STATISTICAL THERMODYNAMIC ESTIMATE OF THE PROPERTIES OF GAS MIXTURES AT HIGHER PRESSURES

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A method is proposed to determine the thermodynamic functions of gas mixtures from the virial expansion in which the second virial coeficient of the mixture is obtained from an exact equation and the higher virial coefficients are estimated from one-liquid or two-liquid approximations. Calculated values of the molar mixing volume V^M and enthalpy H^M in dependence on pressure (up to 100 atm) of argon–nitrogen mixtures are given. At higher pressures the agreement with experiments is not accurate but it is better than with the use of the corresponding states method.

The fundamental equation of state for gases in the form of the virial expansion

$$z = 1 + \sum_{i=2}^{\infty} B_i d^{i-1} , \qquad (1)$$

where z denotes the compressibility factor and d molar density, has been known for many years. The virial coefficients $B_i = B_i(T)$ are given by exact statistical thermodynamic equations which become increasingly more complicated with increasing i values. Based on the Lennard–Jones $12-6$ potential

$$u(r) = 4\varepsilon\left[(\sigma/r)^{12} - (\sigma/r)^6\right] , \qquad (2)$$

only the second through fifth virial coefficients were calculated[1] as functions of the reduced temperature kT/ε.

Eq. (1) holds also for gas mixtures, where the coefficients B_i are functions of temperature and composition; their complexity increases with the i value even more markedly than with pure gases. (The calculation of B_2 is easy, B_3 for mixtures was calculated by Stogryn[2] for the potential according to Eq. (2), but higher virial coefficients of mixtures were for this potential not calculated.) Therefore, approximate methods proposed originally for liquids are used instead of Eq. (1) to calculate the properties of gas mixtures at higher pressures.

In this work we shall describe the thermodynamic properties of multicomponent systems with the aid of the equation of state (1) with the first five terms, where the

second virial coefficient will be given by the exact statistical thermodynamic equation and the other ones will be estimated from those for pure components by the theoreme of the corresponding states.

Principle of the Method

In the one-liquid approximation, Eq. (I) for mixtures can be rewriten as

$$z = 1 + \sum_{i=2}^{5} \left(\tfrac{2}{3}\pi N \bar{\sigma}^3\right)^{i-1} B_i^*(kT/\bar{\varepsilon}) \, d^{i-1} . \tag{3}$$

Here N denotes the Avogadro constant and k Boltzmann constant. The pseudo-interaction parameters $\bar{\varepsilon}$ and $\bar{\sigma}$ are functions of the composition. We modify this equation by replacing the term for $i = 2$ by the exact expression for the second virial coefficient of an s-component mixture:

$$z = 1 + \sum_{k,l=1}^{s} x_k x_l \, \tfrac{2}{3}\pi N \sigma_{kl}^3 B_2^*(kT/\varepsilon_{kl}) \, d + \sum_{i=3}^{5} \left(\tfrac{2}{3}\pi N \bar{\sigma}^3\right)^{i-1} .$$
$$. \, B_i^*(kT/\bar{\varepsilon}) \, d^{i-1} , \tag{4}$$

where x_k denotes molar fraction of the component k.

The equation of state in the two-liquid approximation

$$z = 1 + \sum_{i=2}^{5} \sum_{j=1}^{s} x_j \left(\tfrac{2}{3}\pi N \bar{\sigma}_j^3 d\right)^{i-1} B_i^*(kT/\bar{\varepsilon}_j) \tag{5}$$

can be similarly modified to give

$$z = 1 + \sum_{k,l=1}^{s} x_k x_l \, \tfrac{2}{3}\pi N \sigma_{kl}^3 B_2^*(kT/\varepsilon_{kl}) \, d +$$
$$+ \sum_{i=3}^{5} \sum_{j=1}^{s} x_j \left(\tfrac{2}{3}\pi N \bar{\sigma}_j^3 d\right)^{i-1} B_i^*(kT/\bar{\varepsilon}_j) . \tag{6}$$

Equations (4) and (6) hold exactly at low densities, where the terms with higher powers of d than the first are negligible. They will describe the behaviour of mixtures even at higher densities better than Eqs (3) and (7) as long as the term with the second virial coefficient will have a substantial influence on the compressibility factor.

The sixth and higher virial coefficients in Eqs (3)$-$(6) are neglected (for the $12-6$ potential they are not known). These equations can be therefore used only at such densities at which the remainder of the series, $R = \left| \sum_{i=6}^{\infty} B_i d^{i-1} \right|$, is much smaller than

z. However, the value of R cannot be estimated. Instead, we shall assume that Eqs $(3)-(6)$ can be used at such densities that $|B_s d^4| \leqq 0.001$.

CALCULATION AND RESULTS

To illustrate the proposed method, we shall calculate the molar mixing volume V^M and molar mixing enthalpy H^M of the argon–nitrogen system. The first quantity is given by

$$V^M = V(T, P, x_1, x_2, \ldots, x_s) - \sum_{j=1}^{s} x_j V_j(T, P) . \qquad (8)$$

The volume of the mixture, $V(T, P, x_1, \ldots, x_s)$ is calculated for given values of the variables from the state equation (4) or (6), the volumes of pure components, $V_j(T, P)$, from (3). The mixing enthalpy is given by

$$H^M = H(T, d, x_1, x_2, \ldots, x_s) - \sum_{j=1}^{s} x_j H_j(T, d_j) =$$

$$= RT \left\{ z(T, d, x_1, x_2, \ldots, x_s) - \sum_{j=1}^{s} x_j z_j(T, d_j) - \right.$$

$$\left. - T \frac{\partial}{\partial T} \left[\int_0^d z(T, d, x_1, x_2, \ldots, x_s) \, d\ln d - \sum_{j=1}^{s} x_j \int_0^{d_j} z_j(T, d) \, d\ln d \right] \right\}, \qquad (9)$$

where the density of the mixture, d, is for the given temperature, pressure and composition given by Eq. (4) or (6), the densities of the components, d_j, by Eq. (3). Four alternatives of the method were studied:

1) In Eqs (8) and (9) the density and volume of the mixture is calculated from (4) and the parameters $\bar{\varepsilon}$ and $\bar{\sigma}$ from the relations proposed by Prigogine[3] and Scott[4]:

$$\bar{\varepsilon} = \left(\sum_{i,j=1}^{s} x_i x_j \varepsilon_{ij} \sigma_{ij}^6 \right)^2 \Big/ \sum_{i,j=1}^{s} x_i x_j \varepsilon_{ij} \sigma_{ij}^{12} , \qquad (10a)$$

$$\bar{\sigma} = \left(\sum_{i,j=1}^{s} x_i x_j \varepsilon_{ij} \sigma_{ij}^{12} \Big/ \sum_{i,j=1}^{s} x_i x_j \varepsilon_{ij} \sigma_{ij}^6 \right)^{1/6} . \qquad (10b)$$

2) Use is made of the equation of state (4) and the van der Waals approximation[5] for $\bar{\varepsilon}$ and $\bar{\sigma}$:

$$\bar{\varepsilon} = \bar{\sigma}^{-3} \sum_{i,j=1}^{s} x_i x_j \varepsilon_{ij} \sigma_{ij}^3 , \qquad \bar{\sigma} = \left(\sum_{i,j=1}^{s} x_i x_j \sigma_{ij}^3 \right)^{1/3} . \qquad (11)$$

3) The quantities V^M and H^M are calculated from Eq. (6) and the two-liquid version of the approximation proposed by Prigogine[3] and Scott[4]

$$\bar{\varepsilon}_i = \left(\sum_{j=1}^{s} x_j \varepsilon_{ij} \sigma_{ij}^6\right)^2 \bigg/ \sum_{j=1}^{s} x_j \varepsilon_{ij} \sigma_{ij}^{12} , \qquad (12a)$$

$$\bar{\sigma}_i = \left(\sum_{j=1}^{s} x_j \varepsilon_{ij} \sigma_{ij}^{12} \bigg/ \sum_{j=1}^{s} x_j \varepsilon_{ij} \sigma_{ij}^{6}\right)^{1/6} , \quad i = 1, 2, \ldots, s . \qquad (12b)$$

4) The behaviour of the mixture is described by the equation of state (6), $\bar{\varepsilon}_1$ and $\bar{\sigma}_i$ are determined from the two-liquid version of the van der Waals approximation[6]

$$\bar{\varepsilon}_i = \bar{\sigma}_i^{-3} \sum_{j=1}^{s} x_j \varepsilon_{ij} \sigma_{ij}^{3} , \quad \bar{\sigma}_i = \left(\sum_{j=1}^{s} x_j \sigma_{ij}^{6}\right)^{1/3} , \quad i = 1, 2, \ldots, s . \qquad (13)$$

The following values of ε and σ were used in Eqs $(10)-(14)$ (subscript 1 refers to argon, 2 to nitrogen)[7]: $\varepsilon_1/k = 118\cdot5$ K, $\sigma_1 = 3\cdot41$ Å, $\varepsilon_2/k = 95\cdot5$ K, $\sigma_2 = 3\cdot82$ Å, $\varepsilon_{12}/\sqrt{\varepsilon_1 \varepsilon_2} = 1\cdot005$, $2\sigma_{12}/(\sigma_1 + \sigma_2) = 0\cdot995$. The dependences of V^M and H^M on pressure calculated according to the four mentioned alternatives are shown in Figs 1
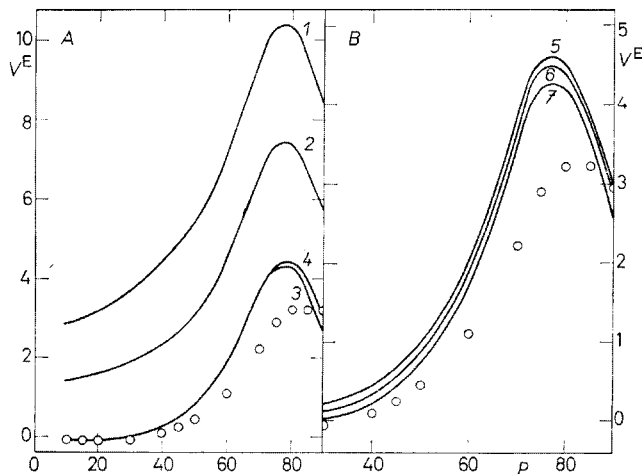

FIG. 1

Dependence of V^M (cm^3/mol) on Pressure (atm) of Argon–Nitrogen Mixture

$T = 170\cdot5$ K; $x_A = 0\cdot5$; *1* Prigogine one-liquid approximation; *2* Prigogine two-liquid approximation; *3* this work, first alternative; *4* third alternative; *5* van der Waals one-liquid approximation; *6* van der Waals two-liquid approximation; *7* this work, second or fourth alternative. Circles denote experimental points.

and 2 in comparison with experimental data[8,9] and with values calculated from the corresponding one- and two-liquid approximations. Numerical values of $V^M(P)$ and $H^M(P)$ were given elsewhere[7].

Fig. 1 shows the dependence of V^M on pressure for an equimolar argon–nitrogen mixture at 170.5 K. Curve *1* was calculated from the one-liquid approximation after Prigogine, Eqs (*3*) and (*10*), curve *2* from the two-liquid approximation after Prigogine, Eqs (*7*) and (*12*); curves *3* and *4* were calculated according to the first and third alternative mentioned above and differ very little from each other They are in excellent agreement with the experimental data at low pressures showing that sufficiently accurate value of ε_i, σ_i, ε_{12} and σ_{12} were used[7]. At higher pressures, the agreement of curves *3* and *4* with the experimental points can be considered good, but the Prigogine approximations (curves *1* and *2*) are unsatisfactory.

The dependences of V^M on pressure calculated according to the second and fourth alternatives are practically the same (Fig. 1, curve *7*) and their agreement with the experimental data is better than in the case of the van der Waals one-liquid (curve *5*) and two-liquid (curve *6*) approximations, which are nevertheless better than the Prigogine ones.

The dependences of H^M on pressure for the same system at 169 K and $x_1 = 0.52$ are shown in Fig. 2; the description of the curves is analogous to Fig. 1. All the mentioned alternatives lead practically to the same results and are therefore not distinguished in the diagram. The agreement with the measured values is (similarly as with
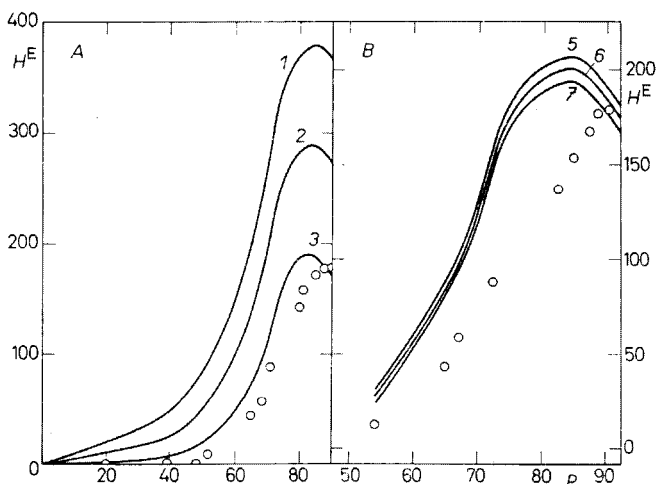

FIG. 2

Dependence of H^M (J/mol) on Pressure P (atm) of Argon–Nitrogen Mixture
$T = 169$ K; $x_A = 0.52$; the curves are described analogously as in Fig. 1.

V^M) much better than with the use of the Prigogine approximations and somewhat better than with the van der Waals approximations.

The mutual comparison of the methods based on the corresponding states theoreme leads to the same conclusions as in the case of liquid mixtures: the van der Waals two-liquid approximation is the best one, the Prigogine one-liquid approximation is the worst. Our method leads to a better agreement with the measured values of the mixing functions than these methods although at higher pressures the agreement is less satisfactory. In the region to the left from the maximum on the $V^M - P$ and $H^M - P$ curves the deviations from the experiments are probably mainly due to the use of approximate relations for the third virial coefficient of the mixture.

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