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PSRK group contribution equation of state: comprehensive revision and extension IV, including critical constants and α-function parameters for 1000 components

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Abstract

As a part of an ongoing process, the predictive Soave–Redlich–Kwong (PSRK) group contribution equation of state was extended by the introduction of additional structural groups (F_2, Cl_2, Br_2, HCN, NO_2, CF_4, O_3 and ClNO) and fitting of the corresponding group interaction parameters. Interaction parameters between already existing main groups were also optimized to the growing literature data base. Overall, 75 new parameter sets are given herein, and typical results are presented for various systems. For the sake of completeness, not only the group new interaction parameters but all available PSRK/UNIFAC interaction parameter sets (more than 900) are given as supplementary material. Moreover, the required pure component properties (critical properties, acentric factors, and Mathias–Copeman constants) were revised and are also included for about 1000 components.
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1. Introduction

The reliable knowledge of the phase equilibrium behavior as function of T, P, x of multicomponent mixtures is a prerequisite for the synthesis and optimization of separation processes such as distillation, absorption or extraction as important topics in chemical engineering. g^E models and equations of state (EoS) are suitable models to predict the behavior of multicomponent mixtures on the basis of binary information. With the development of so-called g^E mixing rules by Huron and Vidal [1] EoS are not any longer limited to the description of non-polar systems. They can also successfully be applied for the description of systems containing polar components. With an EoS even supercritical components can be considered and other thermodynamic quantities like densities

or enthalpies can be obtained directly, which are required as additional information in the γ–φ approach.

The predictive Soave–Redlich–Kwong (PSRK) group contribution EoS by Holderbaum and Gmehling [2] combines the SRK EoS with the UNIFAC group contribution model by the PSRK mixing rule. The advantages of EoS, the local composition concept and the group contribution approach are merged in the PSRK model, which is now widely used in commercial process simulators.

The use of the SRK equation

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

with the pure component parameters a_{ii} and b_i obtained from the critical data T_c and P_c of the pure components

$$a_{ii}(T) = 0.42748 \frac{R^2 T_{c,i}^2}{P_{c,i}} \alpha_i(T) \tag{2}$$

$$b_i = 0.08664 \frac{RT_{c,i}}{P_{c,i}} \tag{3}$$

enables the correct reproduction of pure component vapor pressures with the help of the Mathias–Copeman parameters $c_{1,i}$, $c_{2,i}$ and $c_{3,i}$ [3] fitted to experimental vapor pressure data:

$$\alpha_i(T) = \left[1 + c_{1,i}(1 - \sqrt{T_{r,i}}) + c_{2,i}(1 - \sqrt{T_{r,i}})^2 \right. \\ \left. + c_{3,i}(1 - \sqrt{T_{r,i}})^3\right]^2 \tag{4}$$

or the generalized form using the acentric factor φ [4]:

$$c_{1,i} = 0.48 + 1.574\omega_i - 0.176\omega_i^2, \\ c_{2,i} = 0, \qquad c_{3,i} = 0 \tag{5}$$

Applying EoS to mixtures, the parameters $a(T)$ and b can be calculated using the PSRK mixing rule. Therefore, the pure component parameters $a_{ii}(T)$, b_i and the excess Gibbs energy at a reference state (g_0^E) are required. At the reference state (the liquid at atmospheric pressure) an optimized ratio of the inverse packing fraction $u = v/b = 1.1$ and $v^E = 0$ is assumed, and the following relation is obtained [5]:

$$\frac{a(T)}{bRT} = \sum x_i \frac{a_{ii}(T)}{b_i RT} + \frac{\frac{g_0^E}{RT} + \sum x_i \ln \frac{b}{b_i}}{\ln \frac{u}{u+1}} \tag{6}$$

For the parameter b the classical linear mixing rule is used:

$$b = \sum x_i b_i \tag{7}$$

The Péneloux volume translation [6] can be used to improve the calculation of the liquid density of polar compounds with cubic EoS:

$$v = v_{SRK} - \sum x_i c_i \tag{8}$$

whereby the constant c_i can be estimated from the complete set of critical data for component i:

$$c_i = 0.40768 \frac{RT_{c,i}}{P_{c,i}} \left(0.29441 - \frac{P_{c,i}v_{c,i}}{RT_{c,i}}\right) \tag{9}$$

or from experimental liquid density data.

The published UNIFAC parameters of Hansen and Rasmussen [7] are applied within the PSRK method. While the original UNIFAC parameters are independent of temperature:

$$\Psi_{nm} = \exp\left(-\frac{a_{nm}}{T}\right) \tag{10}$$

new parameters fitted directly for the PSRK group contribution EoS contain the following temperature dependence for the parameter Ψ_{nm}:

$$\Psi_{nm} = \exp\left(-\frac{a_{nm} + b_{nm}T + c_{nm}T^2}{T}\right) \tag{11}$$

However, this temperature dependence is only used if necessary, e.g. for interaction parameters between gases and water, where a large temperature range is covered, or if a strong temperature dependence of the phase equilibrium behavior (e.g. for the Henry coefficients) is observed.

With PSRK, the results of the UNIFAC group contribution method can be reproduced, and furthermore, the model can be used at higher temperatures and pressures even at supercritical conditions. The optimization of a large number of interaction parameters between UNIFAC and new PSRK main groups was performed using the vapor–liquid equilibrium (VLE), gas solubility and critical data stored in the Dortmund Data Bank (DDB). These developments enable the calculation of the phase equilibrium behavior and other thermodynamic properties for various kinds of systems [5,8,9]. Up to now, parameters for the 50 original UNIFAC main groups and 31 new PSRK groups (epoxy group and 30 different gases, such as CO_2, CO, O_2, N_2, CH_4, SF_6, SO_2, etc.) were established.

The aim of this work was to continue this process by the introduction of additional new structural groups (F_2, Cl_2, Br_2, HCN, NO_2, CF_4, O_3 and ClNO) and the fitting of the desired interaction parameters for the new and already existing main groups on the basis of the permanently growing data bank. A few of the obtained results have already been shown within the scope of a thesis [10]. For some of the obtained interaction parameters, also experimental investigations were performed [11].

Recent investigations dealt with the description of asymmetric and polymer systems using a modified mixing rule [12,13]. The ideas of these developments have also led to a volume translated Peng–Robinson (VTPR) EoS [14], where also the description of volumetric properties or vapor–liquid equilibria of polymer systems have been improved. For

Table 1
Van der Waals properties and group assignment for the new PSRK/UNIFAC groups

Main group		Sub group		R_k	Q_k	Component (example)	Increments
78	F_2	142	F_2	0.7500	0.8800	Fluorine	1 F_2
79	Cl_2	143	Cl_2	1.5300	1.4400	Chlorine	1 Cl_2
80	Br_2	144	Br_2	1.9000	1.6600	Bromine	1 Br_2
81	HCN	145	HCN	1.2000	1.1900	Hydrogen cyanide	1 HCN
82	NO_2	146	NO_2	1.0000	1.1000	Nitrogen dioxide	1 NO_2
83	CF_4	147	CF_4	1.7800	1.8200	Tetrafluoromethane	1 CF_4
84	O_3	148	O_3	1.1000	1.2700	Ozone	1 O_3
85	ClNO	149	ClNO	1.4800	1.3400	Nitrosylchloride	1 ClNO

Table 2
New group interaction parameters for the PSRK/UNIFAC model[a]

i	j	a_{ij} (K)	b_{ij}	c_{ij} (K^{-1})	a_{ji} (K)	b_{ji}	c_{ji} (K^{-1})
1	67	205.51			7.1644		
1	79	678.27			−284.66		
1	83	184.05			12.039		
1	85	562.89			−134.73		
2	83	372.06	−0.9896		497.34	−1.6778	
3	55	998.74	−1.6454		534.60	−0.8484	
3	83	87.262			3329.2		
4	55	594.75			432.46		
4	63	348.35			−16.621		
4	83	3339.6			−68.983		
5	61	−111.34			3156.0		
5	83	4479.8			4760.3		
6	59	213.64			−8.5326		
6	81	101.79			−101.54		
7	57	−1573.2	11.993	−0.01225	−1149.1	5.8604	−0.005122
7	80	525.98			944.10		
7	81	261.73			79.524		
11	85	39.903			−98.180		
13	55	322.12			−106.55		
13	61	−96.100			−178.30		
14	55	43.048			49.145		
15	55	17.885			27.888		
16	55	74.728			−45.258		
18	65	−442.89			−369.70		
18	85	0.09021			−75.338		
19	58	434.74			−7.7389		
19	81	−245.39			188.14		
20	57	1102.1			698.17		
20	61	−85.001			671.59		
21	56	−6.3973			41.589		
22	56	337.09			−132.38		
22	63	284.02			288.17		
23	51	126.47			−291.14		
23	55	−237.66			709.31		
23	85	81.611			−36.230		
24	62	589.06			290.17		
24	80	−34.521			236.96		
25	55	347.79			152.67		
25	61	69.383			157.35		
28	57	214.10			42.987		
28	61	162.98			14.907		
28	62	774.56			353.99		
29	57	338.87	−0.8372		26.901	0.8674	
29	61	−0.1486			87.264		
31	51	137.27			156.35		
31	60	1390.3			−150.80		
31	61	521.38			−186.40		
34	35	137.40			−121.00		
34	44	−22.589			−125.98		
36	81	8.7996			−67.392		
37	65	365.54			−43.958		
38	83	37.650			−4.7649		
40	56	332.65			−213.34		
40	62	330.73			136.80		
40	83	288.20			−158.17		
48	57	350.68	−0.5043		146.01	0.003833	
48	61	−151.94			−20.807		
56	67	−108.91			144.40		
56	68	38.274			198.92		
56	79	234.93			109.11		
57	61	511.99	−1.1761		278.10	−0.2300	
57	83	72.986			142.06		
58	84	448.22	−3.5350		373.66	−2.6684	

Table 2 (*Continued*)

i	j	a_{ij} (K)	b_{ij}	c_{ij} (K^{-1})	a_{ji} (K)	b_{ji}	c_{ji} (K^{-1})
59	83	97.117			−58.350		
60	83	19.597	−0.001177		85.380	−0.3801	
62	83	166.92	5.4092		522.68	−1.5559	
65	79	308.78	−0.9455		471.48	−0.3501	
66	82	4516.5	140.84		−3859.3	4.0664	
67	68	0.7920			280.06		
68	83	−243.01			534.14		
69	78	168.03			273.45		
73	78	158.20			630.21		
73	79	515.25			783.19		
74	79	2.0069			132.00		
79	85	584.43			−205.30		

[a] New fitted or revised PSRK parameters from this work and from [10].

this method, also other properties like solid–liquid equilibrium, excess enthalpy data and activity coefficients at infinite dilution are used for the parameter fitting procedure to enable a proper description of the phase equilibrium over a wide temperature range. However, since the PSRK method is used by chemical engineers because of its reliability and wide range of applicability, this model will be developed further on as shown herein or by Kiepe et al. [15,16], where the effect of strong electrolytes on the solubility of gases is predicted with PSRK. Another example for the great acceptance of PSRK is the article of Yoon et al. [17], who applied PSRK for the description of gas hydrate equilibria.

2. Results

Eight new structural groups (F$_2$, Cl$_2$, Br$_2$, HCN, NO$_2$, CF$_4$, O$_3$ and ClNO) were introduced into the PSRK model. The required van der Waals properties (relative volumes R_k and surfaces Q_k) for the new PSRK sub and main groups are listed in Table 1. The van der Waals properties for all PSRK groups are given as supplementary material. They were calculated using the Bondi method [18] or sometimes fitted simultaneously with the group interaction parameters to experimental phase equilibrium data.

In most cases only two binary interaction parameters (a_{ij}, a_{ji}, cf. Eq. (10)) were fitted. In a few cases, linear (b_{ij}, b_{ji}, cf. Eq. (11)) or even a quadratic (c_{ij}, c_{ji}) temperature dependent parameters were required to describe the correct temperature dependence of the phase equilibrium behavior, e.g. for the system CH$_4$ + H$_2$O. The obtained parameters for 75 group pairs are given in Table 2. As for the pure component values, the supplementary material contains all available interactions parameters for the PSRK/UNIFAC method. The current status of the parameter matrix is shown in Fig. 1.

The required pure component parameters, i.e. critical constants $P_{c,i}$, $T_{c,i}$, and $v_{c,i}$ as well as acentric factors ω_i and Mathias–Copeman parameters $c_{1,i}$, $c_{2,i}$ and $c_{3,i}$ are also listed as supplementary material for nearly 1000 components. These parameters are also given for components which can currently not be handled by PSRK. Since these components may be correlated with the SRK EoS, the values are included in the table. If no experimental critical properties were available in the Dortmund Data Bank (DDB 2004) [19], these values were obtained by estimation methods using group contributions, e.g. the methods of Ambrose, Joback, or Constantinou and Gani [20,21]. Furthermore, the groups increments of the components are included.

Some examples for the new introduced structural groups are graphically shown in Figs. 2 and 3 together with the literature data. As can be seen in Fig. 2, the VLE behavior for hydrogen cyanide + water, hydrogen chloride + chlorine, oxygen + ozone and nitrosyl chloride + ethyl acetate can be accurately represented with the model. In Fig. 3 not only the vapor–liquid equilibrium data but also the azeotropic conditions for the chlorine + sulfur dioxide can be described reliably over a larger temperature range using linear temperature dependent parameters.

For deuterium more than 90 binary VLE and gas solubility data sets are available. However, instead of introducing an additional main group, a deuterium sub group was assigned to the hydrogen main group, since both components behave thermodynamically similar. The differences in size were taken into account by the variation of the van der Waals properties (relative volume and surface). They were optimized by correlating several binary systems for D$_2$ (D$_2$ + *n*-heptane, *n*-octane, *iso*-octane, benzene, toluene, water and argon) using the H$_2$ interaction parameters. While for H$_2$ $R_k = 0.4160$ and $Q_k = 0.571$ are applied in the PSRK model, for D$_2$ $R_k = 0.3700$ and $Q_k = 0.527$ were obtained by the optimization. Using these values the description of D$_2$ solubility data in different solvents is as accurate as for H$_2$. Fig. 4 shows the correct prediction of the D$_2$ solubility in *n*-heptane and carbon disulfide. By the annexation of D$_2$ now also D$_2$ systems from structural classes can be described where only H$_2$ data are available. Moreover, the simultaneous correlation of H$_2$ and D$_2$ data allowed to obtain additional PSRK parameters for the hydrogen main group.
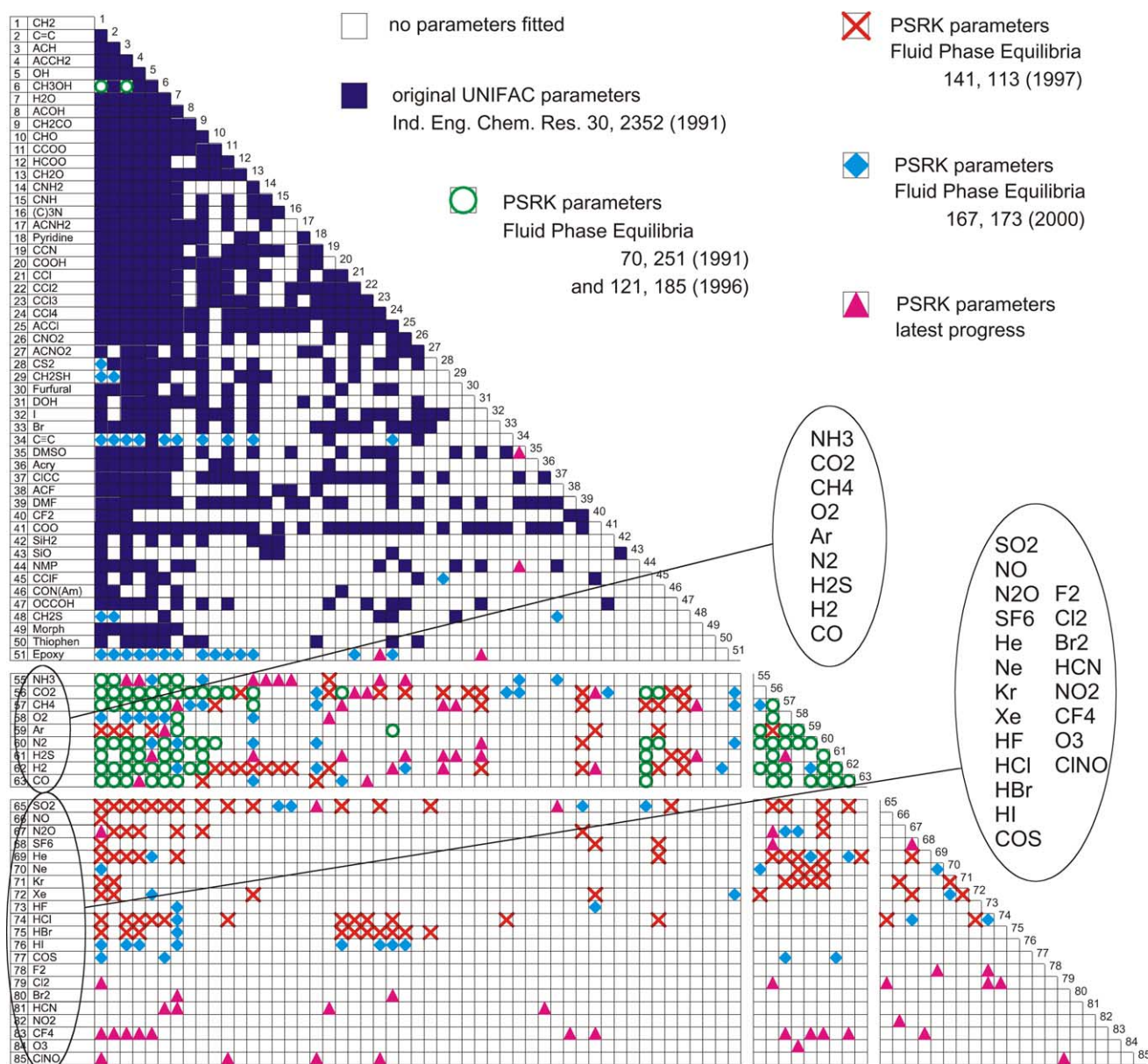
Fig. 1. Current status of the PSRK group interaction parameter matrix.

For water (H_2O) and heavy water (D_2O) this approach is not necessary, since a single neutron has no significant influence on the molecular properties. The reproduction of the D_2O data found in literature is of the same quality as for the systems containing H_2O.

Interaction parameters for diverse systems of already existing PSRK or UNIFAC groups were fitted to the growing data base. Fig. 5 shows examples for the epoxy and alkyne groups, which have been started to be introduced or revised by Horstmann et al. [9]. The system trichloromethane + 1,2-epoxybutane shows an interesting phase equilibrium behavior with a pressure minimum azeotrope which is described correctly.

In the course of a recent research project the PSRK method was extended for the description of the phase equilibrium behavior of electrolyte systems [15]. Especially gas solubility data in solvents containing salts have been investigated. In order to achieve a proper description of the pure solvents as a basis for the occurring salt effects, the parameters for CH_4 and water had to be revised. Fig. 6 shows the temperature dependence of the Henry coefficients for this system calculated with PSRK in comparison to literature data and own measurements [16]. As can be seen, the temperature dependence of the gas solubility showing the typical shape (maximum in Henry coefficient) can be accurately described with the model.
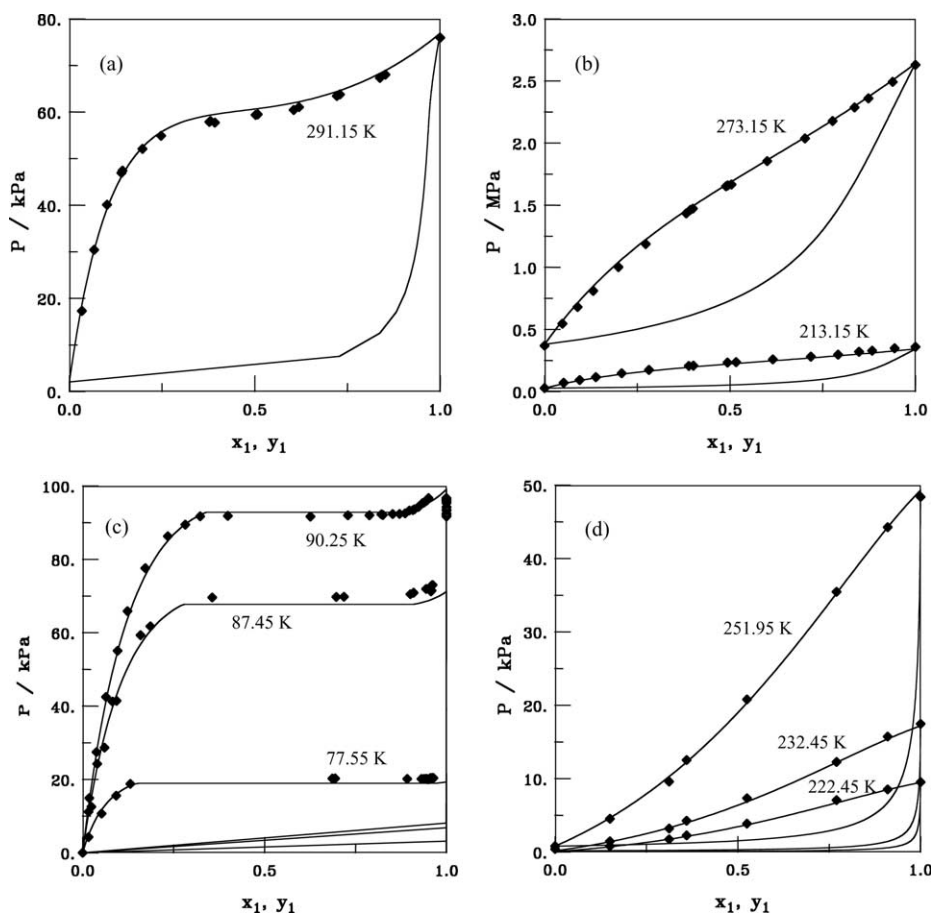
Fig. 2. Vapor–liquid equilibrium data for different systems—(a) hydrogen cyanide (1) + water (2): (♦) experimental data from Shirado [22]; (b) hydrogen chloride (1) + chlorine (2): (♦) experimental data from Wilson and Wilding [23]; (c) oxygen (1) + ozone (2): (♦) experimental data from Jenkins et al. [24]; (d) nitrosyl chloride (1) + ethyl acetate (2): (♦) experimental data from Addison and Sheldon [25]; (—) PSRK.
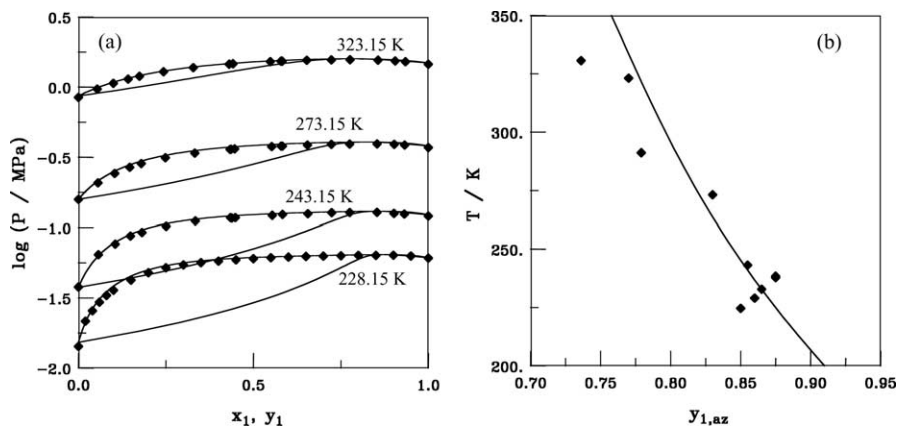

Fig. 3. Phase equilibrium data for the system chlorine (1) + sulfur dioxide (2)—(a) vapor–liquid equilibrium data: (♦) experimental data from Gilot et al. [26] at 228.15 K and from Wilson and Wilding [23] at 243.15, 273.15 and 323.15 K; (b) azeotropic data: (♦) experimental data from Carlson [27], Gilot et al. [26] and Wilson and Wilding [23]; (—) PSRK.
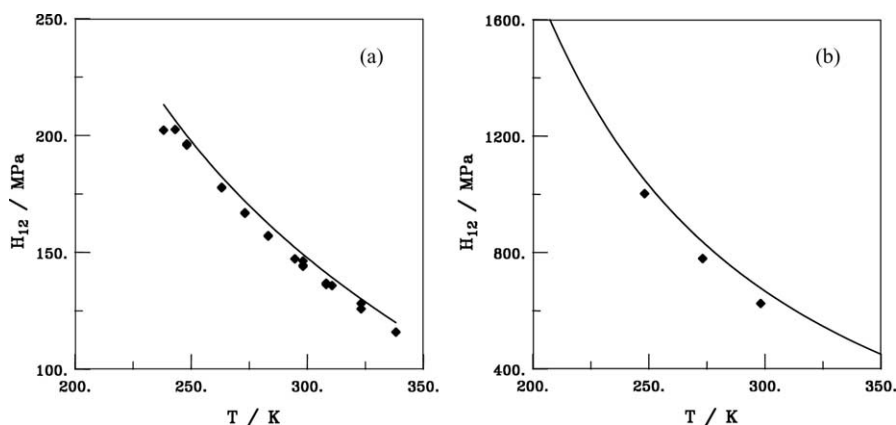
Fig. 4. Henry coefficients for systems with deuterium—(a) deuterium (1) + *n*-heptane (2): (♦) experimental data from Cook et al. [28] and Lachowicz et al. [29]; (b) deuterium (1) + carbon disulfide (2): (♦) experimental data from Cook et al. [28]; (—) PSRK.
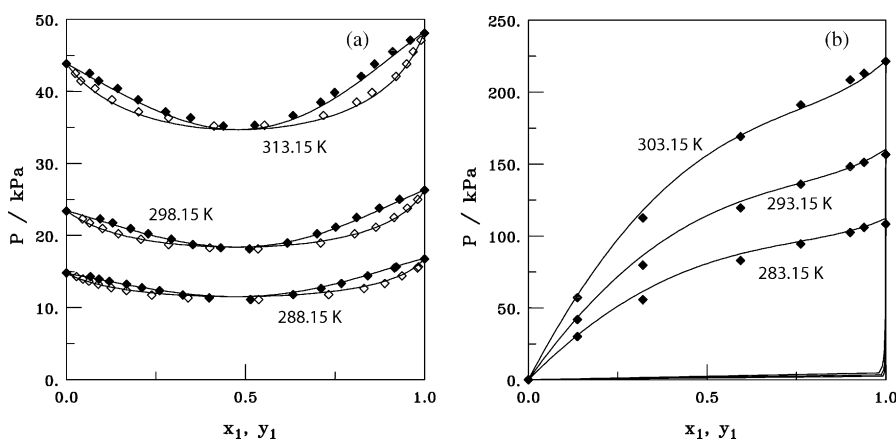

Fig. 5. Vapor–liquid equilibrium data for different systems—(a) trichloromethane (1) + 1,2-epoxybutane (2): (♦, ◊) experimental data from Francesconi et al. [30]; (b) 1-butyne (1) + dimethyl sulfoxide (2): (♦) experimental data from Doering and Preuss [31]; (—) PSRK.

In the past years, also critical data of binary mixtures were calculated with PSRK and also included in the parameter fitting process [32–34]. The obtained parameters from these investigations are included in Table 2. They have already been presented by Horstmann [10].
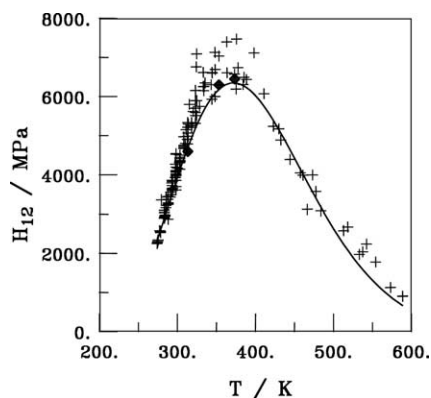

Fig. 6. Henry coefficients for systems methane (1) + water (2): (♦) our experimental data [16]; (+) experimental data from different authors taken from the Dortmund Data Bank [19]; (—) PSRK.

3. Conclusions

The PSRK group contribution EoS was extended by the introduction of eight new structural groups. In total, 75 sets of group interaction parameters for the new and the already existing main groups were fitted to experimental phase equilibrium data (VLE and gas solubility data) and critical data, and selected results were presented. As it was demonstrated, the agreement between experimental and predicted values proves the reliability of PSRK. In these ongoing investigations, also the prediction of asymmetric, polymer [12,13] or electrolyte [15] systems was improved. In the future, further developments of PSRK will be performed in the frame of a company consortium [35]. This article is furthermore a comprehensive summary of all the mixture and pure component parameters which are required for PSRK calculations.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.fluid.2004.11.002.

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