

ON THE APPLICATION OF CUBIC EQUATIONS OF STATE TO SYNTHETIC HIGH-PRESSURE VLE MEASUREMENTS

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ABSTRACT

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A procedure is proposed for the accurate estimation of the compositions of vapour and liquid phases in an equilibrium cell from a knowledge of the weight and composition of the feed and the volume of the vapour phase.

A cubic equation of state (van der Waals or Redlich–Kwong), modified according to Peneloux, is applied. The pure component parameters are determined from vapour pressure and liquid density values. A single binary constant is determined by imposing the value of the vapour phase volume within the cell.

The accuracy of the calculated phase compositions is higher than or comparable to the values obtained by chromatographic analysis, with the advantage of a smaller experimental effort.

INTRODUCTION

Synthetic methods have been widely used for the experimental determination of equilibrium phase compositions (Deiters and Schneider, 1986). Different apparatuses have been developed in the last few years (Fornari et al., 1990), showing a renewed interest in this experimental method.

The basic idea of the method is that no sampling is necessary of either liquid or vapour phases; their compositions are calculated by a material balance, provided that the vapour volume is known and a reasonable model for the vapour phase is available. Consequently, the method is particularly suitable for measuring VLE data in those cases where sampling is the main source of inaccuracy, namely at elevated pressure, near the critical conditions and for complex multiphase systems.

This work aims to verify whether a simple cubic EOS, able to reproduce pure-component saturation and volumetric properties, can be applied successfully in conjunction with the synthetic method to obtain the complete information set (P , T , x , y).

The basic concepts applied here are:

(i) reproduction of liquid-state volumetric properties (the easiest to know and measure) improves the values calculated for the gas state.

(ii) The saturation pressure of a liquid mixture provides enough information about the molecular interactions (parameter mixing rules) to allow an accurate estimation of the vapour composition.

(iii) Finally, the compositions of the phases in equilibrium can be determined from the overall feed composition by applying the usual algorithms.

EQUATIONS OF STATE AND THEIR MODIFICATIONS

In order to limit to a minimum the amount of information needed, a two-parameter, cubic EOS is applied here. In particular, modified forms of the van der Waals (vdW), Redlich-Kwong (RK) and Peng-Robinson (PR) EOSs will be considered.

Of the two parameters in each of these equations, the pure-component covolume, b , is defined by application of the critical constraints, while the mixture values are determined, as usual, by a linear mixing rule.

The second parameter, a , in the attractive part is temperature dependent and for pure components can be determined directly from their vapour pressures (Soave, 1986); mixing rules are treated below.

To improve the volumetric behaviour of the three EOSs, the approach proposed by Peneloux (Peneloux and Rauzy, 1982) was followed. Accordingly, the volume is shifted by a term, c , so that v is replaced by $(v + c)$: modified van der Waals:

$$P = \frac{RT}{v + c - b} - \frac{a}{(v + c)^2} \quad (1a)$$

modified Redlich-Kwong:

$$P = \frac{RT}{v + c - b} - \frac{a}{(v + c)(v + c + b)} \quad (1b)$$

modified Peng-Robinson:

$$P = \frac{RT}{v + c - b} - \frac{a}{(v + c)^2 + 2b(v + c) - b^2} \quad (1c)$$

This volume correction does not affect phase equilibrium conditions, which can be calculated using the original equation.

REPRODUCTION OF PURE-COMPONENT LIQUID DENSITIES AND DETERMINATION OF VAPOUR DENSITIES

In order to determine the volume correction, c , a volumetric datum is needed for each pure component.

The most easily available volumetric property is liquid density, which can be measured as such at the experimental temperature or estimated by extrapolating its value at a different temperature by means of an appropriate equation such as the Rackett correlation:

$$v_L^{\text{sat}} = \frac{RT_c}{P_c} Z_{\text{Ra}}^{1+(1-T_R)^{2/7}} \quad (2)$$

By solving the cubic eqn. (1), a root $(v + c)$ is obtained for the liquid state. From the available liquid density the value of the volume correction, c , which applies to the vapour phase, is obtained.

The problem now arises of whether the c value obtained from liquid density can be used to determine vapour density. This can be decided by comparing calculated values of $(Z_G - Z_L)$ with experimental values; since the latter values are lacking, a comparison can be done, at least for non-polar compounds, with estimates obtained using generalized methods.

In Table 1, a comparison is shown of the $(Z_G - Z_L)$ values at saturation calculated by the three cubic EOSs and the accurate BWR-type Lee-Kesler EOS (Lee and Kesler, 1975) for several values of reduced temperature and acentric factors. Also shown are the $(Z_G - Z_L)$ values estimated from the Pitzer tables (Pitzer and Curl, 1955), with the reduced saturation pressure estimated using the Lee-Kesler equation.

The results (valid for non-polar compounds) lead to the following conclusions:

(i) The vdW and RK EOSs yield practically the same results, while the PR EOS always yields values which are too high.

(ii) The LK EOS is in good agreement (as claimed by the authors, incidentally) with the tabulations by Pitzer.

(iii) The results of the vdW and RK EOSs lie within 1% of the more accurate data by Pitzer, even in the vicinity of the critical temperature.

If the above conclusions can be extended to all types of compounds (which seems reasonable) we can state that the vdW and RK equations can be applied to the calculation of vapour-phase densities, starting from available liquid densities. The PR EOS looks less reliable (although it was conceived especially for a good volumetric behaviour).

TABLE 1

Comparison of ($Z_G - Z_L$) values at saturation (vapour pressures from the Lee-Kesler equation)

T/T_c	ω	vdW	R-K	P-R	L-K	Pitzer
0.60	0.0	0.9566	0.9565	0.9592	0.9510	0.942
	0.2	0.9784	0.9783	0.9795	0.9734	0.961
	0.4	0.9893	0.9892	0.9898	0.9860	0.980
0.64	0.0	0.9336	0.9333	0.9379	0.9269	0.923
	0.2	0.9620	0.9619	0.9642	0.9550	0.946
	0.4	0.9783	0.9782	0.9795	0.9730	0.969
0.68	0.0	0.9038	0.9033	0.9104	0.8964	0.897
	0.2	0.9385	0.9383	0.9424	0.9295	0.925
	0.4	0.9607	0.9606	0.9630	0.9259	0.953
0.72	0.0	0.8665	0.8658	0.8764	0.8590	0.860
	0.2	0.9067	0.9063	0.9132	0.8959	0.894
	0.4	0.9347	0.9344	0.9389	0.9243	0.927
0.76	0.0	0.8209	0.8201	0.8351	0.8141	0.816
	0.2	0.8654	0.8647	0.8754	0.8533	0.854
	0.4	0.8985	0.8980	0.9056	0.8857	0.892
0.80	0.0	0.7658	0.7648	0.7855	0.7609	0.762
	0.2	0.8130	0.8121	0.8280	0.8005	0.802
	0.4	0.8500	0.8493	0.8615	0.8355	0.842
0.84	0.0	0.6994	0.6982	0.7259	0.6976	0.697
	0.2	0.7474	0.7463	0.7689	0.7358	0.738
	0.4	0.7868	0.7858	0.8043	0.7716	0.779
0.88	0.0	0.6183	0.6168	0.6530	0.6212	0.621
	0.2	0.6648	0.6635	0.6949	0.6558	0.659
	0.4	0.7045	0.7032	0.7304	0.6905	0.697
0.92	0.0	0.5153	0.5138	0.5581	0.5252	0.522
	0.2	0.5575	0.5560	0.5976	0.5535	0.555
	0.4	0.5945	0.5931	0.6315	0.5848	0.589
0.96	0.0	0.3721	0.3708	nc	nc	0.392
	0.2	0.4051	0.4037	0.4375	0.4092	0.418
	0.4	0.4347	0.4333	0.4754	0.4345	0.444

Once pure-component vapour densities are estimated accurately, we can assume that the same is also valid for their mixtures; in fact, the mixing rules of parameters play a minor role for a gas phase, and they are defined with sufficient accuracy from the equilibrium conditions, as will be shown below.

ESTIMATION OF THE VAPOUR COMPOSITION (MIXING RULES)

The second assumption made is that knowledge of the system equilibrium conditions provides sufficient information to define the mixing rules of the parameters and finally the vapour composition.

The only available experimental information is the vapour phase volume at the system temperature and pressure. This can be used to define the value of a single interaction parameter, i.e., for binary systems only and for simplified mixing rules, with one adjustable binary parameter.

The simplest solution is to apply the classical mixing rules, containing a single adjustable parameter, $k_{ij} = k_{ji}$:

$$a_M = \sum_i \sum_j x_i x_j a_{ij} = \sum_i \sum_j x_i x_j (1 - k_{ij}) (a_i a_j)^{1/2} \quad (3)$$

$$b_M = \sum_i x_i b_i \quad (4)$$

$$c_M = \sum_i x_i c_i \quad (5)$$

In principle, such mixing rules may not be applied to systems containing polar components but numerical experience has proved that the final results (i.e., the calculated phase compositions) are very little affected by the type of mixing rule employed, so the above expressions can be used for any system.

Given the total mass and composition of the feed, the system temperature and pressure and the measured volume of the vapour phase, the calculation procedure is as follows:

For each component:

(1) estimate the vapour pressure and from it the value of $\alpha_i = a_i(T)/a_i(T_{ci})$; the procedure can be the direct one described by Soave (Soave, 1986).

(2) Calculate the values of the parameters:

$$a_{ii} = \Omega_a \alpha_i R^2 T_{ci}^2 / P_{ci} \quad (6)$$

where $\Omega_a = 0.421875$ (vdW) or 0.42748 (RK) and

$$b_i = \Omega_b R T_{ci} P_{ci} \quad (7)$$

where $\Omega_b = 0.125$ (vdW) or 0.086640 (RK).

(3) Solve the cubic eqn. (1) at $P = P_i^{\text{sat}}$, selecting a liquid-like root ($v_{Li}^{\text{sat}} + c_i$).

(4) Estimate the saturated liquid molar volume, v_{Li}^{sat} (if not available the Rackett equation, eqn. (2), allows an extrapolation of available density values to any other temperature) and, by difference, determine the volume correction, c_i .

The procedure now becomes iterative, as the aim is to determine, by trial and error, the value of the binary interaction constant k_{12} corresponding to the known value of the vapour phase volume.

(5) Assume initial compositions for the vapour and liquid phases.

(6) Assume a starting value for k_{12} and calculate

$$a_{12} = a_{21} = (1 - k_{12})(a_{11}a_{22})^{1/2} \quad (8)$$

Execute steps 7, 8 and 9 for each phase:

(7) calculate mixture parameters:

$$a_M = a_{11}x_1^2 + 2a_{12}x_1x_2 + a_{22}x_2^2 \quad (9)$$

$$b_M = b_1x_1 + b_2x_2 \quad (10)$$

$$c_M = c_1x_1 + c_2x_2 \quad (11)$$

(where x_1, x_2 represent molar fractions in the phase considered).

(8) Solve the cubic eqn. (1) at the system pressure and obtain a root ($v_L + c_M$) or ($v_G + c_M$), according to the phase considered: the molar volume v_L or v_G can be obtained from this.

(9) Calculate fugacity coefficients of components in the phase considered. vdW:

$$\ln \varphi_i = \frac{b_i}{b_M} \left[\frac{P(v + c_M)}{RT} - 1 \right] - \ln \left[\frac{P(v + c_M - b_M)}{RT} \right] - \left(2 \frac{\sum_j x_j a_{ji}}{a_M} - \frac{b_i}{b_M} \right) \frac{a_M}{v + c_M} - \frac{c_i P}{RT} \quad (12)$$

RK:

$$\ln \varphi_i = \frac{b_i}{b_M} \left[\frac{P(v + c_M)}{RT} - 1 \right] - \ln \left[\frac{P(v + c_M - b_M)}{RT} \right] - \left(2 \frac{\sum_j x_j a_{ji}}{a_M} - \frac{b_i}{b_M} \right) \frac{a_M}{RTb_M} \ln \left(1 + \frac{b_M}{v + c_M} \right) - \frac{c_i P}{RT} \quad (13)$$

and vaporization factors:

$$K_i = (y_i/x_i)_{\text{equil.}} = \exp(\ln \varphi_i^L - \ln \varphi_i^G) \quad (14)$$

(10) Calculate phase compositions and vaporization ratio; for binary systems direct expressions apply:

$$x_1 = \frac{1 - K_2}{K_1 - K_2}, \quad x_2 = 1 - x_1 \quad (15)$$

$$y_1 = K_1 x_1, \quad y_2 = 1 - y_1 \quad (16)$$

$$\frac{n^G}{n_{\text{tot}}} = \frac{(K_1 z_1 + K_2 z_2 - 1)}{(K_1 - 1)(1 - K_2)} \quad (17)$$

whence the vapour mole number n^G .

TABLE 2
Pure component properties

	Propylene	Methanol
Critical temperature (K)	364.9	512.6
Critical pressure (bar)	46.0	80.9
Molecular weight	42.081	32.042
Vapour pressure at 25 °C (bar)	11.566	0.169
Saturated liquid volume at 25 °C (cm ³ mol ⁻¹)	83.39	40.73

(11) Compare the calculated vapour volume ($n^G v^G$) with the experimental one, adjust the assumed k_{12} value if necessary and start again from step 6 until the right volume has been found. For the new iteration the calculated liquid and vapour compositions are assumed, so that they stabilize during the search.

The following numerical example is significant in showing the effectiveness of the proposed algorithm, as it applies to a highly asymmetric system (propylene-methanol) at high pressure conditions. The data were taken from a paper by Ohgaki et al. (1988). The paper reports the experimental temperature (25 °C) and pressure, equilibrium phase compositions and pure-component properties (saturated liquid density and vapour pressure). The pure-component properties were used here for the calculations in addition to the critical constants and molecular weights from Reid et al. (1987) (see Table 2).

The experimental points considered and the related experimental data are given in Table 3. Such data were used to synthesize the feed to the equilibrium cell, based on assumed values of the phase volumes. The assumptions were: liquid volume, 800 cm³; vapour volume, 200 cm³.

TABLE 3
Experimental data

	Propylene	Methanol
Liquid molar fractions	0.0779	0.9221
Vapour molar fractions	0.9687	0.0313
Temperature (°C)	25	
Pressure (bar)	4.795	
Liquid molar volume (cm ³ mol ⁻¹)	43.62	

Liquid phase

$$n_L = V_L/v_L = 800 \text{ (cm}^3\text{)}/43.62 \text{ (cm}^3 \text{ mol}^{-1}\text{)} = 18.3402 \text{ mol}$$

$$n_1 = x_1 n_L = 18.3402 \times 0.0779 = 1.4287 \text{ mol}$$

$$n_2 = x_2 n_L = 18.3402 \times 0.9221 = 16.9115 \text{ mol}$$

$$M_L = x_1 M_1 + x_2 M_2 = 32.824 \text{ g mol}^{-1}$$

$$W_L = n_L M_L = 602.000 \text{ g}$$

Vapour phase

Its density is not given and it was estimated by a pressure-explicit virial equation:

$$Z = 1 + BP/RT$$

or:

$$v = RT/P + B$$

The second virial coefficient of the components was derived from the values tabulated by Dymond and Smith (1980), extrapolated to 25°C with the equation proposed by Vetere (1988):

$$B = (A/RT)e^{-kT} \quad (18)$$

The values so determined were: $B_1 = -347 \text{ cm}^3 \text{ mol}^{-1}$, $B_2 = -1485 \text{ cm}^3 \text{ mol}^{-1}$.

For the gas mixture, since no information was available on the combination rule, a linear mixing rule was assumed:

$$B_M = B_1 y_1 + B_2 y_2 = -382.6 \text{ cm}^3 \text{ mol}^{-1}$$

whence:

$$Z_G = 1 - 382.6 \times 4.795 / (83.144 \times 298.15) = 0.92599$$

$$v_G = Z_G RT/P = 4787.24 \text{ cm}^3 \text{ mol}^{-1}$$

$$n_G = V_G/v_G = 200/4787.24 = 0.0418 \text{ mol}$$

$$G_1 = n_G y_1 = 0.0405 \text{ mol}$$

$$G_2 = n_G y_2 = 0.0013 \text{ mol}$$

$$M_G = M_1 y_1 + M_2 y_2 = 41.767 \text{ g mol}^{-1}$$

$$W_G = n_G M_G = 1.745 \text{ g}$$

TABLE 4
Calculation results

	vdW	RK	Experimental
Vapour mole fractions			
propylene	0.9628	0.9628	0.9687
methanol	0.0372	0.0372	0.0313
Vapour compressibility	0.9283	0.9279	(0.9260)
Liquid mole fractions			
propylene	0.0779	0.0779	0.0779
methanol	0.9221	0.9221	0.9221
Liquid molal volume (cm ³ mol ⁻¹)	42.85	42.88	43.62

and finally, for the feed:

$$n_F = n_L + n_G = 18.3820 \text{ mol}$$

$$W_F = W_L + W_G = 603.745 \text{ g}$$

$$F_1 = L_1 + G_1 = 1.4692 \text{ mol}$$

$$z_1 = F_1/n_F = 0.07992$$

The molar fraction of the first component in the feed is 2.6% higher than in the liquid phase; assuming this composition for the liquid (as often done) would introduce a sensible error.

With this feed composition (which is accurate enough, the only assumption relating to the vapour phase compressibility, which has a minor effect) and imposing a value of 200 cm³ for the volume of the vapour phase, calculations by the procedure described above led to the results reported in Table 4.

Both equations of state gave the same results (this was a constant conclusion for all the cases examined).

The calculated vapour density agrees to within less than 1%, with the value calculated by a virial equation of state; vapour phase concentrations also differ by 0.59% from the experimental values but the final effect on liquid-phase composition is negligible, so liquid-phase concentrations agree to within four decimal places with experimental values (and this is a significant result since vapour phase composition is of less importance).

The small inaccuracies found in gas concentrations are mainly due to the types of mixing rules adopted, and it is questionable whether better values could be obtained with different mixing rules.

To investigate this, a different class of mixing rules was applied; this is based on the approach proposed by Vidal and Huron (1979), according to

which the excess value of the ratio a/b is equal to the excess Gibbs energy at infinite pressure:

$$a/b = \sum_i x_i a_i/b_i - g_E^\infty = \sum_i x_i (a_i/b_i - RT \ln \gamma_i^\infty) \quad (19)$$

so that the expression for the fugacity coefficients can be written (for the vdW EOS) as:

$$\ln \varphi_i = \frac{b_i}{b} \left[\frac{P(v+c)}{RT} - 1 \right] - \ln \left[\frac{P(v+c-b)}{RT} \right] - \left(\frac{a_i}{RTb_i} - \ln \gamma_i^\infty \right) \frac{b}{v+c} - \frac{c_i P}{RT} \quad (20)$$

Different expressions can be used for γ^∞ . Some examples are:

Margules:

$$\ln \gamma_1^\infty = A_{12} x_2^2 \quad (21)$$

Hildebrand:

$$\ln \gamma_1^\infty = A_{12} b_1 \phi_2^2 \quad (22)$$

with:

$$\phi_i = b_i x_i / (b_1 x_1 + b_2 x_2) \quad (23)$$

or any other two-parameter expression, provided that a constraint is imposed between the parameters (since a single parameter is required to reproduce the experimental vapour rate).

Repeating the described procedure, with different models, the results were those reported in Table 5.

These results are very similar to those reported above, so a more sophisticated approach is not justified. Although not reported in Table 5, imposing different values on the A_{12}/A_{21} ratio in the Wilson equation did not cause the results to vary notably.

In no case did the calculated vapour composition approach the experimental value, but in all cases it remained sufficiently accurate for the

TABLE 5

Results with different γ^∞ models

γ^∞ model	Z_G	y_1	x_1
Margules	0.9285	0.9631	0.0779
Hildebrand	0.9283	0.9628	0.0779
Wilson ($A_{12} = A_{21}$)	0.9286	0.9630	0.0779
Classical rule	0.9283	0.9628	0.0779
Experimental	(0.9260)	0.9687	0.0779

determination of the liquid composition; the calculated liquid volume ($42.85 \text{ cm}^3 \text{ mol}^{-1}$) was about 2% lower than the experimental value ($43.62 \text{ cm}^3 \text{ mol}^{-1}$), but this difference had no effect on the composition values.

CONCLUSION

The proposed procedure allows the determination of equilibrium phase compositions, starting from the cell feed composition and weight and the volume of the gas phase; the calculated liquid-phase composition is more accurate by far than that obtained by chromatographic analysis, while the gas phase composition is of comparable accuracy.

Calculations prove that the results are very little affected by the type of equation of state adopted and by the parameter mixing rules, so a simple van der Waals-type equation of state, with volume corrections according to Peneloux and classical mixing rules, can be applied with confidence.

The estimated liquid composition is relatively less accurate at higher pressures because of the lower precision of the calculated vapour density and composition. However, this effect is balanced by the relatively low mass of the vapour phase, except in the immediate vicinity of the critical point.

REFERENCES

- Deiters, U.K. and Schneider, G.M., 1986. High pressure phase equilibria: experimental methods. *Fluid Phase Equilibria*, 29: 145-160.
- Dymond, J.H. and Smith, E.B., 1980. *The Virial Coefficients of Pure Gases and Mixtures*. Clarendon Press, Oxford.
- Fornari, R.E., Alessi, P. and Kikic, I., 1990. High pressure fluid phase equilibria: experimental methods and systems investigated (1978-1987). *Fluid Phase Equilibria*, 57: 1-33.
- Lee, B.I. and Kesler, M.G., 1975. A generalized thermodynamic correlation based on three-parameter corresponding states. *AIChE J.*, 21: 510-527.
- Ohgaki, K., Takata, H., Washida, T. and Katayama, T., 1988. Phase equilibria for four binary systems containing propylene. *Fluid Phase Equilibria*, 43: 105-113.
- Peneloux, A. and Rauzy, E., 1982. A consistent correction for Redlich-Kwong-Soave volumes. *Fluid Phase Equilibria*, 8: 7-23.
- Pitzer, K.S. and Curl, R.F., 1955. The volumetric and thermodynamic properties of fluids, I. Theoretical basis and virial coefficients. *J. Am. Chem. Soc.*, 77: 3433-3440.
- Reid, R.C., Prausnitz, J.M. and Poling, B.E., 1987. *The Properties of Gases and Liquids*. 4th edn., McGraw-Hill, New York.
- Soave, G., 1986. Direct calculation of pure-compound vapour pressures through cubic equations of state. *Fluid Phase Equilibria*, 31: 203-207.
- Vetere, A., 1988. An empirical model for calculating second virial coefficients. *Chem. Eng. Sci.*, 43 (12): 3119-3127.
- Vidal, H. and Huron, M.J., 1979. New mixing rules in simple equations of state for representing vapour liquid equilibria of strongly non-ideal mixtures. *Fluid Phase Equilibria*, 3: 255-271.