An interpolation model for the equation of state in binary systems.

S.A.Kukushkin\textsuperscript{1}, A.V.Osipov\textsuperscript{2}, Yu.V.Pavlov, A.S.Sokolov

Institute of Mechanical Engineering, Russian Academy of Sciences, 61 Bolshoy, V.O., St.Petersburg, 199178, Russia

Abstract

The new interpolation model of state of binary mixture is investigated. This model use only two parameters and produce many type of phase diagrams.

Keywords: phase transitions, binary mixture, phase diagrams.

As it is known, at present the virial equation of state is the only theoretically substantiated form for an equation of gaseous state \cite{1}. However, application of this equation to description of behavior of real gases, especially within the range of high densities, presents certain difficulties, since it involves a great number of terms, to be taken into account for virial expansion. Therefore, in practice, various empirical equations of state are often used. In elementary case the equations include two parameters, which can be estimated by the known values of critical magnitudes for temperature, pressure and volume. The Van der Waals equation (see, for instance \cite{2}) and the Redlich-Kwong equation \cite{3} are the most applicable as the two-parametric equations. The Redlich-Kwong model was further extended in papers of G.M.Wilson, G.Soave and others \cite{4}–\cite{7}, where the authors proposed to add a certain function, the so-called \(\alpha\)-function, dependent on the characteristic temperature. One of the main limitations in such modified models is the presence of a great number of parameters, which cannot be rather correctly proved. In the case of analysis of a gaseous mixture, the number of parameters is to be increased. Consequently, to solve this problem, it is necessary to construct a model containing a minimum number of parameters to be defined, and, at the same time, it would be possible to describe the behavior of a real gas’ mixture up to a liquid state within the whole range of changes in pressure and temperature.

\textsuperscript{1}e-mail: ksa@math.ipme.ru
\textsuperscript{2}e-mail: oav@math.ipme.ru
by means of the model. Within the framework of the model presented below, the equation of state for a binary gas mixture is treated, where together with two the Van der Waals parameters of components the only additional parameter of interaction is introduced. Meanwhile, as it is shown below, even within the framework of a such simplified statement the basic types of phase equilibria can be examined and most of phase diagrams presently known can be obtained.

As it is known, the Van der Waals free energy for a gas is defined by the formula (see, for instance, [8]):

$$F = NT \ln \frac{N}{V - Nb} - \frac{N^2a}{V} + Nf(T)$$

(1)

In this work we put forward the following formula of free energy for a mixture of two gases, namely,

$$F = T \left[ N_1 \ln \frac{N_1}{V - (N_1b_1 - N_2b_2)} + N_2 \ln \frac{N_2}{V - (N_1b_1 - N_2b_2)} \right] -$$

$$\left[ \frac{N_1^2a_1}{V} + \frac{N_2^2a_2}{V} \right] + \tilde{A} \frac{N_1N_2}{V} + (N_1 + N_2)f(T)$$

(2)

Here $N_i$ and $b_i$ are the matter content and molecular "volume" of the $i$-th component, respectively; $a_i$ is the positive constant characterizing the interaction of the $i$-th gaseous component. The free energy defined by (2) can be represented in the form of

$$F = F_1 + F_2 + F_{int},$$

where $F_{int} = \tilde{A}N_1N_2/V$, whereas $F_i$ is the free energy of the $i$-th gaseous component in the presence of another component.

Further, we confine ourselves to analysis of a symmetric model, i.e. we assume that $a_1 = a_2 = a$ and $b_1 = b_2 = b$. In addition, in analysis of phase equilibria the last terms in (2) can be neglected, since it does not contribute to the equations for pressure and chemical potentials of different phases.

Now we introduce the dimensionless values, according to formulas

$$V_r = V/V_{crit}, \quad T_r = T/T_{crit}, \quad \rho_i = N_i/V_r,$$

where the critical values of volume and temperature are determined by the following expressions: $V_{crit} = 3b$, $T_{crit} = 8a/(27b)$. Then, the
expression for the reduced density of free energy \( \tilde{F} = F(81b^2)/(8aV) \) takes the form

\[
\tilde{F}(\rho_1, \rho_2 T) = T \left[ \rho_1 \ln \frac{\rho_1}{1-(\rho_1+\rho_2)/3} + \rho_2 \ln \frac{\rho_1}{1-(\rho_1+\rho_2)/3} \right] - \frac{9}{8} [\rho_1^2 + \rho_2^2] + \tilde{A}\rho_1\rho_2.
\]

When instead of gaseous component densities \( \rho_i \) the total density \( \rho \) and "concentration" \( x \) of the first component by formulae \( \rho = \rho_1 + \rho_1 \), \( x = (\rho_1 - \rho_2)/\rho_1 \), \( x \in [-1, 1] \) are introduced, the expression for the density of free energy in the above new variables takes the form:

\[
\tilde{F}(T, \rho, x) = T \rho \ln \frac{\rho}{1-\rho/3} - \frac{9}{8} \rho^2 + \alpha \rho^2(1-x^2) + T \rho \left[ (1+x) \ln(1+x) + (1-x) \ln(1-x) \right].
\]

In the presented expression the parameter \( \alpha = \tilde{A}/4 + 9/16 \) is responsible for the interaction energy of gaseous components. It is easily seen that in the case with an one-component gas \( (x \to \pm 1) \) eqn. (5) takes the form of the Van der Waals equation (1).

From the presented expression for the free energy the formulae for the chemical potentials of gaseous components and pressure are directly followed, namely:

\[
\mu_1 = T \ln \left( \frac{\rho(1+x)}{1-\rho/3} \right) + \frac{T}{1-\rho/3} - \frac{9}{4} \rho + 2\alpha \rho(1-x),
\]

(5)

\[
\mu_2(\rho, x) = \mu_1(\rho, -x),
\]

(6)

\[
P = \frac{T \rho}{1-\rho/3} - \frac{9}{8} \rho^2 + \alpha \rho^2(1-x^2).
\]

(7)

By means of (5) – (7) one can construct phase diagrams with different values of parameter \( \alpha \). Let the pressure in a system be specified. The equality of chemical potentials for gaseous components

\[
\mu_1(\rho, x, T) = \mu_2(\rho, x, T)
\]

is in agreement with conditions of "gas-gas" or "liquid-liquid" phase equilibria at the specified pressure \( P(\rho, x, T) = P_0 \).
The explicit form of the set of equations for the "gas-gas" or "liquid-liquid" equilibria is
\[
\frac{T \rho}{1 - \rho/3} - \frac{9}{8} \rho^2 + \alpha \rho^2 (1 - x^2) = P_0, \quad T \ln \frac{1 + x}{1 - x} = 4\alpha \rho x. \tag{8}
\]

The equality of equilibria in both phases, \( P(\rho_g, x_g, T) = P(\rho_l, x_l, T) = P_0 \) and the equality of chemical potentials of the binary system components are the conditions for "gas-liquid" phase equilibrium, namely,
\[
\mu_1(\rho_g, x_g, T) = \mu_1(\rho_l, x_l, T), \quad \mu_2(\rho_g, x_g, T) = \mu_2(\rho_l, x_l, T),
\]
where lower indices \( g \) and \( l \) refer to gaseous and liquid phases, respectively.

**Discussion**

The set of equations (8) and corresponding system for the "gas-liquid" equilibrium are investigated both numerically and analytically. With different values of determinative parameters of the problem \( \alpha \) and \( P_0 \), various types of diagrams can be obtained, such as, the so-called cigar, pinched cigar, the diagram of eutectic type and so on. In the case with large values of parameters \( \alpha \) and \( P_0 \), the curves of phase equilibrium are of domal shape and they correspond to the "liquid-liquid" phase equilibrium. Here, at \( x \to \pm 1 \) that conforms to the case with an one-component substance, \( F_{int} \to 0 \), and the "liquid-liquid" phase equilibrium is observed at \( T \to 0 \). As \( x \to 0 \) (with large values \( \alpha \)), the contribution to the free energy of an exchange component grows fast and the phase equilibrium is observed at higher temperature.

When the positive interaction energy \( F_{int} \to 0 \) the phase diagrams are represented in the form of eutectic diagrams. This is, first of all, associated with the behavior of free energy curves for gas and liquid phases during changes in the interaction energy (by the analogy with weak solutions).

In the case with negative values of \( \alpha \) there are no "gas-gas" or "liquid-liquid" equilibrium states, that is directly followed from mathematical analysis of the set of equations (8), i.e. at \( \alpha \leq 0 \), solution of the second equation in the system is absent.
So, by means of the present model for a mixture of nonideal gases the authors succeeded in obtaining various types of phase equilibrium diagrams occurred during an experiment.

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