

## PSRK: A Group Contribution Equation of State Based on UNIFAC

T. Holderbaum and J. Gmehling

University of Oldenburg, Chair of Industrial Chemistry, PO Box 2503, D2900 Oldenburg (FRG)

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### ABSTRACT

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  $\gamma$ - $\phi$ -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  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ ,  $\text{C}_4\text{H}_{10}$ ,  $\text{CO}_2$ ,  $\text{N}_2$ ,  $\text{H}_2$  and  $\text{CO}$ .

### THE PSRK EQUATION OF STATE

The PSRK equation is based on the modified Soave-Redlich-Kwong (Soave, 1972) equation of state, which yields good results for vapor-liquid-equilibria (VLE) of nonpolar or slightly polar mixtures:

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

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  $\omega$ :

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

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

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

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:

$$\begin{aligned} f(T) &= [1 + c_1(1-T_r^{0.5}) + c_2(1-T_r^{0.5}) + c_3(1-T_r^{0.5})]^2 & T_r < 1 \\ f(T) &= [1 + c_1(1-T_r^{0.5})]^2 & T_r > 1 \end{aligned} \quad (5)$$

The use of the three adjustable parameters especially improves the description of the pure component vapor pressures for polar components. This is of course important when a reliable prediction of the real behavior of polar mixtures is required.

Table 1 summarizes the required PSRK pure component parameters for some selected substances.

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:

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

TABLE 1

Pure component parameters used in the PSRK equation of state<sup>\*)</sup>

Component	T <sub>c</sub> (K)	P <sub>c</sub> (bar)	c <sub>1</sub>	c <sub>2</sub>	c <sub>3</sub>
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)

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, the PSRK equation is especially suited for conditions, where the use of an  $\gamma$ - $\phi$ -approach is difficult (i.e. when the real behavior of the vapor phase is unknown and not negligible) or inadequate (i.e. when supercritical components are present). The PSRK equation serves as an supplementary model for predicting vapor-liquid-equilibria or gas solubilities and is not designed to replace well known and useful methods like UNIFAC.

Equation (6) is used together with the UNIFAC model (Fredenslund et al., 1975, 1977) and with the linear mixing rule for the parameter b:

$$b = \sum x_i b_i \quad (7)$$

$$b_i = 0.08664 \frac{R T_{c,i}}{P_{c,i}} \quad (8)$$



TABLE 2

VLE Results for different group contribution equation of state

system	data points	T(K)	ref.	extrapolation method		MHV1 $A_1 = -0.593$		(PSRK) MHV1 $A_1 = -0.64663$		MHV2	
				$\Delta P/P$ (x 100)	$\Delta y$	$\Delta P/P$ (x 100)	$\Delta y$	$\Delta P/P$ (x 100)	$\Delta y$	$\Delta P/P$ (x 100)	$\Delta y$
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		

references: a) Griswold and Wong (1952), b) Butcher and Medani (1968), c) Barr and Dodge (1959), d) Campbell et al. (1986), e) Maschke and Thodos (1962), f) Rodrigues et al. (1968), g) Reamer and Sage (1962)

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

of the chosen  $g_0^E$ -model. The PSRK equation and the model proposed by Dahl and Michelsen yield similar results. However, one great advantage of the PSRK equation is evident in Table 2: Ethane- (and also propane- and butane-) systems can be treated without introducing new model parameters. These gases are divided into structure groups in the same way as higher alkanes. Taking into account that ethane-, propane- and butane-systems have never been used to develop the UNIFAC parameter tables, the obtained results are surprisingly good. Figure 1 shows additional VLE predictions for light hydrocarbon systems.

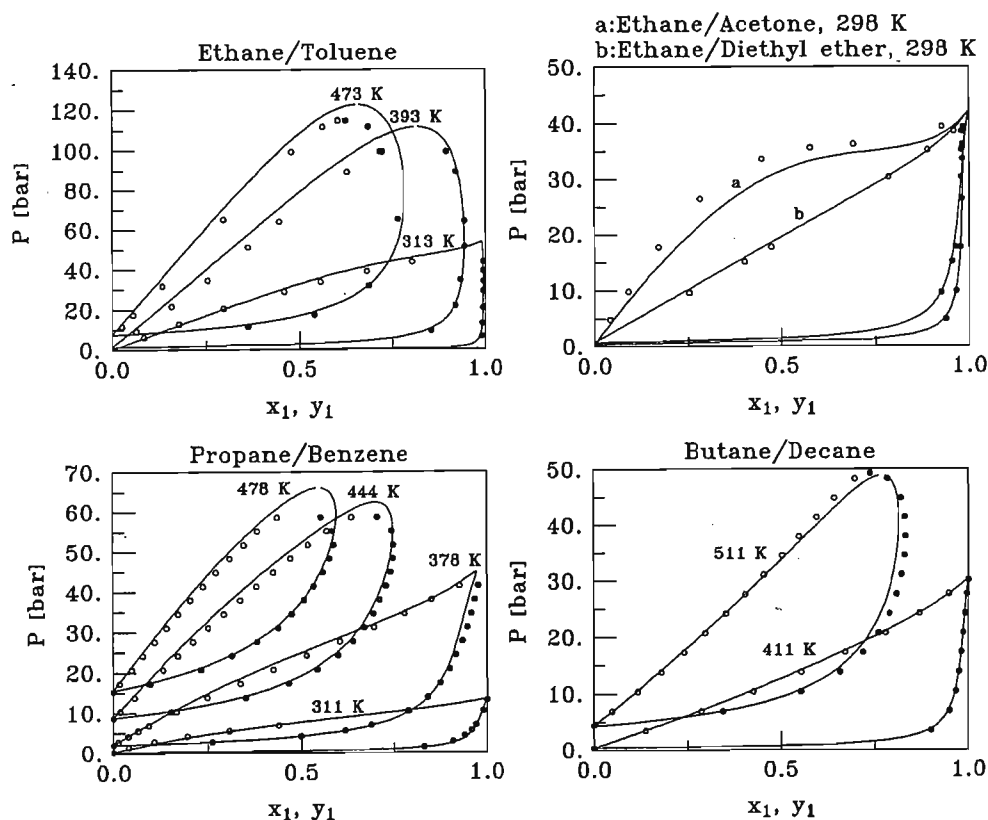


FIGURE 1 VLE predictions with the PSRK equation of state

## ESTIMATION OF NEW PSRK PARAMETERS

The main advantage of equations of state in comparison with  $\gamma$ - $\phi$ -approaches is their ability to calculate phase equilibria of systems containing supercritical components. Therefore, the UNIFAC interaction parameter table was extended as shown in Figure 2. Six gases ( $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{N}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2$ ,  $\text{CO}$ ) are included and parameters for alkane/gas and gas/gas phase equilibria predictions are now available. The missing van der Waals volumes  $r_k$  and surface areas  $q_k$  are summarized in Table 3 and were estimated using Bondi's method (1968). In some cases, slight changes were found useful to improve VLE predictions.

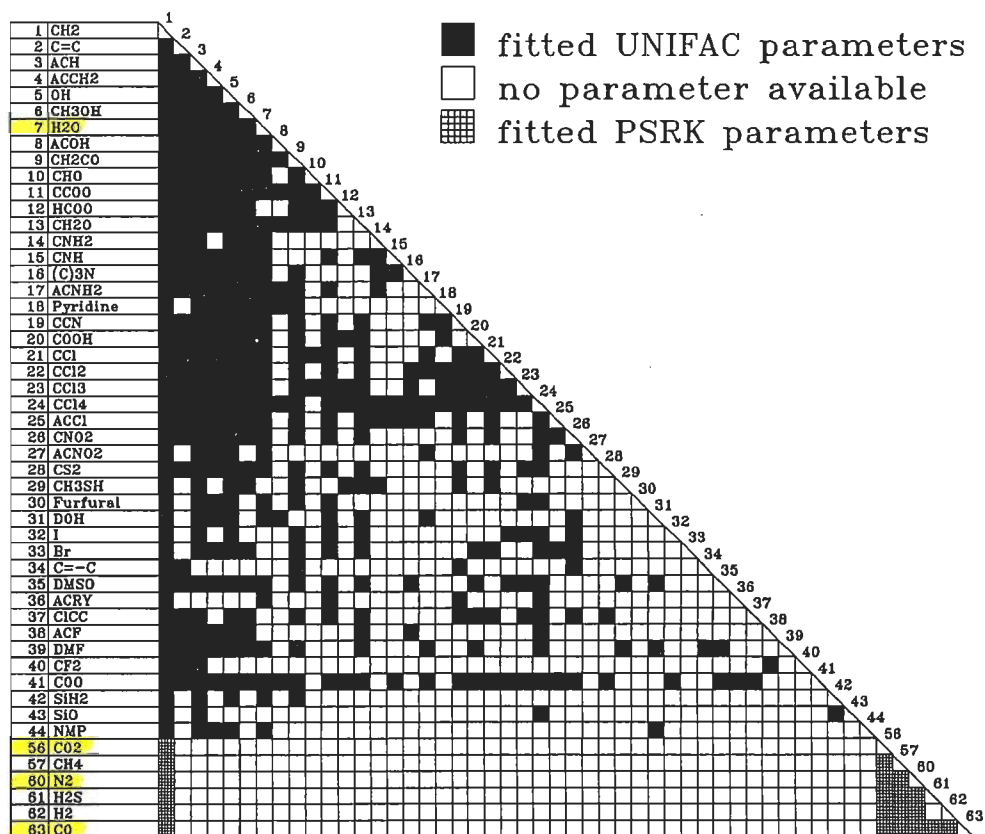


FIGURE 2 PSRK interaction parameter matrix

TABLE 3

Van der Waals properties for the PSRK equation of state

gas	$r_k$	$q_k$
CO <sub>2</sub>	1.300	0.982
CH <sub>4</sub>	1.129	1.124
N <sub>2</sub>	0.856	0.930
H <sub>2</sub> S	1.235	1.202
H <sub>2</sub>	0.416	0.571
CO	0.711	0.828

Nearly all gas/alkane interaction parameters could be estimated using a large binary VLE data base containing alkanes from ethane to decane. For example 107 data sets were used to fit H<sub>2</sub>/CH<sub>4</sub> interaction parameters. The experimental data cover a temperature range from 93 K (H<sub>2</sub>/ethane) to 583 K (H<sub>2</sub>/n-decane). This range is remarkably larger than the one covered by the UNIFAC  $\gamma$ - $\phi$ -approach. Therefore, temperature dependent interaction parameters were introduced and the UNIFAC expression:

$$\psi_{nm} = \exp - \frac{a_{nm}}{T} \quad (9)$$

is replaced by:

$$\psi_{nm} = \exp - \frac{a_{nm} + b_{nm} T + c_{nm} T^2}{T} \quad (10)$$

The parameters  $b_{nm}$  and  $c_{nm}$  are zero for all UNIFAC main groups with numbers up to 44 (see Figure 2). One exception will be discussed later.

Pressures are usually measured more accurately than vapor phase compositions. So only  $x, T, P$  data are used in the following objective function:

$$F = \sum_{i=1}^{nd} \sum_{j=1}^{nv} f_{ij}^2 = \min \quad (11)$$

$nd$  = number of experimental data sets

$nv$  = number of experimental  $x, T, P$ -values

$f_{ij}$  =  $(P_{ij,cal} - P_{ij,exp})/\sigma_{P,ij}$  for isothermal data sets

$f_{ij}$  =  $(T_{ij,cal} - T_{ij,exp})/\sigma_{T,ij}$  for isobaric data sets

$\sigma_{P,ij}$  = assumed standard deviation of the pressure

$\sigma_{T,ij}$  = assumed standard deviation of the temperature



TABLE 4

New interaction parameters for the PSRK equation of state

n	m	$a_{nm}$ [K]	$a_{mn}$	$b_{nm}$	$b_{mn}$	$c_{nm}$ [K <sup>-1</sup> ] (x 100)	$c_{mn}$ (x 100)	temp. range
CO	CH <sub>2</sub> <sup>a)</sup>	165.81	-78.389	-1.1490	1.8727	0.0	0.0	100 - 533 K
CO	CH <sub>4</sub>	71.623	62.419	0.0	0.0	0.0	0.0	91 - 186 K
CO	CO <sub>2</sub>	4.2038	161.54	0.0	0.0	0.0	0.0	223 - 283 K
CO	H <sub>2</sub> S	116.97	665.70	0.0	0.0	0.0	0.0	203 - 293 K
CO	H <sub>2</sub>	494.67	863.18	-8.1869	-12.309	4.7180	4.6316	77 - 125 K
CO	N <sub>2</sub>	6.4230	25.060	0.57946	-0.77261	0.0	0.0	70 - 122 K
H <sub>2</sub> S	CH <sub>2</sub> <sup>a)</sup>	742.31	893.01	-5.7074	-3.1342	1.2651	0.13022	200 - 478 K
H <sub>2</sub> S	CH <sub>4</sub>	295.70	91.023	0.0	0.0	0.0	0.0	189 - 366 K
H <sub>2</sub> S	CO <sub>2</sub>	114.96	78.980	0.0	0.0	0.0	0.0	224 - 366 K
H <sub>2</sub> S	H <sub>2</sub>	- no experimental data available -						
H <sub>2</sub> S	N <sub>2</sub>	648.20	862.84	-0.30072	-2.1569	0.0	0.0	200 - 344 K
N <sub>2</sub>	CH <sub>2</sub> <sup>a)</sup>	-101.96	527.33	0.68629	-2.1596	-0.20660	0.43234	127 - 497 K
N <sub>2</sub>	CH <sub>4</sub>	11.865	64.108	0.0	0.0	0.0	0.0	88 - 183 K
N <sub>2</sub>	CO <sub>2</sub>	694.28	-580.82	-3.0173	3.6997	0.0	0.0	218 - 293 K
N <sub>2</sub>	H <sub>2</sub>	77.701	247.42	0.0	0.0	0.0	0.0	77 - 113 K
CO <sub>2</sub>	CH <sub>2</sub> <sup>a)</sup>	-38.672	919.80	0.86149	-3.9132	-0.17906	0.46309	222 - 594 K
CO <sub>2</sub>	CH <sub>4</sub>	73.563	196.16	0.0	0.0	0.0	0.0	153 - 271 K
CO <sub>2</sub>	H <sub>2</sub>	838.06	3048.9	-1.0158	-10.247	0.0	0.0	220 - 290 K
H <sub>2</sub>	CH <sub>2</sub> <sup>a)</sup>	361.79	175.92	-1.0651	1.1966	0.0	0.0	93 - 583 K
H <sub>2</sub>	CH <sub>4</sub>	128.55	253.92	0.0	0.0	0.0	0.0	90 - 183 K
CH <sub>4</sub>	CH <sub>2</sub> <sup>a)</sup>	68.141	-39.101	-7.3860	.84587	0.0	0.0	130 - 583 K

a) experimental data used:

- CO +ethane (100-273 K), +propane (173-323 K), +n-octane (463-533 K)
- H<sub>2</sub>S +ethane (200-283 K), +propane (217-344 K), +isobutane (278-378 K), +n-pentane (278-378 K), +n-nonane (311-478 K), +n-decane (278-444 K)
- N<sub>2</sub> +ethane (172-290 K), +propane (127-353 K), +isobutane (255-394 K), +n-pentane (277-378 K), +isopentane (278-377 K), +n-hexane (311-444 K), +n-heptane (305-497 K), +methylcyclohexane (311-492 K), +ethylcyclohexane (311-478 K), +isooctane (376-453 K), +n-decane (311-411 K)
- CO<sub>2</sub> +ethane (222-298 K), +propane (233-344 K), +n-butane (227-411 K), +isobutane (250-394 K), +n-pentane (277-378 K), +isopentane (278-378 K), +n-hexane (298-393 K), +n-heptane (311-502 K), +n-decane (278-594 K)
- H<sub>2</sub> +ethane (93-283 K), +propane (172-348 K), +n-butane (200-394 K), +isobutane (311-394 K), +cyclohexane (339-394 K), +n-hexane (311-478 K), +n-heptane (424-499 K), +methylcyclohexane (424-499 K), +isooctane (311-523 K), +n-octane (463-553 K), +n-decane (462-583 K)
- CH<sub>4</sub> +ethane (130-283 K), +propane (130-361 K), +n-butane (144-278 K), +isobutane (311-378 K), +2-methylbutane (344-444 K), +n-pentane (178-461 K), +n-hexane (183-423 K), +n-heptane (200-511 K), +n-octane (223-423 K), +n-nonane (244-423 K), +n-decane (244-583 K)

Some preliminary fits are necessary to check the experimental data base and to determine whether two ( $a_{nm}$ ), four ( $a_{nm}$ ,  $b_{nm}$ ) or six ( $a_{nm}$ ,  $b_{nm}$ ,  $c_{nm}$ ) adjustable parameters are required to describe the experimental data. In these preliminary fits the relative pressure- or temperature-deviation is minimized:

$$\begin{aligned}\sigma_{P,ij} &= P_{ij,\text{exp}} \\ \sigma_{T,ij} &= T_{ij,\text{exp}}\end{aligned}\quad (12)$$



This simplification stresses isothermal data too much. However, this restriction is unimportant, because high pressure VLE data are usually measured isothermally and a few number of isobaric data sets may even be ignored. The final parameter estimation is performed with the better suited relationships:

$$\begin{aligned}\sigma_{P,ij}^2 &= \sigma_P^2 + \left(\frac{\partial P}{\partial x_1}\right)_{ij}^2 \sigma_{x_1}^2 + \left(\frac{\partial P}{\partial T}\right)_{ij}^2 \sigma_T^2 & T = \text{constant} \\ \sigma_{T,ij}^2 &= \sigma_T^2 + \left(\frac{\partial T}{\partial x_1}\right)_{ij}^2 \sigma_{x_1}^2 + \left(\frac{\partial T}{\partial P}\right)_{ij}^2 \sigma_P^2 & P = \text{constant}\end{aligned}\quad (13)$$

The slopes are calculated from the most suited preliminary fit. The errors in temperature, pressure and liquid phase composition could be kept constant to  $\sigma_T = 0.01$  K,  $\sigma_P = (0.001 \text{ bar} + 10^{-3}P)$  and  $\sigma_{x_1} = 0.001$ . Table 4 summarizes the parameters obtained by this procedure. No experimental data were found for the  $\text{H}_2/\text{H}_2\text{S}$  system. A sufficient experimental data base is available in all other cases.

Results for  $\text{H}_2\text{S}$  and  $\text{CO}_2$  systems using the parameters from Table 4 are illustrated in Figure 3 and 4. Additional PSRK predictions for  $\text{H}_2$  systems are already published (Holderbaum and Gmehling (1991), Holderbaum (1991)).

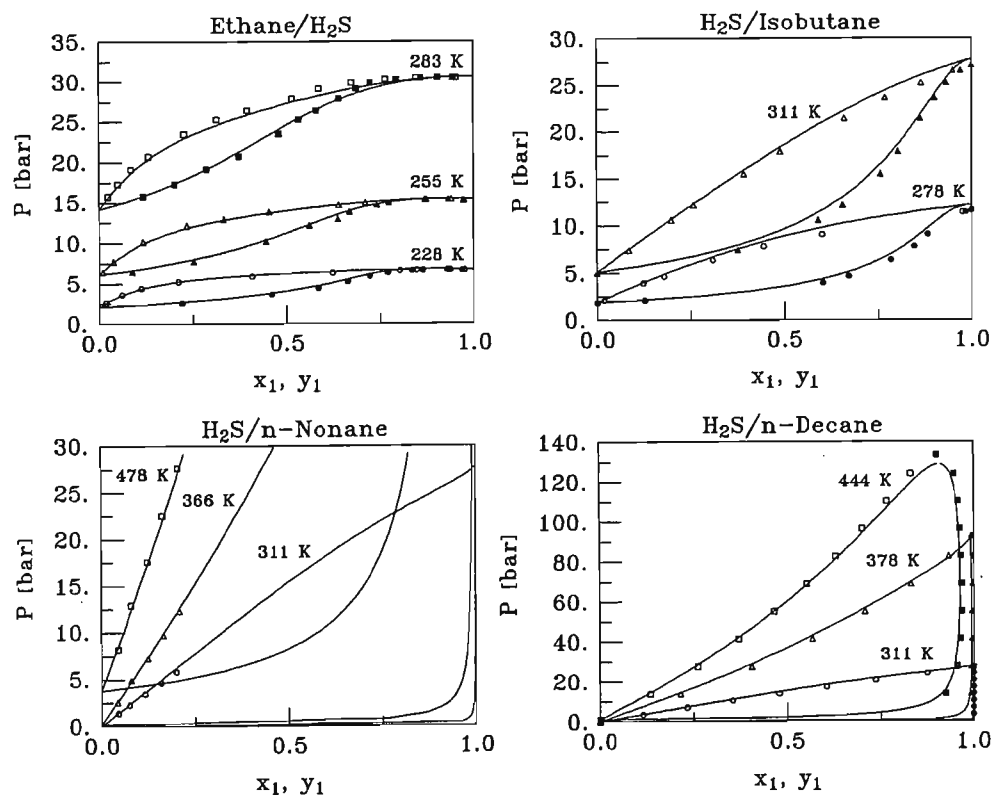
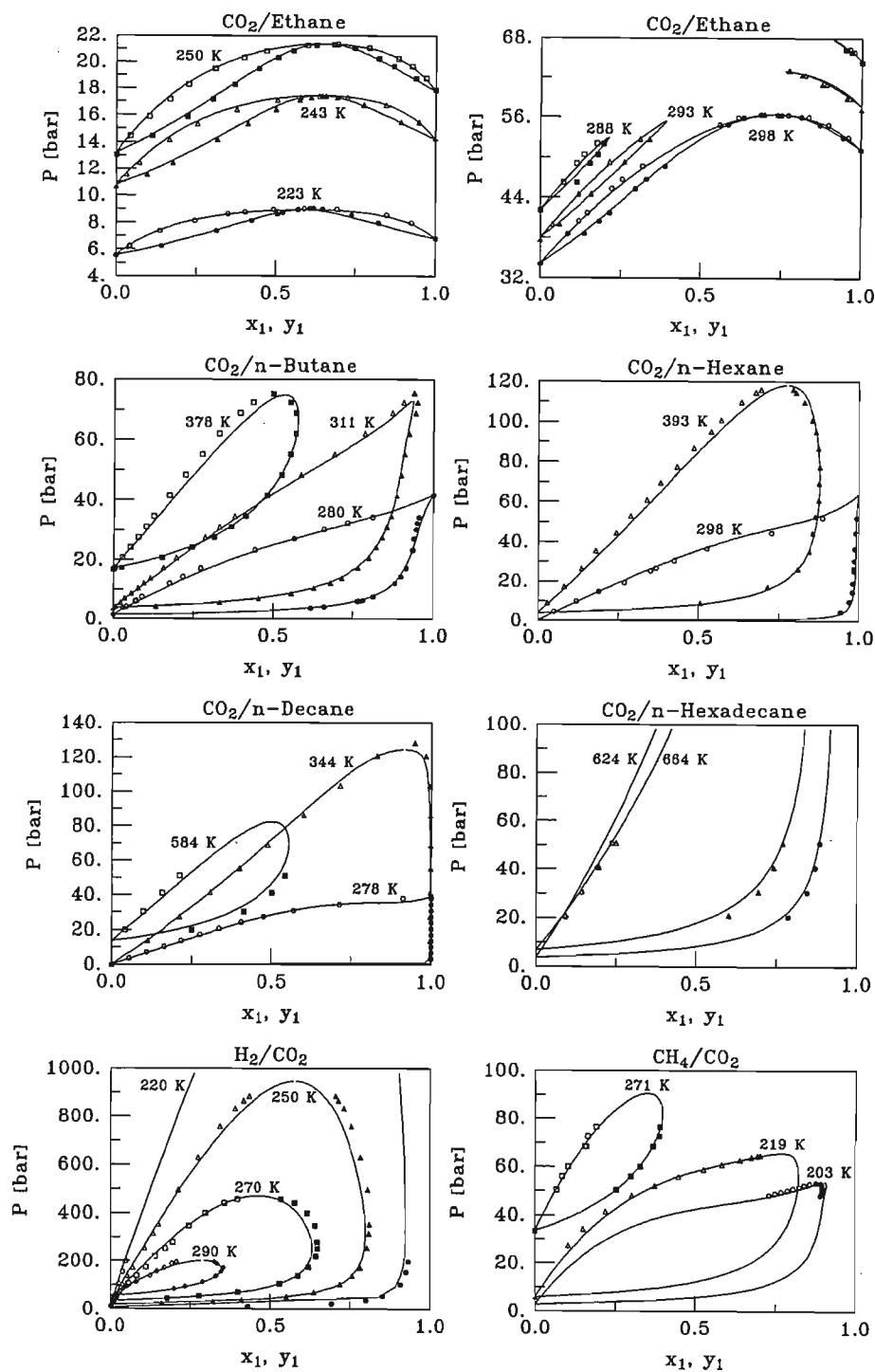


FIGURE 3 PSRK results for  $\text{H}_2\text{S}$  systems

FIGURE 4 PSRK results for  $\text{CO}_2$  systems

## MULTICOMPONENT SYSTEMS

The PSRK equation is based on the SRK equation of state and the UNIFAC method. It is well known, that both underlying models are able to predict multicomponent phase equilibria from binary data only. The most simple procedure to check this ability for the PSRK equation is to generate multicomponent VLE-data at low pressures by the UNIFAC  $\gamma$ - $\phi$ -approach and to compare these data with PSRK predictions. This test shows clearly, that the PSRK equation of state is able to predict multicomponent VLE-data from binary information.

Additional tests have been made using experimental data. Results for a 12-component mixture (Turek et al., 1984) are given in Table 5 and Figure 5. The deviations shown in Table 5 are based on a flash calculation at constant temperature and pressure. Turek et al. used a cubic equation of state with special modifications to improve the results for binary  $\text{CO}_2$  systems. Their approach requires the estimation of 66 binary parameters (if no simplifications are introduced) from experimental VLE-data. The PSRK equation of state is able to predict these K-values by using the model parameters already given in Table 1, 3 and 4. Taking into account, that Turek et al. used an equation of state, that is directly based on binary VLE data and that they performed special modifications to improve their results, it is not surprising that they obtained smaller deviations. However, the pressure dependence shown in Figure 5 is predicted quite well with the PSRK equation of state.

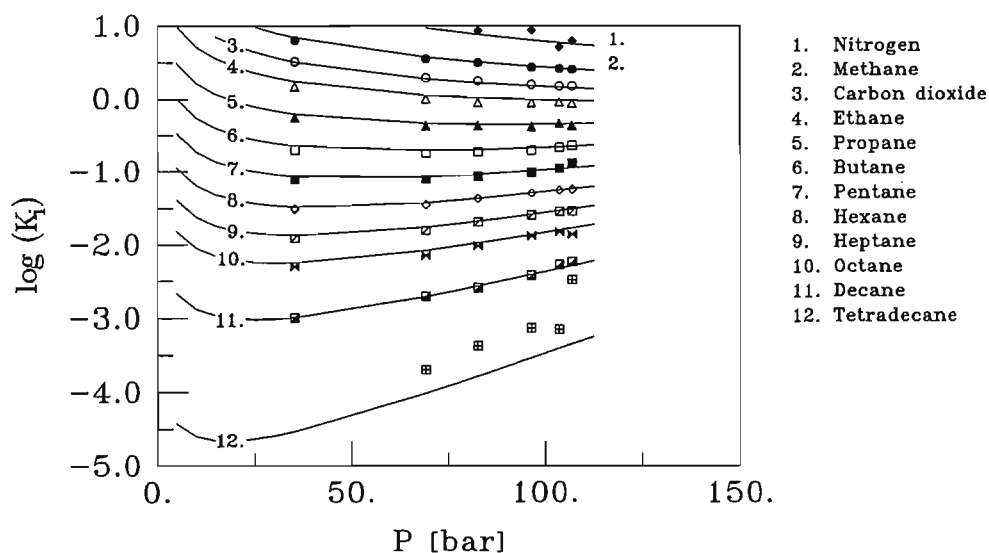


FIGURE 5 Pressure dependence of K-values for a 12-component mixture (feed specified in Table 5) at 322 K



TABLE 5

K-value deviations for a 12-component mixture at 69.29 bar and 322 K

component	exp. Data		Turek et al.	PSRK
	$z_i$	$K_i$	$\Delta K/K$ [%]	$\Delta K/K$ [%]
N <sub>2</sub>	0.00063		-19.7	
CO <sub>2</sub>	0.20000	1.935	0.36	5.1
Methane	0.27551	3.545	3.68	-3.6
Ethane	0.02268	0.989	8.66	13.1
Propane	0.03009	0.426	-0.51	7.7
n-Butane	0.04572	0.181	-1.10	7.7
n-Pentane	0.03154	0.0794	-1.81	7.1
n-Hexane	0.02376	0.0352	-2.09	5.1
n-Heptane	0.03961	0.0157	-2.03	8.3
n-Octane	0.03970	0.0071	-2.41	17.5
n-Decane	0.24968	0.00195	-22.6	-0.5
n-Tetradecane	0.04108	0.0002	-61.0	-6.5

## REVISION OF EXISTING 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.

Additional calculations were performed with binary systems containing methanol and substituted aromatic components like toluene, 1-methyl naphthalene and 1,2,3,4-tetrahydro naphthalene. These calculations require three parameter sets for the MeOH/ACH, MeOH/ACCH<sub>2</sub> and ACH/ACCH<sub>2</sub> interaction. Remarkably better results were obtained with the revised parameters given in Table 6 without a further revision of MeOH/ACCH<sub>2</sub> or ACH/ACCH<sub>2</sub> interaction parameters.

TABLE 6

Methanol/benzene and methanol/naphthalene VLE data

Methanol +	T(K)	P(bar)	ref.	PSRK <sup>*)</sup>		PSRK <sup>**)</sup>	
				$\Delta P/P$ (x 100)	$\Delta y$	$\Delta P/P$ (x 100)	$\Delta y$
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. (1957), e) Butcher and Medani (1968), f) Thies (1985)

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

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

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#### APPENDIX A: CALCULATION OF FUGACITY COEFFICIENTS WITH THE PSRK EQUATION

Assuming, that the linear mixing rule (7) is used for the b parameter and that the mixing rule for parameter a is volume independent, the equation of state (1) yields for the fugacity coefficient of component i in the mixture:

$$\ln \varphi_i = \frac{b_i}{b} \left( \frac{Pv}{RT} - 1 \right) - \ln \frac{P(v-b)}{RT} - \bar{\alpha}_i \ln \left( \frac{v+b}{v} \right) \quad (\text{A1})$$

The dimensionless quantity  $\alpha$  is defined as  $\alpha = a/(bRT)$  for the mixture and  $\alpha_i = a_i/(b_iRT)$  for pure component  $i$ . Thus we obtain from mixing rule (6):

$$\alpha = \frac{1}{A_1} \left( \frac{g_0^E}{RT} + \sum x_i \ln \frac{b}{b_i} \right) + \sum x_i \alpha_i \quad (\text{A2})$$

The partial derivative  $\bar{\alpha}_i$  in equation (A1) is derived easily from equation (A2):

$$\bar{\alpha}_i = \left( \frac{\partial n_T \alpha}{\partial n_i} \right)_{T,P,n_{j \neq i}} = \frac{1}{A_1} \left( \ln \gamma_{0,i} + \ln \frac{b}{b_i} + \frac{b_i}{b} - 1 \right) + \alpha_i \quad (\text{A3})$$

The calculation of fugacity coefficients for given temperature, pressure and composition is performed as follows:

- Calculate the pure component parameters  $a_i$  from equation (2) and (5). Calculate  $\alpha_i = a_i/(b_iRT)$ .
- Calculate the pure component parameters  $b_i$  from equation (8) and the mixture parameter  $b$  from the linear mixing rule (7).
- Determine the activity coefficients  $\gamma_{0,i}$  and  $g_0^E = RT \sum x_i \ln \gamma_{0,i}$  from the UNIFAC model.
- Calculate the mixture parameter  $a$  from mixing rule (6) and determine the mixture volume by solving the cubic equation derived from equation (1). Use the smallest root which satisfies  $v > b$  for liquid phase calculations or the largest root for vapor phase calculations.
- Use equation (A1) and (A3) to calculate the fugacity coefficients.

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