

RESEARCH NOTE

A simple theory for the partial molar volumes of a binary mixture

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A simple theory of mixtures (Snider, N. S. and Herrington, T. M. 1967, *J. chem. Phys.*, **47**, 2248) is applied to calculate the excess volumes and excess partial molar volumes of liquid argon–krypton mixtures at $T = 134.3\text{ K}$ and several pressures. This theory gives a good qualitative description of these quantities. In particular, the theory gives the correct sign and asymmetry for the excess volumes and partial molar volumes and, at high pressures, non-monotonic curves for the excess partial molar volumes. However, the theory predicts that these effects occur at higher pressures than are seen experimentally. As pointed out before (Hamann, S. D. 1992, *High Temp. High Press.*, **24**, 489), such classic theories as regular solution theory and ideal associated mixtures fail to give even the correct sign for these quantities.

1. Introduction

Hamann [1] has collected some of the experimental data for excess molar volumes and excess partial molar volumes of several binary systems and has compared these results with simulations [2] and such classic theories of mixtures as regular solution theory (RST) [3] and ideal associated mixtures (IAM) [4]. He finds that the simulations give reasonable results. This is not surprising as simulations are, apart from statistical problems, exact for the intermolecular potential used. However, Hamann finds that the RST and IAM give poor results. Often the RST and IAM values have an incorrect magnitude and even an incorrect sign. Both the RST and IAM approaches are now rather dated and the poor results that are obtained from these approaches are not too surprising. Of course, one could use just simulations. Indeed, simulations are likely to be the only viable approach for mixtures of complex fluids. However, this approach is likely to be unnecessary for the qualitative description of mixtures of simple fluids. In this paper we consider the simplest

modern theory of mixtures, that of Snider and Herrington [5]; we find that it gives reasonably good agreement with experiment.

2. Theory

The theory of fluids, and by extension, the theory of fluid mixtures, has made great progress during the last three decades. The simplest good theories of fluids and fluid mixtures are perturbation theories where the fluid is regarded as a fluid of hard spheres (or hard sphere mixtures) with the attractive forces having only a perturbing influence. The earliest such theory is that of van der Waals (vdW), where one writes

$$p = p_0 - \rho a. \quad (1)$$

In equation (1) p_0 is the pressure of a hard sphere system, ρ is the density, and

$$a = \sum_{i,j} x_i x_j a_{ij} \quad (2)$$

with

$$a_{ij} = -2\pi \int_{\sigma_{ij}}^{R_{ij}} u_{ij}(r) r^2 dr, \quad (3)$$

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where $u_{ij}(r)$ is the pair interaction potential for a pair of molecules of species i and j , respectively. The quantities σ_{ij} and R_{ij} are the effective molecular diameter and the cutoff of the potential, respectively.

In the original vdW theory, p_0 was approximated by a free volume argument that was valid only for the second virial coefficient. As a result, for years the vdW theory was thought only to be of pedagogical interest. However, three decades ago Longuet-Higgins and Widom [6] showed that equation (1) formed the basis for a reasonably satisfactory theory of fluids if a better expression for the hard sphere pressure, p_0 , is used. Snider and Herrington [5] extended this approach to fluid mixtures by using for p_0 a reliable expression for the pressure of a hard sphere mixture. This is the approach that we have used here.

We use the BMCSL [7] expression for p_0 . For most purposes, this expression gives an excellent description of the thermodynamics of hard sphere mixtures. In our opinion, this expression is written most conveniently in terms of the contact values of the hard sphere distribution functions, $g_{ij}(\sigma_{ij})$. Thus,

$$\frac{p_0 V}{NkT} = 1 + \frac{2\pi}{3} \rho \sum_{i,j} x_i x_j \sigma_{ij}^3 g_{ij}(\sigma_{ij}), \quad (4)$$

where x_i is the fraction of the molecules that are of species i , V is the volume, N is the total number of molecules, k is Boltzmann's constant, T is the temperature, and

$$g_{ij}(\sigma_{ij}) = \frac{1}{1 - \delta_3} + \frac{3\delta_2}{2(1 - \delta_3)^2} \left(\frac{\sigma_{ii}\sigma_{jj}}{\sigma_{ij}} \right) + \frac{\delta_2^2}{2(1 - \delta_3)^3} \left(\frac{\sigma_{ii}\sigma_{jj}}{\sigma_{ij}} \right)^2, \quad (5)$$

where

$$\delta_n = \frac{\pi}{6} \rho (x_1 \sigma_{11}^n + x_2 \sigma_{22}^n). \quad (6)$$

We assume that the hard sphere diameters are additive. Thus,

$$\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2. \quad (7)$$

In calculating the a_{ij} , we use the Lennard-Jones potential,

$$u_{ij} = 4\varepsilon_{ij}(y^{-12} - y^{-6}), \quad (8)$$

where $y = r/\sigma_{ij}$. Also we use $R_{ij} = 2.5\sigma_{ij}$ since, with this value of R_{ij} , the curve for liquid–vapour coexistence obtained from the above theory is similar to that obtained from simulations with the full Lennard-Jones potential. Obviously, this is a result of a cancellation of errors. Further we have assumed that

$$\varepsilon_{12} = \xi_{12}(\varepsilon_{11}\varepsilon_{22})^{1/2}. \quad (9)$$

We use $\xi_{12} = 0.98$ because the most accurate values for the excess heats of mixing of mixtures at low pressures are obtained with values of ξ_{12} very slightly less than unity [8].

Our procedure is to select first a temperature, pressure, and concentration. The theory requires the density as input. Therefore, we iterate until we find the density that corresponds to the chosen pressure. The excess volume of mixing and the excess partial molar volume are calculated from equations (13)–(15) of Hamann [1].

3. Results

Here we confine the application of this theory to an argon–krypton mixture as the theory outlined above is most likely to be useful for a mixture of simple liquids. We use $T = 134.3$ K as this is the temperature for which most of the experimental data [9] were obtained. We chose argon as species 1 and krypton as species 2. The conventional values [10] $\varepsilon_{11}/k = 119.8$ K, $\varepsilon_{22}/k = 171$ K, $\sigma_{11} = 3.405$ Å, and $\sigma_{22} = 3.60$ Å are used. It is convenient to express the values of the σ_{ii} as $N\sigma_{11}^3 = 23.78$ cm³ mol⁻¹ and $N\sigma_{22}^3 = 28.10$ cm³ mol⁻¹.

We have obtained results for the experimental pressures, $p = 10$ MPa, 20 MPa, 30 MPa, 50 MPa, and 70 MPa, and for the higher pressures 100 MPa, 150 MPa, and 200 MPa. For $p = 10$ MPa, we find the molar volumes of the pure species to be $V_1 = 39.50$ cm³ mol⁻¹ and $V_2 = 34.95$ cm³ mol⁻¹, respectively. The value for krypton is fairly close to the experimental value, $V_2 = 35.8$ cm³ mol⁻¹, but the argon value is appreciably larger than the experimental value, $V_1 = 35.5$ cm³ mol⁻¹. This is because the pure fluid version of the theory we have outlined works best in the low temperature and high volume regime. The temperature $T = 134.3$ K is near the critical temperature of argon. The theory presented here becomes less satisfactory as the critical point is approached. No doubt, the results could be improved by adjusting the parameters σ_{ij} , and ε_{ij} . However, we have preferred to have a purely predictive tool.

To save space, we compare our results with experiment only for $p = 10$ MPa and 70 MPa, the smallest and largest of the experimental pressures. In figure 1 we give our results for $p = 10$ MPa for the excess volumes and excess partial molar volumes. The excess partial molar volume is the quantity, $V_J - V_J^*$, that is the amount by which the partial molar volume, V_J , of a component J exceeds the molar volume, V_J^* , of pure component J at the same temperature and pressure. Note that the theoretical results have the correct sign. They are somewhat large in magnitude but are qualitatively correct. Further, note that the theoretical results have the correct asymmetry. Also both the experimental and theoretical par-

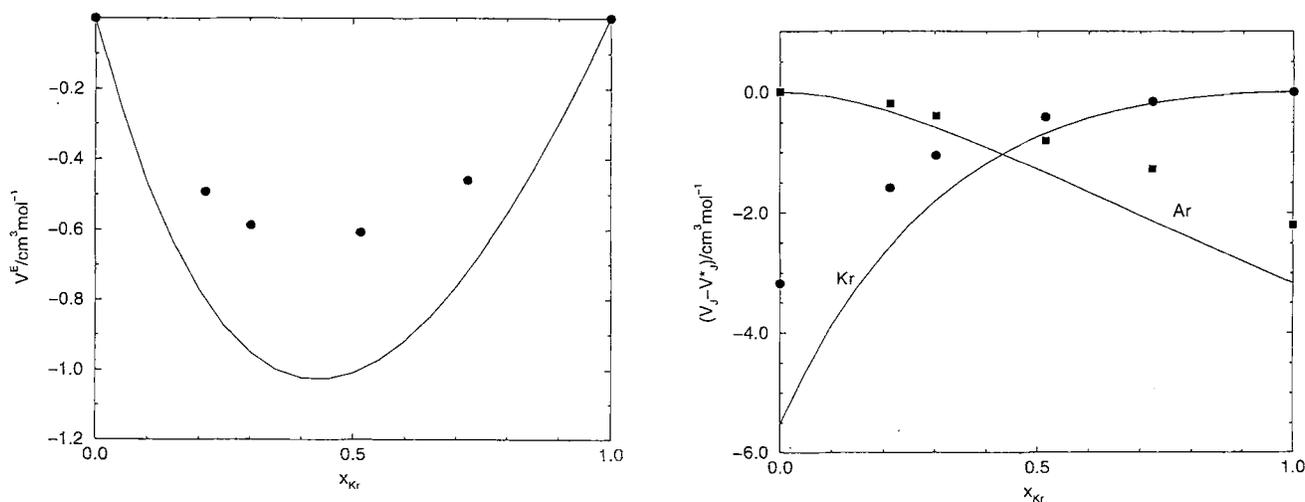


Figure 1. The excess volumes of mixing (a) and excess partial molar volumes (b) of an argon–krypton mixture at $T = 134.3 \text{ K}$ and at $p = 10 \text{ MPa}$. The points give the experimental results and the curves give the theoretical results. In (b), the squares are for argon and the circles are for krypton.

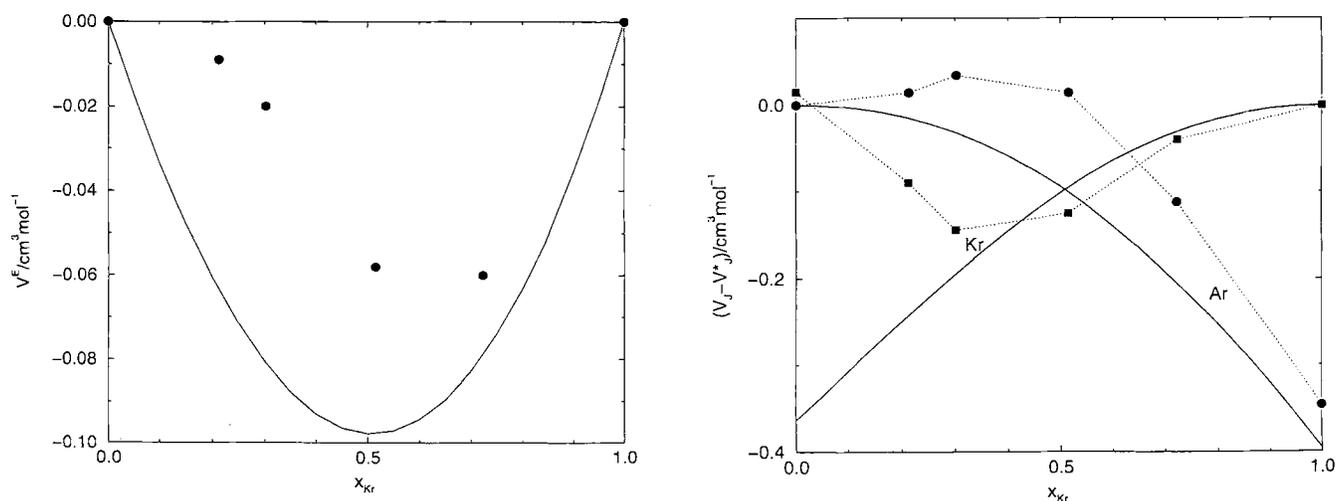


Figure 2. The excess volumes of mixing (a) and excess partial molar volumes (b) of an argon–krypton mixture at $T = 134.3 \text{ K}$ and at $p = 70 \text{ MPa}$. The points and solid curves have the same meaning as in figure 1. The dotted curves are straight lines joining the experimental points and are included only to aid the reader in connecting the points and are not meant to imply that the authors believe that the experimental curve is not smooth.

tial molar volumes are monotonic functions of the concentration.

The theoretical and experimental results for $p = 70 \text{ MPa}$ are compared in figure 2. The asymmetry in the experimental results has shifted. The theoretical results have moved in the same direction but not so far as the experimental results. The theoretical curves are nearly symmetric in the concentration. The experimental results for the partial molar volumes are no longer monotonic; there are even regions with positive values. The theoretical curves do not show this behaviour.

We have calculated results for pressures that exceed those obtained experimentally. These are shown in

figures 3 and 4. For $p = 100 \text{ MPa}$ and 150 MPa , the minimum in theoretical excess volume has now shifted to krypton concentrations that exceed 0.5 and the partial molar volume of krypton is now non-monotonic. Increasing the pressure to 200 MPa , yields partial molar volumes that are non-monotonic in both species and that have regions with positive values. These are similar to the experimental results at the lower pressure of $p = 70 \text{ MPa}$.

4. Summary

We have outlined a simple theory that accounts for the features of the experimentally observed results.

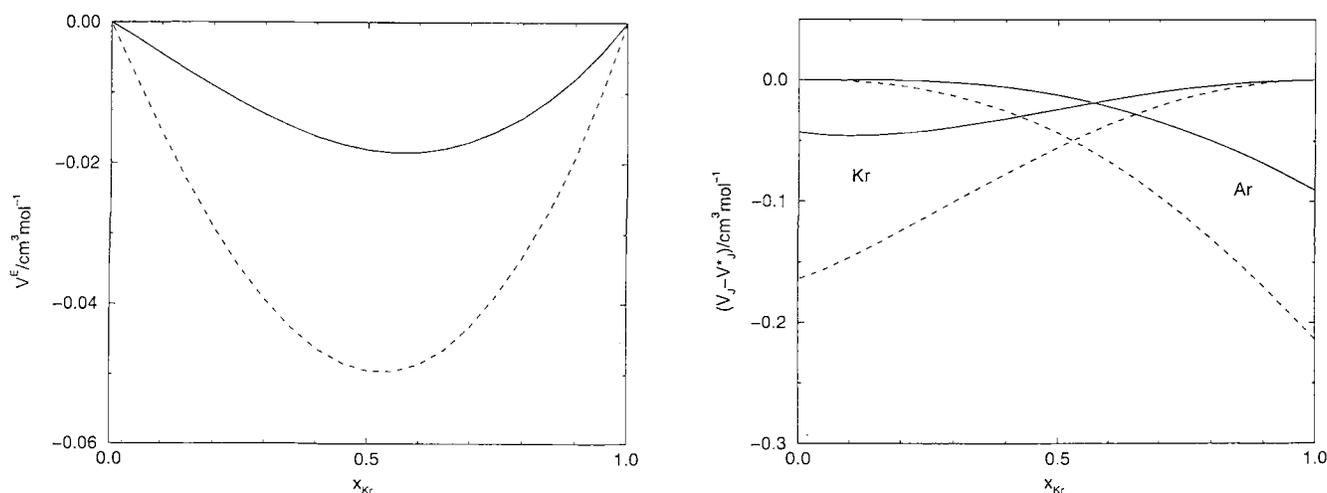


Figure 3. The excess volumes of mixing (a) and excess partial molar volumes (b) of an argon–krypton mixture at $T = 134.3$ K. The solid and broken curves give the theoretical results at 100 MPa and 150 MPa, respectively.

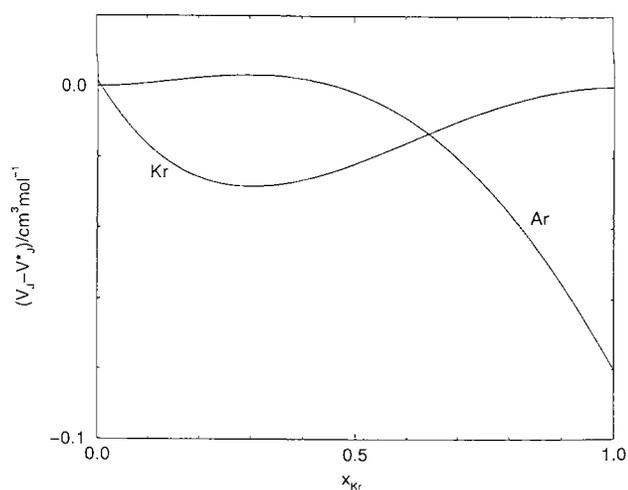


Figure 4. The theoretical excess partial molar volumes of an argon–krypton mixture at $T = 134.3$ K and $p = 200$ MPa.

However, the theory predicts the interesting features seen in the experimental partial molar volumes but at higher pressure than is the case experimentally. This undoubtedly is due to the simple nature of the theory.

The theory developed here is most appropriate for a mixture of simple fluids, such as argon and krypton. However, many of the features seen are found in the experimental results of other mixtures. Thus, the theory outlined here may have a greater application than just to mixtures of inert gases.

The theory is a natural extension of van der Waals theory. In fact, it is the theory that van der Waals might have formulated if he had had a knowledge of the properties of hard sphere mixtures. The theory given here is to be distinguished from the so-called van der Waals 1 (vdW1) theory. The vdW1 theory also has its origin in

the van der Waals theory. van der Waals gave a recipe for writing an equation of state in terms of the single component vdW theory. The vdW1 theory uses this recipe but allows the single component equation of state to come from any source, even a fit of experimental data. The vdW1 theory is a type of conformal solution theory. The vdW1 recipe is valid only for the second virial coefficient. In contrast the theory given here treats the hard core part of the problem, p_0 , at a high degree of accuracy and so should be preferable to the vdW1 theory.

Nevertheless, it is desirable to move beyond the theory outlined here. Perturbation theories, such as that of Barker and Henderson or Weeks, Chandler, and Andersen may not be too appealing in this instance because they give the free energy numerically. Application to this problem would require two numerical differentiations. This is possible but unattractive. Integral equations give the pressure directly and so only one differentiation is required. This may be an advantage. The application of more sophisticated theories will be explored in a later publication.

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