Appendix A
EoS–G^{E} mixing rules: Huron–Vidal and Wong–Sandler

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Self-study note. This material is not lectured; it accompanies four appendix slides.

A.1 The two worlds and why they do not meet

Phase-equilibrium calculation is served by two model families that were developed for different purposes and that fail in complementary ways.

A *cubic equation of state* is a single pressure-explicit function valid for both phases. It is continuous through the critical region, it accepts supercritical components such as methane, nitrogen and hydrogen without a hypothetical standard state, and it delivers densities, enthalpy departures and fugacities from one parameter set. Its weakness is compositional: with the conventional mixing rules it cannot reproduce the strongly non-ideal liquid phases formed by alcohols, water, amines, acids or glycols.

An *activity coefficient model* — Wilson, NRTL, UNIQUAC, UNIFAC — is built precisely for those liquids, and decades of regressed binary parameters exist. Its weaknesses are equally structural: it describes the liquid only, it supplies no density and no vapour-phase model, it is essentially pressure independent, and it cannot treat a supercritical solute, because the pure-component liquid reference state does not exist.

Industrial problems routinely require both capabilities at once: an amine absorber, a methanol synthesis loop, a supercritical extraction with a polar entrainer. An EoS–G^{E} mixing rule inserts the compositional information of an activity coefficient model into the mixture parameters of a cubic equation of state, so that one model retains the pressure and density behaviour of the former and the liquid non-ideality of the latter.

Why the van der Waals one-fluid rule fails

The conventional rule treats the mixture as a hypothetical pure fluid whose parameters are composition averages,

$$a_{\mathrm{mix}} = \sum_i \sum_j x_i x_j a_{ij}, \qquad a_{ij} = \sqrt{a_i a_j}\,(1-k_{ij}), \qquad b_{\mathrm{mix}} = \sum_i x_i b_i. \tag{1}$$

Its origin is the statistical-mechanical result that, for a fluid of molecules interacting through pair potentials, the configurational energy is quadratic in composition *provided the local composition around every molecule equals the bulk composition*. That is the random-mixing assumption. It is a good assumption when the unlike interaction energy is close to the geometric mean of the like energies, which is the case for hydrocarbon mixtures, and it is a poor assumption when it is not.

The consequence can be made quantitative. For a binary, using $\sum_i x_i a_i = \sum_i \sum_j x_i x_j (a_i + a_j)/2$, equation (1) rearranges to

$$a_{\mathrm{mix}} = x_1 a_1 + x_2 a_2 + x_1 x_2 \big(2a_{12} - a_1 - a_2\big). \tag{2}$$

The departure from a linear mole-fraction average is exactly $x_1 x_2$ times a single constant. Section A.2 shows that the excess Gibbs energy implied by a cubic equation of state is controlled by $a_{\mathrm{mix}}/b_{\mathrm{mix}} - \sum_i x_i a_i/b_i$; when the co-volumes are comparable, equation (2) therefore makes the one-fluid rule thermodynamically equivalent to a one-constant (two-suffix) Margules model, $g^{\mathrm{E}} = A\,x_1 x_2$.

That is the whole indictment. A one-constant Margules model is symmetric about $x_1 = 0.5$ and carries a single adjustable parameter. Hydrogen-bonding mixtures are neither: their excess Gibbs energy is strongly skewed towards the associating component, their infinite-dilution activity coefficients differ by orders of magnitude between the two ends of the composition range, and they may exhibit liquid–liquid immiscibility. Fitting k_{ij} harder does not help, because k_{ij} adjusts the magnitude of A, not the shape of the composition dependence. Local-composition models solve exactly this problem by weighting the neighbours of a molecule with Boltzmann factors in the interaction energy differences, so that g^{E} acquires the asymmetric, non-quadratic shape the data demand. The task is to make a cubic equation of state inherit that shape.

A.2 Huron–Vidal: matching at infinite pressure

Huron and Vidal (1979) observed that the excess Gibbs energy is a property both families possess and can therefore serve as the matching variable. The equation of state predicts $g^{\mathrm{E}}(T,P,x)$; the activity coefficient model supplies $g^{\mathrm{E}}(T,x)$. Equating the two at one chosen pressure converts the activity coefficient model into a mixing rule. The choice of that pressure is the entire design decision, and Huron and Vidal chose $P \to \infty$, because that is the limit in which the algebra closes.

The residual Helmholtz energy of a general cubic

Write every two-parameter cubic in the common form

$$P = \frac{RT}{V-b} - \frac{a}{(V+\delta_1 b)(V+\delta_2 b)}. \tag{3}$$

Soave–Redlich–Kwong is $\delta_1 = 1$, $\delta_2 = 0$; Peng–Robinson is $\delta_1 = 1+\sqrt{2}$, $\delta_2 = 1-\sqrt{2}$. The residual Helmholtz energy at fixed T and V follows from integration of the departure integrand,

$$A^{\mathrm{res}}(T,V) = -\int_{\infty}^{V}\Big(P - \frac{RT}{V}\Big)\mathrm{d}V = -RT\ln\frac{V-b}{V} + \frac{a}{b(\delta_1-\delta_2)}\ln\frac{V+\delta_2 b}{V+\delta_1 b}, \tag{4}$$

where the attractive integral was evaluated by partial fractions, $\big[(V+\delta_1 b)(V+\delta_2 b)\big]^{-1} = \big[b(\delta_1-\delta_2)\big]^{-1}\big[(V+\delta_2 b)^{-1} - (V+\delta_1 b)^{-1}\big]$, and both logarithms vanish at the lower limit.

The infinite-pressure limit

As $P \to \infty$ the cubic collapses onto its hard core: $V \to b$. More precisely, the repulsive term dominates equation (3), so $P \simeq RT/(V-b)$ and

$$V - b \longrightarrow \frac{RT}{P}, \qquad V \to b, \qquad Z = \frac{PV}{RT} \to \frac{Pb}{RT}. \tag{5}$$

Substituting into equation (4),

$$A^{\mathrm{res}} \longrightarrow RT\ln\frac{Pb}{RT} + \frac{a}{b(\delta_1-\delta_2)}\ln\frac{1+\delta_2}{1+\delta_1} \equiv RT\ln\frac{Pb}{RT} - C\,\frac{a}{b}, \tag{6}$$

which defines the model constant

$$\boxed{C = \frac{1}{\delta_1-\delta_2}\ln\frac{1+\delta_1}{1+\delta_2}} \tag{7}$$

The first term of equation (6) diverges; the second is finite, and it is the one that carries the composition dependence of the attraction.

Now form the excess Gibbs energy. Since the ideal-gas contributions cancel between mixture and pure components at the same T and P, $g^{\mathrm{E}} = g^{\mathrm{res}}_{\mathrm{mix}} - \sum_i x_i g^{\mathrm{res}}_i$, and $G^{\mathrm{res}} = A^{\mathrm{res}} + RT(Z-1) - RT\ln Z$. Impose the Huron–Vidal choice

$$b_{\mathrm{mix}} = \sum_i x_i b_i \qquad \text{(linear, as in the one-fluid rule)}, \tag{8}$$

so that $V^{\mathrm{E}} \to b_{\mathrm{mix}} - \sum_i x_i b_i = 0$ and the term $RT(Z-1) = PV - RT$ contributes $PV^{\mathrm{E}} = 0$ to the excess. The remaining divergent pieces cancel identically:

$$\underbrace{RT\Big[\ln b_{\mathrm{mix}} - \sum_i x_i \ln b_i\Big]}_{\text{from } A^{\mathrm{res}}} \underbrace{-RT\Big[\ln b_{\mathrm{mix}} - \sum_i x_i \ln b_i\Big]}_{\text{from } -RT\ln Z} = 0, \tag{9}$$

because $Z \to Pb/RT$ and the factor P/RT is common to mixture and pure components. What survives is only the attractive term of equation (6):

$$g^{\mathrm{E}}_{\infty} = -C\,\frac{a_{\mathrm{mix}}}{b_{\mathrm{mix}}} + C\sum_i x_i \frac{a_i}{b_i} = C\Big[\sum_i x_i \frac{a_i}{b_i} - \frac{a_{\mathrm{mix}}}{b_{\mathrm{mix}}}\Big]. \tag{10}$$

Setting g^{E}_{∞} equal to the activity coefficient model $g^{\mathrm{E}}_{\gamma}(T,x) = RT\sum_i x_i \ln\gamma_i$ and solving gives the Huron–Vidal mixing rule:

$$\boxed{a_{\mathrm{mix}} = b_{\mathrm{mix}}\Big[\sum_i x_i \frac{a_i}{b_i} - \frac{g^{\mathrm{E}}_{\gamma}(T,x)}{C}\Big], \qquad b_{\mathrm{mix}} = \sum_i x_i b_i} \tag{11}$$

The signs match physical expectation: a positive g^{E}, meaning unlike interactions weaker than the like average, reduces $a_{\mathrm{mix}}/b_{\mathrm{mix}}$ below the mole-fraction average and so raises the predicted pressure. If g^{E}_{γ} is chosen quadratic in composition, equation (11) reproduces the one-fluid rule — the formal statement of the argument in Section A.1.

The constant C, computed

Equation (7) is arithmetic. For **SRK**, $\delta_1 = 1$ and $\delta_2 = 0$:

$$C_{\mathrm{SRK}} = \frac{1}{1-0}\ln\frac{1+1}{1+0} = \ln 2 = 0.693147. \tag{12}$$

For **Peng–Robinson**, $\delta_1 = 1+\sqrt{2} = 2.414214$ and $\delta_2 = 1-\sqrt{2} = -0.414214$, so $\delta_1 - \delta_2 = 2\sqrt{2} = 2.828427$, $1+\delta_1 = 2+\sqrt{2} = 3.414214$ and $1+\delta_2 = 2-\sqrt{2} = 0.585786$:

$$\frac{1+\delta_1}{1+\delta_2} = \frac{3.414214}{0.585786} = 5.828427 = 3+2\sqrt{2} = (1+\sqrt{2})^2, \tag{13}$$

$$C_{\mathrm{PR}} = \frac{\ln\big(3+2\sqrt{2}\big)}{2\sqrt{2}} = \frac{2\ln(1+\sqrt{2})}{2\sqrt{2}} = \frac{\ln(1+\sqrt{2})}{\sqrt{2}} = \frac{0.881374}{1.414214} = 0.623225. \tag{14}$$

Both quoted values are confirmed in magnitude: $\ln 2$ for SRK and 0.6232 for Peng–Robinson.

Practical caveat, not a derived result. One discrepancy must be recorded rather than concealed. The form circulated in the course brief, $C = (\delta_2 - \delta_1)^{-1} \ln\left[(1+\delta_1)/(1+\delta_2)\right]$, has the index pairing of the prefactor opposite to that of the logarithm and evaluates to -0.623225 for PR and $-\ln 2$ for SRK. The magnitudes are correct; the sign is not, for the convention used here. Two equivalent label-independent forms are $C = (\delta_1 - \delta_2)^{-1} \ln\left[(1+\delta_1)/(1+\delta_2)\right]$, used in equation (7), and $C = (\delta_2 - \delta_1)^{-1} \ln\left[(1+\delta_2)/(1+\delta_1)\right]$; both give $+0.623225$ and $+\ln 2$ whichever root is labelled δ_1. Several texts define instead $C^* = -C$ (so $C^*_{\mathrm{PR}} = \ln(\sqrt{2}-1)/\sqrt{2} = -0.6232$) and write equation (11) with a plus sign. Before transcribing a published mixing rule into code, verify which convention its C carries by testing the limit $g^{\mathrm{E}} = 0$.

The practical cost

Practical caveat, not a derived result. Published low-pressure NRTL, UNIQUAC or Wilson parameters cannot be reused in equation (11). The parameters in the literature were regressed against g^{E} measured at or near atmospheric pressure, whereas equation (10) is an identity at $P \to \infty$, where the liquid is compressed to its hard-core volume. These are not the same function, so a parameter set that reproduces g^{E} at 1 bar does not reproduce g^{E}_{∞}. Huron–Vidal parameters must be re-regressed from phase-equilibrium data for the equation of state in which they will be used, and a set fitted with SRK is not transferable to Peng–Robinson, because C differs. This is why the rule, although thermodynamically sound, did not by itself make cubic equations predictive: it replaces one correlation problem with an identical one over a new database.

A.3 Wong–Sandler: matching at both density limits

Huron–Vidal is exact where it is imposed and unconstrained elsewhere: the linear b_{mix} of equation (8) combined with the non-quadratic a_{mix} of equation (11) violates the one exact composition dependence statistical mechanics supplies. Wong and Sandler (1992) kept the infinite-pressure condition and added that low-density boundary condition.

The second condition

Statistical mechanics requires the second virial coefficient of a mixture to be exactly quadratic in composition,

$$B_{\mathrm{mix}}(T,x) = \sum_i \sum_j x_i x_j B_{ij}(T), \tag{15}$$

because B derives from the sum of interactions over distinct molecular pairs. Expanding equation (3) in $1/V$ gives the second virial coefficient of any cubic,

$$Z = 1 + \frac{1}{V}\left(b - \frac{a}{RT}\right) + O(V^{-2}) \quad \Longrightarrow \quad B = b - \frac{a}{RT}. \tag{16}$$

Equations (15) and (16) together state the Wong–Sandler low-density condition: the group $(b - a/RT)$, not b and not a separately, must be quadratic in composition,

$$b_{\mathrm{mix}} - \frac{a_{\mathrm{mix}}}{RT} = \sum_i \sum_j x_i x_j \left(b - \frac{a}{RT}\right)_{ij} \equiv Q, \tag{17}$$

with the cross term supplied by a combining rule containing one binary parameter,

$$\left(b - \frac{a}{RT}\right)_{ij} = \frac{1}{2}\left[\left(b_i - \frac{a_i}{RT}\right) + \left(b_j - \frac{a_j}{RT}\right)\right](1 - k_{ij}), \qquad k_{ij} = k_{ji}, \quad k_{ii} = 0. \tag{18}$$

The first condition, restated in Helmholtz energy

Because b_{mix} is no longer linear, V^{E} does not vanish at infinite pressure and PV^{E} is indeterminate; the Gibbs form of the match is therefore unusable. The Helmholtz form is not. Repeating the limit of Section A.2 with $a^{\mathrm{E}} = a^{\mathrm{res}}_{\mathrm{mix}} - \sum_i x_i a^{\mathrm{res}}_i - RT\sum_i x_i \ln(V_{\mathrm{mix}}/V_i)$ and $V \to b$, the $\ln b$ terms again cancel in pairs and one obtains, *without* assuming b_{mix} linear,

$$a^{\mathrm{E}}_{\infty} = C\left[\sum_i x_i \frac{a_i}{b_i} - \frac{a_{\mathrm{mix}}}{b_{\mathrm{mix}}}\right]. \tag{19}$$

This is the structural reason Wong and Sandler work with the excess Helmholtz energy.

Practical caveat, not a derived result. The rule is then closed by the approximation $a^{\mathrm{E}}_{\infty} \approx a^{\mathrm{E}}(T, P_{\mathrm{low}}) \approx g^{\mathrm{E}}_{\gamma}(T,x)$. Its justification is empirical rather than exact: the excess Helmholtz energy of a dense liquid is far less pressure dependent than the excess Gibbs energy, so the error incurred is small. It is nevertheless an approximation, and it is what allows literature g^{E} parameters to be used as a starting point in Wong–Sandler — a claim that should be treated as a good initial estimate, not as a licence to skip re-regression when accuracy matters.

Solving the two conditions

Define the dimensionless group implied by equation (19),

$$D \equiv \frac{a_{\mathrm{mix}}}{b_{\mathrm{mix}}RT} = \sum_i x_i \frac{a_i}{b_i RT} - \frac{g^{\mathrm{E}}_{\gamma}(T,x)}{CRT}. \tag{20}$$

Note that D depends only on pure-component parameters and the activity coefficient model, not on a_{mix} or b_{mix}. Substituting $a_{\mathrm{mix}} = RT\, b_{\mathrm{mix}} D$ into equation (17),

$$b_{\mathrm{mix}} - b_{\mathrm{mix}} D = Q \qquad \Longrightarrow \qquad \boxed{b_{\mathrm{mix}} = \frac{Q}{1-D}, \qquad a_{\mathrm{mix}} = RT\,\frac{QD}{1-D}} \tag{21}$$

with Q from equations (17)–(18) and D from equation (20). The two conditions have fixed both parameters simultaneously. Three features deserve attention when implementing this.

- b_{mix} is *not* linear in composition. It is a ratio of a quadratic form to a linear-plus-g^{E} expression, and it is this freedom that lets the rule satisfy the virial constraint while still reproducing an arbitrary g^{E}.
- For a pure component, $Q = b_i - a_i/RT$ and $D = a_i/(b_i RT)$, whence $1 - D = (b_i RT - a_i)/(b_i RT)$ and equation (21) returns $b_{\mathrm{mix}} = b_i$ and $a_{\mathrm{mix}} = a_i$ exactly. The rule is self-consistent by construction, and this identity is the correct unit test for code.
- Fugacity coefficients require $\partial(n^2 Q)/\partial n_i$ and $\partial(nD)/\partial n_i$; because b_{mix} is non-linear in composition, the partial molar derivatives of b must be carried explicitly and cannot be replaced by b_i as in the one-fluid rule. Omitting this is the most common implementation error.

The price of correctness at both ends of the density range is one additional binary parameter, k_{ij}, on top of the two or three parameters of the underlying NRTL or UNIQUAC model. Wong–Sandler consequently reproduces low-pressure VLE about as well as the activity coefficient model alone, extrapolates to high pressure and to supercritical components as an equation of state, and yields correct second virial coefficients in the vapour — which Huron–Vidal does not.

A.4 What the names mean in practice

These rules appear in commercial process simulators as property-method names built from the equation of state, the mixing rule and the G^{E} model. The mapping is mechanical.

Property method	Equation of state	Mixing rule and G^{E} model
PRWS, RKSWS	Peng–Robinson, SRK	Wong–Sandler with NRTL (user parameters plus k_{ij})
PRMHV2, RKSMHV2	Peng–Robinson, SRK	Modified Huron–Vidal second order, usually with UNIFAC
PSRK	SRK (Soave α)	MHV1-type zero-pressure match with UNIFAC
PR/SRK with k_{ij}	Peng–Robinson, SRK	van der Waals one-fluid, equation (1)

Selecting PRWS therefore means: run Peng–Robinson, but compute a_{mix} and b_{mix} from equation (21), taking g^{E} from the NRTL binary parameter form and k_{ij} from the Wong–Sandler parameter form. If those parameters are blank the method degrades silently towards the one-fluid rule and the reason for choosing it has been lost. Confirming that the binary parameters are populated is a required step, not a refinement.

MHV1 and MHV2. Michelsen (1990) proposed matching g^{E} at zero rather than infinite pressure, using the liquid root of the equation of state at $P = 0$; because that reference state is close to the conditions at which published parameters were regressed, MHV1 (a linear approximation of the resulting relation between the dimensionless attraction parameter and g^{E}) and MHV2 (a quadratic, more accurate approximation) *do* allow existing low-pressure UNIFAC and UNIQUAC tables to be used directly — the practical advantage Huron–Vidal lacks, and the reason PSRK (Holderbaum and Gmehling, 1991) is *predictive*: it inherits the whole UNIFAC group-contribution table and needs no binary regression.

The engineering summary is short. Use the one-fluid rule for hydrocarbon and light-gas systems; Wong–Sandler when a polar or associating component coexists with a supercritical or high-pressure one and binary data exist for regression; PSRK or an MHV2 method when no binary data exist and a group-contribution prediction is the only option.

References

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Volume and page numbers are omitted deliberately. Author, year and journal are given with confidence; full bibliographic details should be verified against the journals before these works are cited formally.