Solutions for R&D to Design

Equation of State Model using Group Contribution Method (PSRK Method)

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Introduction

- When performing vapor-liquid equilibrium calculations, activity coefficient models such as the Wilson method and the NRTL method, or equation of state models such as the SRK method and the Peng-Robinson method are commonly used.
- The advantage of the former models is that they provide calculation accuracy for non-ideal solutions. The advantages of the latter models are that they enable estimations to be done with only a limited number of parameters, and that they provide reliable results in the critical region.
- On the other hand, regarding their disadvantages, the former models necessitate parameter fitting using actual measurement data, and the latter models have a limited applicability to non-ideal solutions.
- Here, we will introduce together with information from the scientific literature, features and points of caution regarding the PSRK method which is a group contribution model that compensates for these respective problems.

Predictive SRK Method (1991)

ABSTRACT

J.Gmehling、T.Holderbaum (1991)

A group contribution equation of state called PSRK (Predictive Soave-Redlich-Kwong) which is based on the Soave-Redlich-Kwong equation (Soave, 1972) has been developed. It uses the UNIFAC method to calculate the mixture parameter a and includes all already existing UNIFAC parameters. This concept makes use of recent developments by Michelsen (1990b) and has the main advantage, that vapor-liquid-equilibria (VLE) can be predicted for a large number of systems without introducing new model parameters that must be fitted to experimental VLE-data. The PSRK equation of state can be used for VLE-predictions over a much larger temperature and pressure range than the UNIFAC γ-φ-approach and is easily extended to mixtures containing supercritical compounds. Additional PSRK parameters, which allow the calculation of gas/gas and gas/alkane phase equilibria, are given in this paper. In addition to those mixtures covered by UNIFAC, phase equilibrium calculations may also include gases like CH_4, C_2H_6, C_3H_6, C_4H_{10}, CO_2, N_2, H_2 and CO.

Features of PSRK Method:

1. The SRK equation of state is taken as the base equation and the UNIFAC method group contribution model is applied in the mixing rule of the attractive force parameter term (parameter a).
2. It is possible to predict vapor-liquid equilibrium relationships without using regressions of measured data.
3. Compared to activity coefficient models, it can be applied in wider temperature and pressure ranges, and can handle supercritical components easily (Henry's law is not required).

Solutions for R&D to Design Fluid Phase Equilibria,70 (1991) 251-265 Elsevier Science Publishers B.V., Amsterdam

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SRK Method (1972)

- One of the most successful modifications of the van der Waals equation was introduced by Giorgio Soave in 1972.
- In order to improve the estimation accuracy of the vapor pressure he defined the α function which is dependent of temperature and the acentric factor (ω). Also, to improve the vapor-liquid equilibrium estimation accuracy in multicomponent systems, the empirical parameter (k_{ij}) was adopted and incorporated into the mixing rule .

$$P = \frac{RT}{v_m - b_m} - \frac{a_m}{v_m\left(v_m + b_m\right)}$$

Pure Component Parameters

$$a_i = 0.42748\frac{R^2 T_{ci}^2}{P_{ci}}\alpha_i(T)$$

$$b_i = 0.08664\frac{RT_{ci}}{P_{ci}}$$

SRK Method Mixing Rule

$$\left\{\begin{aligned} a_m &= \sum_i \sum_j x_i x_j \left(a_i a_j\right)^{0.5}\left(1 - k_{ij}\right) \\ b_m &= \sum_i x_i b_i \end{aligned}\right.$$

$$\alpha_i(T) = \left[1 + m_i\left(1 - \sqrt{T_{ri}}\right)\right]^2$$

$$m_i = 0.480 + 1.574\omega_i - 0.176\omega_i^2$$

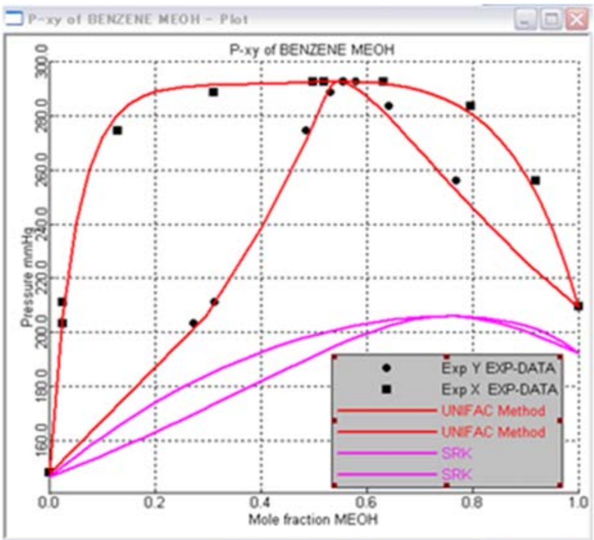
α Function

Application of Equation of State to Polar Molecules

- The original focus of the investigations that made use of the SRK method was on hydrocarbons, which are nonpolar molecules, and, as is shown in the figure, deviations are large when it is applied to polar molecules.
- For the purpose of compensating for this drawback, methods that introduce excess free energy into the mixing rule of the equation of state were introduced (gE-EOS method).
- The following mixing rule was proposed by Huron and Vidal (1979), after which improved mixing rules were proposed by Dahl and Michelsen (MHV2 in 1990), Holderbaum and Gmehling (PSRK in 1991), and Wong and Sandler (WS in 1992).

$$\frac{a}{b} = \sum_i x_i \frac{a_i}{b_i} - \frac{1}{\Lambda} G^E_{m,\ P=\infty}$$

$$\Lambda = \frac{1}{\lambda_1 - \lambda_2} \ln\left(\frac{1+\lambda_1}{1+\lambda_2}\right)$$



MeOH – Benzene
Constant Temperature
VLE (35C)

Modification of α Function
(Pure Component Parameter a)

Two modifications are necessary to obtain an equation of state for predicting vapor-liquid-equilibria of polar as well as nonpolar mixtures. The first modification concerns the temperature dependence of the pure component parameter a, which was originally expressed by Soave in terms of the acentric factor ω:

$$a_i = 0.42748 \frac{R^2 T_{c,i}^2}{P_{c,i}} \boxed{f(T)} \qquad (2)$$

$$f(T) = [\,1 + c_1(1-T_r^{0.5})\,]^2 \qquad (3)$$

$$c_1 = 0.48 + 1.574\omega - 0.176\omega^2 \qquad (4)$$

α Function

Original SRK Method
Parameter a Calculation

This temperature dependence yields sufficiently accurate vapor pressure data for nonpolar substances, but improvements are still necessary for polar components. Therefore, the expression proposed by Mathias and Copeman (1983) is used in the PSRK equation:

$$\boxed{f(T) = [\,1 + c_1(1-T_r^{0.5}) + c_2(1-T_r^{0.5}) + c_3(1-T_r^{0.5})\,]^2 \qquad T_r<1}$$

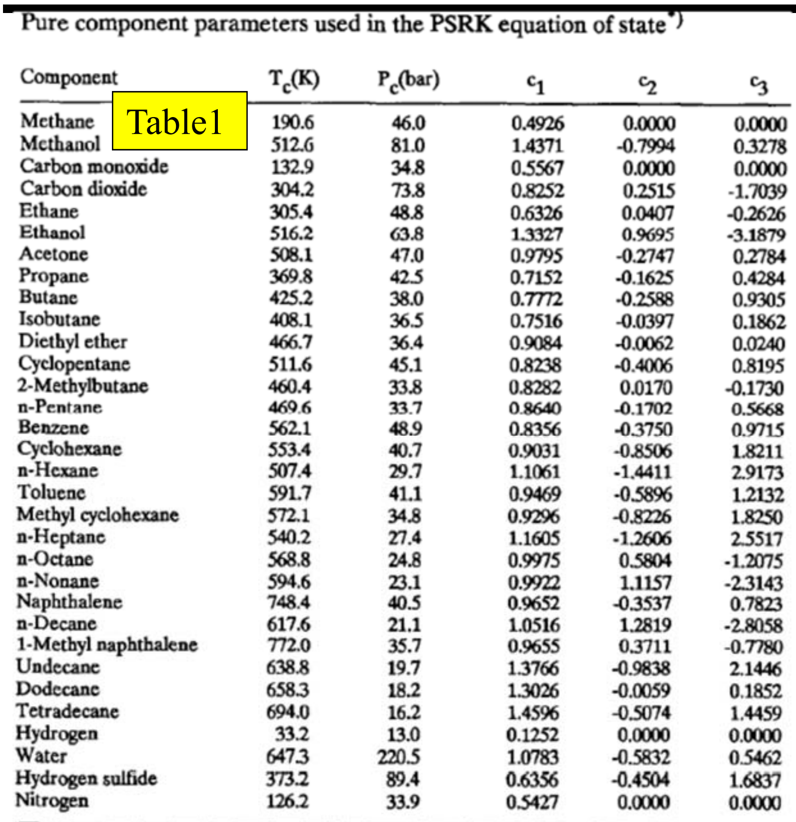
PSRK
method

(5)

$$f(T) = [\,1 + c_1(1-T_r^{0.5})\,]^2 \qquad T_r>1$$

- For components below the reduced critical temperature, the attractive force terms are expressed by parameters c1, c2 and c3.
- For components above the reduced critical temperature , the conventional SRK method is applied. This improves the vapor pressure estimation accuracy of pure substances.

Pure Component Parameters (Tc, Pc, c_1, c_2, c_3)



Pure component parameters used in the PSRK equation of state*)

Table1

Component	T_c(K)	P_c(bar)	c_1	c_2	c_3
Methane	190.6	46.0	0.4926	0.0000	0.0000
Methanol	512.6	81.0	1.4371	-0.7994	0.3278
Carbon monoxide	132.9	34.8	0.5567	0.0000	0.0000
Carbon dioxide	304.2	73.8	0.8252	0.2515	-1.7039
Ethane	305.4	48.8	0.6326	0.0407	-0.2626
Ethanol	516.2	63.8	1.3327	0.9695	-3.1879
Acetone	508.1	47.0	0.9795	-0.2747	0.2784
Propane	369.8	42.5	0.7152	-0.1625	0.4284
Butane	425.2	38.0	0.7772	-0.2588	0.9305
Isobutane	408.1	36.5	0.7516	-0.0397	0.1862
Diethyl ether	466.7	36.4	0.9084	-0.0062	0.0240
Cyclopentane	511.6	45.1	0.8238	-0.4006	0.8195
2-Methylbutane	460.4	33.8	0.8282	0.0170	-0.1730
n-Pentane	469.6	33.7	0.8640	-0.1702	0.5668
Benzene	562.1	48.9	0.8356	-0.3750	0.9715
Cyclohexane	553.4	40.7	0.9031	-0.8506	1.8211
n-Hexane	507.4	29.7	1.1061	-1.4411	2.9173
Toluene	591.7	41.1	0.9469	-0.5896	1.2132
Methyl cyclohexane	572.1	34.8	0.9296	-0.8226	1.8250
n-Heptane	540.2	27.4	1.1605	-1.2606	2.5517
n-Octane	568.8	24.8	0.9975	0.5804	-1.2075
n-Nonane	594.6	23.1	0.9922	1.1157	-2.3143
Naphthalene	748.4	40.5	0.9652	-0.3537	0.7823
n-Decane	617.6	21.1	1.0516	1.2819	-2.8058
1-Methyl naphthalene	772.0	35.7	0.9655	0.3711	-0.7780
Undecane	638.8	19.7	1.3766	-0.9838	2.1446
Dodecane	658.3	18.2	1.3026	-0.0059	0.1852
Tetradecane	694.0	16.2	1.4596	-0.5074	1.4459
Hydrogen	33.2	13.0	0.1252	0.0000	0.0000
Water	647.3	220.5	1.0783	-0.5832	0.5462
Hydrogen sulfide	373.2	89.4	0.6356	-0.4504	1.6837
Nitrogen	126.2	33.9	0.5427	0.0000	0.0000

*) source: Dortmund Data Bank (Gmehling, 1991)

$$m_i = 0.480 + 1.574\omega_i - 0.176\omega_i^2$$

SRK Method : Acentric Factor ω

Aspen Plus DB Values

	ω	C1 Calculated Value	C1 Error
Methane	0.0115478	0.49815	1.1%
Methanol	0.5658310	1.31427	-9.3%
CO2	0.2236210	0.82318	32.4%

- Below the reduced critical temperature , the three *c* parameters are used instead of ω.
- The estimation accuracy of the vapor pressure of nonpolar substances is improved.
- For polar substances, it is indicated that an improvement is required.

Vapor Pressure Estimation Accuracy - Verification Calculations

Nonpolar Substances

	Antoine Eq.	SRK	Error	PSRK	Error
Propane	-42.071	-41.815	-0.11%	-42.086	0.01%
n-Butane	-0.533	-0.119	-0.15%	-0.523	0.00%
CCL4	76.731	77.078	-0.10%	76.785	-0.02%

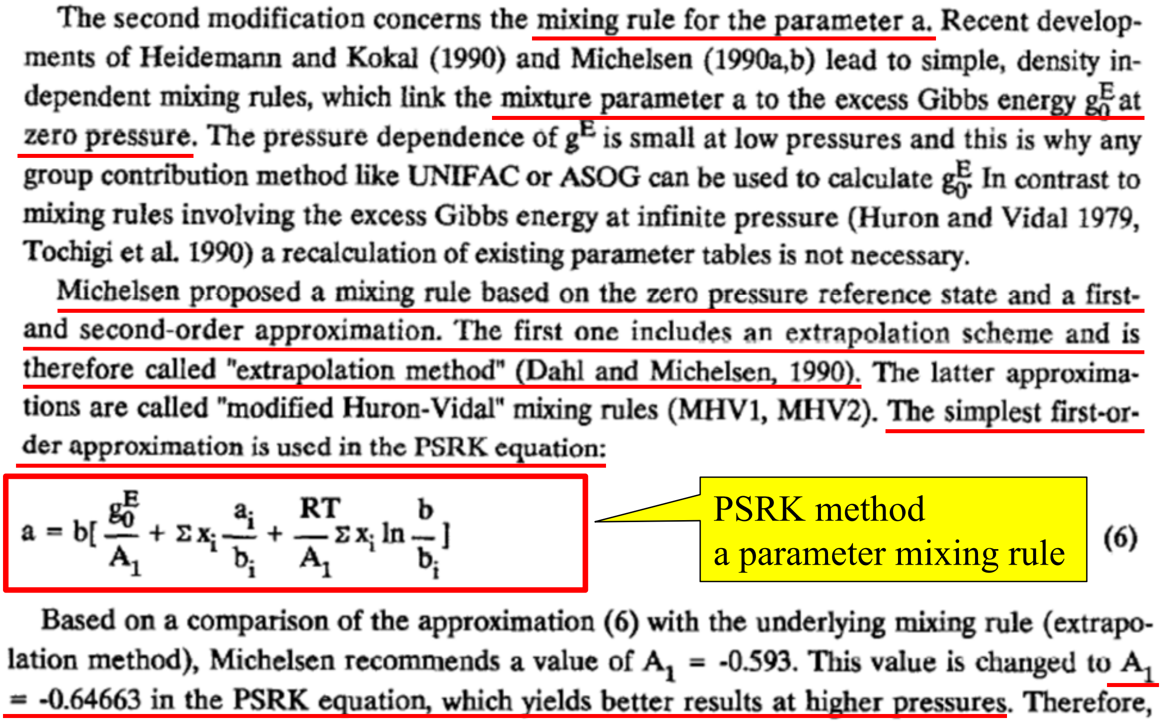
Polar Substances

	Antoine Eq.	SRK	Error	PSRK	Error
Methanol	64.535	64.758	-0.07%	64.555	-0.01%
Water	100.018	102.895	-0.77%	99.946	0.02%
Acetate	118.008	119.314	-0.33%	118.059	-0.01%

A comparison calculation between the SRK method and the PSRK method was carried out by focusing on normal boiling point data.

- Compared with the original SRK method, it was confirmed that the estimation accuracy of the vapor pressure is higher for both nonpolar and polar substances.
- However, caution is required for substances for which the c parameters are not available.

Modification of Mixing Rule (Mixture Parameter a)



The second modification concerns the mixing rule for the parameter a. Recent developments of Heidemann and Kokal (1990) and Michelsen (1990a,b) lead to simple, density independent mixing rules, which link the mixture parameter a to the excess Gibbs energy g_0^E at zero pressure. The pressure dependence of g^E is small at low pressures and this is why any group contribution method like UNIFAC or ASOG can be used to calculate g_0^E. In contrast to mixing rules involving the excess Gibbs energy at infinite pressure (Huron and Vidal 1979, Tochigi et al. 1990) a recalculation of existing parameter tables is not necessary.

Michelsen proposed a mixing rule based on the zero pressure reference state and a first- and second-order approximation. The first one includes an extrapolation scheme and is therefore called "extrapolation method" (Dahl and Michelsen, 1990). The latter approximations are called "modified Huron-Vidal" mixing rules (MHV1, MHV2). The simplest first-order approximation is used in the PSRK equation:

$$\boxed{a = b\left[\frac{g_0^E}{A_1} + \Sigma x_i \frac{a_i}{b_i} + \frac{RT}{A_1} \Sigma x_i \ln \frac{b}{b_i}\right]} \qquad (6)$$

PSRK method
a parameter mixing rule

Based on a comparison of the approximation (6) with the underlying mixing rule (extrapolation method), Michelsen recommends a value of $A_1 = -0.593$. This value is changed to $A_1 = -0.64663$ in the PSRK equation, which yields better results at higher pressures. Therefore,

- Excess Gibbs free energy (g_0^E) at zero pressure is applied to the mixing rule.
- g_0^E is estimated using the UNIFAC or ASOG model.
- A value of -0.64663 is used for A1 parameter.

PSRK Method Summary

$$P = \frac{RT}{v_m - b} - \frac{a(T)}{v_m(v_m + b)}$$

Base Equation of State: SRK method

$$a_i = 0.42748 \frac{R^2 T_{ci}^2}{P_{ci}} \alpha_{i\,(T)}$$

$$b_i = 0.08664 \frac{RT_{ci}}{P_{ci}}$$

Pure Component Parameter

$$\alpha_{i\,(T)} = \left\{1 + c_1\left(1 - T_r^{0.5}\right) + c_2\left(1 - T_r^{0.5}\right) + c_3\left(1 - T_r^{0.5}\right)\right\}^2 \qquad T_r < 1$$

$$\alpha_{i\,(T)} = \left\{1 + c_1\left(1 - T_r^{0.5}\right)\right\}^2 \qquad T_r > 1$$

α Function

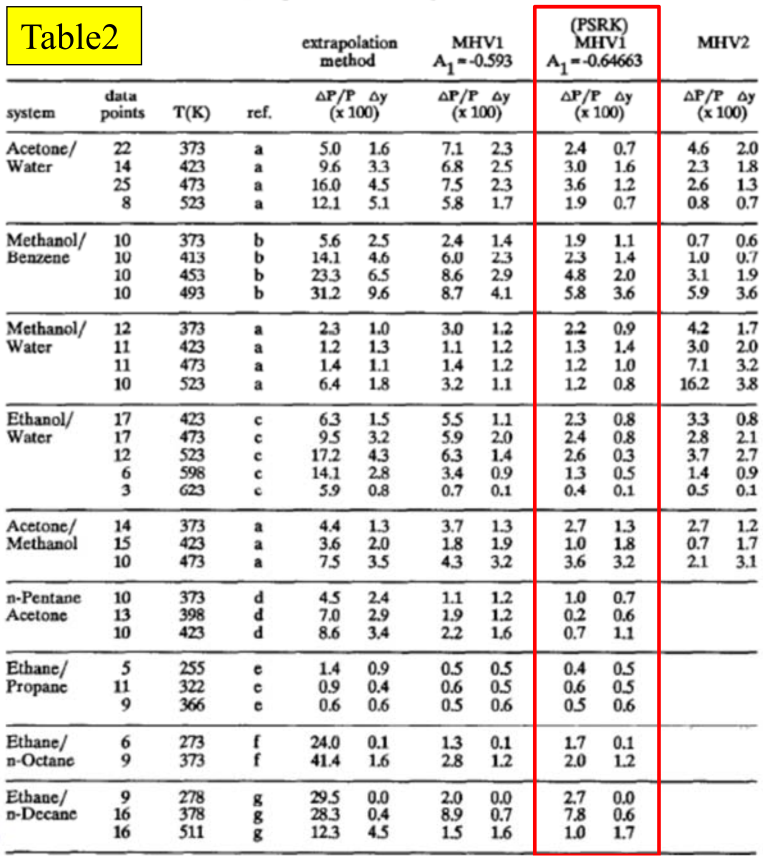
$$a_{mix} = b_{mix}\left[\frac{g_0^E}{A_1} + \sum\left(x_i \frac{a_i}{b_i}\right) + \frac{RT}{A_1}\sum\left(x_i \ln\left(\frac{b_{mix}}{b_i}\right)\right)\right]$$

$$b_{mix} = \sum x_i b_i$$

$$A_1 = -0.64663$$

Mixing Rule

Vapor-Liquid Equilibrium Estimation



VLE Results for different group contribution equation of state

Table2

system	data points	T(K)	ref.	extrapolation method		MHV1 A_1=-0.593		(PSRK) MHV1 A_1=-0.64663		MHV2	
				ΔP/P (x 100)	Δy	ΔP/P (x 100)	Δy	ΔP/P (x 100)	Δy	ΔP/P (x 100)	Δy
Acetone/ Water	22	373	a	5.0	1.6	7.1	2.3	2.4	0.7	4.6	2.0
	14	423	a	9.6	3.3	6.8	2.5	3.0	1.6	2.3	1.8
	25	473	a	16.0	4.5	7.5	2.3	3.6	1.2	2.6	1.3
	8	523	a	12.1	5.1	5.8	1.7	1.9	0.7	0.8	0.7
Methanol/ Benzene	10	373	b	5.6	2.5	2.4	1.4	1.9	1.1	0.7	0.6
	10	413	b	14.1	4.6	6.0	2.3	2.3	1.4	1.0	0.7
	10	453	b	23.3	6.5	8.6	2.9	4.8	2.0	3.1	1.9
	10	493	b	31.2	9.6	8.7	4.1	5.8	3.6	5.9	3.6
Methanol/ Water	12	373	a	2.3	1.0	3.0	1.2	2.2	0.9	4.2	1.7
	11	423	a	1.2	1.3	1.1	1.2	1.3	1.4	3.0	2.0
	11	473	a	1.4	1.1	1.4	1.2	1.2	1.0	7.1	3.2
	10	523	a	6.4	1.8	3.2	1.1	1.2	0.8	16.2	3.8
Ethanol/ Water	17	423	c	6.3	1.5	5.5	1.1	2.3	0.8	3.3	0.8
	17	473	c	9.5	3.2	5.9	2.0	2.4	0.8	2.8	2.1
	12	523	c	17.2	4.3	6.3	1.4	2.6	0.3	3.7	2.7
	6	598	c	14.1	2.8	3.4	0.9	1.3	0.5	1.4	0.9
	3	623	c	5.9	0.8	0.7	0.1	0.4	0.1	0.5	0.1
Acetone/ Methanol	14	373	a	4.4	1.3	3.7	1.3	2.7	1.3	2.7	1.2
	15	423	a	3.6	2.0	1.8	1.9	1.0	1.8	0.7	1.7
	10	473	a	7.5	3.5	4.3	3.2	3.6	3.2	2.1	3.1
n-Pentane Acetone	10	373	d	4.5	2.4	1.1	1.2	1.0	0.7		
	13	398	d	7.0	2.9	1.9	1.2	0.2	0.6		
	10	423	d	8.6	3.4	2.2	1.6	0.7	1.1		
Ethane/ Propane	5	255	e	1.4	0.9	0.5	0.5	0.4	0.5		
	11	322	e	0.9	0.4	0.6	0.5	0.6	0.5		
	9	366	e	0.6	0.6	0.5	0.6	0.5	0.6		
Ethane/ n-Octane	6	273	f	24.0	0.1	1.3	0.1	1.7	0.1		
	9	373	f	41.4	1.6	2.8	1.2	2.0	1.2		
Ethane/ n-Decane	9	278	g	29.5	0.0	2.0	0.0	2.7	0.0		
	16	378	g	28.3	0.4	8.9	0.7	7.8	0.6		
	16	511	g	12.3	4.5	1.5	1.6	1.0	1.7		

- Pure substance parameters Tc, Pc, C1, C2, C3 estimation results using excess free energy g_0^E (UNIFAC).
- By changing the parameter A1, the estimation accuracy under high pressure is improved compared to the value suggested by Michelsen.
- Estimation accuracy is almost equal to MHV2.

Vapor-Liquid Equilibrium Calculation

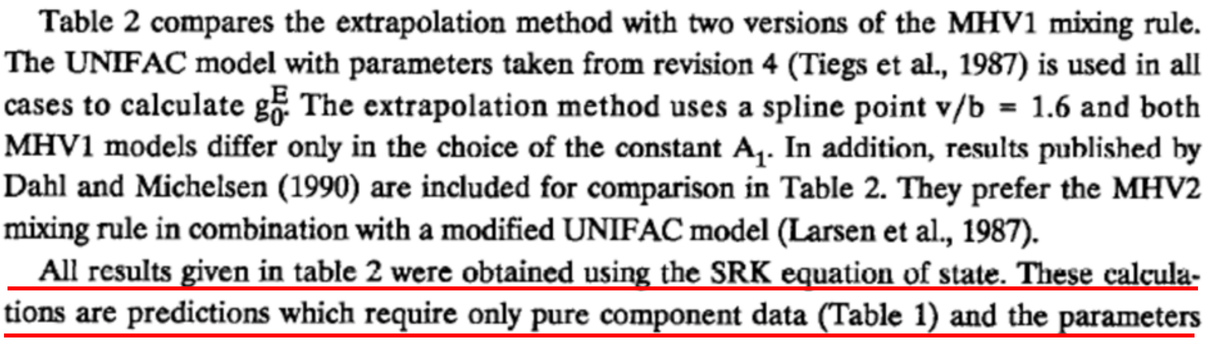


Table 2 compares the extrapolation method with two versions of the MHV1 mixing rule. The UNIFAC model with parameters taken from revision 4 (Tiegs et al., 1987) is used in all cases to calculate g_0^E. The extrapolation method uses a spline point v/b = 1.6 and both MHV1 models differ only in the choice of the constant A_1. In addition, results published by Dahl and Michelsen (1990) are included for comparison in Table 2. They prefer the MHV2 mixing rule in combination with a modified UNIFAC model (Larsen et al., 1987).

All results given in table 2 were obtained using the SRK equation of state. These calculations are predictions which require only pure component data (Table 1) and the parameters

- The results in Table 2 are based on the PSRK method (SRK + UNIFAC), without performing any parameter fitting by actual measurement data. High VLE estimation accuracy is obtained for non-polar substances.

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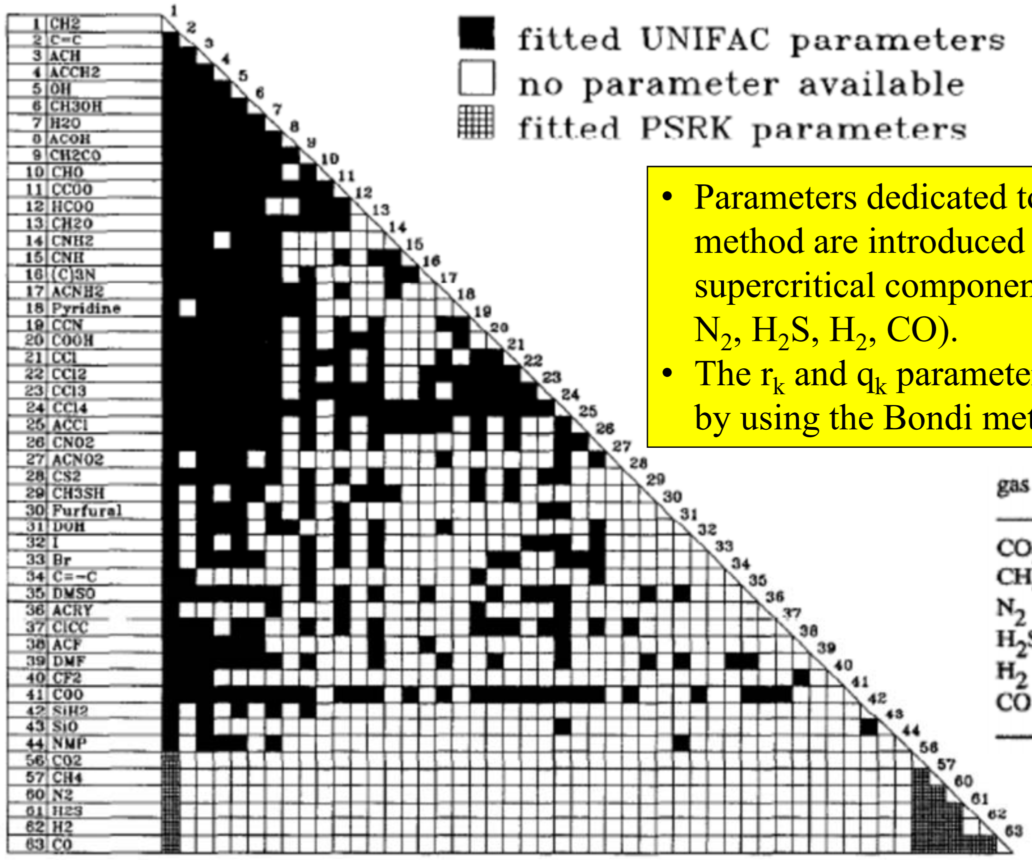
UNIFAC Parameters



- Parameters dedicated to the PSRK method are introduced for supercritical components (CO_2, CH_4, N_2, H_2S, H_2, CO).
- The r_k and q_k parameters are estimated by using the Bondi method.

gas	r_k	q_k
CO_2	1.300	0.982
CH_4	1.129	1.124
N_2	0.856	0.930
H_2S	1.235	1.202
H_2	0.416	0.571
CO	0.711	0.828

Figure2

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Results using New Parameters (P-xy Diagram)

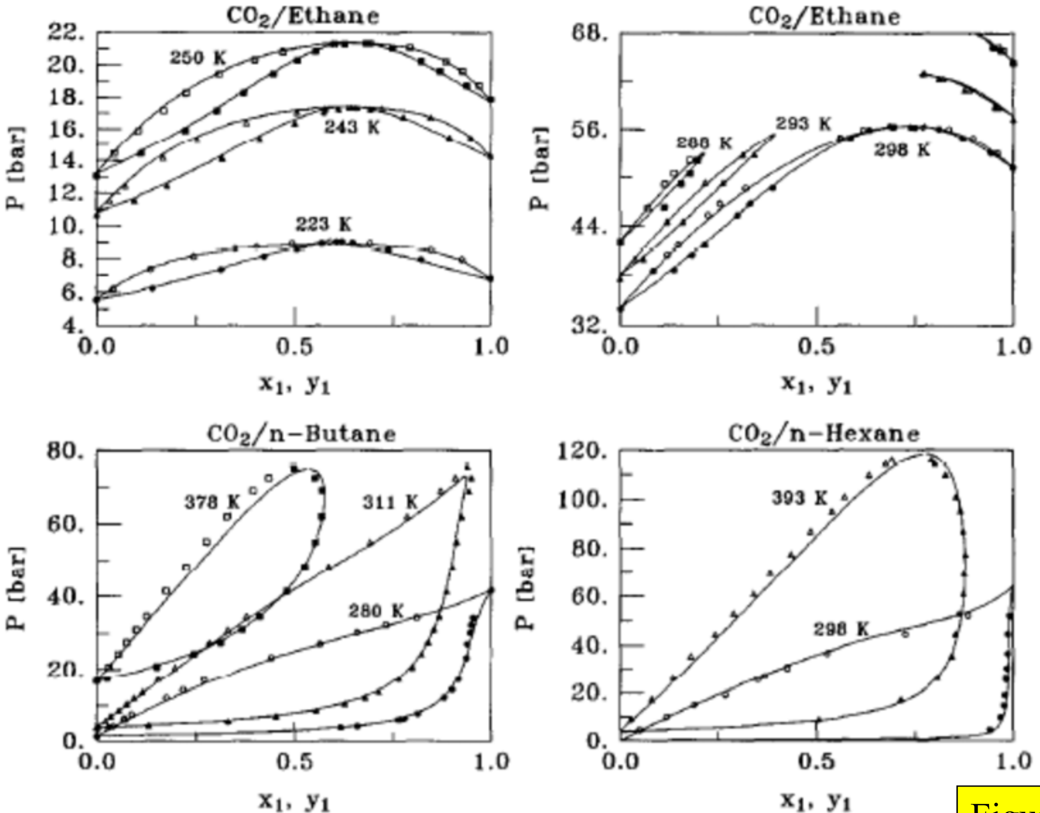


Figure4

Application to Multicomponent Systems

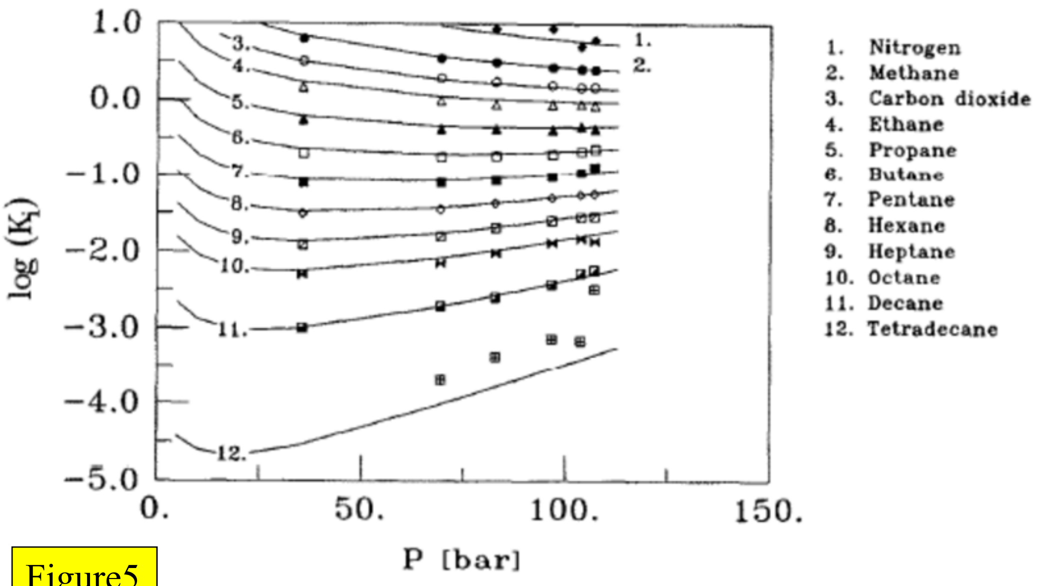
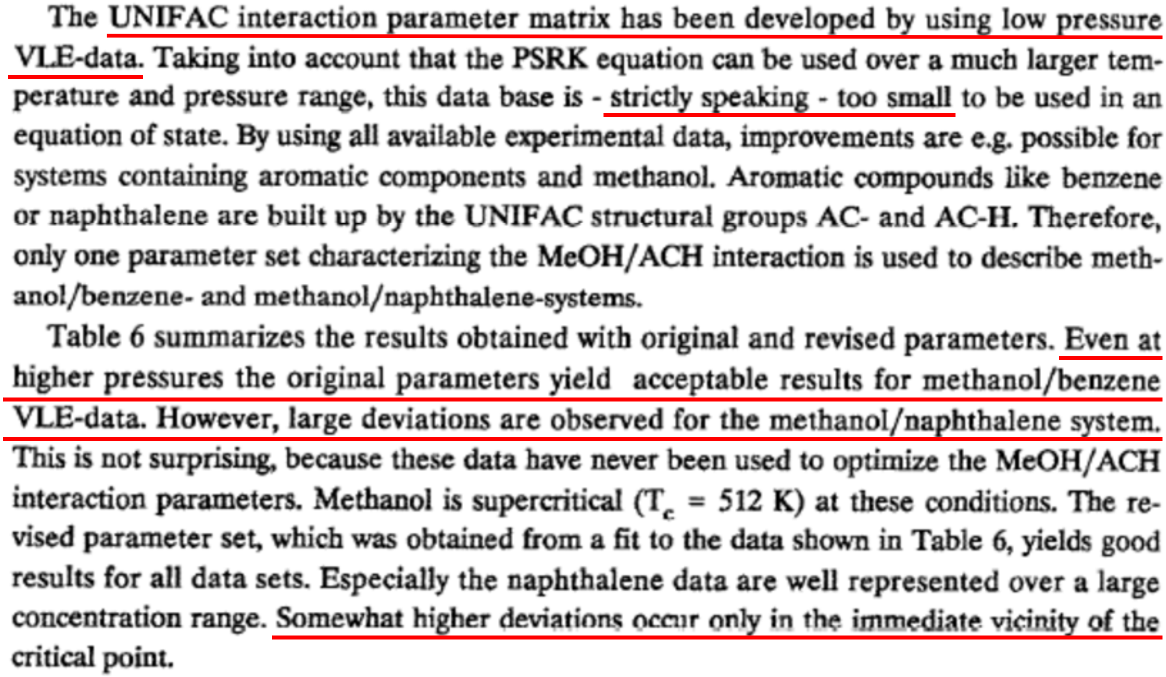


Figure5

FIGURE 5 Pressure dependence of K-values for a 12-component mixture (feed specified in Table 5) at 322 K

- Both the SRK method and the UNIFAC method can be extended to multiple components from two component parameters.
- Even when extended to multiple components, PSRK can be expressed accurately.

Modification of UNIFAC Parameters



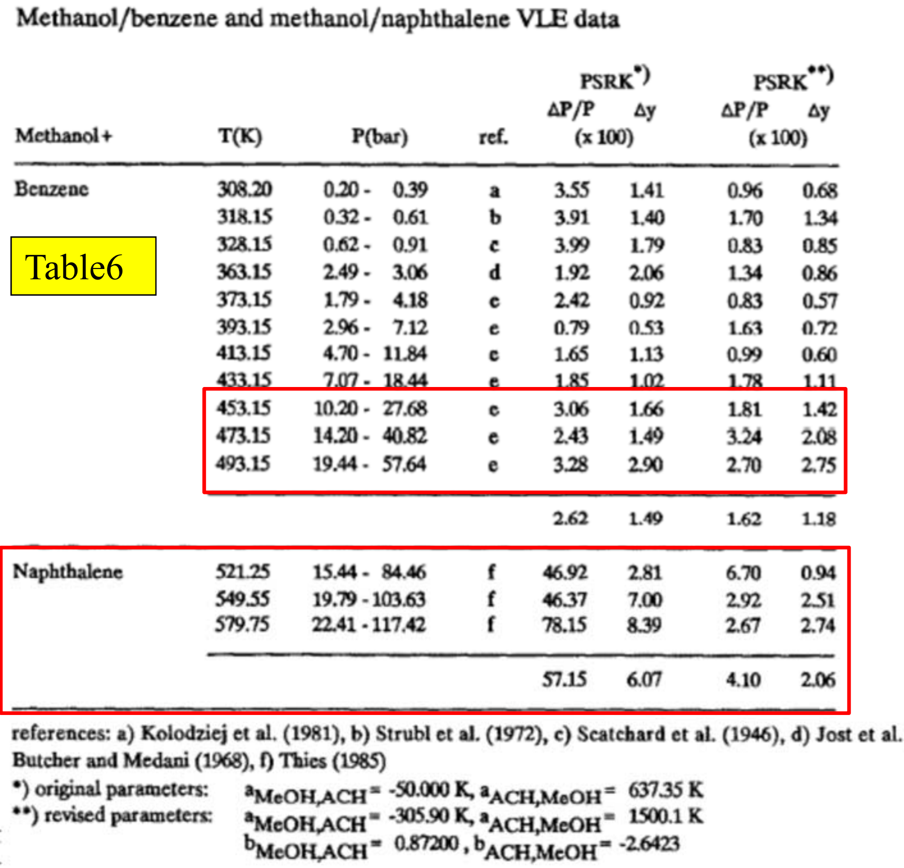
The UNIFAC interaction parameter matrix has been developed by using low pressure VLE-data. Taking into account that the PSRK equation can be used over a much larger temperature and pressure range, this data base is - strictly speaking - too small to be used in an equation of state. By using all available experimental data, improvements are e.g. possible for systems containing aromatic components and methanol. Aromatic compounds like benzene or naphthalene are built up by the UNIFAC structural groups AC- and AC-H. Therefore, only one parameter set characterizing the MeOH/ACH interaction is used to describe methanol/benzene- and methanol/naphthalene-systems.

Table 6 summarizes the results obtained with original and revised parameters. Even at higher pressures the original parameters yield acceptable results for methanol/benzene VLE-data. However, large deviations are observed for the methanol/naphthalene system. This is not surprising, because these data have never been used to optimize the MeOH/ACH interaction parameters. Methanol is supercritical (T_c = 512 K) at these conditions. The revised parameter set, which was obtained from a fit to the data shown in Table 6, yields good results for all data sets. Especially the naphthalene data are well represented over a large concentration range. Somewhat higher deviations occur only in the immediate vicinity of the critical point.

- The UNIFAC interaction parameter matrix has been developed by using low pressure VLE-data, and there is a possibility that deviations become large near the critical point.
- It is necessary to consider correcting parameters by using measured data.

Modification of UNIFAC Parameters

Table6



Methanol/benzene and methanol/naphthalene VLE data

Methanol+	T(K)	P(bar)	ref.	PSRK*) ΔP/P (x 100)	PSRK*) Δy	PSRK**) ΔP/P (x 100)	PSRK**) Δy
Benzene	308.20	0.20 - 0.39	a	3.55	1.41	0.96	0.68
	318.15	0.32 - 0.61	b	3.91	1.40	1.70	1.34
	328.15	0.62 - 0.91	c	3.99	1.79	0.83	0.85
	363.15	2.49 - 3.06	d	1.92	2.06	1.34	0.86
	373.15	1.79 - 4.18	e	2.42	0.92	0.83	0.57
	393.15	2.96 - 7.12	e	0.79	0.53	1.63	0.72
	413.15	4.70 - 11.84	e	1.65	1.13	0.99	0.60
	433.15	7.07 - 18.44	e	1.85	1.02	1.78	1.11
	453.15	10.20 - 27.68	e	3.06	1.66	1.81	1.42
	473.15	14.20 - 40.82	e	2.43	1.49	3.24	2.08
	493.15	19.44 - 57.64	e	3.28	2.90	2.70	2.75
				2.62	1.49	1.62	1.18
Naphthalene	521.25	15.44 - 84.46	f	46.92	2.81	6.70	0.94
	549.55	19.79 - 103.63	f	46.37	7.00	2.92	2.51
	579.75	22.41 - 117.42	f	78.15	8.39	2.67	2.74
				57.15	6.07	4.10	2.06

references: a) Kolodziej et al. (1981), b) Strubl et al. (1972), c) Scatchard et al. (1946), d) Jost et al. Butcher and Medani (1968), f) Thies (1985)

*) original parameters: $a_{MeOH,ACH}$ = -50.000 K, $a_{ACH,MeOH}$ = 637.35 K

**) revised parameters: $a_{MeOH,ACH}$ = -305.90 K, $a_{ACH,MeOH}$ = 1500.1 K
$b_{MeOH,ACH}$ = 0.87200 , $b_{ACH,MeOH}$ = -2.6423

Estimation accuracy in the high pressure range is improved by using corrected parameters.

In other words, it is better to consider that deviations will be large in the high pressure region unless corrected parameters are applied.

High Pressure VLE - Azeotropic Point Estimation Accuracy Verification

Components	Temperature [C]	Azeotropic Composition	
1. Ethyl Acetate-Cyclohexane	71.60	0.5490	Measured Data
P = 101.33 kPa	70.68	0.5360	UNIFAC
	1.29%	2.36%	UNIFAC Error
	71.519	0.5397	PSRK
	0.11%	1.70%	PSRK Error
	72.004	0.5358	NRTL
	-0.56%	2.41%	NRTL Error

Components	Temperature [C]	Azeotropic Composition	
2. Ethyl Acetate-Cyclohexane	160.15	0.6834	Measured Data
P = 902 kPa	155.39	0.6058	UNIFAC
	2.98%	11.35%	UNIFAC Error
	158.54	0.6509	PSRK
	1.00%	4.76%	PSRK Error
	162.98	0.8734	NRTL
	-1.77%	-27.79%	NRTL Error

The azeotropic point of ethyl acetate - cyclohexane was calculated and verified under normal pressure and high pressure conditions.

- With the NRTL method and the UNIFAC method, the accuracy worsens in the high pressure condition that approaches the critical region.
- On the other hand, with the PSRK method it appears that a high accuracy can be expected in both the normal pressure and the high pressure regions.

However, caution is required as this depends on the estimation accuracy of UNIFAC.

Conclusion

- The PSRK method is based on the SRK method, and the α function is corrected below the reduced critical temperature in order to improve the vapor pressure estimation accuracy of pure substances. Therefore, this is why pure component parameters c1, c2 and c3 are required for calculation.
- The UNIFAC method (g_0^E) is applied to the mixing rule of parameter a. Therefore, for non-ideal solutions, it is possible to expect the same estimation result as the UNIFAC method without using actual measurement data. On the other hand, vapor-liquid equilibrium calculations cannot be performed for components with structures that do not belong to the UNIFAC groups.
- Group parameters for supercritical components are added, UNIFAC parameter corrections for high pressure vapor-liquid equilibrium calculation are performed, and the calculation accuracy becomes higher than the calculation by the UNIFAC method alone under the same conditions.
- The PSRK method is an excellent model that enables performing vapor-liquid equilibrium calculations with few parameters even if there is no actual measurement data, but it is essential to verify results by way of actual measurement data when dealing with non-ideal solutions.