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## A MODIFICATION OF THE REDLICH-KWONG-SOAVE EQUATION OF STATE AND THE DETERMINATION OF ITS PARAMETERS ON THE BASIS OF SATURATED VAPOUR PRESSURES AND SECOND VIRIAL COEFFICIENTS OF PURE SUBSTANCES

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The temperature dependence of parameter  $a = a(T_r)$  of the Redlich-Kwong-Soave equation of state was modified. To calculate the corresponding individual parameters, an effective algorithm applying the Newton method was proposed. The parameters were determined for 60 substances, and the new modification correlates saturated vapour pressures from the values of  $p_r = 0.001$  to  $p_r = 1.0$  with the accuracy which is usually better than 0.2% and is comparable with that attained in terms of the Wagner equation. The modification proposed is utilized above all when applying the equation of state to the calculation of vapour-liquid equilibrium.

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Two approaches are used for calculating vapour-liquid equilibrium: The classical approach employs activity coefficients which characterize the liquid phase behaviour. The vapour phase is (usually) considered to be an ideal gas or it is described by the virial equation of state truncated after the second term. On the basis of saturated vapour pressures of pure substances and experimental equilibrium data, the activity coefficients are determined and then correlated by a suitable equation.

The main advantage of this approach is its relative simplicity when calculating back the equilibrium and particularly the fact that for the systems with small deviations from ideality, the experimental data are described with high accuracy. This high accuracy is attained among others because the experimental data on saturated vapour pressures of pure substances or the correlation equations which reproduce these data in limits of experimental errors are used. On the other hand, a great disadvantage of this method is its limitation to low pressures and impossibility to be applied in the critical region.

The second, recently considerably elaborated approach, stems from the equation of state which is applied to both the phases. In this direction, the most different versions of the van der Waals or Redlich-Kwong equations<sup>1</sup> are applied most often. Especially large extension has reached the Soave<sup>2</sup> modification of the Redlich-Kwong equation (hereafter RKS equation) and the Peng-Robinson equation<sup>3</sup>.

This approach suffers from two disadvantages which did not allow its wider practical employment before computers having been introduced. These are partly more complicated calculations of equilibria and partly an insufficiently accurate description of saturated vapour pressures in terms of the generalized equations of state.

As it has been mentioned, the calculation of vapour-liquid equilibrium is conditioned to a considerable degree by the accuracy of saturated vapour pressures of pure substances. To attain a better agreement in saturated vapour pressures on using the Redlich-Kwong equation, Soave<sup>2</sup> modified the temperature dependence of parameter  $a$  in this equation. The generalized dependence obtained represents very well the behaviour of hydrocarbons and weakly polar substances. The accuracy of calculated saturated vapour pressures lies within 1–3% according to various authors, see, e.g., Sandarusi and coworkers<sup>4</sup>.

In this work an algorithm is proposed based on the Newton method making it possible to establish the required number of individual substance parameters on the basis of data on saturated vapour pressures and, if need be, on second virial coefficients.

#### CALCULATIONS

The modified Redlich-Kwong equation was used here in the form

$$p = RT/(V_m - b) - a/[V_m(V_m + c)], \quad (1)$$

where the temperature dependence of parameters  $a$ ,  $b$ ,  $c$  was considered in the general form

$$\begin{aligned} a &= a_c \exp\left(\sum_{k=1} a_k (T_r^{m_k} - 1)\right), \\ b &= b_c(1 + b_1(T_r^{b_2} - 1)), \\ c &= c_c(1 + c_1(T_r^{c_2} - 1)). \end{aligned} \quad (2)$$

The dependence of parameter  $a = a(T_r)$  can be regarded to be an extension of the dependence used by Heyen<sup>5</sup> and/or by other authors<sup>6–8</sup>. A temperature dependence of parameter  $b$  was considered by Heyen<sup>5</sup> and Fuller<sup>9</sup>. Further dependences for  $a = a(T_r)$  can be found in the literature<sup>2,4,10–14</sup>.

The values of constants  $a_c$ ,  $b_c$ ,  $c_c$  were determined from the conditions valid at the critical point – see Appendix 1. The calculations were carried out always for a firmly chosen set of exponents  $\{m_k\}$  and/or  $b_2$ ,  $c_2$ , too.

Parameters  $\{a_k\}$  and/or  $b_1$ ,  $c_1$  were chosen so that the criterion function

$$F = \sum_{i=1}^{n_p} [(p_{i,\text{exp}}^{\circ} - p_{i,\text{calc}}^{\circ})/p_{i,\text{exp}}^{\circ}]^2 + w \sum_{j=1}^{n_B} (B_{j,\text{exp}} - B_{j,\text{calc}})^2 \quad (3)$$

should acquire a minimum value.

When suggesting criterion function (3), we started from the assumption that the variance of relative deviation of experimental vapour pressure data was approximately constant in the whole temperature range. Further we started from the idea that especially for substances with a low value of critical temperature (hydrogen, nitrogen, oxygen, methane, etc.) it would be necessary to include higher temperature data (e.g., virial coefficient) into the calculation to describe well the  $P$ - $V$ - $T$  behaviour of the substance even in the supercritical region.

The algorithm itself of the calculation of parameters  $\{a_k\}$  — if need be also considered parameters  $b_i$ ,  $c_i$  are included in the set — consists of the following steps:

1. The initial approximation of  $\{a_k\} = \{a_k^0\}$  is chosen; usually we take  $a_k^0 = 0$  for all the values of index  $k$  considered.

2. From the equilibrium conditions

$$\begin{aligned} p(T, V_m^L, \mathbf{a}) &= p(T, V_m^g, \mathbf{a}), \\ \ln f(T, V_m^L, \mathbf{a}) &= \ln f(T, V_m^g, \mathbf{a}) \end{aligned} \quad (4)$$

we determine the molar volumes of saturated liquid ( $V_m^L$ ) and vapour ( $V_m^g$ ) phases for each temperature  $T = T_i$ ,  $i = 1, 2, \dots, n_p$ , and on inserting into the left- or right-hand side of the first equation of set (4) we determine the value of  $p_{i,\text{calc}}^0$ .

3. On applying the Newton-Raphson method to the calculation of  $M$  parameters  $\{a_k\}$ , we solve in each iteration step the system of linear equations

$$\begin{aligned} \sum_{j=1}^M \left( \sum_{i=1}^{n_p} w_i \frac{dp_i^0}{da_k} \frac{dp_i^0}{da_j} + w \sum_{i=1}^{n_B} \frac{dB_i}{da_j} \frac{dB_i}{da_k} \right) \Delta a_j &= \\ = \sum_{i=1}^{n_p} w_i (p_{i,\text{exp}}^0 - p_{i,\text{calc}}^0) \frac{dp_i^0}{da_k} + w \sum_{i=1}^{n_B} (B_{i,\text{exp}} - B_{i,\text{calc}}) \frac{dB_i}{da_k}, \\ k &= 1, 2, \dots, M, \quad w_i = (p_{i,\text{exp}}^0)^{-2}. \end{aligned} \quad (5)$$

The value of  $(dp_i^0/da_j)$  is determined so that the left- and right-hand side of system of equations (4) is differentiated with respect to parameter  $a_j$  at point  $T = T_i$ . We obtain the system of two equations

$$\begin{aligned} (\partial p / \partial V_m^L)_T (\partial V_m^L / \partial a_j)_T + (\partial p / \partial a_j)_{T, V_m^L} &= (\partial p / \partial V_m^g)_T (\partial V_m^g / \partial a_j)_T + (\partial p / \partial a_j)_{T, V_m^g}, \quad (6) \\ (\partial \ln f / \partial V_m^L)_T (\partial V_m^L / \partial a_j)_T + (\partial \ln f / \partial a_j)_{T, V_m^L} &= \\ = (\partial \ln f / \partial V_m^g)_T (\partial V_m^g / \partial a_j)_T + (\partial \ln f / \partial a_j)_{T, V_m^g} \end{aligned}$$

for two unknowns  $(\partial V_m^L / \partial a_j)_T$  and  $(\partial V_m^g / \partial a_j)_T$ . After its solution and following insertion into the left- or right-hand side of the first equation of system (6), we obtain the required value of  $(dp_i^0/da_j)_T$ .

The values of derivatives ( $dB/da_k$ ) are determined easily from the relation

$$B = b - a/(RT). \quad (7)$$

The relationships for calculating the thermodynamic quantities and their derivatives are given in Appendix 2.

4. After solving system (5), the new approximation of adjustable parameters is determined from the relation

$$a_k^{(1)} = a_k^{(0)} + \eta \Delta a_k, \quad k = 1, 2, \dots, M, \quad (8)$$

where  $\eta$ ,  $\eta \in \langle 0, 1 \rangle$ , is the relaxation (reduction) parameter. We usually required  $\max |\eta \Delta a_k| \leq 1$ . If  $\|\Delta a_k\| < \varepsilon$  (e.g.,  $\varepsilon = 10^{-4}$ ), then the iteration process is finished. In opposite case, the calculation is repeated starting from point 2.

The input data of  $p_{i,\text{exp}}^0$  were obtained in two ways: Firstly, "pseudoexperimental" data were concerned obtained by using the tabulated constants<sup>15</sup> of the Wagner equation<sup>16</sup> using 10 K step within the whole region of validity of this equation. In case of n-hydrocarbons and several other substances, special data<sup>17-19</sup> were used. The virial coefficients were taken from the books by Dymond and Smith<sup>20</sup> and Dymond and coworkers<sup>21</sup>.

Since the assumption of constant variance of relative error of saturated vapour pressure data is not fulfilled for the temperatures close to the triple point temperature, we confined ourselves usually to the temperature interval for which  $p_r^0 > 0.001$  holds.

## RESULTS AND DISCUSSION

The calculations were performed for more than 60 substances for various temperature dependences of parameters  $a$ ,  $b$ ,  $c$  chosen and various values of weight  $w$ . On their basis, the following conclusions were drawn:

1. The effect of the chosen temperature dependence of parameters  $b$ ,  $c$  on the value of  $\sigma_p$  is quite negligible, which agrees with the information of Adachi and coworkers<sup>22</sup>. Also the difference between the cases  $z_c = 1/3$  (i.e.,  $b_c = c_c$ , and only the values of  $T_c$  and  $p_c$  are employed to determine the values of  $b_c$ ,  $a_c$ ) and  $z_c = p_c V_{mc}/RT_c$  (i.e., generally  $b_c \neq c_c$ , and the knowledge of critical values  $T_c$ ,  $p_c$ ,  $V_{mc}$  is required) is, from the point of view of  $\sigma_p$  values, quite negligible. For these reasons we have considered for final calculations (see Appendix 1)

$$\begin{aligned} b &= c = b_c = 0.08664RT_c/p_c, \\ a_c &= 0.42748R^2T_c^2/p_c. \end{aligned} \quad (9)$$

It is evident from Eq. (7) that the calculated value of the second virial coefficient does not depend on the value of parameter  $c$ . It was also one of reasons why we differentiated between parameters  $b$  and  $c$  in equation of state (1) (unlike the original version of the RKS equation). We assumed that by choosing suitably the temperature dependence  $c = c(T)$ , we should attain a substantial improvement of the value of  $\sigma_p$  without influencing the value of  $\sigma_B$ . This assumption proved to be incorrect for the value of  $\sigma_p$  depended only little on the chosen temperature dependence  $c = c(T)$ .

2. The dominant effect on the value of  $\sigma_p$  is shown by the number of adjustable parameters chosen in the prescription for the temperature dependence  $a = a(T)$ . To reach the value  $\sigma_p < 0.2\%$ , it is usually sufficient to take four parameters (in some cases even less). It is documented for methane, n-decane, and water in Table I.

3. Two sets of exponents were tested, viz.

$$A_1 = 1, 1.5, 3, 6 \text{ and}$$

$$A_2 = 1, 0.5, -0.5, -1.$$

A so-called Wagner set of exponents  $A_1$  usually yielded better (however, not considerably) results, i.e., a lower value of  $\sigma_p$ . The comparison of the set of exponents  $A_1$  and  $A_2$  for hydrocarbons (the same number of parameters is always considered) is given in Table II.

It is apparent at first sight that from propane to hexane the deviations are higher than 0.25%. It is caused by the fact that all the data recommended by the authors of paper<sup>17</sup> were included into the calculation. That not all the data are in perfect order, it is shown in Fig. 1 where the dependence of the value of  $\Delta p_i/p_i$  on temperature for propane is plotted. It is clear that the relative high value of  $\sigma_p$  is not brought about by the correlation relation but by the experimental points which have too large variance.

TABLE I

The dependence of the  $\sigma_p$  value for methane, decane, and water on the number of parameters used (set  $A_1$ ,  $w = 0$ )

Number of parameters	Methane	Decane	Water
1	0.62	0.46	2.75
2	0.55	0.46	1.54
3	0.14	0.076	0.27
4	0.04	0.074	0.17

4. The choice of a non-zero weight  $w$  usually decreased the value of  $\sigma_B$  only unstrikingly, however, increased considerably the value of  $\sigma_p$ . For this reason we considered  $w = 0$  in final calculations, i.e., the values of second virial coefficients were not included into the calculation. Despite with substances for which the data on second virial coefficient were available, we determined the value of  $\sigma_B$ , i.e., we judged the agreement between the experimental and predicted values of the second virial coefficient. The presentation of values  $\sigma_B$  for individual substances need not be sufficiently informative for the absolute value of deviation ( $B_{i,\text{exp}} - B_{i,\text{calc}}$ )

TABLE II

The comparison of values of  $\sigma_p$  for the sets of exponents  $A_1$  and  $A_2$  for n-hydrocarbons ( $w = 0$ )

Substance	Number of parameters $M$	Set $A_1$	Set $A_2$
Methane	4	0.043	0.102
Ethane	4	0.277	0.276
Propane	4	0.470	0.492
Butane	4	0.381	0.407
Pentane	4	0.483	0.484
Hexane	4	0.420	0.607
Octane	4	0.153	0.240
Nonane	3	0.273	0.245
Decane	3	0.076	0.074
Tetradecane	3	0.139	0.146
Pentadecane	3	0.123	0.105
Hexadecane	3	0.170	0.106

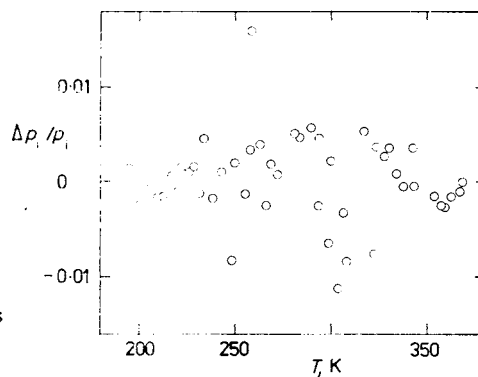


FIG. 1

The values of  $\Delta p_i/p_i$  at single temperatures for propane

decreases considerably with increasing temperature. Omitting the value of the second virial coefficient at the lowest temperature from the data set usually causes a significant decrease in  $\sigma_B$ . Altogether the data on the second virial coefficient for more than 30 substances were available. The value of  $\sigma_B$  lay within 20–400 cm<sup>3</sup>/mol in dependence on the substance and on the temperature range (above all at its lower limit) in which the value of the second virial coefficient were considered ( $\sigma_B$  increased with the molecule size). At low temperature the calculated virial coefficients were always larger than experimental ones.

Surprisingly very good agreement was attained between the calculated and experimental values of the second virial coefficient even for substances with very low value of critical temperature (see Table III). The reason of good extrapolation of temperature dependence  $a = a(T)$  high above the critical temperature is probably the suitably chosen exponential form of this dependence and the fact that the adjustable parameter at expression  $(T_r^6 - 1)$  is always negative, which implies (see Eq. (7)) the validity of the relation

$$\lim_{T \rightarrow \infty} B(T) = b \quad (=b_c). \quad (11)$$

5. The importance of good description of saturated vapour pressures can be demonstrated on the 1,3-butadiene(1)–butane(2) system. In these calculations we started from the smoothed  $p$ - $x_1$ - $y_1$  data reported by Flebbe and coworkers<sup>23</sup>. These data comprise the whole concentration range and the temperatures of 278·15, 298·15, 318·15, and 338·15 K (pressure range 0·12 to 0·82 MPa). The  $p$ - $x_1$  curve at 278·15 J is plotted in Fig. 2 from which follows as well that the system forms an azeotropic mixture ( $x_{1,az} = 0·825$ ).

TABLE III

The comparison of experimental and calculated values of the second virial coefficient of hydrogen ( $w = 0$ ,  $M = 4$ , set  $A_1$ ,  $\sigma_p = 0·06\%$ )

$T$ , K	$B_{exp}$ , cm <sup>3</sup> mol <sup>-1</sup>	$B_{exp} - B_{calc}$ , cm <sup>3</sup> mol <sup>-1</sup>
14	-254	-50
25	-110	-4
50	-33	-20
100	-2	-10
200	11	-7
300	15	-3
400	16	-3

In Fig. 2 we depict as well the calculated  $p(x_1)$  curves for the RKS ( $\omega_1 = 0.1814$ ,  $\omega_2 = 0.193$ ) and modified RKS equations of state. The classical combination rules ( $b = c$ ) were applied in these calculations:

$$b = \sum_{i=1}^N x_i b_{ii},$$

$$a = \sum_{i=1}^N \sum_{j=1}^N x_i x_j a_{ij}, \quad (12)$$

$$a_{ij} = (1 - k_{ij})(a_{ii} a_{jj})^{1/2}, \quad k_{ij} = k_{ji}.$$

As it can be seen in Fig. 2, the use of  $k_{12} = 0$  predicts in both cases practically an ideal mixture, the RKS equation, with respect to the fact that it intersects the experimental boiling point curve, giving better agreement in calculated pressure than the proposed modification of the RKS equation.

The optimum values of  $k_{ij}$  were determined by minimizing the function

$$S = \sum_{i=1}^{n_{LV}} \min S_i = \sum_{i=1}^{n_{LV}} \min \left\{ \left( \frac{x_{1,\text{calc}} - x_{1,\text{exp}}}{\sigma_{x_1}} \right)^2 + \left( \frac{y_{1,\text{calc}} - y_{1,\text{exp}}}{\sigma_{y_1}} \right)^2 + \left( \frac{p_{\text{calc}} - p_{\text{exp}}}{\sigma_{pLV}} \right)^2 \right\}, \quad (13)$$

where  $x_{1,\text{calc}}$ ,  $y_{1,\text{calc}}$ ,  $p_{\text{calc}}$  are the calculated values of the liquid and vapour phase compositions and the pressure in the system at the given temperature (assuming that it is determined with an accuracy higher than that of remaining variables). The procedure for calculating  $x_{1,\text{calc}}$ ,  $y_{1,\text{calc}}$ , and  $p_{\text{calc}}$  is outlined in Appendix 3. The standard deviations of values  $x_1$ ,  $y_1$ ,  $p$  were chosen to be  $\sigma_{x_1} = \sigma_{y_1} = 0.001$ ,  $\sigma_{pLV} = 0.005 p_{\text{exp}}$ .

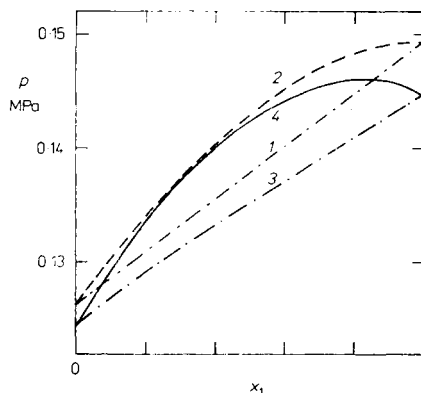


FIG. 2

The dependence of  $p-x_1$  in the 1,3-butadiene-(1)-butane(2) at the temperature of 5°C for RKS (1, 2) and modified RKS (3, 4) equations; 1, 3  $k_{12} = 0$ , 2  $k_{12} = 0.0126$ , 4  $k_{12} = 0.0168$



On using the optimum  $k_{ij}$  values, the situation is changed drastically, and with the modified RKS equation, the values are obtained which differ only slightly from the experimental ones. For instance, the mean deviation in pressure on the 278·15K isotherm is 0·32 kPa (0·22%) whereas for the RKS equation, it is the value of 1·08 kPa (0·78%).

The dependence of quantities  $S_y$ ,  $S_{pLV}$ , and  $\sigma_c = \sqrt{(S/(n_{LV} - 1))}$ , where  $S$  is the used objective function determined by Eq. (13), on the chosen parameter  $k_{ij}$  is illustrated for both the equations of state in Fig. 3. The points on all four isotherms were considered in these calculations. With the RKS equation, for the point of minimum of function  $\sigma_c = f(k_{ij})$  holds  $k_{ij} = 0\cdot0126$  which lies between the minimum of the  $S_y$  and  $S_{pLV}$  functions. However, nor this optimum value of  $k_{ij}$  ensures the existence of azeotropic point in this system. Just at still higher values of  $k_{ij}$  ( $\approx 0\cdot02$ ), a maximum appears on curve  $p = p(x_1)$  needed for the existence of azeotropic point.

For the modified RKS equation, the points of minimum of functions  $\sigma_c$ ,  $S_{pLV}$ ,  $S_y$  (and analogical  $S_x$  as well) practically coincide and  $k_{ij} = 0\cdot0168$  holds. This equation yields also much lower values of deviations ( $S_x = 0\cdot04$ ,  $S_y = 0\cdot04$ ,  $S_{pLV} = 0\cdot0146$ ,  $\sigma_c = 0\cdot81$ ) unlike the original RKS equation ( $S_x = 0\cdot24$ ,  $S_y = 0\cdot22$ ,  $S_{pLV} = 1\cdot41$ ,  $\sigma_c = 4\cdot81$ ).

### CONCLUSION

When applying the equations of state to the calculation of vapour-liquid equilibrium, it is necessary that the equation of state should describe well the saturated vapour pressures of pure substances. For this purpose an effective procedure is proposed in this work which makes it possible, on the basis of saturated vapour

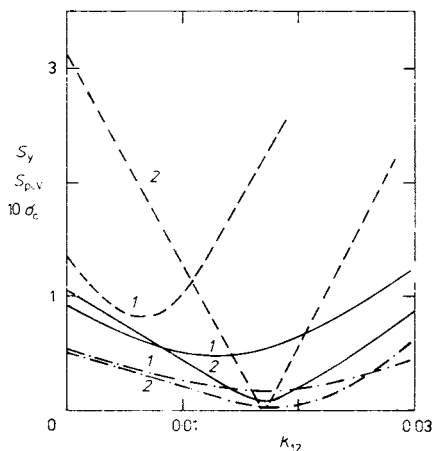


FIG. 3

The dependence of  $S_y$ ,  $S_p$ ,  $\sigma_c$  on  $k_{12}$  in the 1,3-butadiene(1)-butane(2) system: -----  $S_{pLV}$ , - - - - -  $S_y$ , ———  $\sigma_c$ , 1 RKS equation, 2 modified RKS equation

pressures of pure substances (or if need be of further quantities), to determine the temperature dependence of parameter  $a = a(T_r)$  in cubic equations of state for different substances. It was found that if the mean percent deviation between the calculated and experimental values of saturated vapour pressures is to be lower than 0.2% for the temperature range  $T_r \in \langle 0.55, 1 \rangle$ , it is usually necessary to take 4 parameters. The accuracy obtained is comparable with that obtained in terms of the Wagner equation. The substance-specific parameters were calculated for 60 substances and are given in Table IV.

On using the butadiene-butane system it is shown that the classical Soave equation of state, considering that it is unable to describe saturated vapour pressures of these substances with sufficient accuracy, fails when describing the vapour-liquid equilibrium in this system.

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## APPENDIX 1

### Calculation of Constants of Equation of State from Critical Constants

The way of determination of constants  $a_c$ ,  $b_c$ ,  $c_c$  in Eq. (2) is described briefly. Equation of state (1) is rewritten into the form

$$\beta_0 V_m^3 + \beta_1 V_m^2 + \beta_2 V_m + \beta_3 = 0, \quad (A1-1)$$

where

$$\begin{aligned} \beta_0 &= p, & \beta_1 &= p(c - b) - RT, & (A1-2) \\ \beta_2 &= -pbc - RTc + a, & \beta_3 &= -ab. \end{aligned}$$

Critical point  $T_c$ ,  $p_c$ ,  $V_{mc}$  is a threefold root of Eq. (A1-1), and therefore it must hold

$$\begin{aligned} \beta_0 V_{mc}^3 + \beta_1 V_{mc}^2 + \beta_2 V_{mc} + \beta_3 &= 0, \\ 3\beta_0 V_{mc}^2 + 2\beta_1 V_{mc} + \beta_2 &= 0, & (A1-3) \\ 6\beta_0 V_{mc} + 2\beta_1 &= 0. \end{aligned}$$

After inserting relations (A1-2) into system of equations (A1-3), the system of equations can be rearranged into the equivalent form

$$\begin{aligned} b^3 + b^2 V_{mc}(2 - 3z_c)/z_c + b V_{mc}^2(3z_c^2 - 3z_c + 1)/z_c^2 - V_{mc}^3 &= 0, \\ ab &= p_c V_{mc}^3, & (A1-4) \\ b - c &= (3z_c - 1) RT_c / p_c. \end{aligned}$$

TABLE IV

The values of parameters  $a_k$  for the modified RKS equation (set of exponents  $A_1$ )

Substance	$T_c$ , K	$p_c$ , MPa	$a_1$	$a_2$
Argon	150.65	4.8580	0.170844	-0.948845
Hydrogen	33.19	1.3096	2.712114	-3.196732
Nitrogen	126.20	3.39961	-0.587035	-0.200463
Oxygen	154.70	5.08987	0.163397	-1.08478
Carbon monoxide	132.85	3.4935	-0.77261	-0.0787449
Carbon dioxide	304.15	7.37499	7.47947	-9.38156
Water	647.13	22.055	-1.213043	0.217229
Methane	190.55	4.599	-0.402502	-0.285776
Ethane	305.34	4.871	-1.612079	0.907125
Ethylene	282.55	5.05088	-0.856937	-0.0337492
Acetylene	308.30	6.1389	0.886426	-2.13783
Propane	369.85	4.246	-1.608355	0.744260
Butane	425.14	3.784	0.137977	-1.379693
Isobutane	408.14	3.65801	-0.402591	-0.744602
1-Butene	419.57	4.0176	-1.047337	-0.0164517
cis-2-Butene	435.6	4.205	-1.50597	0.494440
trans-2-Butene	428.6	4.1037	0.246551	-1.50278
Isobutene	417.90	4.00706	-0.244438	-0.911925
1,3-Butadiene	425.0	4.3266	-0.4379348	-0.7385931
1-Butyne	463.70	4.7116	3.51879	-5.98171
Pentane	469.69	3.364	-1.789687	0.800788
Isopentane	460.43	3.3859	-0.904341	-0.218300
Hexane	507.50	3.0120	0.785063	-2.312098
Isohexane	498.10	3.03252	-0.403115	-0.866969
3-Methylpentane	504.4	3.12171	-0.370379	-0.868740
2,2-Dimethylbutane	489.4	3.1127	0.230666	-1.56623
2,3-Dimethylbutane	500.3	3.1458	-0.153026	-1.13825
Heptane	540.10	2.7324	-0.877431	-0.456462
2,2-Dimethylpentane	433.77	3.1979	-0.539688	-0.673205
2,2,3-Trimethylbutane	531.17	2.9491	0.0929908	-1.41796
Octane	568.83	2.487	-0.179474	-1.395738
Nonane	594.60	2.288	-2.44444	1.338401
Decane	617.40	2.104	-3.64083	2.538059
Undecane	638.80	1.966	-3.89121	2.76242
Dodecane	658.20	1.824	-3.81897	2.64177
Tridecane	676.0	1.720	-4.24070	3.04385
Tetradecane	693.0	1.620	-4.69102	3.478924
Pentadecane	707.0	1.530	-5.86483	4.68264
Hexadecane	722.0	1.450	-6.01671	4.78870
Cyclohexane	553.64	4.0753	-0.350706	-0.915668
Benzene	562.10	4.8956	-1.63780	0.548579
Toluene	591.72	4.1064	-0.740226	-0.478415

TABLE IV  
(Continued)

$a_3$	$a_4$	$T_{\min}$ , K	$T_{\max}$ , K	$\sigma_p$ , %	Note
0.415027	-0.091351	85	150	0.0375	a
1.00776	-0.220709	14	33	0.064	a
0.233627	-0.0711056	65	125	0.054	a
0.5451308	-0.1353647	70	145	0.060	a
0.241548	-0.0776285	68	132	0.0477	b
2.57301	-0.339154	220	300	0.018	a
0.0293666	-0.05456365	273	623	0.170	c
0.211163	-0.0627246	90	189	0.04	d
-0.1093375	-0.0196467	90	303	0.27	d
0.220648	-0.0727288	135	275	0.07	a
0.785537	-0.152451	190	300	0.039	e
-0.00882805	-0.0471752	180	367	0.44	d
0.628285	-0.139818	210	420	0.38	d
0.461251	-0.123093	200	400	0.079	a
0.2417197	-0.0856401	210	410	0.07	a
0.0884511	-0.0610806	215	425	0.082	e
0.683994	-0.170303	220	420	0.082	e
0.476284	-0.116501	210	410	0.069	a
0.488620	-0.139840	210	420	0.086	e
2.48835	-0.443975	230	455	0.034	e
-0.0292675	-0.0452141	246	461	0.48	d
0.295650	-0.098310	230	450	0.08	a
0.935978	-0.200262	262	503	0.42	d
0.470680	-0.117149	260	490	0.066	a
0.452015	-0.112198	265	495	0.064	a
0.716396	-0.166150	245	485	0.085	a
0.582144	-0.144115	255	495	0.075	a
0.379682	-0.115396	285	525	0.079	a
0.469871	-0.122328	260	428	0.041	e
0.646520	-0.145143	270	530	0.068	a
0.718362	-0.185759	304	548	0.153	d
-0.249255	0	325	511	0.273	d
-0.487378	0	344	445	0.076	d
-0.540136	0	362	498	0.095	d
-0.519515	0	379	520	0.106	d
-0.605702	0	395	540	0.081	d
-0.694457	0	410	559	0.139	d
-0.945254	0	424	577	0.123	d
-0.960467	0	438	594	0.170	d
0.537822	-0.129771	300	540	0.056	a
0.128747	-0.0754409	280	550	0.080	a
0.380103	-0.111972	310	580	0.072	a

TABLE IV  
 (Continued)

Substance	$T_c$ , K	$p_c$ , MPa	$a_1$	$a_2$
<i>o</i> -Xylene	630.25	3.7330	-0.514507	-0.775655
<i>m</i> -Xylene	616.97	3.5368	-0.202150	-1.12988
<i>p</i> -Xylene	616.15	3.5130	-0.383564	-0.930286
Ethylbenzene	617.12	3.6019	-0.127021	-1.25222
Naphthalene	748.40	4.053	-1.324625	-0.0449344
Methanol	512.64	8.0850	1.09039	-2.30599
Ethanol	513.92	6.13087	3.98848	-5.78227
1-Propanol	536.78	5.15111	3.86014	-6.01698
2-Propanol	508.30	4.7424	4.21376	-6.43670
1-Butanol	563.05	4.4126	5.18609	-7.87457
2-Butanol	536.01	4.18975	3.91386	-6.59239
1-Pentanol	588.15	3.90945	9.36328	-13.1866
1-Octanol	652.50	2.87376	5.99078	-9.75229
Acetone	508.10	4.69993	-1.02282	-0.0780193
Methyl Ethyl Ketone	536.78	4.22177	0.723920	-2.200431
Diethyl Ether	466.74	3.6461	-0.891355	-0.351476
Methylamine	430.0	7.4333	0.593761	-2.21029
Dimethylamine	437.7	5.3033	2.04958	-4.25281
Trimethylamine	433.3	4.08396	-1.17641	0.128988
Ethylamine	456.35	5.64137	-1.33135	-0.0862948
Diethylamine	496.45	3.7054	0.229037	-1.75148
Propylamine	497.0	4.8067	-1.36550	-0.0435724
Monofluoromethane	315.0	5.55736	-0.910626	0.0270614
Difluoromethane	351.54	5.8270	0.176755	-1.40142
Trifluoromethane	299.06	4.8409	0.520617	-1.87910
Monochloromethane	416.27	6.69718	-1.93639	1.11960
Trichloromethane	536.40	5.36576	-1.39193	0.366198
Tetrachloromethane	556.40	4.55078	-0.834464	-0.382380

<sup>a</sup> Parameters of the Wagner equation were used as reported by McGerry<sup>15</sup>, and the substance is inserted into the group for which reliable data on saturated vapour pressures exist; <sup>b</sup> see ref.<sup>19</sup>; <sup>c</sup> see ref.<sup>18</sup>; <sup>d</sup> see ref.<sup>17</sup>; <sup>e</sup> parameters of the Wagner equation were used as reported by McGerry<sup>15</sup>,

From the first equation we determine the value of  $b = b_c$ , from the second the value of  $a = a_c$ , and in the end from the third equation,  $c = c_c$ . If  $z_c = 1/3$ , then the first equation can be written in the form

$$(x + 1)^3 - 2 = 0, \quad (A1-5)$$

TABLE IV  
(Continued)

$a_3$	$a_4$	$T_{\min}, K$	$T_{\max}, K$	$\sigma_p, \%$	Note
0.449273	-0.123275	340	625	0.066	<i>a</i>
0.532670	-0.131893	330	610	0.065	<i>a</i>
0.495236	-0.134242	330	610	0.069	<i>a</i>
0.608946	-0.145799	350	610	0.065	<i>a</i>
0.428092	-0.171579	400	730	0.096	<i>e</i>
0.474958	-0.0815079	288	508	0.041	<i>a</i>
1.41617	-0.168150	303	503	0.021	<i>a</i>
1.66488	-0.189126	310	530	0.024	<i>a</i>
1.74618	-0.190999	300	500	0.020	<i>a</i>
2.41671	-0.315513	325	555	0.037	<i>a</i>
2.15051	-0.281483	315	535	0.029	<i>a</i>
4.38818	-0.704750	340	580	0.097	<i>a</i>
3.79128	-0.733729	385	645	0.135	<i>a</i>
0.179575	-0.0751514	270	500	0.067	<i>a</i>
0.860058	-0.186661	305	535	0.072	<i>a</i>
0.346457	-0.103562	250	460	0.064	<i>a</i>
0.987597	-0.215508	230	420	0.073	<i>a</i>
1.84012	-0.387439	240	430	0.093	<i>a</i>
0.186072	-0.073486	220	430	0.067	<i>a</i>
0.400139	-0.118334	245	455	0.061	<i>a</i>
0.768983	-0.150700	260	490	0.059	<i>a</i>
0.376408	-0.115818	265	495	0.064	<i>a</i>
0.0729527	-0.0327844	160	310	0.059	<i>a</i>
0.564097	-0.133417	180	348	0.077	<i>a</i>
0.764736	-0.169792	155	293	0.074	<i>a</i>
-0.0991497	-0.0461333	175	415	0.135	<i>a</i>
0.116636	-0.0661480	275	535	0.066	<i>a</i>
0.447401	-0.139580	280	550	0.080	<i>a</i>

and the substance is inserted into the group for which less reliable data on saturated vapour pressures exist.

where  $b = xV_{mc}$ ,  $x = 2^{1/3} - 1$ . From relation  $V_{mc} = RT_c/(3p_c)$  then follow the well-known relations

$$a_c = 0.42748R^2T_c^2/p_c, \quad b_c = c_c = 0.08664RT_c/p_c. \quad (A1-6)$$

## APPENDIX 2

*Relationships for Calculating Thermodynamic Quantities*

The relationships for calculating thermodynamic quantities in Eqs (4)–(6) can be derived from the thermodynamic relation<sup>24,25</sup>

$$\ln f = \ln (RT/V_m) - (RT)^{-1} \int_{\infty}^m (p - RT/V_m) dV_m + pV_m + pV_m/(RT) - 1 \quad (A2-1)$$

and its derivative with respect to volume

$$(\partial \ln f / \partial V_m)_T = (\partial p / \partial V_m)_T V_m / (RT). \quad (A2-2)$$

For equation of state (1) therefore holds

$$(\partial p / \partial V_m)_T = -RT / (V_m - b)^2 + a(2V_m + c) / [V_m^2(V_m + c)^2], \quad (A2-3)$$

$$\ln f = \ln [RT / (V_m - b)] + a(cRT)^{-1} \ln [V_m / (V_m + c)] + b / (V_m - b) - a / [RT(V_m + c)]. \quad (A2-4)$$

Calculation of the values of derivatives  $(\partial p / \partial a_j)_{T, V_m}$  and/or  $(\partial \ln f / \partial a_j)_{T, V_m}$  is apparently simple.

## APPENDIX 3

*Calculation of the Value of min  $S_i$* 

The minimum value of  $S_i$  (min  $S_i$ ) in objective function (13) or the values of  $x_{1, \text{calc}}$ ,  $y_{1, \text{calc}}$ ,  $p_{\text{calc}}$  of the  $i$ -th experimental point which yield the minimum value of  $S_i$  were determined in the following way:

At a constant temperature we can write

$$\begin{aligned} x_{1, \text{calc}}^{\text{new}} &= x_1^{\text{old}} + \Delta x_1, \\ y_{1, \text{calc}}^{\text{new}} &= y_1^{\text{old}} + \Delta y_1 = y_1^{\text{old}} + (\partial y_1 / \partial x_1)_T \Delta x_1 = y_1^{\text{old}} + k_y \Delta x_1, \quad (A3-1) \\ p_{\text{calc}}^{\text{new}} &= p^{\text{old}} + \Delta p = p^{\text{old}} + (\partial p / \partial x_1)_T \Delta x_1 = p^{\text{old}} + k_p \Delta x_1. \end{aligned}$$

After inserting these relations into the relation for  $S_i$  in Eq. (13) we get, from condition  $(\partial S_i / \partial \Delta x_1) = 0$ , the relation

$$\begin{aligned} \Delta x_1 &= [(x_{1, \text{exp}} - x_1^{\text{old}}) / \sigma_{x_1}^2 + (y_{1, \text{exp}} - y_1^{\text{old}}) / \sigma_{y_1}^2 + (p_{\text{exp}} - p^{\text{old}}) / \sigma_p^2] \cdot \\ &\quad \cdot [1 / \sigma_{x_1}^2 + (k_y / \sigma_{y_1})^2 + (k_p / \sigma_p)^2]^{-1}. \quad (A3-2) \end{aligned}$$

On the basis of the calculated value of  $\Delta x_1$  we obtain next approximation of  $x_1$  and as soon as the increments in composition of phases and in pressure decrease below the prescribed limit, the calculation is finished. The values of  $k_y$  and  $k_p$  are given by the relations

$$k_y = (\partial y_1 / \partial x_1)_T = (G11)^L \sum_{i=1}^2 x_i (\bar{V}_{mi}^g - \bar{V}_{mi}^L) / [(G11)^g \sum_{i=1}^2 y_i (\bar{V}_{mi}^g - \bar{V}_{mi}^L)], \quad (A3-3)$$

$$k_p = (\partial p / \partial x_1)_T = (G11)^L (y_1 - x_1) RT / \sum_{i=1}^2 y_i (\bar{V}_{mi}^g - \bar{V}_{mi}^L),$$

where

$$G11 = \{ \partial^2 [G_m / (RT)] / \partial x_1^2 \}_{T,p}. \quad (A3-4)$$

On using the formerly defined dimensionless  $Q$  quantities<sup>25</sup>, it holds

$$\sum_{i=1}^2 x_i (\bar{V}_{mi}^g - \bar{V}_{mi}^L) = V_m^g - V_m^L + (V_m^g / Q_d^g) (x_1 \bar{z}_1^g + x_2 \bar{z}_2^g - z^g),$$

$$\sum_{i=1}^2 y_i (\bar{V}_{mi}^g - \bar{V}_{mi}^L) = V_m^g - V_m^L - (V_m^L / Q_d^L) (y_1 \bar{z}_1^L + y_2 \bar{z}_2^L - z^L), \quad (A3-5)$$

$$(G11)^L = 1 / (x_1 x_2) + (\partial Q_{F,1} / \partial x_1)^L - (\partial Q_{F,2} / \partial x_1)^L - (\bar{z}_1^L - \bar{z}_2^L)^2 / Q_d^L,$$

$$(G11)^g = 1 / (y_1 y_2) + (\partial Q_{F,1} / \partial y_1)^g - (\partial Q_{F,2} / \partial y_1)^g - (\bar{z}_1^g - \bar{z}_2^g)^2 / Q_d^g.$$

The procedure of calculation is as follows:

a) For the given experimental point at temperature  $T$  we choose  $x_1^{\text{old}}$  (which may be, e.g., the experimental value of  $x_1$ ).

b) By means of the procedure for calculating the boiling point pressure (see, e.g., ref.<sup>25</sup>) we determine the values of  $p^{\text{old}}$  and  $y_1^{\text{old}}$  for the values of  $T$ ,  $x_1^{\text{old}}$ .

c) From relations (A3-3)–(A3-5) we calculate the respective quantities and on their basis,  $\Delta x_1$  from Eq. (A3-2). As soon as the increments in composition of phases and in pressure are sufficiently low, the calculation is finished.

*Note 1.* Another procedure which considers also the possible errors in temperature was suggested by Aim and coworkers<sup>26</sup>.

*Note 2.* Considering that in the proposed modification of the RKS equation changes only the temperature dependence of parameters  $a_i$  of pure substances, it is possible to apply – for calculating the fugacity coefficient of component  $i$ , the compressibility factor,  $Q_d$ , etc. – the procedures for calculating these quantities valid for the RKS equation (naturally, on changing the calculation of the individual  $a_i(T)$  parameters).



## LIST OF SYMBOLS

$a, b, c$	constants of equation of state
$B$	second virial coefficient
$c$	subscript, quantity corresponding to critical point
$d$	molar density
$f$	fugacity
$G_{11}$	$= (\partial^2 [G_m / (RT)] / \partial x_1^2)_{T,p}$
$G_m$	molar Gibbs energy of mixing
$k_{12}$	interaction parameter (Eq. (12))
$M$	number of adjustable parameters $a_1, \dots, a_M$ considered
$N$	number of components in system
$n_p, n_B, n_{LV}$	number of experimental data points on saturated vapour pressures, virial coefficients, vapour-liquid equilibrium, respectively
$p, p^0$	pressure, saturated vapour pressure, respectively
$Q_d$	$= z + d(\partial z / \partial d)_{T,x}$ dimensionless quantity
$Q_F$	$= \int_0^z (z-1) \ln d$ dimensionless quantity
$Q_{F,1}$	$= Q_F + x_2(\partial Q_F / \partial x_1)_{T,d}$ dimensionless quantity (valid for $N=2$ )
$Q_{F,2}$	$= Q_F - x_1(\partial Q_F / \partial x_1)_{T,d}$ dimensionless quantity (valid for $N=2$ )
$R$	gas constant
$r$	subscript, reduced quantity
$S$	objective function (Eq. (13))
$S_y$	$= (\sum_{i=1}^{n_{LV}}  y_{1,exp} - y_{1,calc} _i) / n_{LV}$
$s_{pLV}$	$= (\sum_{i=1}^{n_{LV}}  p_{exp} - p_{calc} _i) / n_{LV}$
$T$	thermodynamic temperature
$V_m$	molar volume
$\bar{V}_{mi}$	partial molar volume of $i$ -th component
$w$	weight
$x_i$	mole fraction of $i$ -th component in liquid phase
$y_i$	mole fraction of $i$ -th component in vapour phase
$z$	compressibility factor
$\tilde{z}_1$	$= z + x_2(\partial z / \partial x_1)_{T,d}$ auxiliary quantity (valid for $N=2$ )
$\tilde{z}_2$	$= z - x_1(\partial z / \partial x_1)_{T,d}$ auxiliary quantity (valid for $N=2$ )
$\sigma_B$	$= \{ [\sum_{i=1}^{n_B} (B_{exp} - B_{calc})_i^2] / (n_B - M) \}^{1/2}$
$\sigma_p$	$= 100 \{ \langle \sum_{i=1}^{n_p} [(p_{exp}^0 - p_{calc}^0) / p_{exp}^0]_i^2 \rangle / (n_p - M) \}^{1/2}$
$\sigma_c$	$= [S / (n_{LV} - 1)]^{1/2}$
$\sigma_x, \sigma_y, \sigma_{pLV}$	standard deviations in composition of liquid and vapour phases and in pressure, respectively, of vapour-liquid equilibrium
$\omega$	acentric factor
$\Delta p_i / p_i$	$= (p_{exp}^0 - p_{calc}^0) / p_{exp}^0$ for $i$ -th point

## REFERENCES

1. Kolasinska G.: *Fluid Phase Equilib.* 27, 289 (1986).
2. Soave G.: *Chem. Eng. Sci.* 27, 1197 (1972).
3. Peng D. Y., Robinson D. B.: *Ind. Eng. Chem., Fundam.* 15, 59 (1976).
4. Sandarusi J. A., Kidnay A. J., Yesevage V. F.: *Ind. Eng. Chem., Process Des. Dev.* 25, 957 (1986).
5. Heyen G.: *A Cubic Equation of State with Extended Range of Application, 2nd World Congress of Chemical Engineering, Montreal 1981*; cited by ref.<sup>1</sup>.
6. Adachi Y., Lu B. C.-Y.: *AIChE J.* 30, 991 (1984).
7. Yu J.-M., Lu B. C.-Y.: *Fluid Phase Equilib.* 34, 1 (1987).
8. Trebble M. A., Bishnoi P. R.: *Fluid Phase Equilib.* 35, 1 (1987).
9. Fuller G. G.: *Ind. Eng. Chem., Fundam.* 15, 254 (1976).
10. Grabowski M. S., Daubert T. E.: *Ind. Eng. Chem., Process Des. Dev.* 18, 300 (1979).
11. Mathias P. M., Copeman T. W.: *Fluid Phase Equilib.* 13, 91 (1983).
12. Stryjek R., Vera J. H.: *Can. J. Chem. Eng.* 64, 820 (1986).
13. Lielmezs J., Merriman L. H.: *Thermochim. Acta* 105, 383 (1986).
14. Gibbons R. M., Laughton A. P.: *J. Chem. Soc., Faraday Trans. 2*, 80, 1019 (1984).
15. McGerry J.: *Ind. Eng. Chem., Process Des. Dev.* 22, 313 (1983).
16. Wagner W.: *Cryogenics* 13, 470 (1973).
17. Salerno S., Cascella M., May D., Watson P., Tasso D.: *Fluid Phase Equilib.* 27, 15 (1986).
18. Haar L., Gallagher J. S., Kell G. S.: *NBS/NRC Steam Tables*. Hemisphere, Washington D.C. 1984.
19. Goodwin R. D.: *J. Phys. Chem. Ref. Data* 14, 899 (1985).
20. Dymond J. H., Smith E. B.: *The Virial Coefficients of Pure Gases and Mixtures*. Clarendon Press, Oxford 1980.
21. Dymond J. H., Cholinski J. A., Szafranski A., Wyrzykowska-Stankiewicz D. in: *Measurement, Evaluation and Prediction of Phase Equilibria* (H. V. Kehiaian and H. Renon, Eds). Elsevier, Amsterdam 1986.
22. Adachi Y., Lu B. C.-Y.: *Can. J. Chem. Eng.* 63, 497 (1985).
23. Fiebbe J. L., Barclay D. A., Manley E. D.: *J. Chem. Eng. Data* 27, 405 (1982).
24. Rowlinson J. S.: *Liquids and Liquid Mixtures*. Butterworths, London 1969.
25. Novák J. P., Růžička V., Maličevský A., Matouš J., Linek J.: *Collect. Czech. Chem. Commun.* 50, 1 (1985).
26. Aim K., Boublik T.: *Fluid Phase Equilib.* 29, 583 (1986).

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