METHODOLOGY OF SELECTING A MOLECULAR SUBSTANTIATED OPTIMAL CUBIC EQUATION OF STATE

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Abstract. The results related to the possibility of choosing the optimal cubic equations of state (ES) are presented. The study is carried out in the framework of a new model among three-term ES based on the molecular model of interacting point centers (IPC) and the well-known two-term ES of the van der Waals type. Manifestations of acting between molecules-points of attraction and repulsion forces are reflected in the structure and parameters of the ES belonging to the basic one-parameter family. The selection technique presented earlier was based on the possibility to obtain a consistent set of parameters that form the optimal equation. As a generalization of the limit variants of the ES with various manifestations of forces, a simple three-term four-parameter ES is proposed and investigated. All parameters make sense. Two relative parameters form the equation. It is shown that the known ES of Ishikawa, Chang, and Lu after the transformation become a special case of the ES of the IPC and cannot be considered as a general one. The technique was tested by calculating the critical isotherms of a number of substances, including argon, isopentane, carbon dioxide, etc. The next step should be to connect to the analysis a more finely structured control parameter.

1. Introduction
Thermal low-parametric equations of state (ES) are still of interest. Most of these equations consist of cubic equations, which are in demand in engineering and technological calculations due to their simplicity and profitability. Moreover, the very simplicity of form gives hope to obtain a physically (molecularly) justified equation of state, the structure, form of a contributions and the meaning of the parameters of which are associated with the molecular level, that is, a model with predictive value. Here we present some of the results related to the new built-up model (ES based on the simplest molecular model of interacting point centers (IPC)), as well as the results regarding the methods for choosing molecular-based optimal ES.

2. Van der Waals equation of state and its modifications. Systematization of ES. Problems
The famous van der Waals equation of state was the first one to be based on a molecular model. This ES has the form (1) (for one mole, the notation is standard; parameter $b$ is an attribute associated with
the objects own volume, parameter \(a\) is responsible for their attraction). The first contribution of ES (1) is accepted to be related to the repulsion of rigid spheres, the second – to their attraction. Depending on the fact, which form of contribution to (1) is considered correct, three modification methods can be implemented. Over a century and a half, a number of independent low-parametric ES (from 2 to 5 parameters) had been obtained [1,2] and called now the ES of van der Waals (vdW)-type.

\[
P = \frac{RT}{V - b} - \frac{a}{V^2}
\]

(1)

2.1. ES vdW-type: \(RT \div (V - b) = idem\)

The binomial ES are the largest group, which can be written in the form with the same first contribution

\[
P = \frac{RT}{V - b} - P (\text{attr})
\]

A new ES were obtained by modifying the second ES contribution (1) related to attraction. Perhaps this is because van der Waals himself did not insist on this form's verity. The most famous modification of the van der Waals ES is considered to be the Redlich – Kwong ES. The new ES itself has become the source of a huge number of modifications.

\[
P = \frac{RT}{V - b} - \frac{a}{\sqrt{TV}(V + b)}
\]

(2)

Our analysis [3] showed that the three-parameter implementation is a common form for many ES

\[
P = \frac{RT}{V - b} - \frac{a}{V (V + c)}
\]

(3)

(We study the temperature and volume dependences of the configurational contributions separately. First, we will search for the optimal functional form \(P(V)\) of the equation of state). The equations of state of a similar form were proposed [see 4] almost a hundred years after the Van der Waals ES by different authors, including Himpan, Usdin and MacAuliff, Adashi, Fuller, Eberhart. We emphasize that introducing the third parameter into the ES the authors do not discuss its meaning. At the same time, attributing the specific responsibility to the two parameters (parameter \(b\) is responsible for the repulsion, parameter \(a\) - for the attraction), the authors are faced with the fact that parameter \(c\) is responsible for nothing. To a single form (3), one can bring a lot of ES. At the same time, the contribution corresponding to attraction in the original ES must be reformatted [5] so that for parameter \(c\) two positions are possible: \(c = \text{const}\) or \(c\) depends on the density. The authors of such ES were Redlich and Kwong, Robinson and Peng, Schmidt and Wenzel, Abbott, Harmens and Knapp, and many others.

2.2. ES vdW-type: \(a/V^2 = idem\)

The second group includes ES of the general form

\[P = P (\text{rep}) - a/V^2.\]

The second contribution related to attraction remains unchanged. The problem of modifying the first contribution of ES vdW (1) is solved by a much smaller number of researchers. The leader of this direction is the work of Carnahan – Starling [6], in which a theoretically substantiated (corresponding to the so-called perturbed rigid sphere model) cubic equation is proposed

\[
P = \frac{RT}{V} \left[ 1 + \eta + \eta^2 - \frac{\eta^3}{(1 - \eta)^3} \right], \quad \eta = \frac{b}{4V}
\]

(4)
Adding to this equation (4) the “tail” responsible for attraction from the ES vdW, the authors obtained a two-term two-parameter ES. However, a significant improvement in the description of the properties did not happen, and the ES ceased to be cubic – it lost some of its magnetism and simplicity.

The three-term three-parametrical ES obtained by A.B. Kaplun and A.B. Meshalkin [7] belongs to the same set, in which “the spirit of the van der Waals ideas” was preserved:

$$P = \frac{RT}{V} (1 + \frac{d}{(V - b)}) - \frac{a}{V^2}.$$  

The authors did not find the physical meaning of the new, third, parameter $d$. Situations with two ES, namely (3) and (5) turned out to be similar. Taking into account the generally accepted meaning of the parameters $b$ and $a$, the meaning of the third parameters in both ES makes no sense!

2.3. Both contributions change shape

The smallest third group is the ES vdW - type, in which both contributions are changed. The general form of similar binomial equations is

$$P = P(\text{rep}) + P(\text{attr}).$$

Such ES includes, for example, a two-parameter cubic ES by Ishikawa, Chung, and Lu [8]

$$P = \frac{RT}{V} \frac{2V + b}{2V - b} - \frac{a(T)}{V(V + b)}.$$  

The authors decided that (6) is optimal among 12 different ES obtained by a combination of individual contributions included in a number of known ES. The first contribution is in the form proposed by Scott. The equation (6) was applied to the calculation of the properties of 22 substances.

2.4. Problems of the third parameter and the first contribution

Even such a superficial analysis of the ES vdW reveals two problems: of the first contribution and the third parameter. Moreover, if the emerging third parameter has no meaning at all, the first contribution poses the problem of choosing its meaning.

It is accepted that the first contribution $RT / (V - b)$ is due to the repulsion of spheres – objects of the vdW model. At the same time, in the publications, this equation has been known as the ES with a covolume. An empirical ES of non-interacting spheres takes into account only the presence of objects with their own volume. We have to choose from mutually exclusive provisions. Probably, this will have to affect the choice of ES as a model of the thermodynamic level, which is based on a specific molecular model. At the same time, such a method for classifying ES (according to molecular models) is absent. Why? Because the authors of the ES vdW modifications believe that the basis of their empirical ES is the same model of rigid spheres ("the simplest and physically clear"). Besides, they have the same meaning of two parameters $b$ and $a$ like the van der Waals ES.

When looking for another model, we again have a paradox. The molecular model of van der Waals was a significant step forward: it recognized the real existence of molecules with their own geometric characteristics. However, real molecules can be simulated by models of varying complexity, and the model of a molecule in the form of a rigid sphere is not the simplest.

3. The model of interacting point centers (IPC)

The simplest model of a molecule is a point center, a point that does not have its own spatial characteristics. Its properties are manifested in the nature of the interaction: attraction and repulsion.
For this IPC model, it is possible to obtain a cluster of molecularly substantiated three-member ES, all of whose parameters have a meaning associated with the manifestation of the intermolecular interaction forces.

3.1. ES IPC. The meaning of the parameters

The first of the obtained ES [3] was a three-term three-parameter one. Three contributions: the first is the ES of non-interacting potential PC, the other two are configurational ones, caused by their repulsion and attraction. The repulsion is rigid, the attraction is optimized, i.e., the condition of weakness, which was agreed upon by van der Waals, had been removed. In standard notation (for one mole), the ES IPC has the form

\[ P = \frac{RT}{V} + \frac{RTb}{V(V - b)} - \frac{a}{V(V + c)} \]  

(7)

All three parameters \( b, c, \) and \( a \) of the equation of state (7) make sense. Moreover, it is different from the meaning of the parameters of the ES vdW. Two parameters are equal to changes in the volume available for the point centers, caused by the action of attractive and repulsive forces, respectively \( c = -\Delta Vf (\text{attr}), b = \Delta Vf (\text{rep}) \) (\( c \) and \( b \) are positive), the third parameter \( a \) is related to \( c \) and appears as a result of the difference in the nature of the acting forces.

3.2. Control parameter \( \chi \) of the thermodynamic level of the model

The established sense of the parameters (see above) of the new ES made it possible [3,9] to introduce a physically determined parameter \( \chi = c / b \), the value of which shows the ratio of the influence of attractive and repulsive forces between PC in relation to the volume available for movement. This gives the following form of ES IPC:

\[ P = \frac{RT}{V} + \frac{RTb}{V(V - b)} - \frac{a}{V(V + \chi b)} \]  

(8)

The resulting equation (8) is three-parameter \( b, a, \chi \) one. The ES IPC (8) was studied primarily under the standard assumption that \( b \) and \( c \) are constant. (A separate consideration is required by the question of which states correspond to this condition).

Let us turn to the reduced with respect to critical parameters variables. The equation (8) will take the form

\[ P_r = \frac{1}{Z_c(\chi)} \left[ \frac{\tau}{V_r} + \frac{\tau \beta(\chi)}{V_r(V_r - \beta(\chi))} - \frac{\alpha(\chi)}{V_r(V_r + \chi \beta(\chi))} \right] \]  

(9)

In the case of \( \chi = \text{const} (\chi \neq 0, \text{the case } \chi = 0 \text{ is considered separately}) \), the expressions for all parameters of the reduced ES are obtained in the form of explicit functions of \( \chi \) [10]:

\[ \beta = \frac{1}{\chi} \left( \frac{1}{\sqrt{1 + \chi}} - 1 \right), \quad \sigma = \left( \frac{1}{\sqrt{1 + \chi}} - 1 \right), \quad Z_c = \frac{\chi}{\chi(\chi + 1)(\chi - 1) + 2\chi + 1} \]  

(10)

3.3. A One-parameter family of ES. New similarity criterion

A consistent set of parameters has been obtained, which excludes the possibility of arbitrary values for some of them. The importance of the result can hardly be overestimated: the three-parameter ES IPC is transformed into a one-parameter family of the ES IPC: \( \pi = \pi (\varphi, \tau, \chi) \). This makes it possible to distinguish and compare the ES by the value of one parameter \( \chi \), which was called the control
parameter of the thermodynamic level. Obviously, the meaning of this factor is the same as that of the well-known similarity criteria by Pitzer, Riedel, and Filippov, which appeared after the first in row one – the critical compressibility factor (CCF). The difference of the new criterion is that it (the only one among all) clearly associated with the manifestation of the forces of attraction and repulsion and not with the properties of substances such as pressure, temperature, and volume. The performed calculations show that the family includes the equations of state with realistic values of the CCF: 0.29–0.26. These ES are given by the values of the control parameter from the interval 3–7 (see Table 1). Analysis at the molecular level showed [3] that such values are characteristic for the following structures: simple cubic (7), volume (2.5), and face-centered one (3.5).

Table 1. Control parameter of the model and the critical compressibility factor

| χ₀ | 0   | 1   | 2   | 3   | 4   | 5   | 7   |
|----|-----|-----|-----|-----|-----|-----|-----|
| Z₀ | 0.375 | 0.3333 | 0.3105 | 0.294 | 0.283 | 0.270 | 0.259 |

4. Adjustment equations of state of vdW-type to the model of interacting point centers. ES analogues

In this physically justified model of the interacting point centers, it is possible to fit many ES from the first group of the vdW-type [11]. Moreover, as a result, all their parameters are getting meaning. The essence of the transition is as follows. The first contribution of the two-term vdW-type equation gets the true meaning of the ES with a covolume, i.e., ES of non-interacting hard spheres. This makes it possible to transfer to rigidly repulsing PC by the following ES transformation:

\[ \frac{R T}{V - b} = \frac{R T}{V} + \frac{R T b}{V((V - b))} \]

The contributions corresponding to the attraction are reduced to the form adequate to the IPC ES (7). The form of the ES itself will find information on the parameter χ. As a result, in the IPC family, we obtain a new ES, which is an analogue of the original, where configuration contributions are clearly distinguished. In this case, a set of independent ES vdW-type turns into equations of one IPC family, the difference between which is determined by the difference in the ratio of intermolecular forces manifestations ensured by different values of the parameters χ. The result is a physical basis for a direct comparison of the equations of state.

5. Another modification of the ES vdW. Two "ultimate" equations of state

We will show some possibilities for the new approach. Let's start with the transformation (as described above) of the "foremost" binomial equation – ES vdW. We get a three-term analogue of the ES vdW, corresponding to it in the family of the IPC ES. Here, the repulsion of the point centers is rigid, and the attraction is very weak. At the thermodynamic level, the assumption of weak attraction forces in the IPC model is expressed in the fact that the change in free volume caused by these forces, i.e., parameter c, will be equal to zero. ES-analogue of the ES vdW has the form

\[ P = \frac{R T}{V} + \frac{R T b}{V(V - b)} - \frac{a}{V(V + 0*b)}, \chi=0. \]

This specific nature of the attraction and repulsion forces allows two ways to optimize the equation, which give two "ultimate" by the nature of the acting forces equations of state:

1. Rigid repulsion with optimized (not weak) attraction
The equations (see above) differ in the value of the control parameter, a new criterion for thermodynamic similarity.

2. Weak (by vdW) attraction with softened repulsion

\[ P = \frac{RT}{V} + \frac{RTb}{V(V-b)} - \frac{a}{V(V+c)} \]

We have already studied the family of such ES [12] and have shown that the control parameter is the quantity \( \gamma = \frac{d}{b} \) determined by the ratio of the quantities \( d \) and \( b \), in the value of which the repulsive forces — softened and rigid — are manifested.

The equations of state of this family differ in the value of the parameter \( \gamma \). They do not give CCF values equal to the experimental ones (and they cannot give them, primarily because the attraction forces do not manifest themselves). As for the values of the control parameter, for a number of technically important substances, they can be found in [7]. Comparison of the ES found by Kaplun and Meshalkin, and the option just considered, namely the generalized ES vdW, gives their coincidence. The values recovered in [7] lie in the range from 1.8 (for methane) to 3.3 (for carbon dioxide).

6. The methodology for choosing the IPC ES in a one-parameter family of equations \((\chi = \text{const})\)

Here are some of the most popular ES vdW, in which the first contribution is in the form of \( \frac{RT}{(V-b)} \), which allows to compare the ES analogue in the IPC family on the values of CCF: 0.375 (VdW); 0.333 (Redlich ‒ Kwong); 0.315 (Ishikawa et al. ); 0.3074 (Peng ‒ Robinson); 0.286 (Harmens ‒ Knapp). There is an obvious trend: CCF values are close to those that are characteristic of specific substances.

We define as an optimal the ES for which the CCF calculated according to the ES (as its characteristic) will coincide with the experimental value of the CCF for a particular substance.

The proposed methodology is based on the formulae for calculating parameters as functions of the control parameter \( \chi \) [10] obtained for the IPC model with rigid repulsion. The algorithm of actions is as follows: from the known (experimental) value of the CCF \( Z_C \) of a particular substance, using formula (6), we restore the value of the parameter \( \chi \). Next, based on the found value, we calculate the coordinated values of the ES parameters (all of them are determined by one value of the control parameter). The technique was tested by calculating the critical isotherms of a number of substances: Ar, NH\(_3\), C\(_4\)F\(_8\), C\(_2\)H\(_4\), CHF\(_3\), and isopentane.

Let us calculate the pressure at the critical isotherm for argon from the found IPC (rigid repulsion) [13,14]. By the value of the critical compressibility factor for argon \( Z_C = 0.291 \), we find the value of the parameter \( \chi = 3.3 \) using the formula (10). Coordinated with it values for the parameters of the equation of state in the case \( \chi = \text{const} \) are equal \( \beta = 0.18973 \), \( \sigma = 0.62615 \), \( \alpha = 1.53374 \). The reduced ES IPC for the critical isotherm Ar has the form

\[ P_R = \frac{1}{0.291V_R} \left[ 1 + \frac{0.18973}{V_R - 0.18973} - \frac{1.53374}{V_R + 0.62615} \right] \]

The reduced densities varied from 0.01 to 0.625. We have compared the calculation results obtained by this ES IPC (11), by ES of Martin proposed in [15] for argon as the best, and ES of Redlich ‒ Kwong (2). The comparison showed the following: average absolute deviations (%) of the results from those according to the ES of the National Bureau of Standards (NIST, USA) chosen by Martin as
the reference in [15], respectively, amounted to 1.67; 4.3; and 5.78%. That is, the ES selected in the IPC family turned out to be “better than the best”.

The same result was obtained for another substance. **Isopentane.** The parameters \( \beta = 0.1598, \sigma = 0.8566, \alpha = 1.69717 \) have been found from \( Z_C = 0.270 \) and \( \chi = 5.4 \). An interval of values \( V_R:120.7 – 2.48 \). Average absolute deviations (%) - 1.3.

**Perfluorocyclobutane.** \( \text{C}_4\text{F}_8 \). The parameters \( \beta = 0.17, \sigma = 0.765, \alpha = 1.63626 \) have been found from \( Z_C = 0.278 \) and \( \chi = 4.5 \). An interval of values \( V_R:15.8 – 0.69 \). Average absolute deviations (%) - 1.33.

**Carbon dioxide.** \( \text{CO}_2 \). The parameters \( \beta = 0.1643, \sigma = 0.81, \alpha = 1.66939 \) have been found from \( Z_C = 0.2745 \) and \( \chi = 4.9 \). An interval of values \( V_R:12.6 – 0.67 \). Average absolute deviations (%) - 2.8. (Peng-Robinson – 2.76, Martin – 3.92).

7. The choice of the optimal ES from the general equations of state in the model of IPC
The rigid nature of repulsion is generally unrealistic (the Sutherland potential describes the situation). Therefore, we have to assume the possibility of “softening” the nature of repulsion, that is, a modification of the repulsive configurational contribution to the equation of state. Presumably, it will be of the form \( RTd / V (V - b) \), \( d > b \). As a result, the general ES, which is based on “realistic” repulsion and attraction, will have the form

\[
P = \frac{RT}{V} + \frac{Rtd}{V(V - b)} - \frac{a}{V(V + c)}.
\]

Let us denote the ratio of the parameters \( c/b = \chi_0 \) and \( d/b = \chi_1 \), accounting that they are control parameters for two ES “ultimate” in the nature of the interaction. We represent (12) as cubic equation by volume \( V \) and use the condition that the roots are equal at the critical point; this gives a set of three equations, resulting in a cubic equation for the parameter \( \beta \nabla
\]

\[
\beta^3(\chi_0 + (\chi_0 - 1)f) + 3f\beta^2 + 3\beta - 1 = 0.
\]

Let \( f(\chi_0, \chi_1) = \chi_1(\chi_0 + 1) - 1 \).

The value of the parameter \( \beta \) found from Eq. (13) will determine the value of the critical coefficient \( K_C \) (the inverse of the CCF \( Z_C \))

\[
K_C = 3 + (\chi_0 - 1)\beta \quad K_C = 3 + \sigma - \beta
\]

The direct connection of this quantity with the forces of intermolecular interaction is of undoubted interest. If the manifestations of forces are balanced, then \( K_C = 3 \) (CCF = 1/3) and this is the state that describes the Redlich – Kwong ES. Then expression (14) can be generalized

\[
K_C^{ES} = K_C^{R-Kw} + \sigma - \beta
\]

The last parameter of the reduced ES (12) is determined by the expression

\[
\alpha = \frac{Z_C}{\beta} - \beta\chi_0(\chi_1 - 1)
\]

8. Example: Ishikawa equation of state
In order to the general equation of state of the IPC (12) could work, in the described version, it is necessary to know two numbers in which the ratios of the acting forces are accumulated. As an
example, we take the equation of state (6) of Ishikawa, Chung, and Lu, according to which the authors performed calculations:

\[ P = \frac{RT}{V} \left( \frac{2V}{2V+b} \right) \left( \frac{2V-b}{V(V+b)} \right) - \frac{a(T)}{V(V+b)}. \]

We transform the original ES by writing its analogue in the form (16) of the ES IPC

\[ P = \frac{RT}{V} + \frac{RTb}{V(V-b/2)} - \frac{a}{V(V+b)}. \] (16)

We redefine the parameters of the ES (16) and find the relative parameters

\[ b = b/2, \ d = b, \ c = b, \ \chi_0 = c/b = b/(b/2) = 2, \ \chi_1 = d/b = 2 \]

We can say now that the manifestation of repulsive forces is softened, according to the value of the parameter \( \chi_1 = 2 \), and the contribution responsible for attraction differs from the same in the Redlich ‒ Kwong ES, since \( \chi_0 = 2 \) and this means that attraction is more active.

Using the parameters of ES (16), the equation has been obtained:

\[ 7\beta^3 + 15\beta^2 + 3\beta - 1 = 0 \]

The parameters \( \beta = 0.1726, \ \sigma = 0.3452, \ \delta = 0.3452, \ \alpha = 1.48098 \) have been found from (14) and (15).

For this coordinated system, the ES of critical isotherm for argon is constructed (an analogue of the Ishikawa ES):

\[ P_R = \frac{1}{0.3152V_R} \left[ 1 + \frac{0.3452}{V_R - 0.1726} - \frac{1.48098}{V_R + 0.3452} \right]. \] (17)

This ES for argon turned out to be quite functional (table 2). Simultaneously, a preliminary conclusion can be made: the ES proposed by Ishikawa, Chung, and Lu in [8] cannot be considered a general ES. It describes only those states that are formed by well-defined specific relationships of forces.

| Table 2. The critical isotherm of argon for the Ishikawa et al. equation of state |
|-----------------------------------------------|
| \( V_R \) | \( P_R(\text{rep}) \) | \( P_R(\text{attr}) \) | \( P_R(\text{*}) \) | \( P_R(\text{res}) \) | \( \Delta(\%) \) |
|------|-----------------|-----------------|-----------------|-----------------|---------------|
| 100  | 0.003458        | 0.014758        | 0.031725        | 0.03136         | 7.6           |
| 20   | 0.017410        | 0.072792        | 0.158629        | 0.14984         | 7.55          |
| 5    | 0.071508        | 0.277067        | 0.634517        | 0.50408         | 6.77          |
| 2.5  | 0.14832         | 0.520518        | 1.269           | 0.79668         | 4.5           |
| 1.25 | 0.320400        | 0.928397        | 2.53807         | 0.99493         | 0.06          |
| 10/9 | 0.36781         | 1.01694         | 2.8553          | 1.00184         | 0.24          |
| 1    | 0.417210        | 1.109936        | 3.172588        | 1.003407        | 0.34          |
| 10/11| 0.468709        | 1.180816        | 3.490279        | 1.004826        | 0.42          |
| 10/12| 0.52247         | 1.25663         | 3.80720         | 1.012106        | 0.62          |
| 2/3  | 0.698785        | 1.463708        | 4.759359        | 1.11895         |              |
| 10/16| 0.763041        | 1.526468        | 5.07614         | 1.287           | 15.61         |
| ½    | 1.054367        | 1.752224        | 6.34517         | 1.917148        |              |

9. Calculations and forecast for substances

It seems logical to combine the results for the two limiting ES IPC and check whether this ES is better than the initial ones taken separately. Let us turn to the general equation of state for the interaction point centers proposed by us and consider the equation of state for argon.
“Reasonable” and independent of each other values of the control parameters are equal to $\chi_0 = 3.3$ (found by formula (6) for the “rigid” ES IPC) and $\chi_1 = 1.93$ (data of A. Kaplun).

1. We kept the initial values of the parameters. From the general equation (12), we obtained the cubic equation for the parameter $\beta$:

$$20.215\beta^3 + 21.95\beta^2 + 3\beta - 1 = 0.$$ 

Then we found $\beta = 0.1489$, $\delta = 0.287373$, $\sigma = 0.492859$, $\alpha = 1.5522929$, $K_C = 3.3424$, and $Z_C = 0.2991$. CCF is overestimated in comparison with the experimental value. No calculations were performed. The above considerations about the relationship between the CCF and the interaction forces show that it is possible to go to a state with a lower CCF if the $\chi_0$ is increased.

2. It was decided to round these values to the nearest integers: $\chi_0 = 4$ and $\chi_1 = 2$.

Solving the equation, we obtained $\beta = 0.13728$. This gave the value for $K_C = 3.41184$ and $Z_C = 0.293$.

The corresponding ES has the form

$$31\beta^3 + 27\beta^2 + 3\beta - 1 = 0.$$ 

Solving the equation, we obtained $\beta = 0.146$, $\delta = 0.2482$, $\sigma = 0.584$, $\alpha = 1.583438$, $K_C = 3.438$. For $Z_C$ we have got the value 0.29086.

The equation of state of interacting point centers for argon is

\begin{equation}
\begin{bmatrix}
V_R & P_r^\text{(NBS)} & P_r^\text{ES(18)} & \Delta_r, \% & P_r^\text{ES(19)} & \Delta_r, \% & R-Kwong & \Delta_r, \% \\
1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 \\
100 & 0.03395 & 0.033927 & -0.168 & 0.034229 & -0.82 & 0.03394 & -0.03 \\
20 & 0.16209 & 0.160825 & -0.78 & 0.160641 & -0.89 & 0.16187 & -0.13 \\
5 & 0.54073 & 0.528393 & -2.28 & 0.526271 & -2.67 & 0.53993 & -0.15 \\
2.5 & 0.83428 & 0.818798 & -1.85 & 0.813201 & -2.52 & 0.83837 & +0.5 \\
1.25 & 0.99556 & 1.003461 & 0.79 & 0.9929 & +0.26 & 0.99936 & +0.38 \\
10/9 & 0.99946 & 1.009748 & 1.029 & 0.998513 & 0.094 & 1.0000 & +0.06 \\
1 & 1.0000 & 1.011353 & 1.13 & 0.999349 & +0.06 & 1.0033 & +0.38 \\
10/11 & 1.0006 & 1.013001 & 1.239 & 1.000166 & 0.043 & 1.0195 & +1.9 \\
10/12 & 1.0058 & 1.019048 & 1.317 & 1.005236 & 0.05 & 1.0598 & +5.4 \\
10/14 & 1.0685 & 1.06047 & -0.75 & 1.043962 & 2.29 & 1.2646 & +18.0 \\
10/16 & 1.3426 & 1.1669 & -13.109 & 1.146311 & 14.62 & 1.7432 & +30.0 \\
average absol. deviation & <2.2> & <2.2> & 14.62 & 14.62 & 14.62 & 14.62 & 14.62 \\
10/18 & 2.1534 & 1.36568 & -36.58 & 1.338464 & 37.84 & 2.6716 & +24.0 \\
average absol. deviation & <4.88> & <5.1> & <7.3> & <7.3> & <7.3> & <7.3> & <7.3> \\
\end{bmatrix}
\end{equation}

3. The values $\chi_1 = 1.7$ and $\chi_0 = 4$ are chosen:

$$26.5\beta^3 + 22.5\beta^2 + 3\beta - 1 = 0.$$ 

Solving the equation, we obtained $\beta = 0.146$, $\delta = 0.2482$, $\sigma = 0.584$, $\alpha = 1.583438$, $K_C = 3.438$. For $Z_C$ we have got the value 0.29086.

The equation of state of interacting point centers for argon is
\[ P_R = \frac{1}{0.291 V_R} \left( 1 + \frac{0.2482}{V_R - 0.146} - \frac{1.583438}{V_R + 0.584} \right) \]  

The average absolute deviation 0.97% was for the same region of reduced densities (up to the first “splash” of calculation errors). The most interesting area (1.25 – 0.8) of \( V_R \) is described with an accuracy of 0.1%.

10. Conclusion

The results obtained are of undoubted interest, especially from the standpoint that we consider physically reasonable equations of state associated with the molecular properties of the objects. Moreover, at the moment, this is the simplest version of the equation of state obtained under the condition \( \chi = \text{const} \). At the same time, a more general (structured) ES has already been obtained when the demand of constancy is removed from the parameters. All parameters of the ES are determined by a set of two generating numbers \( k_1 \) and \( k_2 \), which it turns out to be possible to associate with the two types of movements available to the point center. These preliminary data confirm the possibility of further optimization of the constructed molecular thermodynamic model.

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