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APPLICATION OF THE HOLE THEORY TO STUDY THE P-V-T-X RELATIONS OF THE $\text{CO}_2\text{-CH}_4$ AND THE $\text{CO}_2\text{-N}_2$ SYSTEMS*

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The hole theory is applied to represent the P-V-T-X relations at the phase boundary of the $\text{CO}_2\text{-CH}_4$ and the $\text{CO}_2\text{-N}_2$ systems. As these systems contain super-critical components, Henderson's approximation for free volume was simplified and adopted for these expanded solutions. An equation of state was derived by introducing two characteristic parameters, which were determined from the heat of vaporization and the saturated densities of liquid and vapor of the pure substance.

The equation of state successfully explains the P-V-T-X relations of the above systems with the aid of combining rules for characteristic parameters.

Introduction

Several workers^{2-10,13-17}) have studied liquids and their mixtures on the basis of statistical mechanics. An excellent application for simple liquids has recently been reported by Eckert *et al.*^{3,4,16}) based on the cell model in conjunction with a three-parameter theory of corresponding states. As described in their articles^{4,13}), the treatment does not hold in the expanded liquid region since it is based on the cell model. However, expanded liquid mixtures consisting of super-critical components are often used in the chemical industry, so that a successful approach to such an expanded solution becomes important.

The present investigation was undertaken to develop a solution model available for expanded liquids and their mixtures. We put our theoretical basis on the hole theory, which seemed adequate for our purpose, and derived an equation of state introducing two characteristic molecular parameters concerning potential energy and cell volume. These parameters were determined by using the heat of vaporization and the volumetric data of the saturated liquid and vapor. The equation of state was then extended to binary mixtures with the aid of the combining rules for the two characteristic parameters. By using these equations, the P-V-T-X relations for the $\text{CO}_2\text{-CH}_4$ and the $\text{CO}_2\text{-N}_2$ systems were calculated and compared

with the experimental data presented in a previous paper¹). As a result it was found that the P-V-T-X relations of binary mixtures composed of simple molecules may be satisfactorily explained by the hole theory.

1. Equation of State of Pure Substance

It has been generally admitted,^{2,5}) through X-ray or neutron diffraction studies, that the density and the apparent number of nearest neighbours decrease when most substances melt. As the temperature of the liquid is raised, both the density and the apparent number of nearest neighbours decrease still further. These facts suggest to us that the presence of vacant lattice sites or holes should be taken into account in considering the structure of liquids. Thus we adopted the hole theory to study liquids and their mixtures. In the hole theory we could, if we wished, postulate that the cell size remains constant (independent of density and temperature) so that the whole of the thermal expansion is due to the increasing number of holes. From statistical mechanics all thermodynamic properties of a system can be derived by considering the canonical ensemble.

The canonical partition function, Z , is given by

$$Z = Z_k Z_i Q \quad (1)$$

where Z_k includes the translational kinetic energy of molecules, Z_i is related to the intramolecular degrees of freedom and Q is contributed by the potential energy of molecules. An equation of state can be

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derived from the partition function by using the following equations.

$$F = -kT \ln Z \quad (2)$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_T \quad (3)$$

Since Eq.(3) means the differentiation of Helmholtz free energy by volume at constant temperature, our attention is confined to calculating the configurational integral, Q , if Z_k and Z_i are dependent on temperature alone. This assumption holds for simple molecules having no complicated intermolecular interaction such as hydrogen bonds or orientation effects due to polarity. This condition holds for the simple liquids studied here.

On the basis of the hole theory, the configurational integral, Q , can be formulated as²⁾

$$Q = \frac{(N+N')!}{N!N'!} \{v_f\}^N \exp[-U^\circ/kT] \quad (4)$$

where N is the number of molecules, N' is the number of holes, U° is the total potential energy and v_f is the free volume of a molecule. The total potential energy, U° , and the free volume, v_f , were determined in the following manner.

As simple molecules interact by London dispersion forces having short range effect, the total potential energy can be replaced by the sum of the potential energies of the nearest-neighbour pairs. When random distribution of molecules at the lattice sites is assumed, the number of nearest-neighbour pairs is readily obtained as

$$N_{11} = \frac{z}{2} \frac{N^2}{N+N'} \quad (5)$$

The total potential energy is then given by

$$U^\circ = N_{11}\epsilon \quad (6)$$

where ϵ is the pair potential energy.

Although several different forms for the free volume have been published^{5,10)}, Henderson's approximation^{5,8)} seems best. This is the linear combination of the free volume of a molecule with all of its neighbouring sites occupied, v_f^0 , and that of a molecule with all of its neighbouring sites empty, ω ; that is

$$v_f = (1-\alpha)v_f^0 + \alpha\omega \quad (7)$$

where

$$\alpha = \frac{N'}{N+N'} \quad (8)$$

and

$$\omega = \frac{V}{N+N'} \quad (9)$$

The v_f^0 is in general considered as the free volume in the solid state. This volume, of course, is much less than the unit cell volume, ω . In view of the fact that the amplitude of a vibrating molecule in the solid state near the melting point is about 10% of the lattice distance, the magnitude of v_f^0 can be estimated as

$$v_f^0 \leq \omega \times 10^{-3} \quad (10)$$

On the other hand, the value of α can be given by the expression

* For instance, the ratio of critical volume to solid state volume is 3.2 for methane.

$$\alpha = \frac{V-V_0}{V} \quad (11)$$

At the critical region, the volume of the liquid is nearly three times larger* than that of the solid, V_0 . That is, the value of α near the critical region is about 0.7, so that the first term in Eq.(7) may be negligible in comparison with the second term. From the above discussion, the free volume can finally be written in the simple form

$$v_f = \alpha\omega \quad (12)$$

This equation may not cause serious error except near the solid-like high density region.

An equation of state based on the hole theory is derived by combining Eqs.(2) to (6) and Eq.(12). In carrying out the calculations, Eq.(3) was rewritten as

$$P = -\frac{1}{\omega} \left(\frac{\partial F}{\partial N'}\right)_T \quad (13)$$

because the change of volume is due to the change in number of holes. The equation of state then obtained is

$$P = \frac{1}{2} \frac{zN^2\epsilon}{\omega M^2} + \left(\frac{V_0}{V}\right) \frac{RT}{V-V_0} + \frac{RT}{V_0} \ln\left(\frac{V}{V-V_0}\right) \quad (14)$$

where $N+N'$ is denoted by M . In this equation, the characteristic parameters are the coordination number, z , the pair potential energy, ϵ , and the unit cell volume, ω . The value of the coordination number can hardly be determined for liquids. It is generally given by 6 to 12. The pair potential energy estimated by the force constant does not successfully represent the liquid behaviour quantitatively. So we tried to determine the characteristic properties along the saturation curve of the pure liquid. In this study the heat of vaporization and the volumetric data of the coexisting liquid and vapor were used. To avoid complication in dealing with Eq.(14), the coordination number and the pair potential energy were incorporated in the internal energy and then were related as

$$U^\circ = \frac{1}{2} \frac{zN^2}{M} \epsilon \quad (15)$$

From Eqs.(14) and (15), an equation of state is finally given by

$$P = \frac{U^\circ}{V} + \left(\frac{V_0}{V}\right) \frac{RT}{V-V_0} + \frac{RT}{V_0} \ln\left(\frac{V}{V-V_0}\right) \quad (16)$$

The characteristic parameters remaining unknown are now U° and V_0 . These were determined by the following procedure. In this treatment the equation of state derived here was assumed to be applicable to both liquid and vapor. First the initial value of V_0 was assumed and the internal energy was calculated for each phase by using the vapor pressure and the volumetric data of the saturated liquid and vapor. The internal energy change of vaporization is calculated as

Fig. 1 Internal energy change of vaporization for nitrogen

Fig. 2 Internal energy change of vaporization for methane

$$\Delta U = U_v^\circ - U_l^\circ \quad (17)$$

On the other hand, the experimental value of the internal energy change of vaporization is

$$\Delta U = \Delta H - P\Delta V \quad (18)$$

A value for V_0 which would suit ΔU from Eq.(17) to that from Eq.(18) was found by the iterative procedure. The value of V_0 finally determined and the internal energy change for molecules studied here are shown in **Figs. 1 to 3**. As shown in these figures, the internal energy changes of simple molecules can be well correlated by using the constant values of V_0 . For the sake of comparison, the calculated results for the internal energy change are illustrated with dotted lines when the values of V_0 were approximated by solid volumes. As shown in these figures, the value best fitted to ΔU is slightly larger than that from solid density. However, the present work seems

Fig. 3 Internal energy change of vaporization for carbon dioxide

Fig. 4 Internal energy curves for nitrogen, methane and carbon dioxide

to be satisfactory, because the internal energy change can be well represented by the constant value of V_0 , and its value is not far different from that of the solid. The profiles of the internal energies are shown in **Fig. 4**. These curves are represented as a function of volume from liquid region to vapor region through the critical points.

2. Extension to Binary Mixtures

Theoretical consideration of the thermodynamics of liquid mixtures contributes to a fundamental understanding of molecular behaviour in solutions and is of direct use in the prediction and correlation of

Fig. 5 Orthobaric density for the carbon dioxide-methane system at 0°C

physical properties of mixtures.

In this study we discussed the P-V-T-X relations around the phase boundary of simple liquid mixtures consisting of super-critical components. The CO₂-CH₄ and the CO₂-N₂ systems were studied. The saturation pressures of the binary systems were calculated by using Eq.(16) with the aid of the combining rules, described below, for two characteristic parameters, U° and V_0 .

2-1. Combining rule for U°

The internal energies of both liquid and vapor mixtures were evaluated by the expression:

$$U_m^\circ = x_1^2 U_1 + 2x_1 x_2 U_{12} + x_2^2 U_2 \quad (19)$$

where U_i is the internal energy of i -th component in a solution. It was assumed that U_i could be given by the internal energy of the pure component at the same volume as that of the mixture in question; that is,

$$U_i = U_i^\circ(V_m) \quad (20)$$

where $U_i^\circ(V)$ is given in Fig. 1 as a function of volume. The internal energy between unlike molecules, U_{12} , was given by

$$U_{12} = m_U \sqrt{U_1 U_2} \quad (21)$$

where m_U is the factor to correct the deviation from the geometric mean. Based on the well-known London formula^{10,17)}, the correction factor, m_U , will have the following physical meaning

$$m_U = \frac{2\sqrt{I_1 I_2}}{I_1 + I_2} \frac{2^6 \sigma_1^3 \sigma_2^3}{(\sigma_1 + \sigma_2)^6} \quad (22)$$

where I is the ionization potential and σ is the collision diameter. Eq.(22) shows that m_U is expected to be always less than unity.

2-2. Combining rule for V_0

The following approximation was used for the V_0 of a mixture

$$V_0 = x_1^2 V_{01} + 2x_1 x_2 m_V \sqrt{V_{01} V_{02}} + x_2^2 V_{02} \quad (23)$$

where m_V is an essentially empirical factor to fit Eq.(16) to actual liquid mixtures. This is considered to be due to the packing manner of unlike molecules.

Fig. 6 Orthobaric density for the carbon dioxide-nitrogen system at 0°C

The correction factors m_U and m_V cannot be independently determined from the experimental P-V-T-X relations. The requirements for each factor should be decided from the consideration of the features of the system.

2-3. Comparison of calculation with experiment

The pressures of the CO₂-CH₄ and the CO₂-N₂ systems were computed by using the experimental data for compositions, molar volumes and temperatures. As the critical volumes of these binary mixtures are less than those of the pure components¹⁾, the internal energy of the pure substance in the liquid region is used for each component in the vapor mixture near the critical point.

2-3-1 The CO₂-CH₄ system The values of V_0 of both components of this system are identical. Therefore, we assumed $m_V = 1$ and then the V_0 for this mixture became equal to that of each component. The factor, m_U , was found to be 0.955 by fitting the calculated results to those of the experiment, and it was shown to be almost independent of temperature and composition. The value mentioned above for m_U was smaller than 0.999 as estimated by Eq.(22). Representative comparison of the calculation with the experiment is demonstrated with success in Fig. 5. When m_U was assumed to be unity, the calculated pressure near the critical point was about 10% smaller than that of the experiment.

2-3-2 The CO₂-N₂ system In this system, the values of V_0 of both components are different. When m_V remained unity, the factor, m_U , became larger than unity to correlate the experimental results well. This fact contradicts Eq.(22). Therefore, a desirable value of m_V was sought by letting m_U equal unity; that is, the deviation from the experimental results was considered due to the fault of the combining rule for V_0 . The most desirable value of m_V was found to be 0.985 in this calculation. In Fig. 6 the calculated results are compared with the experimental data. They agree well. When m_V was assumed to be unity, the calculated pressure near the critical

point was about 5% larger than that of the experiment. The value of 0.985 for m_v was also suitable for other temperatures, 15°C and -20°C.

Conclusion

The hole theory was applied to simple liquids and their mixtures containing super-critical components. The equation of state derived here was shown to be successful in quantitatively representing the P-V-T-X relations of binary mixtures. Although the present treatment is restricted to simple molecules having no polar effects, it will provide an introductory study of expanded liquids and their mixtures.

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Nomenclature

F	= Helmholtz free energy
ΔH	= heat of vaporization
I	= ionization potential
k	= Boltzmann's constant
m_U	= correction factor used in combining rule for potential energy
m_v	= correction factor used in combining rule for unit cell volume
M	= number of lattice sites ($N+N'$)
N	= number of molecules
N'	= number of holes
N_{11}	= number of nearest-neighbour pairs
P	= pressure
Q	= configurational integral
R	= gas constant
T	= temperature
U°	= total potential (internal) energy of pure component
U_m°	= total potential (internal) energy of mixture
U_i	= molar internal energy of i -th component in mixture
V	= molar volume
V_m	= molar volume of mixture
v_f	= free volume of a molecule
v_f^0	= free volume of a molecule in solid state
V_0	= molar volume in solid state
x	= mole fraction
z	= coordination number

Z	= canonical partition function
Z_i	= factor in Z for internal degrees of freedom
Z_k	= kinetic energy factor in Z for translational degrees of freedom
<Greek letters>	
α	= hole fraction
ϵ	= pair potential energy
σ	= collision diameter
ω	= unit cell volume ($=V/(N+N')=V_0/N$)
<Subscripts>	
v	= vapor
l	= liquid

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