1) have a clear reading: the first two are the repulsive contribution,

positive in sum here because $-\ln(Z-B)$ dominates $Z-1$, and the third is the attractive contribution, always negative for a positive a. Their near cancellation is typical: the fugacity coefficient of a dense fluid is a small residue of two large opposing effects, which is why the algebra must be carried at full precision even though the answer is quoted to four figures.

5. The integrand of the verification integral, sampled along the isotherm:

P / bar	0	17.5	35.0	52.5	70.0
$(Z-1)/P$ / bar^{-1}	−0.004394	−0.004539	−0.004720	−0.004956	−0.005289

The integrand is smooth, finite at the origin and monotone, so the quadrature converges rapidly and no root switching can have occurred on the path.

Check. Numerical quadrature of $(Z-1)\,\mathrm{d}P/P$ from $P=0$ to 70 bar, with Z obtained by solving the cubic at each quadrature node, gives $\ln\varphi = -0.3330935$ with an estimated quadrature error of 3.7×10^{-15}. The two routes differ by 8.3×10^{-16} in $\ln\varphi$ and by 7.7×10^{-16} relative in φ, that is at the level of double-precision rounding. The integrand behaves as it must: at $P\to0$ it equals $B_2/(RT)$ with $B_2 = b - a/(RT) = -116.9\,\mathrm{cm^3\,mol^{-1}}$, giving $-0.004\,394\,\mathrm{bar^{-1}}$, and it varies smoothly to $-0.005\,289\,\mathrm{bar^{-1}}$ at 70 bar, so no root switching occurred anywhere on the path.

Engineering comment. At this condition $\varphi = 0.7167$, so treating carbon dioxide as an ideal gas would overstate its fugacity, and therefore its escaping tendency in any phase or reaction equilibrium, by 40 %. The agreement between the closed form and the quadrature is not a formality: it is the standard acceptance test for an equation-of-state implementation, because it exercises the cubic solver, the root selection and the fugacity algebra simultaneously, and it fails loudly if any of the three is wrong.

Example 7: Vapour pressure of propane by the isofugacity condition

Problem. For propane at $T = 300\,\mathrm{K}$ ($T_\mathrm{c} = 369.8\,\mathrm{K}$, $P_\mathrm{c} = 42.48\,\mathrm{bar}$, $\omega = 0.152$), solve $\varphi^L P = \varphi^V P$ for the saturation pressure with the Peng–Robinson equation. Show the first iterations explicitly, report the converged P^{sat} and the saturated liquid and vapour molar volumes, and obtain the enthalpy of vaporization from the Clapeyron equation with $\mathrm{d}P^{sat}/\mathrm{d}T$ evaluated numerically.

Strategy. At equilibrium the fugacities of the two phases are equal; at a common pressure this reduces to $\varphi^L = \varphi^V$, where both fugacity coefficients come from Equation (1.1) evaluated at the smallest and largest roots of the same cubic. The condition is solved by successive substitution, $P_{k+1} = P_k\,\varphi^L_k/\varphi^V_k$, which is the classical scheme because the ratio is the factor by which the pressure must move to equalize the fugacities. The starting estimate is the Wilson expression $P_0 = P_\mathrm{c}\exp[5.373(1+\omega)(1-T_\mathrm{c}/T)]$. The Clapeyron equation $\mathrm{d}P^{sat}/\mathrm{d}T = \Delta H^{vap}/[T(V^V - V^L)]$ then gives the latent heat without any further model.

Solution.

1. $T_\mathrm{r} = 0.8112$ and $P_0 = 42.48\exp[5.373(1.152)(1-369.8/300)] = 10.06\,\mathrm{bar}$.
2. Successive substitution:

k	P_k / bar	Z^L	Z^V	φ^L	φ^V	φ^L/φ^V
0	10.06332	0.035005	0.813278	0.836232	0.841165	0.9941350
1	10.00430	0.034802	0.814582	0.840992	0.842086	0.9987010
2	9.991306	0.034757	0.814869	0.842048	0.842289	0.9997140
3	9.988448	0.034747	0.814932	0.842281	0.842334	0.9999371
4	9.987820	0.034745	0.814946	0.842332	0.842344	0.9999862
5	9.987682	0.034744	0.814949	0.842343	0.842346	0.9999970

The iteration is linearly convergent: the relative errors of the successive iterates are 7.577×10^{-3}, 1.668×10^{-3}, 3.667×10^{-4}, 8.060×10^{-5}, 1.772×10^{-5} and 3.894×10^{-6}, whose ratios are 0.2201, 0.2199, 0.2198, 0.2198 and 0.2198. Each iteration therefore gains rather more than half a

decimal digit, and the contraction factor is constant, which is the signature of a fixed-point scheme rather than a Newton scheme.

3. Converged result, refined by a bracketed root solve on $\ln\varphi^V - \ln\varphi^L$:

$$P^{sat}(300\,\mathrm{K}) = 9.988\,\mathrm{bar}, \qquad Z^L = 0.03474, \qquad Z^V = 0.8150,$$

with a residual $|\ln\varphi^V - \ln\varphi^L| = 3.6\times10^{-13}$.

4. Saturated molar volumes: $V^L = Z^L RT/P^{sat} = 86.77\,\mathrm{cm^3\,mol^{-1}}$ and $V^V = 2035\,\mathrm{cm^3\,mol^{-1}}$, so $V^V - V^L = 1948\,\mathrm{cm^3\,mol^{-1}}$. The saturated liquid density is $M/V^L = 508.2\,\mathrm{kg\,m^{-3}}$ with $M = 44.097\,\mathrm{g\,mol^{-1}}$.

5. Quality of the initial estimate. The Wilson expression gave 10.06 bar against the converged 9.988 bar, an error of 0.7577 %. That is why the successive substitution needed only five steps: the correlation is designed to be accurate enough to place the starting pressure inside the three-root window, which is the only requirement the scheme imposes on it.

6. Clapeyron slope by central difference: $P^{sat}(299.5\,\mathrm{K}) = 9.862\,\mathrm{bar}$ and $P^{sat}(300.5\,\mathrm{K}) = 10.11\,\mathrm{bar}$, so $\mathrm{d}P^{sat}/\mathrm{d}T = 0.2523\,\mathrm{bar\,K^{-1}}$.

7. Enthalpy of vaporization, using $1\,\mathrm{bar\,cm^3} = 0.1\,\mathrm{J}$:

$$\Delta H^{vap} = T\left(V^V - V^L\right)\frac{\mathrm{d}P^{sat}}{\mathrm{d}T} = (300)(1948.4)(0.25230)(0.1) = 14\,747\,\mathrm{J\,mol^{-1}} = 14.75\,\mathrm{kJ\,mol^{-1}}.$$

Check. Two independent verifications agree. First, the Maxwell equal-area construction: integrating $P(V) - P^{sat}$ along the model isotherm from V^L to V^V gives a residual of $9.1\times10^{-9}\,\mathrm{bar\,cm^3\,mol^{-1}}$, that is 4.7×10^{-11} percent of $P^{sat}(V^V - V^L)$, confirming that the isofugacity root is also the equal-area root, as it must be. Second, the latent heat computed from the Peng–Robinson residual enthalpies of the two saturated phases, $H^{res,V} = -1288\,\mathrm{J\,mol^{-1}}$ and $H^{res,L} = -16\,035\,\mathrm{J\,mol^{-1}}$, is their difference, $14\,747\,\mathrm{J\,mol^{-1}}$, which differs from the Clapeyron value by 0.0009 %; the residual is entirely attributable to the finite difference used for the slope.

Engineering comment. A saturation pressure of 9.988 bar at ambient temperature fixes the design pressure of every propane storage vessel, and the saturated liquid density of $508.2\,\mathrm{kg\,m^{-3}}$ fixes the mass in it. The latent heat obtained here comes from the same equation and the same two roots, with no separate correlation, which is exactly the economy that made a single cubic acceptable for whole flowsheets: pressure, density and latent heat are three consequences of one PVT surface, and they cannot become mutually inconsistent.

Example 8: Binary vapour–liquid equilibrium and K-values

Problem. An equimolar mixture of methane and *n*-butane is at $T = 350\,\mathrm{K}$ and $P = 20\,\mathrm{bar}$. Using the Peng–Robinson equation with the van der Waals one-fluid mixing rules

$$a_{mix} = \sum_i\sum_j y_i y_j \sqrt{a_i a_j}\,(1 - k_{ij}), \qquad b_{mix} = \sum_i y_i b_i,$$

and with $k_{ij} = 0$ assumed for this pair, compute the K-values of both components and perform one Rachford–Rice iteration, reporting the residual function and the updated vapour fraction. State what changes if $k_{ij} \neq 0$.

Strategy. For a mixture the fugacity coefficient of a component follows from the same integration as Equation (1.1) applied to the partial molar residual Gibbs energy:

$$\ln\hat{\varphi}_i = \frac{b_i}{b_{mix}}(Z-1) - \ln(Z-B) - \frac{A}{2\sqrt{2}\,B}\left(\frac{2\sum_j y_j a_{ij}}{a_{mix}} - \frac{b_i}{b_{mix}}\right)\ln\left(\frac{Z + (1+\sqrt{2})B}{Z + (1-\sqrt{2})B}\right), \tag{1.2}$$

and $K_i = \hat{\varphi}_i^L/\hat{\varphi}_i^V$. Trial phase compositions are needed before Equation (1.2) can be evaluated, so the Wilson expression $K_i = (P_{c,i}/P)\exp[5.373(1+\omega_i)(1 - T_{c,i}/T)]$ initializes the calculation. The vapour

fraction ψ then follows from the Rachford–Rice residual $F(\psi) = \sum_i z_i(K_i - 1)/[1 + \psi(K_i - 1)] = 0$, which is monotonically decreasing in ψ and therefore has at most one root in $[0, 1]$.

Solution.

1. Pure-component parameters at 350 K: $a_1 = 1.848 \times 10^6$ and $a_2 = 1.698 \times 10^7\,\mathrm{bar\,cm^6\,mol^{-2}}$, $b_1 = 26.81$ and $b_2 = 72.44\,\mathrm{cm^3\,mol^{-1}}$, with the cross term $a_{12} = \sqrt{a_1 a_2}(1 - k_{12}) = 5.602 \times 10^6\,\mathrm{bar\,cm^6\,mol^{-2}}$.
2. Initialization: the Wilson expression gives $K_1 = 27.36$ and $K_2 = 0.4758$, and solving $F(\psi) = 0$ with these values returns $\psi = 0.9349$, hence trial compositions $x = (0.01950, 0.9805)$ and $y = (0.5334, 0.4666)$.
3. Mixture parameters and roots. For the liquid trial phase, $a_{mix} = 1.654 \times 10^7\,\mathrm{bar\,cm^6\,mol^{-2}}$, $b_{mix} = 71.55\,\mathrm{cm^3\,mol^{-1}}$, $A = 0.3906$, $B = 0.04917$ and $Z^L = 0.07640$, that is $V^L = 111.2\,\mathrm{cm^3\,mol^{-1}}$. For the vapour trial phase, $a_{mix} = 7.010 \times 10^6\,\mathrm{bar\,cm^6\,mol^{-2}}$, $b_{mix} = 48.10\,\mathrm{cm^3\,mol^{-1}}$, $A = 0.1656$, $B = 0.03306$ and $Z^V = 0.8611$, that is $V^V = 1253\,\mathrm{cm^3\,mol^{-1}}$.
4. Fugacity coefficients from Equation (1.2) and the resulting K-values:

component	$\hat{\varphi}_i^L$	$\hat{\varphi}_i^V$	K_i
methane	9.277	1.025	9.055
n-butane	0.4128	0.7274	0.5675

5. One Rachford–Rice iteration at $\psi = 0.9349$ with these K-values:

$$F(\psi) = \underbrace{\frac{0.5(9.055-1)}{1+0.9349(9.055-1)}}_{+0.4721} + \underbrace{\frac{0.5(0.5675-1)}{1+0.9349(0.5675-1)}}_{-0.3630} = +0.1091, \qquad \frac{\mathrm{d}F}{\mathrm{d}\psi} = -0.7093,$$

   so the Newton update is $\psi_{new} = 0.9349 - (0.1091)/(-0.7093) = 1.089$.
6. Interpretation of the update. The residual is positive at both ends of the interval, $F(0) = 3.811$ and $F(1) = 0.06380$, so F has no root in $[0, 1]$ and the Newton step correctly leaves the interval. The Peng–Robinson K-values therefore state that the equimolar feed at 350 K and 20 bar is a single superheated vapour, not a two-phase mixture.

Check. Three verifications were performed. First, setting the composition of either component to unity in Equation (1.2) reproduces the pure-component fugacity coefficient of Chapter 10 exactly, $\hat{\varphi} = 0.9757409$ for methane and 0.4127765 for *n*-butane, to 2×10^{-16}. Second, the dew-point pressure of this feed at 350 K, obtained by solving $\sum_i y_i/K_i = 1$ with the same model, is 22.77 bar, above the specified 20 bar, which confirms the single-phase verdict by an independent route. Third, the identical procedure applied at 40 bar, inside the two-phase region, converges to $\psi = 0.6930$, $K = (4.372, 0.4057)$, $x = (0.1498, 0.8502)$ and $y = (0.6551, 0.3449)$, with an isofugacity residual $\max_i |x_i\hat{\varphi}_i^L - y_i\hat{\varphi}_i^V| = 7.3 \times 10^{-14}$ and a material balance residual of 1.1×10^{-16}.

Engineering comment. Two lessons follow. The first is that the bracketing test on $F(\psi)$, and not the Newton step, is what detects a single-phase feed; a flash routine that iterates without testing $F(0)$ and $F(1)$ will either diverge or return a physically meaningless negative-flow split. The second concerns k_{12}. Setting it to zero is an assumption, not a neutral choice:

k_{12}	K_1	K_2	change in K_2	converged ψ at 40 bar
0	9.055	0.5675	reference	0.6930
0.02	8.919	0.6043	6.472 %	0.7359
0.05	8.671	0.6627	16.76 %	0.8177

A binary interaction parameter of a few hundredths, well within the range regressed for light hydrocarbon pairs, moves the vapour fraction by 6.19 % and 17.99 % respectively, which is the difference

between a column that meets specification and one that does not. The geometric mean $\sqrt{a_1 a_2}$ is a statement about the unlike pair potential, and setting $k_{12} = 0$ asserts that the methane to *n*-butane attraction is exactly the geometric mean of the like attractions; for molecules of such different size that assertion is optimistic, and it must be recorded in the calculation basis rather than left implicit.

Example 9: Departure functions and a compressor duty

Problem. For carbon dioxide ($T_c = 304.2\,\mathrm{K}$, $P_c = 73.83\,\mathrm{bar}$, $\omega = 0.224$) at $T = 350\,\mathrm{K}$ and $P = 80\,\mathrm{bar}$, evaluate $H - H^{ig}$ and $S - S^{ig}$ from the Peng–Robinson equation. Then compute the isentropic duty of a compressor handling $100\,\mathrm{kmol\,h^{-1}}$ of carbon dioxide from 10 bar to 80 bar with an inlet temperature of 350 K, and compare with the answer obtained by neglecting the departure functions. Assume a constant ideal-gas heat capacity $C_P^{ig} = 42.0\,\mathrm{J\,mol^{-1}\,K^{-1}}$, representative of carbon dioxide between 350 K and 541 K; the reference state for both routes is the ideal gas at the same temperature and pressure, so it cancels from every difference taken below.

Strategy. Applying the departure-function chain of Chapter 1 to the Peng–Robinson equation gives, with $\mathscr{L} = \ln\{[Z + (1+\sqrt{2})B]/[Z + (1-\sqrt{2})B]\}$,

$$H - H^{ig} = RT\,(Z-1) + \frac{T\,\mathrm{d}a/\mathrm{d}T - a}{2\sqrt{2}\,b}\,\mathscr{L}, \qquad S - S^{ig} = R\ln(Z-B) + \frac{\mathrm{d}a/\mathrm{d}T}{2\sqrt{2}\,b}\,\mathscr{L}, \tag{1.3}$$

with $\mathrm{d}a/\mathrm{d}T = -a_c\kappa\left[1 + \kappa(1-\sqrt{T_r})\right]/\sqrt{T T_c}$. An isentropic compression is then located by solving $C_P^{ig}\ln(T_2/T_1) - R\ln(P_2/P_1) + S^{res}(T_2,P_2) - S^{res}(T_1,P_1) = 0$ for T_2, and the duty follows from $W_s = C_P^{ig}(T_2 - T_1) + H^{res}(T_2,P_2) - H^{res}(T_1,P_1)$.

Solution.

1. Parameters in SI units: $a_c = 0.396\,141\,\mathrm{Pa\,m^6\,mol^{-2}}$, $b = 2.665\,115 \times 10^{-5}\,\mathrm{m^3\,mol^{-1}}$, $\kappa = 0.7066$. At 350 K, $T_r = 1.151$, $a = 0.355\,203\,\mathrm{Pa\,m^6\,mol^{-2}}$ and $\mathrm{d}a/\mathrm{d}T = -8.137\,746 \times 10^{-4}\,\mathrm{Pa\,m^6\,mol^{-2}\,K^{-1}}$.
2. State: $A = 0.3368$, $B = 0.07327$, $Z = 0.7217$ and $V = 262.5\,\mathrm{cm^3\,mol^{-1}}$, with $\mathscr{L} = 0.2622$.
3. Prefactors in Equation (1.3): $(T\,\mathrm{d}a/\mathrm{d}T - a)/(2\sqrt{2}b) = -8508\,\mathrm{J\,mol^{-1}}$ and $(\mathrm{d}a/\mathrm{d}T)/(2\sqrt{2}b) = -10.80\,\mathrm{J\,mol^{-1}\,K^{-1}}$. Hence

$$H - H^{ig} = (8.314)(350)(0.7217-1) + (-8508)(0.26218) = -3041\,\mathrm{J\,mol^{-1}} = -3.041\,\mathrm{kJ\,mol^{-1}},$$

$$S - S^{ig} = (8.314)\ln(0.72169 - 0.07327) + (-10.7955)(0.26218) = -6.432\,\mathrm{J\,mol^{-1}\,K^{-1}}.$$

4. Inlet state and isentropic outlet. The entropy balance $C_P^{ig}\ln(T_2/T_1) - R\ln 8 + \Delta S^{res} = 18.2844 - 17.2885 - 0.9959 = 0$ is satisfied at $T_2 = 540.9\,\mathrm{K}$. The two states are

state	T / K	P / bar	Z	H^{res} / J mol^{-1}
suction	350.0	10	0.9668	−322.4
discharge	540.9	80	0.9651	−1066

   with $S^{res} = -0.6462\,\mathrm{J\,mol^{-1}\,K^{-1}}$ at suction and $-1.642\,\mathrm{J\,mol^{-1}\,K^{-1}}$ at discharge. Both compressibility factors are close to unity because the discharge is hot; the residual properties are nevertheless not negligible, which is the point of the example.
5. Duty:

$$W_s = (42.0)(540.92 - 350.00) + (-1066.17) - (-322.39) = 7275\,\mathrm{J\,mol^{-1}},$$

   and with $\dot{n} = 100\,\mathrm{kmol\,h^{-1}} = 27.78\,\mathrm{mol\,s^{-1}}$ the shaft power is 202.1 kW.
6. Ideal-gas-only route: $R/C_P^{ig} = 0.19795$, so $T_2 = 350 \times 8^{0.19795} = 528.2\,\mathrm{K}$ and $W_s = C_P^{ig}(T_2 - T_1) = 7486\,\mathrm{J\,mol^{-1}}$, that is 207.95 kW.
7. Comparison of the two routes:

route	T_2 / K	W_s / J mol^{-1}	duty / kW
ideal gas only	528.2	7486	207.95
Peng–Robinson departures	540.9	7275	202.08
difference	−12.68	−211.4	−5.872

The ideal-gas answer is 2.824 % high in duty and 12.68 K high in discharge temperature.

Check. The three departure functions are derived separately and must satisfy $H^{res} - TS^{res} = G^{res} = RT\ln\varphi$. Evaluating each independently gives $-3040.52 - (350)(-6.432194) = -789.26\,\mathrm{J\,mol^{-1}}$ against $RT\ln\varphi = -789.26\,\mathrm{J\,mol^{-1}}$, agreeing to 9×10^{-13}. As a second and stronger test, S^{res} was recomputed as $-(\partial G^{res}/\partial T)_P$ by central difference on $RT\ln\varphi$, giving $-6.4322\,\mathrm{J\,mol^{-1}\,K^{-1}}$ against the analytic $-6.4322\,\mathrm{J\,mol^{-1}\,K^{-1}}$, a difference of 8×10^{-7}; this exercises the temperature derivative of the alpha function, which is where errors in departure functions usually hide.

Engineering comment. The residual enthalpy at the discharge condition is $-1.066\,\mathrm{kJ\,mol^{-1}}$ and at suction $-0.322\,\mathrm{kJ\,mol^{-1}}$; the difference is only about ten percent of the shaft work, yet it moves the duty by 5.9 kW on a 202 kW machine. Two consequences follow. The ideal-gas calculation is conservative here, so it does not create a safety problem, but it does create a capital one, since a machine specified 2.8 % large is paid for. More seriously, the predicted discharge temperature is 12.7 K too high, which propagates into intercooler duty, material selection and, on a multistage machine, into the stage distribution itself.

Example 10: Corresponding states and the acentric factor in practice

Problem. For *n*-butane ($T_c = 425.1$ K, $P_c = 37.96$ bar, tabulated $\omega = 0.200$), recover the acentric factor from the Peng–Robinson saturation curve at $T_r = 0.7$ and compare with the tabulated value. Then estimate Z at $T_r = 1.2$ and $P_r = 1.5$ from three-parameter corresponding states, compare with the direct Peng–Robinson result, and discuss the discrepancy.

Strategy. The acentric factor is defined by $\omega = -1 - \log_{10} P_r^{sat}$ evaluated at $T_r = 0.7$, so any model that predicts a saturation curve also predicts an acentric factor, and the comparison with the tabulated value measures how faithfully the $\kappa(\omega)$ correlation inverts. For the second part the three-parameter corresponding-states expansion $Z = Z^{(0)} + \omega Z^{(1)}$ is used, with $Z^{(0)}$ from the Lee–Kesler simple fluid and $Z^{(1)} = (Z^{(r)} - Z^{(0)})/\omega^{(r)}$ from its *n*-octane reference fluid, $\omega^{(r)} = 0.3978$. This is a genuinely independent model, fitted to experimental PVT data rather than derived from a cubic, so the comparison is a test and not a tautology.

Solution.

1. At $T_r = 0.7$, $T = 0.7(425.1) = 297.6$ K. The Peng–Robinson isofugacity solution gives $P^{sat} = 2.387$ bar, hence $P_r^{sat} = 2.38678/37.96 = 0.06288$ and $\log_{10} P_r^{sat} = -1.2015$.
2. Recovered acentric factor: $\omega = -1 - (-1.20151) = 0.2015$, against the tabulated 0.200. The deviation is $+0.001514$, that is 0.7570 %.
3. Three-parameter corresponding states at $T_r = 1.2$, $P_r = 1.5$: the Lee–Kesler simple fluid gives $Z^{(0)} = 0.6605$ and the reference fluid gives $Z^{(r)} = 0.7193$, hence

$$Z^{(1)} = \frac{Z^{(r)} - Z^{(0)}}{\omega^{(r)}} = \frac{0.71927 - 0.66052}{0.3978} = 0.1477,$$

$$Z = Z^{(0)} + \omega Z^{(1)} = 0.66052 + (0.200)(0.14769) = 0.6901.$$

4. Direct Peng–Robinson result at the same reduced state, that is $T = 510.1$ K and $P = 56.94$ bar: $Z = 0.6831$, corresponding to $V = 508.8\,\mathrm{cm^3\,mol^{-1}}$ against $514.0\,\mathrm{cm^3\,mol^{-1}}$ from the corresponding-states estimate.
5. Summary of the estimates at $T_r = 1.2$, $P_r = 1.5$:

route	Z	V / cm^3 mol^{-1}
two-parameter corresponding states, $Z^{(0)}$ only	0.6605	492.0
three-parameter corresponding states, $Z^{(0)} + \omega Z^{(1)}$	0.6901	514.0
Peng–Robinson, direct	0.6831	508.8

6. Discrepancy: $Z^{PR} - Z^{CS} = -0.006991$, that is $-1.013\,\%$. For perspective, dropping the acentric term entirely and using two-parameter corresponding states would give $Z = Z^{(0)} = 0.6605$, an error of $-4.281\,\%$; the acentric correction is worth $\omega Z^{(1)} = +0.02954$ in Z, four times the residual disagreement between the two models.

Check. The Lee–Kesler implementation was verified in three ways. At $T_\mathrm{r} = 2$ and $P_\mathrm{r} = 1 \times 10^{-4}$ it returns $Z^{(0)} = 0.99999714$, and the implied second virial coefficient $(Z^{(0)} - 1)T_\mathrm{r}/P_\mathrm{r} = -0.057232$ reproduces the analytic $B(T_\mathrm{r})$ of the same correlation, -0.057233. At its own critical point it returns 0.2918 against the correlation's stated $Z_\mathrm{c} = 0.2901$, the residual being the accuracy attainable at a triple root. The corresponding test on the Peng–Robinson cubic, whose three roots at the critical point have mean $(1 - B)/3$, returns 0.307400 against the design value 0.30740. A truncated virial route is not available as a check here: the Pitzer correlation $B^{(0)} = -0.2322$, $B^{(1)} = 0.05902$ would give $Z = 0.7245$, but its validity criterion $P_\mathrm{r} < T_\mathrm{r}/2 = 0.60$ is violated at $P_\mathrm{r} = 1.5$, which is exactly the reason a full corresponding-states correlation is needed at this density.

Engineering comment. Two conclusions of different kinds follow. The recovered acentric factor differs from the tabulated one by less than one percent, which shows that the $\kappa(\omega)$ correlation inverts almost exactly, and repeating the calculation for propane gives $\omega = 0.1530$ against a tabulated 0.152, so the small positive offset is a property of the correlation and not of one substance. The one percent disagreement in Z at $T_\mathrm{r} = 1.2$, $P_\mathrm{r} = 1.5$ is of a different nature. It is not an arithmetic residual but a genuine model difference: the Lee–Kesler correlation is a multiparameter fit to measured volumetric data, whereas the cubic carries only two substance constants and a mean-field attraction. In the dense near-critical region the two constructions cannot agree better than this, and a one percent uncertainty in Z is a reasonable expectation for any cubic equation there, which is the practical warning to carry away from all ten examples.

Closing remarks on the ten examples

Three threads run through the set. The first is that a single dimensionless number, the compressibility factor, converts directly into money and metal: 640 kg of methane in Example 1, 25.8 t of misassigned *n*-butane in Example 3, 5.9 kW of compressor duty in Example 9. None of these errors announces itself; each is simply carried forward.

The second is that almost every quantity a process calculation needs is a functional of the same PVT surface. The fugacity coefficient of Example 6, the saturation pressure and latent heat of Example 7, the K-values of Example 8 and the departure functions of Example 9 were all obtained from one cubic with three tabulated constants per substance. This is the economy that made the cubic equation of state the industrial standard, and it is also the reason an error in the volumetric closure cannot be confined: it reappears in the enthalpy balance, the phase split and the equipment size at the same time.

The third is that verification is cheap and non-negotiable. Every example above carries an independent check, and the checks used only four techniques: a limiting case, a second analytic route, a numerical quadrature or derivative, and a units argument. Where the closed form and the quadrature agreed to 1×10^{-15} the implementation may be trusted; where the two routes agreed only to one percent, as in Example 10, the residual is a real difference between models and must be reported as an uncertainty rather than resolved by refining the arithmetic.

The examples also record, in one place, the numerical acceptance criteria a working implementation should meet. The closed-form and quadrature routes to $\ln\varphi$ must agree to machine precision, as they did in Examples 4 and 6 at the level of 1×10^{-15}. The isofugacity saturation pressure must satisfy the Maxwell

equal-area construction, as in Example 7, where the residual was $9.1 \times 10^{-9}\,\mathrm{bar\,cm^3\,mol^{-1}}$. The three departure functions must satisfy $H^{res} - TS^{res} = RT\ln\varphi$ and $S^{res} = -(\partial G^{res}/\partial T)_P$, as in Example 9. The mixture fugacity coefficient must reduce to the pure-component value when a mole fraction is set to unity, as in Example 8. A flash must close its material balance and its isofugacity condition simultaneously. None of these tests requires experimental data, and each one fails loudly when an implementation is wrong; together they are cheaper than a single misdiagnosed simulation.