

## ISOTOPE EFFECTS ON FLUID-FLUID SEPARATION OF H<sub>2</sub>-He MIXTURES AT HIGH PRESSURES

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*The fluid-fluid phase separation of H<sub>2</sub>-He mixtures has been studied theoretically at 100 K. It is found that phase separation is promoted by heavier helium isotopes or by lighter hydrogen isotopes. This can be accounted for by a simple size analysis of the components.*

It is well-known that the location of phase transitions at high pressures depend strongly on intermolecular interactions. For example in the case of freezing, the solid phase occurs at lower density when the size parameter of the intermolecular potential increases and the freezing temperature increases with the energy parameter.<sup>1</sup> Fluid-fluid separation in binary mixtures is promoted by a large difference in size (or energy) parameter between the different species but it also depends on the interaction between the different species: demixing is favored by increasing size parameter and by increasing energy parameter of the unlike interaction.<sup>2</sup>

An interesting question is what is the effect of isotopic substitution. For He and H<sub>2</sub>, the freezing density decreases with decreasing mass as expected, due to the increased zero-point motion. However, the freezing pressure does not necessarily decrease, since at a given density the pressure increases with decreasing mass.<sup>3</sup> In this paper, the isothermal phase separation curves are investigated for mixtures of different isotopes of H<sub>2</sub> and He.

The calculations were done with the van der Waals one fluid approximation (vdW1f), that assumes the properties of the mixed fluid to be equal to those of a single, hypothetical, pure fluid (see ref. 4). The free energy of the effective fluid is calculated using thermodynamic perturbation theory.<sup>5</sup> Ree<sup>4</sup> has shown that these methods yield results that

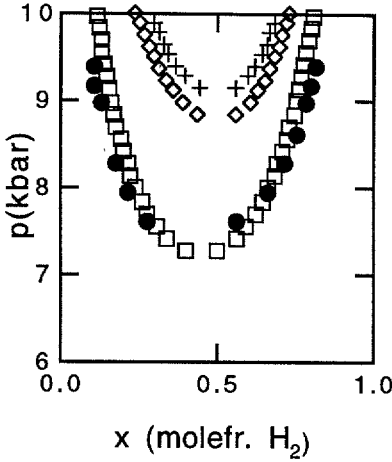


Figure 1. Phase separation curves of mixtures of  $^4\text{He}$  with  $\text{H}_2$  (squares),  $\text{D}_2$  (diamonds), and  $\text{T}_2$  (crosses) at 100 K in a pressure-composition diagram. The filled dots indicate the experimental results of Streett (ref. 9).

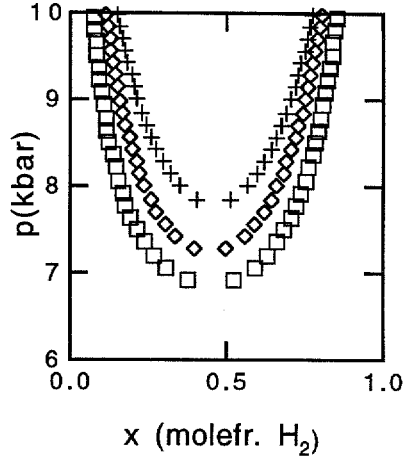


Figure 2. Phase separation curves of mixtures of  $\text{H}_2$  with  $^3\text{He}$  (crosses),  $^4\text{He}$  (diamonds), and a hypothetical  $^{1000}\text{He}$  (squares) isotope in a pressure-composition diagram at 100 K.

are in excellent agreement with computer simulations. Quantum effects are incorporated by using the Wigner-Kirkwood expansion up to second order in  $\hbar^2$  (the next term is of order  $\hbar^4$ ), which gives the following extra term:

$$F^{W-K} = \frac{\hbar^2 \rho}{24 \pi m k_B T} \int \nabla^2 \phi(r) g(r) d\vec{r} \quad (1)$$

with  $\rho$  the density,  $m$  the mass,  $T$  the temperature,  $\phi(r)$  the intermolecular potential, and  $g(r)$  the radial distribution function as a function of intermolecular distance  $r$ . The intermolecular potential of  $\text{H}_2$ ,  $\text{He}$ , and  $\text{H}_2\text{-He}$  was taken from refs. 6-8 and is of the Buckingham exponential-6 form:

$$\phi(r) = \frac{\varepsilon}{(\alpha - 6)} \left( 6 \exp \left( \alpha \left( 1 - \frac{r}{r^*} \right) \right) - \alpha \left( \frac{r^*}{r} \right) \right) \quad (2)$$

The well depth  $\varepsilon$ , the separation  $r^*$  of the well and the stiffness  $\alpha$  of the repulsive wall have been fitted to high-pressure thermodynamic properties. The good agreement between experimental results of Streett<sup>9</sup> on  $^4\text{He}\text{-H}_2$  and the calculations can be observed in fig. 1.

The phase separation curves were obtained by constructing double

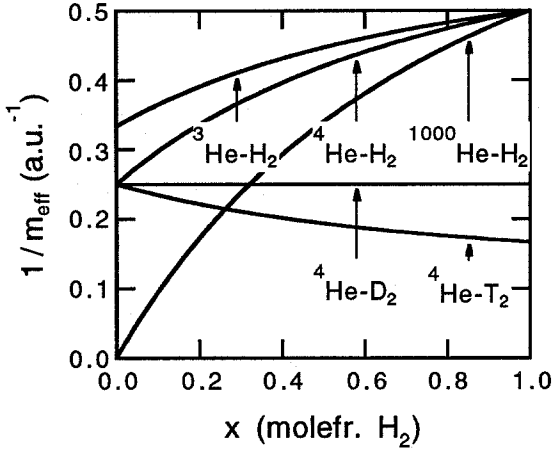


Figure 3. The inverse of the mass of the effective one-component system (given by eq. 3) for several isotopic He-H<sub>2</sub> mixtures as a function of the composition.

tangents on Gibbs' free enthalpy  $G$  versus composition  $x$  curves. The calculations were done at a temperature of 100 K, high enough to justify the convergence of the Wigner-Kirkwood expansion,<sup>4</sup> and low enough to obtain sizable differences between the isotopic pairs. In fig. 1 the results are shown for the mixtures of <sup>4</sup>He with H<sub>2</sub>, D<sub>2</sub>, and T<sub>2</sub>. At lower pressure the mixtures are completely miscible while the curves indicate the thermodynamic conditions under which the mixtures separate at higher pressure. It can be seen that the curves increase in pressure with increasing mass of the hydrogen component. Similar results are obtained for <sup>3</sup>He. Fig. 2 contains the phase separation curves for H<sub>2</sub> with <sup>3</sup>He, <sup>4</sup>He and a hypothetical <sup>1000</sup>He. Here, the curves decrease in pressure with increasing mass of the helium component. Again, a similar result was obtained for D<sub>2</sub> and T<sub>2</sub>.

It is obvious that the differences between the mixtures arise from the quantum part of the free energy (eq. 1) and more specifically from the behavior of the effective mass, since it was assumed that the isotopes have the same intermolecular interaction. The effective mass is defined as:

$$\frac{1}{m_{\text{eff}}} = \frac{1}{\alpha_{\text{eff}} \epsilon_{\text{eff}} (r_{\text{eff}}^*)^3} \sum_i \sum_j \left( \frac{1}{m_i} \epsilon_{i,j} \alpha_{i,j} (r_{i,j}^*)^3 \right) \quad (3)$$

where  $(i,j)$  labels the species (He,H<sub>2</sub>) and the other effective properties  $\epsilon_{\text{eff}}$ ,  $r_{\text{eff}}^*$ , and  $\alpha_{\text{eff}}$  are defined in a similar fashion.<sup>4</sup> In fig. 3, the inverse of  $m_{\text{eff}}$  as a function of composition for several mixtures has been plotted. This function is seen to be concave whenever the hydrogen isotope is

lighter than the helium one and convex whenever the opposite occurs. The convexity or concavity increases with increasing mass difference and is of course zero for the same masses ( $^4\text{He-D}_2$ ). A more convex  $1/m_{\text{eff}}$  (as for the series  $^4\text{He}$  with  $\text{H}_2$ ,  $\text{D}_2$ , and  $\text{T}_2$ ) will make the free energy more convex, thus effectively lowering the free enthalpy of the mixture and favoring mixing, which is indeed observed in fig. 1. On the other hand, a more concave  $1/m_{\text{eff}}$  ( $\text{H}_2$  with  $^3\text{He}$ ,  $^4\text{He}$ , and  $^{1000}\text{He}$ ) will raise the free enthalpy of the mixture and thus favor phase separation (see fig. 2).

It is also possible to give a simple physical interpretation of the behavior. The molecules become effectively larger when their masses decrease due to the increased zero-point motion. Therefore, if the mass of the hydrogen component increases, the 'size' will decrease. Since hydrogen is larger than helium, the difference between the species decreases, and this will favor mixing (see fig. 1). On the other hand, if the helium component becomes heavier, its 'size' will also decrease, but this will increase the difference between the components and favor demixing, as seen in fig. 2.

Of course, the behavior predicted here remains to be studied experimentally.

### ACKNOWLEDGMENTS

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