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## MIXING RULES FOR THE BACK EQUATION OF STATE

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Van der Waals type of mixing rule for the energy parameter  $u_s$  together with the mixing rules introduced previously for parameters  $\alpha_s$  and  $V_s^0$  of the BACK equation were employed in evaluating excess properties of mixing, Henry's law constant and high pressure vapour-liquid equilibria. A comparison with the experimental data reveals that the BACK equation together with the suggested mixing rules could provide good prediction of equilibrium properties of mixtures of relatively simple molecules.

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The available equations of state may be separated into three groups: (i) cubic equations of the van der Waals type, (ii) equations that followed from the exactly derived expressions of the perturbation theory of fluids, and (iii) the so-called augmented van der Waals equations of state. The first group includes the currently popular equations such as the Redlich-Kwong equation as modified by Soave<sup>1</sup> and the Peng-Robinson equation<sup>2</sup>. These equations can yield good representation of equilibrium properties, such as vapor-liquid equilibrium (VLE) values, and are simple to use. However, their abilities for describing volumetric properties are less than desirable. It is difficult to modify the expressions of these equations due to their empirical nature. Equations of state that follow from the perturbation theory employ precise relationships for the description of repulsive forces together with perturbation terms given by contribution of attractive forces. While this approach represents an exact way of characterizing the equilibrium behaviour of gases and liquids from the first principles (see, for example, ref.<sup>3</sup>), these equations are not very suitable for engineering calculations. The equations of the third group represent a reasonable compromise. They are formulated by combining an exact expression for the compressibility factor of hard bodies of different shape and size with the contribution of attractive forces expressed in the form of a series the constants of which are usually determined from the behaviour of pure compounds with simple structures and precisely known PVT and other property values.

The BACK equation, proposed by Chen and Kreglewski<sup>4-6</sup>, belongs to the third group. It is an augmented equation of the van der Waals type, relatively simple to use, and is accurate in representing equilibrium values for compounds of low molecular weights.

In addition to the mixing rules used by Simnick and co-workers<sup>7</sup> new sets have been proposed by Boublík<sup>8</sup>, and Machát and Boublík<sup>9</sup>, to improve systematically the mixing rules for parameters in the repulsive term. In these modifications, the

close relationship to the perturbation theory was retained. In this study, mixing rules for the attractive term have been considered.

### THEORETICAL

The BACK equation is of the form

$$z = PV/RT = z^r + z^a \quad (1)$$

$$z^r = \frac{1 + (3\alpha - 2)y + (3\alpha^2 - 3\alpha + 1)y^2 - \alpha^2 y^3}{(1 - y)^3} \quad (2)$$

$$z^a = \sum_{m=1}^4 \sum_{n=1}^9 n D_{mn} \left( \frac{u}{kT} \right)^m \left( \frac{V^0}{V} \right)^n, \quad (3)$$

where  $k$  is the Boltzmann constant,  $z$  is the compressibility factor, and  $\alpha$  is the parameter of non-sphericity; it is equal to unity for spheres, but greater than one for other hard convex bodies. The quantity  $y$  stands for the packing fraction, and

$$y = 0.74048V^0/V. \quad (4)$$

Chen and Kreglewski expressed the close-packed volume of the hard core molecules by means of

$$V^0 = V^{00} [1 - C \exp(-3u^0/kT)]^3 \quad (5)$$

and the energy parameter  $u$  of Eq. (3) by means of

$$u = u^0(1 + \eta/kT) \quad (6)$$

with  $\eta = 0$  for spheres and  $\eta > 0$  for acentric and polar molecules.

The BACK equation comprises of 24  $D_{mn}$  constants, which are generally valid for all compounds, and five characteristic parameters for individual substances,  $V_i^{00}$ ,  $\alpha$ ,  $u_i^0$ ,  $\eta_i$ , and  $C$ . However, Chen and Kreglewski suggested that  $C$  be given the value of 0.12 for all nonpolar substances but hydrogen.

For solutions, different mixing rules for  $V^0$ ,  $\alpha$  and  $u$  are available in the literature. Simnick and co-workers<sup>7</sup> adopted the following:

$$V_s^0 = \sum_i \sum_j x_i x_j V_{ij}^0 \quad (7)$$

$$\alpha_s = \sum_i x_i \alpha_i \quad (8)$$

$$u_s = \sum \sum x_i x_j u_{ij} . \quad (9)$$

Machát and Boublík<sup>9</sup> proposed that

$$V_s^0 = \sum x_i V_i^0 \quad (10)$$

$$\alpha_s = V_s^{-1} \sum x_i (\alpha_i V_i^0)^{1/3} \sum x_i (\alpha_i V_i^0)^{2/3} \quad (11)$$

and used Eq. (9) for  $u_s$ . In these equations,  $x$  stands for mole fraction and the subscript  $s$  stands for solution properties. The combining rules for obtaining the cross interaction terms  $V_{ij}^0$  and  $u_{ij}$  adopted by Simnick and co-workers were expressed by

$$V_{ij}^0 = \frac{1}{8} (V_i^0)^{1/3} + V_j^0)^3 (1 + v_{ij}) \quad (12)$$

and

$$u_{ij} = (u_{ii} u_{jj})^{1/2} (1 - k_{ij}) , \quad (13)$$

where the dimensionless cross-interaction constants,  $v_{ij}$  and  $k_{ij}$  were determined from mixture properties.

To conform with the perturbation theory, Eq. (10) should be used for obtaining  $V_s^0$ : Eq. (2) after substitution from (10) and (11) is exact up to the second term in the special case of hard sphere solutions of spheres with different diameters; it gives also quite accurate values of the excess entropy of mixing of model systems of hard spheres and prolate spherocylinders. In the work of Machát and Boublík, Eqs (9) and (10) were used together with Eq. (13) for  $u_{ij}$ .

The close resemblance of the BACK equation and the equation of state from the perturbation theory offers the possibilities of using revised mixing rules, such as expressing the attractive term by including explicit contributions of all the possible pairs of molecules:

$$z^a = \sum \sum x_i x_j \sum \sum n D_{mn} \left( \frac{u_{ij}}{kT} \right)^m \left( \frac{V_{ij}^0}{V} \right)^n . \quad (14)$$

This would be an exact analogy of the perturbation expansion up to the first order perturbation term. (The higher-order terms of the perturbation theory, however, would be expressed by more complicated functions of mole fractions than Eq. (14).)

As the quantity  $V_{ij}^0$  of Eq. (14) corresponds to  $\sigma_{ij}^3$  in the perturbation theory  $\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j)$  and  $\sigma_i$  is the zero-energy distance, we adopted Eq. (12) for its determination, but to determine  $y_s$ , we employed

$$y_s = \sum x_i y_i . \quad (15)$$

Eq. (13) was used for the determination of  $u_{ij}$ .

The use of Eq. (14) instead of Eq. (3) in the calculation demands a considerable increase in computer time, it is therefore desirable to select suitable mixing rules for  $u_s$  and  $V_s^0$  to reduce the computing time.

It is known that for simple mixtures (see *e.g.*<sup>10</sup>) the so-called van der Waals rules,

$$\bar{\varepsilon}_s = \frac{\sum \sum x_i x_j \varepsilon_{ij} \sigma_{ij}^3}{\sum \sum x_i x_j \sigma_{ij}^3}, \quad (16)$$

and

$$\bar{\sigma}_s^3 = \sum \sum x_i x_j \sigma_{ij}^3, \quad (17)$$

are applicable in theoretical expressions for mixtures. These rules are known to be exact for low density region, and useful for solutions of roughly spherical molecules at high densities. The quantity  $\varepsilon$  is the minimum energy value of the interaction pair potential and  $\sigma$  corresponds to its zero value.

This is the reason that we used in this study

$$u_s = \sum \sum x_i x_j u_{ij} V_{ij}^0 / V_s^0 \quad (18)$$

together with Eq. (13) for  $u_{ij}$  and Eq. (10) for  $V_s^0$ , with the adjustable binary parameter  $k_{ij}$  determined from the properties of a binary mixture.

## APPLICATIONS

### *Excess Properties of Binary Mixtures of Liquids*

At low pressures, the determination of the excess properties of mixtures as a function of composition represents a suitable characterization of their equilibrium behaviour, and only simple calculations are involved. At these conditions the small differences in densities of liquids at 0.1 to 0.2 MPa or zero pressure can be neglected, thus all the properties can be determined at the  $P \rightarrow 0$  condition.

During the calculation the volumes of pure components and their mixtures were evaluated first from Eq. (1) for  $z = 0$  by a Newton method. Their differences provide immediately the values of  $V^E$ . These volume values are then used to determine the Helmholtz free energy from the expression

$$(F - F^*)/RT = (\alpha^2 - 1) \ln(1 - y) + \frac{3\alpha y}{(1 - y)} + \frac{\alpha^2 y}{(1 - y)^2} + \sum \sum D_{mn} \left( \frac{u}{kT} \right)^m \left( \frac{V^0}{V} \right)^n \quad (19)$$

for pure components and their mixtures. Since the ideal gas free energies  $F_1^*$  and  $F_s^*$  are considered at volumes  $V_1$  and  $V_s$ , the corresponding term  $\sum x_i \ln(V_s/V_i)$  must be

subtracted to obtain  $G^E \approx F^E$ . The difference  $U - U^*$  in the internal energy follows from the expression

$$\frac{U - U^*}{RT} = (z - 1) \left( \frac{T}{V^0} \frac{\partial V^0}{\partial T} \right) + \left[ 2\alpha \ln(1 - y) + \frac{3y}{(1 - y)} + \frac{2\alpha y}{(1 - y)^2} \right] \left( -T \frac{\partial \alpha}{\partial T} \right) + \sum m D_{mn} \left( \frac{u}{kT} \right)^m \left( \frac{V^0}{V} \right)^n \left( 1 - \frac{T}{u} \frac{\partial u}{\partial T} \right). \quad (20)$$

For a solution, the expressions  $(-T/V_s^0)(\partial V_s^0/\partial T)$ ,  $(-T\partial\alpha_s/\partial T)$ , and  $(-T/u_s)(\partial u_s/\partial T)$  have, in accord with the mixing rules (10), (11), and (18), the following forms for mixtures:

$$(-T/V_s^0)(\partial V_s^0/\partial T) = (3/V_s^0) \sum x_i V_i^0 f_i \quad (21)$$

$$-T(\partial\alpha_s/\partial T) = \alpha_s \left[ -\frac{T}{V_s^0} \frac{\partial V_s^0}{\partial T} + \frac{\sum x_i (\alpha_i V_i^0)^{1/3} f_i}{\sum x_i (\alpha_i V_i^0)^{1/3}} + 2 \frac{\sum x_i (\alpha_i V_i^0)^{2/3} f_i}{\sum x_i (\alpha_i V_i^0)^{2/3}} \right] \quad (22)$$

and

$$(-T/u_s)(\partial u_s/\partial T) = (-T/V_s^0)(\partial V_s^0/\partial T) + (1/u_s V_s^0) \sum \sum x_i x_j u_{ij} V_{ij}^0 \left[ \frac{1}{2} \left( \frac{u_i^0}{u_i} + \frac{u_j^0}{u_j} - 2 \right) + 3 \frac{V_i^0{}^{1/3} f_i + V_j^0{}^{1/3} f_j}{V_i^0{}^{1/3} + V_j^0{}^{1/3}} \right], \quad (23)$$

where

$$f_i = (3u_i^0/kT)(V_i^0/V_i^0)^{1/3} - 1. \quad (24)$$

In the case that Eq. (14) for  $z^a$  is considered, we have

$$\begin{aligned} \frac{U - U^*}{RT} &= (z^r - 1) [(-T/V^0)(\partial V^0/\partial T)] + \\ &+ \left[ 2\alpha \ln(1 - y) + \frac{3y}{(1 - y)} + \frac{2\alpha y}{(1 - y)^2} \right] (-T\partial\alpha/\partial T) + \\ &+ \sum \sum x_i x_j \sum \sum D_{mn} \left( \frac{u_{ij}}{kT} \right)^m \left( \frac{V_{ij}^0}{V} \right)^n \{ n(-T/V_{ij}^0)(\partial V_{ij}^0/\partial T) + \\ &+ m[1 + (-T/u_{ij})(\partial u_{ij}/\partial T)] \}. \end{aligned} \quad (25)$$

The derivatives of the last term of Eq. (25) could be evaluated from the expressions analogous to Eqs (21) and (23). At the limiting condition  $P \rightarrow 0$ ,

$$H^E/RT \approx (U_s - U_s^*)/RT - \sum x_i (U_i - U_i^*)/RT. \quad (26)$$

In the calculation of the excess properties of mixtures, values of  $D_{mn}$  constants as given by Chen and Kreglewski<sup>4</sup> were used. The parameter values of pure compounds used in the calculation are given in Table I. The calculated excess thermodynamic properties depend on the  $k_{12}$  values, increasing with their increase. The  $k_{12}$  values were adjusted to give the best overall agreement for all three excess functions with slightly weight given to  $H^E/RT$ . A comparison of the calculated excess free energy,  $G^E$ , excess enthalpy,  $H^E$  and excess volume  $V^E$  of equimolar solutions with experimental data for the mixing rule set consisting of Eqs (10), (11), and (18) is given in Table II. An attempt was made to perform similar calculations using the other set of mixing rules (Eqs (10), (11), and (14)), but we obtained, for  $k_{12} = 0$ , systematically higher values of  $V^E$  than the experimental ones. For example, for the equimolar mixture of Ar and Kr,  $V_{cal}^E = -0.33$  while  $V_{exp}^E = -0.52 \text{ cm}^3 \text{ mol}^{-1}$ . By changing the value of  $k_{12}$  in the physically acceptable range ( $k_{12} \geq 0$ ), more positive values of  $V^E$  resulted. It was therefore concluded that the latter set of mixing rules would not provide a fair description of mixtures. On the other hand, the set of rules using Eqs (10), (11), and (18) yielded good calculated values, especially for mixtures of compounds with low molecular weights. The parameters  $V^{00}$ ,  $\alpha$ ,  $u^0$ , and  $\eta$  are generally known with better accuracy for these compounds than those with high molecular weights. However, a fair agreement between the calculated and experiment values of three excess properties was obtained for the benzene-n-hexane system at 298.15 K as shown in Fig. 1.

The proposed approach yielded acceptable values of excess thermodynamic functions for a variety of binary mixtures, as shown in Table II and Fig. 1, using a single  $k_{12}$  value for each mixture. The only exception is the system benzene-n-octane, where the deviations are large. This disagreement is probably more due to the inaccuracy of the parameter values of n-octane and the fact that the BACK equation does not describe properly properties of systems of larger molecules than due to the mixing rules.

### Henry's Law Constant

Henry's law constant is another thermodynamic quantity that can be easily evaluated together with the heat of solution and the partial molar volume of solute from equations of state of mixtures. As it usually comprises systems formed by one small molecule (solute) and one higher molecular compound, it provides information on the quality of the equilibrium behaviour description for systems of unlike substances.

From thermodynamics of fluids (see *e.g.* Goldman<sup>11</sup>)

$$\ln H_\infty = (\mu_2/kT)_\infty^1 - (\mu_2^0/kT)^g, \quad (27)$$

where  $\mu_2$  stands for the chemical potential of solute *per* one molecule;  $k$  is the Boltz-

TABLE I  
BACK equation parameters

Compounds	$V^{00}$ $\text{cm}^3 \text{mol}^{-1}$	$\alpha$	$u^0/k, \text{K}$	$\eta/k, \text{K}$	$C$	Ref.
Argon	16.290	1.000	150.86	0.00	0.12	5
Krypton	20.506	1.000	208.32	0.00	0.12	5
Nitrogen	19.457	1.000	123.53	3.00	0.12	5
Oxygen	16.062	0.998	152.82	2.02	0.12	10
Carbon monoxide	19.797	1.004	129.70	3.90	0.12	10
Carbon dioxide	19.728	1.061	279.00	48.00	0.12	10
Methane	21.859	1.002	190.29	1.00	0.12	10
Ethane	31.430	1.022	295.05	19.00	0.12	10
Propane	42.598	1.041	353.11	34.00	0.12	5
n-Butane	53.907	1.057	402.46	52.00	0.12	10
n-Pentane	65.751	1.057	435.83	70.72	0.12	7
Neopentane	65.518	1.050	409.59	51.28	0.12	7
n-Hexane	77.228	1.072	468.33	90.11	0.12	7
n-Heptane	88.351	1.080	491.00	113.77	0.12	7
n-Octane	96.556	1.098	517.52	134.50	0.12	7
Cyclo-hexane	64.772	1.058	522.46	70.72	0.12	7
Benzene	54.383	1.059	532.12	71.50	0.12	7
Carbon tetrachloride	57.950	1.050	515.89	64.70	0.12	7

TABLE II  
Comparison of the calculated and experimental equimolar excess functions

System	T, K	$k_{ij}$	$G^E$		$H^E$		$V^E$		Ref.
			$\text{J mol}^{-1}$		$\text{J mol}^{-1}$		$\text{cm}^3 \text{mol}^{-1}$		
			cal.	exp.	cal.	exp.	cal.	exp.	
Ar-Kr	115.7	0.0215	99.6	83.9	43.1	43(T=117)	-0.53	-0.52	11
Ar-N <sub>2</sub>	83.8	0.003	44.1	34.4	41.1	51	-0.18	-0.18	11
Ar-O <sub>2</sub>	83.8	0.012	30.7	37.1	59.1	60	0.14	0.14	11
Ar-CO	83.8	0.015	62.4	56.7	80.2	—	0.00	0.09	11
Ar-CH <sub>4</sub>	91.0	0.027	76.4	75.0	105.4	—	0.12	0.18	11
N <sub>2</sub> -CO	83.8	0.012	30.3	23.0	47.4	—	0.09	0.13	11
CO-CH <sub>4</sub>	90.7	0.021	127.4	121.0	105.0	105.0	-0.28	-0.32	11
C <sub>6</sub> H <sub>6</sub> -n-C <sub>5</sub> H <sub>12</sub>	298.1	0.024	501.3	422.0	853.2	856.5	0.10	—	15
C <sub>6</sub> H <sub>6</sub> -n-C <sub>6</sub> H <sub>14</sub>	298.1	0.033	454.3	384.0	797.3	800.0	0.66	0.50	16-18
C <sub>6</sub> H <sub>6</sub> -n-C <sub>7</sub> H <sub>16</sub>	298.1	0.030	418.8	415.0	825.2	933.2	0.79	0.60	15
C <sub>6</sub> H <sub>6</sub> -n-C <sub>8</sub> H <sub>18</sub>	298.1	0.015	118.9	614.0	1085.2	969.0	1.40	—	15

mann constant  $l$ , and  $g$  denote liquid and gaseous phases, respectively; superscript  $^{\circ}$  denotes a standard state of pure gas at  $P = 1$  atm, and  $\infty$  refers to the infinitely dilute condition. Neglecting the small differences in behaviour of solute in the gaseous phase at  $P = 1$  atm from that of an ideal gas, and the difference in densities of solvent at  $P = 1$  and  $P \rightarrow 0$ , we can write

$$\ln H_{\infty} = \ln (RT/\bar{V}_1) + (\mu_{2\infty}^1 - \mu_2^*)/kT. \quad (28)$$

The second term of the right-hand side follows from the derivative of  $(F - F^*)/kT$  with respect to the number of molecules  $N$ .

From Eq. (19) one can obtain

$$\begin{aligned} \ln H_{\infty} = & \ln (RT/\bar{V}_1) + (F^0 - F^*)/RT + \\ & + \left[ 2\alpha \ln(1-y) + \frac{3y}{(1-y)} + \frac{2\alpha y}{(1-y)^2} \right] \varphi_{\infty} + (z^f - 1)(1 + \psi_{\infty}) + \\ & + \sum \sum D_{mn} \left( \frac{u}{kT} \right)^m \left( \frac{V^0}{V} \right)^n + \sum \sum D_{mn} \left( \frac{u}{kT} \right)^m \left( \frac{V^0}{V} \right)^n [mv_{\infty} + n(1 + \psi_{\infty})]. \quad (29) \end{aligned}$$

$\bar{V}_1$  is the partial molar volume of the solvent at  $x_2 \rightarrow 0$ ;  $\alpha$ ,  $y$ ,  $F^0 - F^*$ ,  $z$ ,  $u$ , and  $V^0$

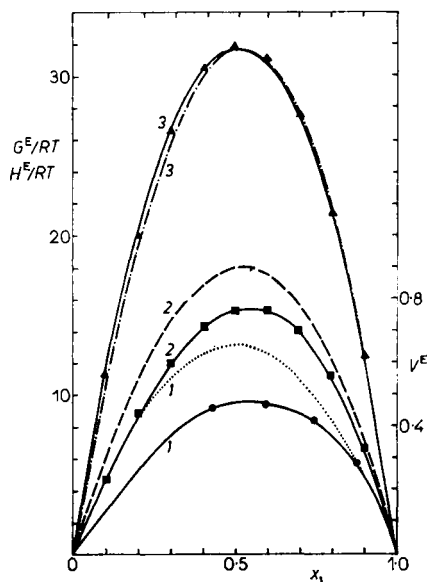


FIG. 1

Comparison of calculated and experimental excess properties of the benzene-n-hexane system at 298.15 K (full lines fit the experimental points, interrupted curves — calculated 1  $V^E$ ,  $\text{cm}^3 \text{mol}^{-1}$ ; ref.<sup>18</sup>; 2  $10^2 \cdot G^E/RT$ , ref.<sup>17</sup>; 3  $10^2 \cdot H^E/RT$ , ref.<sup>16</sup>)



are all properties of the mixture at  $x_2 \rightarrow 0$ , whereas  $\varphi_\infty$ ,  $\psi_\infty$ , and  $v_\infty$  are defined by

$$\varphi_\infty = \left[ \left( \sum N_i \right) \frac{\partial \alpha}{\partial N_2} \right]_{x_2 \rightarrow 0} \quad (30)$$

$$\psi_\infty = \left[ \left( \sum N_i / V_s^0 \right) (\partial V_s^0 / \partial N_2) \right]_{x_2 \rightarrow 0} \quad (31)$$

and

$$v_\infty = \left[ \left( \sum N_i / u_s \right) (\partial u_s / \partial N_2) \right]_{x_2 \rightarrow 0} \quad (32)$$

For the above mentioned set of mixing rules (Eqs (10), (11), and (18))

$$\psi_\infty = (V_2^0 / V_1^0) - 1 \quad (33)$$

$$v_\infty = 2[(u_{12} V_{12}^0 / u_{11} V_1^0) - 1] - \psi_\infty \quad (34)$$

and

$$\varphi_\infty = \alpha_1 [(\alpha_2 V_2^0 / \alpha_1 V_1^0)^{1/3} + (\alpha_2 V_2^0 / \alpha_1 V_1^0)^{2/3} - 2 - \psi_\infty], \quad (35)$$

where  $u_{12}$  and  $V_{12}^0$  are given by Eqs (13) and (12), respectively, but with  $v_{ij} = 0$ . Differentiating  $\ln H_\infty$  with respect to pressure yields the partial molar volume of the solute in the given solvent at  $x_2 \rightarrow 0$ ,

$$(\bar{V}_2 / RT)_\infty = \bar{q}_1^{-1} (\partial \bar{q}_1 / \partial P) + (kT)^{-1} (\partial / \partial \bar{q}_1) (\mu_{2\infty}^1 - \mu_2^*) (\partial \bar{q}_1 / \partial P). \quad (36)$$

It follows from Eq. (29) that,

$$\begin{aligned} (\bar{V}_2 / RT)_\infty = & \beta_1 \{ 1 + (z^r - 1) + (1 + \psi_\infty) y [(3\alpha + 1) + \\ & + (6\alpha^2 - 2) y + (-3\alpha^2 + 1) y^2] / (1 - y)^4 + \\ & + \varphi_\infty y [3 + (6\alpha - 3) y - 2\alpha y^2] / (1 - y)^3 + \\ & + \sum n D_{mn} \left( \frac{u}{kT} \right)^m \left( \frac{V^0}{V} \right)^n [1 + m v_\infty + n(1 + \varphi_\infty)] \}, \end{aligned} \quad (37)$$

where

$$\beta_1 = \bar{q}_1^{-1} (\partial \bar{q}_1 / \partial P). \quad (38)$$

The relationship for the heat of solution,  $\Delta H_\infty$ , is more complicated, as both the system variables and the derivatives depend on temperature. The derivative of  $\ln H_\infty$  with respect to temperature was determined numerically.

With the inclusion of one adjustable parameter,  $k_{12}$ , the experimental value of  $H_\infty$  can be easily reproduced at the given temperature. A more demanding task is to obtain proper  $H_\infty$  values at different temperatures. Calculation of  $H_\infty$  was carried out for systems of methane, ethane, propane and carbon dioxide in butane and methane and nitrogen in n-hexane in the temperature ranges considered by Prausnitz and Chueh<sup>12</sup>. The calculated results are presented in Figs 2 and 3. Good agreement between the calculated values and those obtained from the correlation of Prausnitz and Chueh was observed for the majority of the systems.

A comparison of the calculated and experimental values of  $H_\infty$ , partial molar volume  $\bar{V}_2$  and the heat of solution  $\Delta H_\infty$  at infinite dilution is presented in Table III. In the calculation, one  $k_{12}$  value was used to determine the three properties for each binary system, but its values were adjusted to yield approximate agreement between the calculated and experimental  $H_\infty$  values. The calculation yielded consistently higher values of  $\Delta H_\infty$  and  $\bar{V}_2$ , and this trait was more pronounced for systems containing benzene. It is worthy to note that this calculation yielded higher  $\bar{V}_2$  values than experimental ones, whereas the majority of theories (see Handa and Benson<sup>13</sup>) underestimate it.

#### *High Pressure Vapor-Liquid Equilibria*

One of the most important applications of equations of state is their use for describing high pressure vapor-liquid equilibria. The BACK equation was recently applied for this purpose (Machát and Boublík<sup>10</sup>) using Eqs (9), (10), (11), and (13). Although a fair accord with experimental values was obtained for mixtures consisting of simple compounds, large deviations were obtained for systems containing carbon dioxide and higher n-alkanes. For this reason, a series of carbon dioxide-n-alkane systems was studied using the van der Waals mixing rule for  $u_s$ . In the process of calculation, the equilibrium pressure  $P$  was determined from Eq. (1) together with Eqs (2) and (3). The fugacity coefficient of a component  $i$  was evaluated from

$$\begin{aligned} \ln \varphi_i = & (F^0 - F^*)/RT + \left[ 2\alpha \ln(1 - y) + \frac{3y}{(1 - y)} + \frac{2\alpha y}{(1 - y)^2} \right] \phi_i + \\ & + (z^f - 1)(1 + \psi_i) + \sum \sum D_{mn} \left( \frac{u_s}{kT} \right)^m \left( \frac{V_s^0}{V} \right)^n + \\ & + \sum \sum D_{mn} \left( \frac{u_s}{kT} \right)^m \left( \frac{V_s^0}{V} \right)^n [m v_i + n(1 + \psi_i)] - \ln z \end{aligned} \quad (39)$$

with

$$\psi_i = V_i^0/V_s^0 - 1 \quad (40)$$

$$v_i = 2 \left[ \frac{(\sum x_k u_{ik} V_{ik}^0)/(u_s V_s^0) - 1}{2} \right] - \psi_i \quad (41)$$

TABLE III

 Comparison of the calculated Henry's law constant,  $H_\infty$ , the solution heat  $\Delta H_\infty$  and the partial molar volume,  $\bar{V}_2$  at infinite dilution with the experimental data at 298.15 K (refs<sup>13,19</sup>)

System	$k_{12}$	Calculated			Experimental		
		$H_\infty$ , MPa	$\Delta H_\infty$ , J mol <sup>-1</sup>	$\bar{V}_2$ , cm <sup>3</sup> mol <sup>-1</sup>	$H_\infty$ , MPa	$\Delta H_\infty$ , J mol <sup>-1</sup>	$\bar{V}_2$ , cm <sup>3</sup> mol <sup>-1</sup>
C <sub>6</sub> H <sub>6</sub> -Ar	0.24	115.4	4.69	51.2	115.0	1.24	44.6
C <sub>6</sub> H <sub>6</sub> -N <sub>2</sub>	0.23	231.9	7.88	58.4	227.2	4.25	52.6
C <sub>6</sub> H <sub>6</sub> -O <sub>2</sub>	0.26	120.7	4.83	51.0	124.1	1.71	46.1
C <sub>6</sub> H <sub>6</sub> -CH <sub>4</sub>	0.12	50.7	1.69	59.0	48.0	-1.28	54.4
C <sub>6</sub> H <sub>6</sub> -CO <sub>2</sub>	0.16	10.6	-6.65	51.3	10.4	-9.31	47.6
CCl <sub>4</sub> -Ar	0.22	74.8	0.69	49.3	75.0	-0.43	44.0
CCl <sub>4</sub> -N <sub>2</sub>	0.23	156.6	3.78	57.0	156.4	2.36	53.1
CCl <sub>4</sub> -O <sub>2</sub>	0.24	78.2	0.83	49.1	84.4	0.03	45.2
CCl <sub>4</sub> -CH <sub>4</sub>	0.12	37.0	-1.84	57.8	35.3	-2.99	52.3
CCl <sub>4</sub> -CO <sub>2</sub>	0.16	8.7	-9.18	49.4	9.6	—	47.9

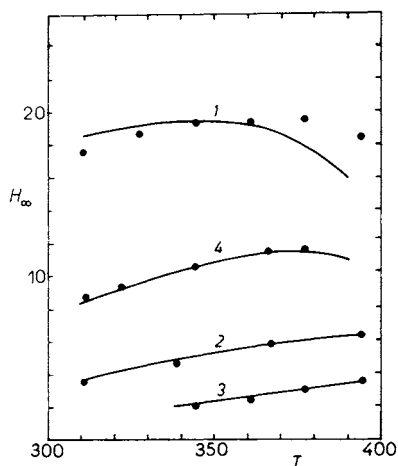


FIG. 2

Dependence of Henry's law constant  $H_\infty$ , MPa, of methane, ethane, propane, and carbon dioxide in butane on temperature ( $T$ , K; points — recalculated values from the correlation of Prausnitz and Chueh<sup>12</sup>; curves — calculated)

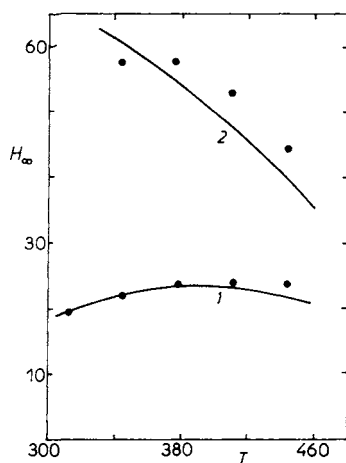


FIG. 3

Dependence of Henry's law constants,  $H_\infty$ , MPa, of methane and nitrogen in n-hexane on temperature ( $T$ , K; points — recalculated values from the correlation of Prausnitz and Chueh<sup>12</sup>; curves — calculated)

TABLE IV  
Comparison of calculated and experimental vapor-liquid equilibrium values for carbon dioxide and n-paraffins

T, K	Proposed mixing rules			Previous mixing rules			Peng-Robinson Eq.			Ref.
	$k_{12}$	$ P _{lav}$ %	$ \Delta y $	$k_{12}$	$ P _{lav}$ %	$ \Delta y $	$k_{12}$	$ P _{lav}$ %	$ \Delta y $	
	<b>CH<sub>4</sub>-CO<sub>2</sub></b>									
219.26	0.0655	1.66	0.0093	0.0781	1.65	0.0097	0.0943	2.2	0.0139	20
230.00	0.0610	1.15	0.0119	0.0717	0.85	0.0124	0.0928	1.2	0.0133	21
233.15	0.0605	0.44	0.0122	0.0683	1.60	0.0130	0.0930	1.7	0.0057	22
250.00	0.0566	1.72	0.0101	0.0650	1.44	0.0177	0.0985	2.5	0.0126	21
253.15	0.0582	1.19	0.0184	0.0681	1.44	0.0194	0.1005	1.7	0.0057	22
270.00	0.0620	1.82	0.0096	0.0735	1.90	0.0097	0.1154	1.7	0.0067	21
273.15	0.0559	1.46	0.0178	0.0660	1.57	0.0187	0.1191	2.1	0.0045	22
	<b>C<sub>2</sub>H<sub>6</sub>-CO<sub>2</sub></b>									
250.00	0.1131	1.45	0.0099	0.1225	2.19	0.0106	0.1304	0.5	0.0060	21
283.15	0.1086	0.78	0.0050	0.1386	2.20	0.0067	0.1352	1.1	0.0022	23
	<b>C<sub>3</sub>H<sub>8</sub>-CO<sub>2</sub></b>									
266.48	0.1283	1.91	0.0063	0.1263	7.79	0.0179	0.1271	2.0	0.0058	24
277.59	0.1319	1.71	0.0086	0.1215	6.06	0.0134	0.1271	1.6	0.0066	25
310.93	0.1373	1.69	0.0081	0.1616	8.15	0.0268	0.1351	0.6	0.0166	25

$C_4H_{10}-CO_2$											
255-98	0-1654	5-99	0-0070	0-1093	11-51	0-0141	0-1279	5-8	0-0172	26	
310-93	0-1602	2-22	0-0096	0-1190	11-30	0-0053	0-1259	1-5	0-0065	27	
$C_5H_{12}-CO_2$											
277-65	0-1780	5-83	0-0039	0-0920	12-07	0-0081	0-1271	5-2	0-0047	26	
311-04	0-1758	3-92	0-0042	0-0972	13-54	0-0092	0-1192	3-0	0-0075	26	
344-15	0-1818	4-02	0-0168	0-0938	9-66	0-0149	0-1260	2-5	0-0164	26	
$C_6H_{14}-CO_2$											
298-15	0-1998	7-07	0-0053	0-0914	19-59	0-0044	0-1156	5-2	0-0062	28	
313-15	0-1885	6-13	0-0043	0-0842	17-85	0-0044	0-1153	6-3	0-0038	28	

and

$$\varphi_i = \alpha_s [(\alpha_i V_i^0)^{1/3} / \sum x_k (\alpha_k V_k^0)^{1/3} + (\alpha_i V_i^0)^{2/3} / \sum x_k (\alpha_k V_k^0)^{2/3} - 2 - \psi_i]. \quad (42)$$

At the condition of infinite dilution,  $x_2 \rightarrow 0$ , Eqs (40)–(42) reduce to Eqs (33)–(35).

A bubble-point calculation was performed and results obtained for the carbon dioxide–*n*-alkane systems at several arbitrarily selected temperatures are summarized in Table IV. The  $k_{12}$  values were obtained by an optimization procedure with the objective function given by the squares of relative deviations in pressure and vapor phase mole fraction. For comparison, the results obtained from the Peng–Robinson equation of state and the values obtained using the old mixing rule for  $u$  (Eq. (9) instead of Eq. (18)) are included in Table IV. The present set of mixing and combining rules yielded better results than the older set, especially for systems containing higher members of the *n*-alkane. The description of VLE values by means of the BACK equation is as good as that from the empirical Peng–Robinson equation.

In their attempt to describe VLE values for systems such as methane–carbon dioxide, Kreglewski and Hall<sup>14</sup> found it necessary to introduce a semi-empirical correction for the vanishing ordering effect. This correction was not required in the present calculation as shown in Fig. 4, in which the calculated and experimental

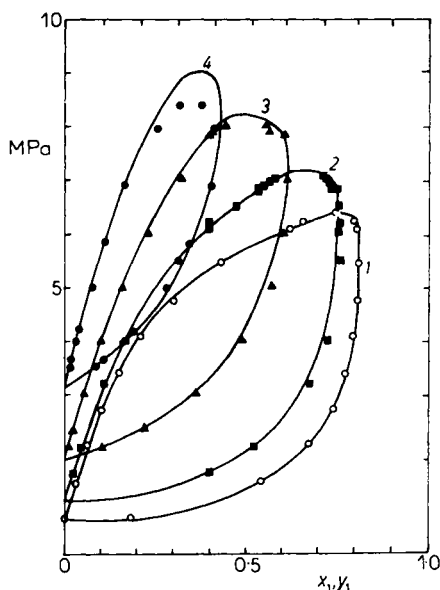


FIG. 4

Vapor-liquid equilibria in the methane–carbon dioxide system at four isothermal conditions 1 219.6, 2 230, 3 250, 4 270 K (refs see Table IV)

values for the methane-carbon dioxide system at several temperatures are compared. With the exception of VLE values at the highest temperature considered, excellent agreement was obtained. In passing, we notice that the result of Kreglewski and Hall for the same temperature indicated similar disagreement.

We can thus conclude that the BACK equation, an augmented van der Waals equation, makes it possible to calculate several thermodynamic properties of liquids with good accuracy. The main advantage of this type of equation over an empirical equation is the possibility of systematic improvement of the equation by considering the exact results of statistical thermodynamics of fluids and mixtures. For example, the expression of Eq. (2) could be modified by a three-term expression (see Boublik<sup>3</sup>) involving mean radius and surface area parameters.

Another advantage of this type of equations is their versatility. Enthalpy and volume of mixtures can be predicted without modifying the mixing rules.

The BACK equation yields sufficiently accurate results for the low molecular substances, for which "van der Waals" mixing rule is adequate. With the increase of size and with more complex shape of molecules results become consequently worse. In such cases, a good fit cannot be obtained by simple variation of  $k_{12}$ . An introduction of more appropriate characterization of interaction forces of molecules differing in size, shape and electrostatic moments would be required.

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#### REFERENCES

1. Soave G.: Chem. Eng. Sci. 27, 1197 (1972).
2. Peng D. Y., Robinson D. B.: Ind. Eng. Chem. Fundam. 15, 59 (1976).
3. Boublik T.: Fluid Phase Equil. 1, 37 (1977).
4. Chen S. S., Kreglewski A.: Ber. Bunsenges. Phys. Chem. 81, 1048 (1977).
5. Kreglewski A., Chen S. S.: J. Chim. Phys. 75, 347 (1978).
6. Kreglewski A., Chen S. S.: Adv. Chem. Ser. 182, 197 (1979).
7. Simnick J. J., Lin H. M., Chao K. C.: Adv. Chem. Ser. 182, 209 (1979).
8. Boublik T.: This Journal 48, 2713 (1983).
9. Machát V., Boublik T.: Fluid Phase Equil. 21, 1 (1985).
10. Rowlinson J. S.: *Liquids and Liquid Mixtures*. 3rd ed., Butterworth, London 1982.
11. Goldman S.: J. Phys. Chem. 81, 1428 (1977).
12. Prausnitz J. O., Chueh P. L.: *Computer Calculations for High-Pressure Vapor-Liquid Equilibria*. Prentice-Hall, Englewood Cliffs. New York 1969.
13. Handa Y. P., Benson C. G.: Fluid Phase Equil. 8, 161 (1982).
14. Kreglewski A., Hall K. R.: Fluid Phase Equil. 15, 11 (1983).
15. Kehiaian H. V. (Ed.): *Selected Data on Mixtures*, Int. Data Series. Thermodynamic Research Center, Texas A & M University 1973-1984.
16. Smith B. D., Muthu O., Duvau A.: J. Phys. Chem. Reference Data 12, 389 (1983).
17. Murray R. S., Martin M. L.: J. Chem. Thermodyn. 7, 839 (1975).
18. Schmidt R. L., Randal J. C., Clever H. L.: J. Phys. Chem. 70, 3912 (1966).

19. Boublik T., Lu B. C.-Y.: *J. Phys. Chem.* **82**, 2801 (1978).
20. Donnelly H. G., Katz D. L.: *Ind. Eng. Chem.* **46**, 511 (1954).
21. Davalos J., Anderson W. R., Phelps R. E., Kidnay A. J.: *J. Chem. Eng. Data* **21**, 81 (1976).
22. Kaminishi G., Arai Y., Saito S., Maeda M.: *J. Chem. Eng. Jpn.* **1**, 109 (1968).
23. Ohgaki K., Katayama T.: *Fluid Phase Equil.* **1**, 27 (1977).
24. Hamam S. E. M., Lu B. C.-Y.: *J. Chem. Eng. Data* **21**, 200 (1976).
25. Reamer H. H., Sage B. H., Lacey W. N.: *Ind. Eng. Chem.* **43**, 2515 (1951).
26. Kalra H., Krishan T. R., Robinson D. B.: *J. Chem. Eng. Data* **21**, 222 (1976).
27. Besserer G. J., Robinson D. B.: *Can. J. Chem. Eng.* **49**, 651 (1971).
28. Besserer G. J., Robinson D. B.: *J. Chem. Eng. Data* **18**, 416 (1973).

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