NEW SEMI-EMPIRICAL RULES FOR ESTIMATING CROSS SECOND VIRIAL COEFFICIENTS

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By using the statistical-thermodynamic interpretation of the theorem of corresponding states, new rules have been derived for estimating cross second virial coefficients.

Second virial coefficients are very often used to describe the volumetric behaviour of gases at low pressures. These quantities are determined from the experimental $P-V-T$ data and are tabulated as a function of temperature for a number of substances (*e.g.* in the monograph by Dymond and Smith[1]). The experimental values of second virial coefficients of mixtures, on the contrary, are known only seldom and therefore the interest in various possibilities of their estimation is obvious.

For the second virial coefficient of a binary mixture, the relation holds

$$B = B_{11}x_1^2 + 2x_1x_2B_{12} + B_{22}x_2^2 , \qquad (1)$$

where x_1, x_2 are the mole fractions and B_{11}, B_{22} the virial coefficients of pure components. With regard to Eq. (*1*), the problem of estimation of the virial coefficient of mixture reduces to the determination of the cross virial coefficient B_{12}. The simplest estimation rules for B_{12} are as follows:

$$B_{12}(T) = (1/2)\left[B_{11}(T) + B_{22}(T)\right] , \qquad (2)$$

$$B_{12}(T) = \text{sign}\left[B_{11}(T)\right]\left[B_{11}(T)\,B_{22}(T)\right]^{0.5} , \quad B_{11}(T)\,B_{22}(T) > 0 , \qquad (3)$$

$$B_{12}(T) = (1/8)\left[B_{11}^{1/3}(T) + B_{22}^{1/3}(T)\right]^3 . \qquad (4)$$

The empirical relations given are rather popular for their simplicity even though their accuracy is usually low. Rather more accurate estimates can be obtained when applying the empirical relations for virial coefficients of pure components (*e.g.* by Pitzer and Curl, McGlashan and Potter, Black, *etc.*) on using various combination rules for parameters of these relations[2].

In this work, new relations are derived for estimating B_{12} in terms of the corresponding states theorem. The relations obtained are used, in addition, to judge the range of validity of empirical rules $(2)-(4)$.

Derivation of Relations for B_{12}

Let us assume that it holds

$$u_{ij}(r) = \varepsilon_{ij} f(r/\sigma_{ij}), \quad i, j = 1, 2, \tag{5}$$

$$\varepsilon_{12} = [\varepsilon_{11}\varepsilon_{22}]^{1/2}, \tag{6}$$

$$\sigma_{12} = (1/2)(\sigma_{11} + \sigma_{22}), \tag{7}$$

where u_{ij} is the pair potential for interactions between molecules of the kinds i, j, f is the universal function of the reduced distance r/σ_{ij}, and ε_{ij}, σ_{ij} are parameters characterizing the interacting molecules. An example of the general dependence (5) is the well-known Lennard–Jones potential. Relation (5) is a necessary condition of the validity of the theorem of corresponding states. Relations (6) and (7) are familiar combination rules[3] whose accuracy is sufficient for the purposes of this work. From Eq. (5) it is possible to derive[4] the following relations between the interaction parameters and the critical quantities

$$\varepsilon = k_\varepsilon T_c, \tag{8}$$

$$\sigma = k_\sigma V_c^{1/3}, \tag{9}$$

where k_ε, k_σ are the constants independent of the kind of substance. From Eq. (5) it follows as well

$$B_{ij}(T) = \sigma_{ij}^3 \varphi(T/\varepsilon_{ij}) = \sigma_{ij}^3 \psi(T/T_{cij}), \tag{10}$$

where $T_{cij} = \varepsilon_{ij}/k_\varepsilon$, φ and ψ are the universal functions of reduced temperatures T/ε, T/T_c.

By means of the above-mentioned relations we shall express $B_{ij}(T)$ through the virial coefficients of pure components. For the component 1 at a temperature of $T(T_{c1}/T_{c2})^{1/2}$, we can write with regard to Eq. (10)

$$B_{11}[T(T_{c1}/T_{c2})^{1/2}] = \sigma_{11}^3 \psi[T/(T_{c1}T_{c2})^{1/2}]$$

and for the component 2 at a temperature $T(T_{c2}/T_{c1})^{1/2}$

$$B_{22}[T(T_{c2}/T_{c1})^{1/2}] = \sigma_{22}^3 \psi[T/(T_{c1}T_{c2})^{1/2}].$$

On rearranging these equations we get

$$(1/2) \left\{ B_{11}^{1/3} \left[T(T_{c1}/T_{c2})^{1/2} \right] + B_{22}^{1/3} \left[T(T_{c2}/T_{c1})^{1/2} \right] \right\} =$$
$$= (1/2)(\sigma_1 + \sigma_2) \, \psi^{1/3} \left[T/(T_{c1} T_{c2})^{1/2} \right].$$

The expression on the right-hand side is, with respect to Eqs $(6)-(8)$, (10), the third root of the cross second virial coefficient at a temperature T

$$B_{12}(T) = (1/8) \left\{ B_{11}^{1/3} \left[T(T_{c1}/T_{c2})^{1/2} \right] + B_{22}^{1/3} \left[T(T_{c2}/T_{c1})^{1/2} \right] \right\}^3. \qquad (11)$$

If we employ in addition Eq. (9) we can get another relation for B_{12}

$$B_{12}(T) = (1/16)(V_{c1}^{1/3} + V_{c2}^{1/3})^3 \left\{ V_{c1}^{-1} \, B_{11} \left[T(T_{c1}/T_{c2})^{1/2} \right] + \right.$$
$$\left. + V_{c2}^{-1} \, B_{22} \left[T(T_{c2}/T_{c1})^{1/2} \right] \right\}. \qquad (12)$$

If the starting assumptions $(5)-(7)$ hold the relations (11) and (12) lead to the same result. Both terms in braces of Eq. (12) are then as well identical which can be employed for testing *a priori* the relations derived. If we do not know sufficiently accurately the values of critical volumes of components we can replace V_{ci} by the ratio T_{ci}/P_{ci} in Eq. (12).

Generally it is possible to expect that the proposed relations (11), (12) will predict well the values of B_{12} for substances with spherical, charge-symmetrical substances; for strongly polar substances they can fail. In the next paragraph we will show that the conditions of the validity of the empirical rules $(2)-(4)$ are much harder.

Limits of Validity of Empirical Rules $(2)-(4)$

In relation (11), the cross virial coefficient is given by the Lorenz average of the coefficients for pure components at temperatures $T(T_{c1}/T_{c2})^{1/2}$ and $T(T_{c2}/T_{c1})^{1/2}$. Consequently, for $T_{c1} = T_{c2}$, Eq. (11) turns into (4). The rule of arithmetic mean (2) is obtained from Eq. (12) for $T_{c1} = T_{c2}$ and $V_{c1} = V_{c2}$. The rule of geometric mean (3) can be derived from Eq. (12) just for the following particular type of the dependence of second virial coefficient on temperature:

$$\psi(T/T_c) = \text{const.} \, (T/T_c)^r, \qquad (13)$$

where r is a real number. Then

$$B_{12}(T) = (1/8) \left[(V_{c1}/V_{c2})^{1/6} + (V_{c1}/V_{c2})^{-1/6} \right]^3.$$
$$. \left[B_{11}(T) B_{22}(T) \right]^{1/2}. \qquad (14)$$

For $V_{c1} = V_{c2}$, Eq. (14) turns into (3). The rule of the geometric mean could seem to be successful in case of substances with near values of critical volumes irrespective of the values of critical temperatures. We will prove that it is not so. Relation (14) can be rearranged to

$$B_{12}(T) = (1 + \delta^2/12) \left[B_{11}(T) \, B_{11}(T) \right]^{1/2},\qquad (15)$$

where $\delta = (V_{c1} - V_{c2})/V_{c2}$. It is evident that the values of critical volumes have no effect on B_{12} in the given relation. If the critical volumes of components differ e.g. by 50%, the results of Eq. (15) and Eq. (3) differ only by 2%. The effect of critical temperatures does not manifest itself explicitly but in terms of Eq. (13). The more remote the critical temperatures of components will be, the worse will Eq. (13) approximate the real temperature dependence of virial coefficients in the range of reduced temperatures $\langle T/T_{c1}, T/T_{c2} \rangle$.

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Translated by J. Linek.