International Journal of Thermophysics, Vol. 10, No. 1, 1989

Phase Behavior of Mixtures at Very High Pressures[1]

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The invention of the diamond anvil cell (DAC) has been an enormous stimulus to high-pressure research. This technique has only recently been used to investigate the behavior of binary systems, probably because of the extra experimental problems which arise in the study of mixtures. It will be shown that a variety of aspects of the behavior of the mixture can, nevertheless, be studied under extreme conditions. Although the first investigations were carried out only recently, some very interesting results have already been obtained. A variety of two-components systems has been studied, e.g., He–Kr, Ne–Xe, He–H_2, NH_3–H_2O, and N_2–He_2. Some of these results are discussed. Finally, a comparison is made between experimental results and theoretical calculations.

KEY WORDS: diamond anvil cell; high pressure; mixtures; phase equilibria; solutions.

1. INTRODUCTION

The study of the properties of matter at high density was stimulated considerably by the invention of the diamond anvil cell (DAC) and the development of the ruby pressure scale. Application of these techniques to mixtures was delayed by more than 10 years, but this field of research is now growing rapidly. One of the reasons for this rapid growth may be that the majority of research in the field of mixtures is concerned with the study of technically important multicomponent systems. For most applications, a pressure range of a few kilobars is sufficient. It is, however, very difficult to give an accurate theoretical description of the phase behavior of mixtures,

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[1] Invited paper presented at the Tenth Symposium on Thermophysical Properties, June 20–23, 1988, Gaithersburg, Maryland, U.S.A.

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even at these relatively low pressures. It is now recognized that the study of pure substances at high pressures not only reveals a wealth of new and interesting phenomena but affords better insight into the behavior of matter, also at lower pressures. There is no reason to believe that the same will not also be true for multicomponent systems.

The purpose of this paper is to demonstrate that the study of mixtures under extreme conditions is very interesting and that a theoretical description for at least the simple mixtures is possible with reasonable accuracy. Moreover, it will be shown that a variety of phenomena can be studied with the modern techniques.

2. EXPERIMENTAL METHODS

The sample space in a diamond anvil cell can be filled easily with either a solid or a liquid. A permanent gas can also be distilled into the system without any problem. A mixture, however, cannot be transferred to the sample space in this way since, in general, the mixture will separate into two phases during the distillation process. It is not yet possible to determine the composition of an arbitrary mixture in a DAC at high pressure. The sample space must, therefore, be filled with a mixture of known composition. This problem has been solved in different ways by several investigators [1–3] and is not discussed further here.

Several methods have been used for the determination of phase transitions. A simple and powerful method is visual observation of the sample using a microscope system [4]. The temperature is varied at constant pressure, or vice versa, until a phase transformation takes place. These transformations can be observed easily in the case of fluid–fluid, fluid–solid, and fluid–fluid–solid phase equilibria. If more than one solid phase is involved, the use of rotating crossed polarizers is recommended [5].

In many cases, three-phase equilibria fluid–fluid–solid and fluid–solid–solid can be detected by plotting the pressure as a function of temperature. When the volume is kept constant, these phase transitions are accompanied by an abrupt change in pressure.

Loubeyre et al. [6] studied the system helium–hydrogen using Raman spectroscopy. They determined the change in the frequency of the H_2 vibron as a function of pressure at constant temperature and bulk composition. The frequency changes discontinuously at the phase transition.

Kimura et al. [8] developed a method for the determination of the ultrasonic velocity of the coexisting phases in a binary mixture using a piston-cylinder apparatus. The sound velocity changes discontinuously both at the transition from gaseous to liquid-like phases and at the transition from fluid to solid phases. Of course, any physical property which shows an abrupt change can be used to detect phase transitions. A more detailed description of these methods is given in Ref. 7.

3. EXPERIMENTAL RESULTS

We present some results of the systems helium–hydrogen and helium–nitrogen. Although these systems seem to be quite simple, it turns out that the phase diagram of helium–nitrogen is rather complicated and that helium–hydrogen exhibits some peculiar properties. A discussion of these systems will, therefore, give good insight into the possibilities and difficulties of studying mixtures in a diamond anvil cell.

3.1. Helium–Hydrogen

Measurements on the phase behavior of this system by Streett [9] revealed that at least up to 10 kbar, the critical line and the three-phase line fluid–fluid–solid diverge. From an experimental point of view, this makes helium–hydrogen a good candidate for the investigation of fluid–fluid equilibra at high pressure. Moreover, the phase diagrams of the pure systems are relatively simple. One might, therefore, expect a simple phase diagram for the helium–hydrogen system in the pressure range up to 100 kbar and at temperatures above 50 K. Yet the mixture exhibits seven different types of phase equilibria under these conditions.

The system has been studied up to about 100 kbar by Loubeyre et al. [6, 10] and by Schouten and van den Bergh [11–13]. Visual observation, Raman spectroscopy, and the p–T method were used to obtain the phase diagram. Although a combination of detection methods is very useful, all seven different phase equilibria can, in fact, be detected by visual observation.

Usually the results are presented in the form of isotherms or isobars. The experimental results, however, are obtained along lines of constant composition. The p–T projection of four lines of constant composition is given in Fig. 1. We show that these lines may also be useful for a theoretical interpretation. A typical plot of some isobars is given in Fig. 2, which shows that the temperature range for the existence of fluid–fluid equilibrium increases from about 20 K at 25 kbar to about 40 K at 75 kbar. This suggests that the fluid–fluid region will persist up to very high pressures.

The general shape of the isotherms given in Refs. 6 and 13 is the same, yet there are some marked differences which need further experimental verification. For example, Loubeyre et al. reported a cusp in the helium-

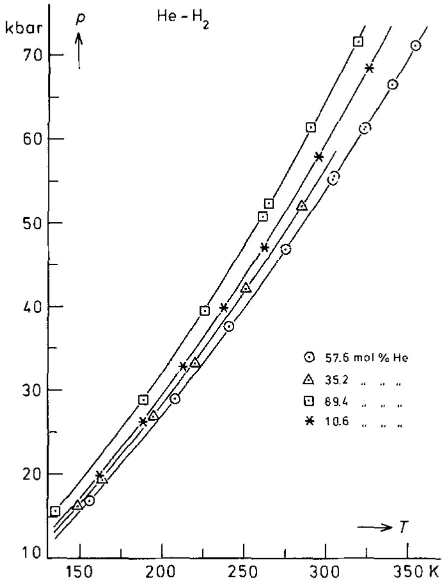

Fig. 1. p–T projection of some lines of constant composition in the system He–H_2.

rich fluid branch of the isotherms which is not present in the work of van den Bergh et al. This may have important consequences for the behavior of the system at very high pressures. Other differences concern the curvature of the line representing the equilibrium between a hydrogen-rich fluid and solid hydrogen and, moreover, the composition of the hydrogen-rich fluid at the three-phase line.

It is worth mentioning that critical phenomena can also be studied in a diamond anvil cell. When the temperature in an inhomogeneous mixture with critical bulk composition is increased slowly, the meniscus will first straighten and then appear as a broad dark band. Large fluctuations have been observed within this band. Critical demixing is obtained starting with a homogeneous mixture and decreasing the temperature slowly. Critical fluctuations will then appear throughout the whole sample space.

Another important point is the solubility of gases in solids. If there is any solubility of helium in solid hydrogen, it must be a very small amount. Experiments have been performed with a mixture containing only 3 mol% helium. At low temperatures and high pressures the mixture separates into a helium-rich fluid phase and a solid consisting predominantly of hydrogen. This means that the solubility of helium in hydrogen is less than 3%. In

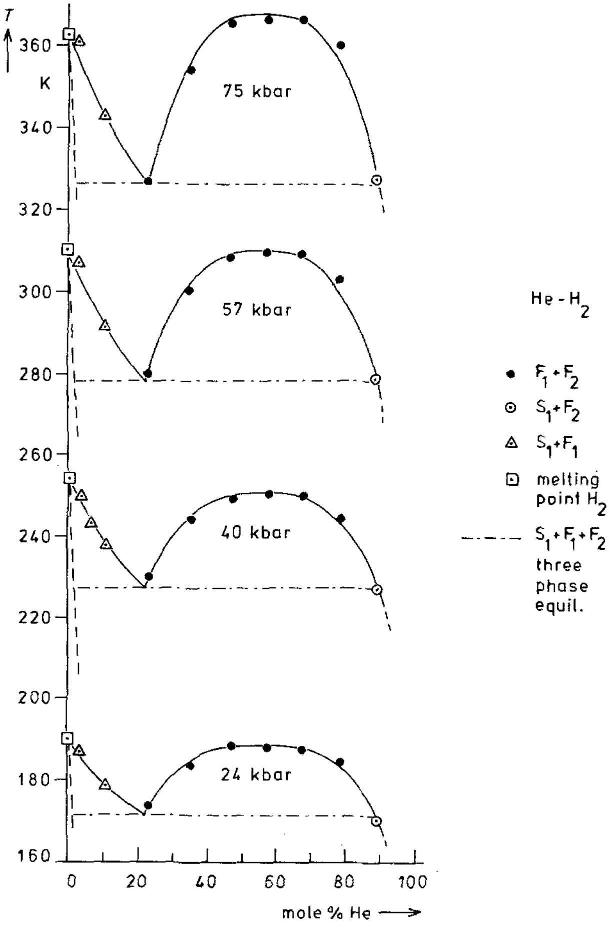

Fig. 2. Isobars in the system He–H_2.

order to be able to draw definitive conclusions, experiments should be carried out in a range of pressures and temperatures.

Streett [9] suggested that density inversions might occur between the hydrogen-rich fluid and solid hydrogen (although pure liquid hydrogen is less dense than solid hydrogen along the melting line) if the fluid contains 15 mol% helium. Experiments have been carried out with mixtures of different bulk compositions [12]. It turns out that a few percent of helium is sufficient to realize a complete inversion of the densities. At the three-phase line, the solid floats on top of the hydrogen-rich liquid, which in its turn, floats on top of the helium-rich gas. With low helium concentrations, equilibrium exists only between a solid and a fluid, in which case the solid floats on top of the fluid.

On the basis of the above results, some conclusions can be drawn regarding the models for the giant planets Jupiter and Saturn. These conclusions are presented in Section 4.2.

3.2. Helium–Nitrogen

The phase diagram of pure N_2 has been studied extensively up to about 200 kbar [14]. One triple point has been detected along the melting line at 99 kbar and 578 K. Below 100 kbar and above 200 K, only two different solid phases exist. Since helium does not show any phase transition in the experimental range considered here, one would expect a relatively simple phase diagram for helium–nitrogen.

The mixture has been investigated by Streett and Erickson [15] up to 10 kbar and by van den Bergh and Schouten [16] up to 100 kbar. The experimental results of both investigations are consistent. The solid lines on the left-hand side in Fig. 3 represent the experimental results for the critical line and the three-phase line. The critical line moves continuously to

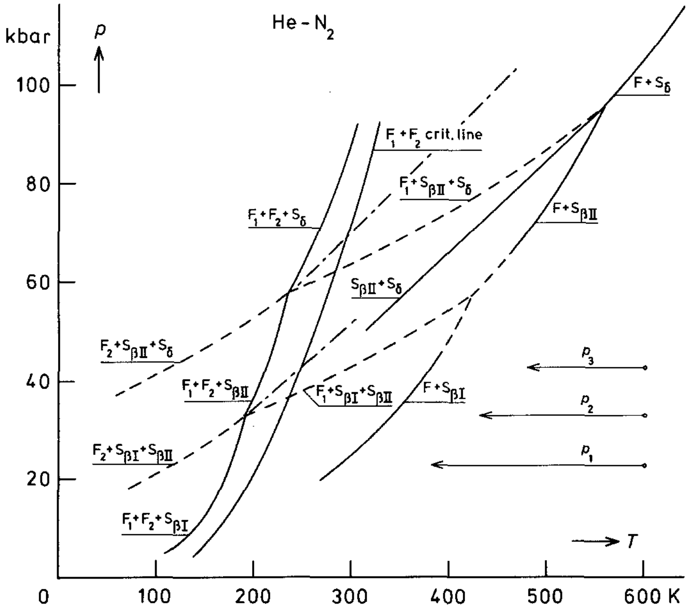

Fig. 3. Suggested phase diagram for the system helium–nitrogen. Solid lines have already been determined experimentally.

higher temperatures at high pressures without any tendency toward the occurrence of a maximum in temperature.

The most interesting point is the presence of two cusps on the three-phase line. A cusp on a three-phase line represents a quadruple point at which four phases are in equilibrium. From phase theoretical considerations, it follows that each quadruple point is the end point of four three-phase lines. Moreover, it can be shown that the angles between the three-phase lines are related to the possibilities for the metastable extensions of the three-phase lines. And last, but not least, phase theoretical arguments provide prescriptions for the possible two-phase equilibria in the p–T regions between the three-phase lines.

It was observed that along all three parts of the three-phase line, two of the coexisting phases are fluids. Therefore, the third phase—the solid—must be different in the three equilibria. In pure nitrogen, however, only two different solids are present in this temperature and pressure range. Of course, one of the cusps should be connected directly to the triple point of nitrogen via a three-phase line, and a three-phase line in He–N_2 must

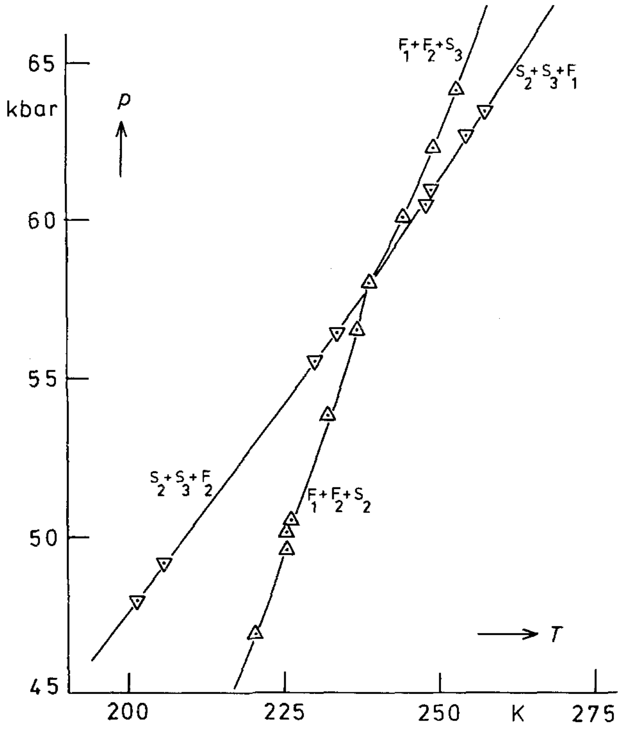

Fig. 4. Three-phase lines of He–N_2 near the quadruple point.

coincide with a two-phase line in pure N_2 if helium does not dissolve in solid N_2.

On the basis of these arguments, van den Bergh and Schouten [17] considered two possibilities for the phases diagram of helium–nitrogen, as indicated by the dash-dotted lines in Fig. 3. The conclusion is that either one of the two-phase lines in nitrogen has shifted considerably due to the solubility of helium in the solid or a new phase transition in nitrogen has been detected. A combination of these possibilities cannot be excluded.

Figure 4 shows that it is possible to investigate the behavior of a binary system under high pressures even in the neighborhood of a quadruple point. It should be pointed out that such an investigation is rather complicated due to the hysteresis in solid transitions, the large metastability range of fluids in the stable solid range, and the appearance of metastable fluid–fluid and even metastable fluid–solid A equilibria in the range of stable fluid–solid B equilibria. A more elaborate discussion of these phenomena is given in a paper by Vos et al. from this conference.

4. CALCULATION OF PHASE EQUILIBRIA AT HIGH PRESSURES

Most straightforward is the use of an equation of state for the calculation of the Gibbs free energy, but in general, the quantitative agreement with experiment is insufficient, particularly at high pressures.

In recent years, many modifications of perturbation theory have been developed quite successfully. In these theories, mixing rules have to be applied on the microscopic potential parameters which do have a physical meaning. We present a calculation based on perturbation theory and an as yet phenomenological description based on the Simon–Glatzel equation.

4.1. Correlation with the Simon–Glatzel Equation

The lines of constant composition at high pressures are plotted in a p–T diagram in Fig. 1. The shape of these lines is very similar to the shape of the melting lines of simple substances. This suggests a representation of these curves by the Simon–Glatzel equation, which describes the melting lines of pure substances remarkably well [18]. It should be pointed out, however, that the curves are very complicated at low pressures, i.e., near the pressure of the critical double point or lower. Therefore, the following description is valid only at higher pressures.

We have fitted the lines of constant composition in the range from 10 to 90 mol% helium by the Simon–Glatzel equation of the form $p = AT^C - B$, where p is given in kbar and T in K. The most important parameter is C, which regulates the steepness of the curves in a p–T plot. The values of the three parameters are given as a function of composition in Figs. 5a, b, and c. These values have been obtained by including the high-pressure data points of Streett [9]. The parameters can be represented by a quadratic expression of the form: $(x-x_0)=d(y-y_0)^{0.5}$, where d, x_0, and y_0 are constants, x is the composition in mole percent helium,

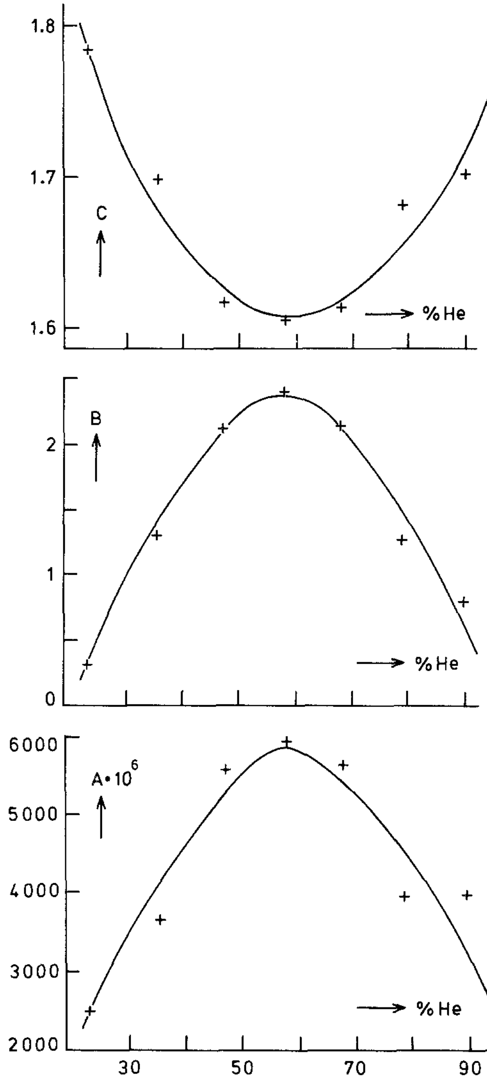

Fig. 5. Dependence on composition of the parameters *A*, *B*, and *C* in the *S–G* equation.

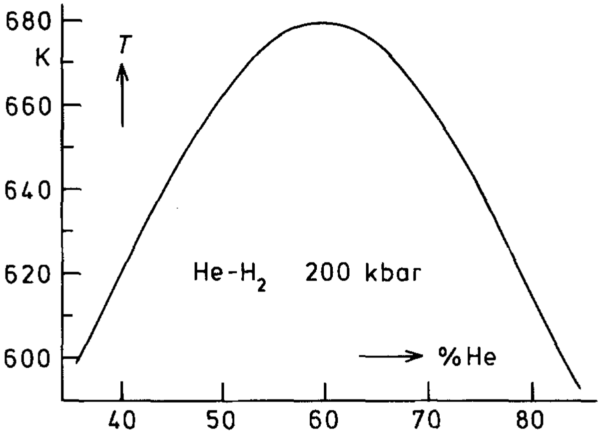

Fig. 6. Calculated isobar for He–H_2.

and y is the parameter A, B, or C. In this way, a simple analytic expression for the coexistence surface of the fluid–fluid equilibrium is obtained. This expression might be used to calculate the isobars or isotherms. A typical example is shown in Fig. 6, where the calculated isobar at 200 kbar is given.

The use of the Simon–Glatzel equation has some important advantages. Of course, the lines of constant composition can also be fitted with a series expansion in T, but it is well known that such a fit cannot be used for extrapolation outside the experimental range. The Simon–Glatzel equation, however, can be used for extrapolation to much higher pressures [18]. It is remarkable that the parameters A, B, and C are smooth functions of composition as shown in Fig. 5. Moreover, the extreme values for the parameters are obtained at the same composition (about 60 mol% helium), which is also the critical composition. An explanation for this behavior is not yet available. Experiments on the systems He–N_2 and He–CH_4 are in progress to investigate whether this behavior is more general.

4.2. Calculation with Perturbation Theory

Recently, Ree [19] has calculated the fluid–fluid phase behavior of He–H_2 up to 100 K and 10 kbar using the variational hard-sphere perturbation theory in combination with a modified Van der Waals one-fluid model for the mixture. Perturbation theory is most easily applied if the mixture is considered as an effective one-component system. It is well known that a two-parameter potential does not give a good description of the thermodynamic properties of substances at high pressures. If a three-parameter potential is used, an additional mixing rule should be developed. Usually, the exponential-6 (exp-6) potential is chosen, which is of the form

$$\phi(r)=\frac{\varepsilon}{\alpha-6}\{6\exp[[\alpha(1-r/r^*)]-\alpha(r^*/r)^6\}$$

The parameters ε and r^* represent, as usual, the attractive well depth and the range of interaction, respectively. The parameter α regulates the stiffness of the repulsion. Ree [20] developed a mixing rule for α of the form

$$\alpha=\sum_{i,j} x_i x_j \alpha_{ij}\frac{\varepsilon_{ij}}{\varepsilon}\frac{(r_{ij}^*)^3}{(r^*)^3}$$

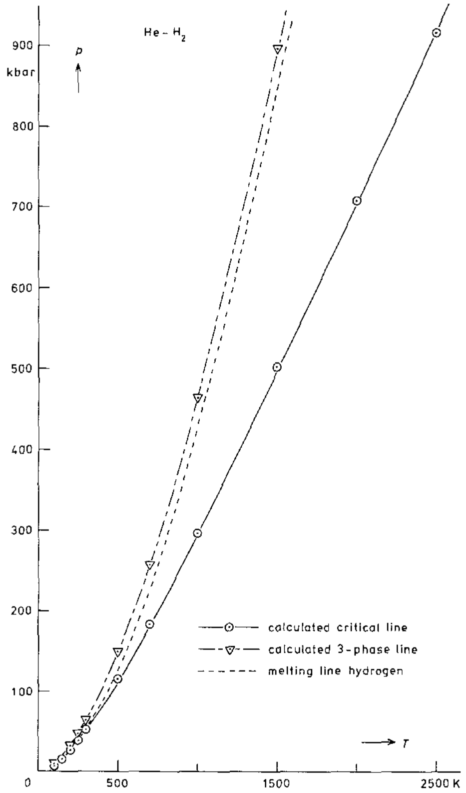

Fig. 7. Calculated critical line and three-phase line for He–H_2.

MacGowan et al. [21] have given a theoretical justification for this equation. For the parameters ε and r^* the usual mixing rules were applied.

van den Bergh and Schouten [22] have extended the work of Ree to describe their experimental data up to 75 kbar. On the basis of these results, they predicted the phase behavior of He–H_2 up to 1 Mbar and 2500 K. In Fig. 7 the calculated p–T diagram of He–H_2 is presented for pressures up to 1 Mbar. The agreement with experimental data up to 75 kbar is reasonable. A few important conclusions can be drawn with respect to the existing models for the atmosphere of Jupiter and Saturn. These models suggest that the envelope of Jupiter and Saturn, consisting mainly of 90 mol% H_2 and 10 mol% He, is gaseous up to pressures of 2 Mbar and temperatures of 8000 K. At higher pressures (and temperatures) solid or liquid (metallic) hydrogen will appear. However, extrapolation of the critical line and the three-phase line in Fig. 7 shows that at 2 Mbar the critical temperature is about 5000 K and the triple-point temperature about 3000 K. According to perturbation theory, therefore, the homogeneous gaseous envelope will not separate into two phases at 8000 K and 2 Mbar. In fact, since the experimental slope of the lines is slightly higher than the calculated ones in the range up to 75 kbar, we expect the above-mentioned temperatures to be upper limits. Even if a phase transformation takes place, the phase density inversions, as mentioned above, will prevent the formation of a core of solid hydrogen. These conclusions are valid only if the system is molecular. Theoretical calculations suggest that,

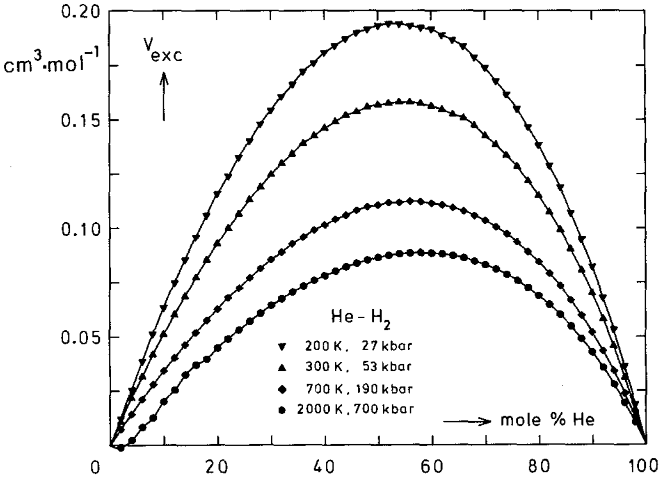

Fig. 8. Calculated excess molar volume of He–H_2 as a function of composition.

at about 3 Mbar, liquid or solid metallic hydrogen may be the stable phase, but this has not yet been confirmed by experiment. An increased solubility in the metallic phase could prevent phase density inversions and explain the depletion of helium in the outer layers of the atmospheres.

Under these extreme pressures, the excess volume is an important quantity. It determines largely whether or not a system will show phase separation. In Fig. 8 the calculated excess volume is plotted as a function of composition for a few pressures and temperatures. It is interesting to note that, e.g., for a mixture with 60 mol% helium, the relative value of the excess volume with respect to the molar volume is nearly constant, namely, 2.5 %.

Young et al. [23] reported that the hard-sphere packing fraction $\eta = \pi d^3 \rho / 6$ (where d is the hard-sphere diameter and ρ the density) is nearly constant ($\eta = 0.44$) along the melting line of helium and nitrogen. However, the melting pressure is very sensitive to small variations in η. van den Bergh and Schouten [22] modified this principle in the following way for mixtures. At each temperature, the packing fraction of helium and hydrogen at the melting line was calculated using perturbation theory. It was then assumed that the value of η varied linearly along the freezing line of the mixture at constant temperature: $\eta(x) = \eta(0) + x[\eta(1) - \eta(0)]$. The slope of the freezing line with $\eta = \eta(x)$ differs somewhat from the slope with $\eta =$ constant and is in better agreement with experiment.

ACKNOWLEDGMENT

This is the 356th publication of the Van der Waals Laboratory.

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