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D. Dimitrelis and J.M. Prausnitz

December 1985

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**Comparison of Two Hard-Sphere Reference Systems  
for Perturbation Theories for Mixtures**

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## Abstract

The Carnahan-Starling equation of state for hard spheres can be extended to mixtures using either a one-fluid theory or the generalization of the scaled-particle or the Percus-Yevick theory proposed by Boublik and by Mansoori and coworkers, respectively. (These two generalizations are identical). The two reference systems are combined with a perturbation term of the van der Waals form; they are then used to correlate the phase behavior of binary mixtures of nonpolar molecules differing significantly in molecular size. In each case, one adjustable binary parameter ( $a_{12}$ ) is used to correlate vapor-liquid equilibria over the entire composition range. Predicted Henry's constants and liquid densities for the saturated mixture are compared with experiment. The Boublik-Mansoori hard-sphere-mixture equation is superior, especially in the dilute region.

## Introduction

When we try to describe quantitatively the thermodynamic properties of a real system, the conventional procedure is first to idealize the system, that is, to abstract from reality the primary essential features while neglecting secondary characteristics. The idealized system, often called the reference system, is described quantitatively using some theory with well-defined assumptions. Corrections are then added to account for differences between the real and the idealized system; these corrections, called perturbations, are often based on semitheoretical models. The better the reference system, the lower the magnitude and complexity of the perturbation term needed to represent highly nonideal mixtures. For correlation and prediction of phase behavior, an oft-used reference system is a hard-sphere mixture.

While recent literature has given much attention toward refining the perturbation term, relatively little attention has been given to the reference term. In other words, most recent literature has focussed on the tail, rather than the dog. In this work we reverse that procedure. We use a very simple perturbation term, focussing attention on two possible reference terms.

Based on the Percus-Yevick theory for hard spheres, Carnahan and Starling (1969) proposed for the compressibility factor  $Z$  of a system of equi-sized hard spheres

$$Z^{CS} = \frac{P}{\rho RT} = \frac{1 + \xi + \xi^2 - \xi^3}{(1 - \xi)^3} \quad (1)$$

where superscript CS denotes Carnahan-Starling and reduced density  $\xi$  is given

by

$$\xi = b\rho/4 . \quad (2)$$

Here  $\rho$  is the molar density and  $b$  is the van-der-Waals covolume parameter;  $P$  is the pressure,  $R$  is the gas constant and  $T$  is the absolute temperature. As usual,

$$b = \frac{2}{3} \pi N_A \sigma^3 \quad (3)$$

where  $N_A$  is Avogadro's number and  $\sigma$  is the hard-sphere diameter.

A common method for extension to a mixture of hard spheres is provided by the one-fluid-theory mixing rule. In that event, Equation (1) is used with

$$b = \sum_{i=1}^m \sum_{j=1}^m x_i x_j b_{ij} \quad (4)$$

where  $m$  is the number of components in the mixture and  $x$  is the mole fraction. For the cross-parameter  $b_{12}$  we use the cube-root combining rule<sup>1</sup>

$$b_{12} = \left( \frac{b_1^{1/3} + b_2^{1/3}}{2} \right)^3 . \quad (5)$$

Working independently and following somewhat different phenomenological arguments based on scaled-particle and on Percus-Yevick theory respectively, Boublik (1970) and Mansoori et al. (1971) derived the following expression for

<sup>1</sup>In Appendix II we compare the cube-root with the arithmetic-mean combining rule.

the compressibility  $Z$  of a mixture of hard spheres<sup>2</sup>

$$Z^{BM} = \frac{1 + \left(\frac{3DE}{F} - 2\right)\xi + \left(\frac{3E^3}{F^2} - \frac{3DE}{F} + 1\right)\xi^2 - \frac{E^3}{F^2}\xi^3}{(1 - \xi)^3} \quad (6)$$

where superscript BM denotes Boublik-Mansoori and where

$$b = \frac{2}{3} \pi N_A F \quad (7)$$

with

$$F = \sum_{i=1}^m x_i \sigma_i^3 \quad (8)$$

$$E = \sum_{i=1}^m x_i \sigma_i^2 \quad (9)$$

$$D = \sum_{i=1}^m x_i \sigma_i \quad (10)$$

For mixtures of equi-sized spheres, the Boublik-Mansoori form is identical to that of Carnahan and Starling. However, for other mixtures there exists an appreciable difference, as illustrated in Figure 1 for an equimolar binary mixture.

We compare the Carnahan-Starling One-Fluid (CS) and the Boublik-Mansoori (BM) reference systems. We base our comparison on experimental data for the

<sup>2</sup>In Appendix I we give a convenient expression for the fugacity coefficient for the Boublik-Mansoori form.



phase behavior of mixtures of nonpolar molecules that differ significantly in molecular size. We examine mixtures for which the intermolecular attractive forces can be reasonably modelled by a van der Waals perturbation term, e.g. mixtures containing simple fluids or hydrocarbons.

### Procedure

For reduction of experimental vapor-liquid-equilibrium (VLE) data we use the equation of state

$$z = z^{\text{ref}} - \frac{a(T,x) \cdot \rho}{RT} \quad (11)$$

where

$$a(T,x) = \sum_{i=1}^m \sum_{j=1}^m x_i x_j a_{ij}(T) . \quad (12)$$

We introduce binary parameter  $k_{12}$  to correct for small deviations from the geometric-mean combining rule for the attractive-force cross coefficient

$$a_{ij}(T) = \sqrt{a_i(T)a_j(T)} (1 - k_{ij}) . \quad (13)$$

While the van der Waals covolume parameter  $b$  is here taken as temperature independent, the attractive-force parameter  $a$  depends on temperature according to the convenient function

$$a_i(T) = \frac{R^2 T_{c,i}^2}{P_{c,i}} \frac{a_i^{(0)} + a_i^{(1)} \frac{T}{T_{r,i}}}{1 + a_i^{(2)} \frac{T^2}{T_{r,i}^2}} \quad (14)$$

where  $a_i^{(0)}$ ,  $a_i^{(1)}$  and  $a_i^{(2)}$  are empirical coefficients. Also, we define  $b_i^{(0)}$ :

$$b_i = \frac{R T_{c,i}}{P_{c,i}} b_i^{(0)} \quad (15)$$

Here subscript c refers to the critical point and

$$T_r = \frac{T}{T_c} \quad (16)$$

Pure-component parameters are fitted to vapor-pressure, liquid-density and supercritical-density data. Binary VLE data (K-factors) are used to fix the temperature-independent binary interaction parameter  $k_{ij}$ . The numerical procedure is described elsewhere (Topliss, 1985, pp. 359-405). Table 1 gives all pure-component and binary parameters used here. In all cases, the optimal binary interaction parameter  $k_{ij}$  is larger for the case of the Carnahan-Starling One-Fluid reference system than for the Boublik-Mansoori reference system.

## Results and Discussion

Figure 2 shows calculated and experimental (Streett, 1967) phase equilibria for the system neon/argon at 129.93 K. The critical-volume ratio for this system is

$$\frac{v_{c,Ar}}{v_{c,Ne}} = 1.8 \quad .$$

For this system which contains molecules of similar size, there appears to be

no essential difference between the two reference systems. Both do poorly in the critical region, as expected from an equation of state of the van der Waals form.

The value of  $k_{12}$  obtained from VLE data in the concentrated region is used to predict Henry's constants for neon in argon and saturated-mixture liquid densities. As shown in Tables 2 and 3, the two reference systems give similar results.

Figure 3 shows calculated and experimental (Rogers and Prausnitz, 1971) phase equilibria for the system argon/neopentane at 323.15 K. The critical-volume ratio for this system is

$$\frac{v_{c_{\text{neo-C}_5\text{H}_{12}}}}{v_{c_{\text{Ar}}}} = 4.$$

For this system containing molecules with a larger size difference, the Boublik-Mansoori form correlates the liquid phase better than the Carnahan-Starling One-Fluid form. Both do equally well in the vapor but there is a significant difference in the liquid. Table 4 gives predicted and experimental (Rogers and Prausnitz, 1971) saturated-mixture liquid densities; deviations from experiment are similar for both reference systems.

Figure 4 shows calculated and experimental (7) phase equilibria for the system methane/n-decane at two temperatures, 310.93 and 510.93 K. The critical-volume ratio for this system is

$$\frac{v_{c_{\text{n-C}_{10}\text{H}_{22}}}}{v_{c_{\text{CH}_4}}} = 6.1$$

The Carnahan-Starling form fails to reproduce correctly the phase behavior for this system over a wide range of temperatures<sup>3</sup>.

Figure 5 shows predicted and experimental (Beaudoin and Kohn, 1967) Henry's constants for methane in n-decane. The predictions use binary parameter  $k_{12}$  as determined from binary VLE data in the concentrated region. Predicted Henry's constants, based on the Carnahan-Starling One-Fluid<sup>4</sup> form, are in serious error, especially at low temperatures.

Table 5 gives predicted and experimental (Reamer et al., 1942) saturated-mixture liquid densities for the system methane/n-decane. Results based on the Boublik-Mansoori form are significantly better than those based on the Carnahan-Starling One-Fluid form.

Figure 6 shows calculated<sup>5</sup> and experimental (Nichols et al., 1967) phase equilibria for the system hydrogen/n-hexane at 277.59 K (Note the discontinuity in scale in the horizontal axis). The critical-volume ratio for this system is

$$\frac{v_{c_{n-C_6H_{14}}}}{v_{c_{H_2}}} = 5.7$$

<sup>3</sup>In Appendix III we discuss the advantage of using Prigogine's parameter  $3c$  for modelling n-decane as a chain of spheres.

<sup>4</sup>In Appendix IV we show calculated Henry's constants for this system using the van der Waals reference system.

<sup>5</sup>For these calculations, the van-der-Waals covolume parameter  $b$  for hydrogen depends on temperature according to the relation

$$b(T) = \frac{RT_c}{P_c} \frac{b^{(0)} + b^{(1)}T_r^2}{1 + b^{(2)}T_r^2} \quad (17)$$

The Boublik-Mansoori form correlates the vapor-liquid equilibria for this highly asymmetric system significantly better than the Carnahan-Starling One-Fluid form.

Figure 7 shows predicted and experimental (Katayama and Nitta, 1976) Henry's constants for hydrogen in n-hexane; predictions based on the Carnahan-Starling One-Fluid form are in error by one order of magnitude at lower temperatures. These predictions also give a qualitatively incorrect temperature dependence.

Table 6 gives predicted and experimental (Nichols et al., 1967) saturated-mixture liquid densities for the system hydrogen/n-hexane. Results based on the Boublik-Mansoori form are significantly better than those based on the Carnahan-Starling One-Fluid form, especially at higher pressures.

The results shown above lend support to the computer-simulation studies of Shing and Gubbins (1982), comparing Henry's constants based on Monte-Carlo calculations for Lennard-Jones molecules with those based on van der Waals one-fluid theory. Shing and Gubbins (1982) systematically varied the molecular-size ratio  $0.5(\sigma_1 + \sigma_2)/\sigma_2$  holding the well-depth-parameter ratio  $\epsilon_{12}/\epsilon_2$  constant and vice versa (In this calculation  $\epsilon_{12} = \sqrt{\epsilon_1 \epsilon_2}$ ). They conclude that Henry's-constant predictions are more sensitive to differences in molecular size than to differences in energy.

Figure 8 follows from the work of Shing and Gubbins (1982). It shows Henry's constants for Lennard-Jones molecules with  $\epsilon_1 = \epsilon_2 = \epsilon_{12}$  as a function of the critical-volume ratio solvent/solute. The one-fluid theory shows large

deviations from the Monte-Carlo calculations for values of the molecular-size ratio  $0.5(\sigma_1+\sigma_2)/\sigma_2$  differing significantly from unity.

The shaded region in Figure 8 indicates the range of molecular-size ratio covered in this investigation. While the energy-parameter ratios were not constant, Shing and Gubbins conclusively show that these ratios are of minor importance in the prediction of Henry's constants. Within this limitation, the results of our work follow the findings of Shing and Gubbins. The Carnahan-Starling One-Fluid form (corresponding to the one-fluid calculations of Shing and Gubbins) underestimates Henry's constants as calculated from the Boublik-Mansoori form (corresponding to the Monte-Carlo calculations of Shing and Gubbins). The error is larger the further the critical-volume ratio  $v_{c2}/v_{c1}$  (or molecular-size ratio  $0.5(\sigma_1+\sigma_2)/\sigma_2$ ) departs from unity.

### Computing-Time Requirements

Computing-time requirements for the two reference systems are comparable. Solving for the density or calculating the fugacity coefficient (Topliss, 1985) with the Boublik-Mansoori form requires about 30% more CPU time than that required with the Carnahan-Starling One-Fluid form. This additional computing-time requirement is negligible compared to the CPU time required for the same operations using modern perturbation theories (Luedecke and Prausnitz, 1985); those theories require computing times about a factor of 10 larger than those used here.

## Conclusion

The calculations presented here suggest that the Boublik-Mansoori reference system and the Carnahan-Starling One-Fluid reference system correlate equally well the phase behavior of nonpolar binary systems of spherical molecules up to size ratios  $(\sigma_1/\sigma_2)^3$  of (about) 2. However, it appears that phase behavior of binary mixtures of molecules with size ratios greater than 2 can be correlated significantly better with the Boublik-Mansoori reference system. The difference between the two reference systems is particularly apparent when experimental data at high concentrations are used to predict Henry's constants.

**Nomenclature**

A	Helmholtz energy
a	attractive-force parameter
b	van der Waals covolume parameter
c	Prigogine's parameter
D,E,F	defined in Equations (8) through (10)
H	Henry's constant
k	binary interaction parameter (defined in Equation (13))
m	number of components
$N_A$	Avogadro's number
N	total number of moles
n	number of moles
P	pressure
R	gas constant
T	temperature
v	molar volume
x	mole fraction
Z	compressibility factor

**Greek letters:**

$\epsilon$	well-depth parameter
$\xi$	reduced density
$\rho$	molar density
$\sigma$	hard-sphere diameter
$\phi$	fugacity coefficient



**Subscripts:**

c        critical  
i        component i  
ij       interaction between components i and j  
r        reduced

**Superscripts:**

BM        Boublik-Mansoori  
CS        Carnahan-Starling One-Fluid  
CCS       Chain-Carnahan-Starling  
exp       experimental  
r        residual  
ref       reference  
(0)       0th coefficient etc. (see Equations (14), (15) and (17))  
~        reduced molar residual Helmholtz energy (see Appendix I)

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**Appendix I: Fugacity coefficient for the Boublik-Mansoori reference system.**

Following Topliss (1985, pp. 11-16), we express the fugacity coefficient  $\phi_i(\rho, T, x)$  for the Boublik-Mansoori reference system as

$$\ln \phi_i = \left( \frac{\partial (\tilde{N}\tilde{A})}{\partial n_i} \right)_{\rho, T, n_{j \neq i}} + (Z - 1) - \ln Z. \quad (I-1)$$

$\tilde{A}$  is the reduced molar residual Helmholtz energy  $A^F/NRT$ ,  $n_i$  is the number of moles of component  $i$  and  $N$  is the total number of moles. Residual is here defined with respect to a mixture of ideal gases at the same  $(\rho, T, x)$ .

The compressibility factor  $Z$  is given by Equation (6). The derivative<sup>6</sup> of  $\tilde{A}$  with respect to the number of moles of component  $i$  is

$$\left( \frac{\partial (\tilde{N}\tilde{A})}{\partial n_i} \right)_{\rho, T, n_{j \neq i}} = \tilde{A} + \left( \frac{D\tilde{A}}{Dx_i} \right)_{\rho, T, x} - \sum_{\substack{j=1 \\ (j \neq i)}}^m x_j \left( \frac{D\tilde{A}}{Dx_j} \right)_{\rho, T, x} \quad (I-2)$$

with

$$\tilde{A} = \frac{\frac{3DE}{F} \xi - \frac{E^3}{F^2}}{(1 - \xi)} + \frac{\frac{E^3}{F^2}}{(1 - \xi)^2} + \left( \frac{E^3}{F^2} - 1 \right) \ln(1 - \xi). \quad (I-3)$$

Writing  $\tilde{A}$  as a function of  $\rho$  and three parameters  $\beta_1=D$ ,  $\beta_2=E$ , and  $\beta_3=F$ , which in turn depend on mole fraction, i.e.

$$\tilde{A} = \tilde{A}(\rho, \beta_1 = D(x), \beta_2 = E(x), \beta_3 = F(x)),$$

<sup>6</sup>We use the differential operator  $(D/Dx_i)_x$ , to indicate differentiation with respect to  $x_i$  where all other  $x_j$  are held constant (Topliss, 1985, p. 12).

we can perform the differentiation

$$\left(\frac{D\tilde{A}}{Dx_1}\right)_{\rho, T, x'} = \sum_{\kappa=1}^3 \frac{\partial \tilde{A}}{\partial \beta_{\kappa}} \frac{\partial \beta_{\kappa}}{\partial x_1} \quad (\text{I-4})$$

with

$$\frac{\partial \tilde{A}}{\partial \beta_1} = \frac{\partial \tilde{A}}{\partial D} = \frac{\frac{3E\xi}{F}}{(1-\xi)} \quad (\text{I-5})$$

$$\frac{\partial \tilde{A}}{\partial \beta_2} = \frac{\partial \tilde{A}}{\partial E} = \frac{\frac{3D\xi}{F} - \frac{3E^2}{F^2}}{(1-\xi)} + \frac{\frac{3E^2}{F^2}}{(1-\xi)^2} + \frac{3E^2}{F^2} \ln(1-\xi) \quad (\text{I-6})$$

$$\begin{aligned} \frac{\partial \tilde{A}}{\partial \beta_3} = \frac{\partial \tilde{A}}{\partial F} = & \frac{\frac{\xi}{F} + \frac{E^3}{F^3}(2-\xi)}{(1-\xi)} + \frac{\frac{3DE}{F} \frac{\xi^2}{F} - \frac{E^3}{F^3}(2+\xi)}{(1-\xi)^2} + \\ & \frac{\frac{2E^3\xi}{F^3}}{(1-\xi)^3} - 2 \frac{E^3}{F^3} \ln(1-\xi) \end{aligned} \quad (\text{I-7})$$

The partial derivatives of the parameters  $\beta_{\kappa}$  with respect to mole fraction  $x_1$  of component 1 are

$$\frac{\partial \beta_1}{\partial x_1} = \frac{\partial D}{\partial x_1} = \sigma_1 \quad (\text{I-8})$$

$$\frac{\partial \beta_2}{\partial x_1} = \frac{\partial E}{\partial x_1} = \sigma_1^2 \quad (\text{I-9})$$

$$\frac{\partial \beta_3}{\partial x_1} = \frac{\partial F}{\partial x_1} = \sigma_1^3 \quad (\text{I-10})$$

The expressions for  $\xi$ ,  $D$ ,  $E$ , and  $F$  are given by Equations (2), (7), (8), (9),

and (10).

**Appendix II: Effect of combining rule for van der Waals covolume cross-coefficient  $b_{12}$ .**

Figure 9 shows calculated and experimental (Nichols et al., 1967) phase equilibria for the system hydrogen/n-hexane at 277.59 K. In addition to the Boublik-Mansoori form for the reference system, we present also results for the Carnahan-Starling One-Fluid form using two different combining rules for van der Waals covolume cross-coefficient  $b_{12}$ .

The first combining rule is

$$b_{12} = \left( \frac{b_1^{1/3} + b_2^{1/3}}{2} \right)^3 \quad (\text{II-1})$$

and the second combining rule is

$$b_{12} = \frac{b_1 + b_2}{2} . \quad (\text{II-2})$$

Equation (II-1) gives a much better representation of the phase behavior for this highly asymmetric binary system, in particular in the liquid region. Further, when Equation (II-2) is used, we obtain a physically unreasonable value for  $k_{12}$  of -0.38. This unreasonable  $k_{12}$  means that an unrealistic perturbation term is needed to compensate for a faulty reference system.



**Appendix III: Effect of Prigogine's parameter 3c on modelling chain-like molecules.**

Figure 10 shows calculated and experimental (Reamer et al., 1942) phase equilibria for the system methane/n-decane at 310.93 K. In addition to the Boublik-Mansoori form, we present results for the "Chain-Carnahan-Starling" form. Following the suggestion of Beret (1975), we modify the reference term, using Prigogine's parameter 3c, to take into account density-dependent rotational and vibrational degrees of freedom. The compressibility factor for the reference system becomes

$$z^{CCS} = 1 + c \frac{4\xi - 2\xi^2}{(1 - \xi)^3}. \quad (\text{III-1})$$

Following Donohue (1978), we use the following mixing rules for the reference system

$$\xi = bp/4 \quad (\text{III-2})$$

$$b = \sum_{i=1}^m x_i b_i \quad (\text{III-3})$$

and

$$c = \sum_{i=1}^m x_i c_i. \quad (\text{III-4})$$

The perturbation term is given by Equations (11) through (14).

For mixtures of small spherical molecules,  $c=1$  for every component; in

that event, Equation (III-1) reduces to Equation (1). For chain-like molecules (e.g. n-decane),  $c > 1$ .

Pure-component and binary parameters are obtained as described in the main body of this paper. For methane, since  $c=1$ , the values for the parameters are the same as those given in Table 1. For n-decane we obtain

$$\begin{aligned} a^{(0)} &= 0.61375 & b^{(0)} &= 0.14243 \\ a^{(1)} &= 0.000134 & c &= 1.26 \\ a^{(2)} &= 0.33333 \end{aligned}$$

Binary adjustable parameter  $k_{ij}$  is  $-0.09$ .

The value for  $c$  for n-decane may be lower than expected, probably because our perturbation term is of the simple van der Waals form and not scaled properly on a segmental basis as in the perturbed-hard-chain theory.

The Chain-Carnahan-Starling form correlates the phase behavior for the system methane/n-decane better than the original Carnahan-Starling One-Fluid form. This is not surprising, since a perturbed-hard-chain model for n-decane should represent the experimental data more accurately than the original Carnahan-Starling One-Fluid form. It is surprising, however, that even when parameter  $c$  is included, the Chain-Carnahan-Starling form is not as good as the Boublik-Mansoori form without  $c$ .

While tentative conclusions based on these results must be examined with additional calculations, they suggest that it may be worthwhile to use the

Boublik-Mansoori form as the starting point for perturbation theories for mixtures of large, chain-like molecules rather than the Carnahan-Starling One-Fluid form, as used in the past (Donohue and Prausnitz, 1978).

Appendix IV: Comparison with the van der Waals reference system.

Figure 11 shows predicted and experimental (Beaudoin and Kohn, 1967) Henry's constants for methane in n-decane. In addition to the Boublik-Mansoori and Carnahan-Starling One-Fluid forms for the reference term, we present results using the van der Waals reference term

$$z^{vdW} = \frac{1}{1 - 4\xi} \quad (IV-1)$$

Reduced density  $\xi$  is given by Equations (2), (4) and (5).

Pure-component and binary parameters for the van der Waals reference term are obtained as described in the main body of this paper; for the system methane/n-decane they are

	$a^{(0)}$	$a^{(1)}$	$a^{(2)}$	$b^{(0)}$
Methane	0.469	0.17557	0.3715	0.094161
<u>n</u> -Decane	0.72711	0.94746	1.305	0.084301

Binary adjustable parameter  $k_{1j}$  is -0.11.

The predictions of the van der Waals reference system are significantly worse than those from both the Boublik-Mansoori and the Carnahan-Starling One-Fluid forms. Further, they require an unreasonably low value for the covolume parameter  $b$  (Wong and Prausnitz, 1985).

**List of Table Captions:**

**Table 1:** Pure-component and binary parameters

**Table 2:** Percent deviations from experimental (Karasz and Halsey, 1958)  
Henry's constants for neon in argon

**Table 3:** Percent deviations from experimental (Streett, 1967) saturated-  
mixture liquid densities for the system neon/argon

**Table 4:** Percent deviations from experimental (Rogers and Prausnitz, 1971)  
saturated-mixture liquid densities for the system argon/neopentane.

**Table 5:** Percent deviations from experimental (Reamer et al., 1942) saturated-  
mixture liquid densities for the system methane/n-decane.

**Table 6:** Percent deviations from experimental (Nichols et al., 1967)  
saturated-mixture liquid densities for the system hydrogen/n-hexane.

Table 1

Pure-Component Parameters (Equations (14) and (15))

	$a^{(0)}$	$a^{(1)}$	$a^{(2)}$	$b^{(0)}$	$b^{(1)}$	$b^{(2)}$
Neon	0.50907	0.19059	0.333333	0.19154		
Argon	0.48936	0.16307	0.333333	0.17753		
Methane	0.49539	0.16199	0.333333	0.17841		
Neopentane	0.54047	0.070014	0.333333	0.16540		
<u>n</u> -Hexane	0.56831	0.030037	0.333333	0.16173		
<u>n</u> -Decane	0.60509	-0.045415	0.333333	0.15906		
Hydrogen <sup>7</sup>	0.16306	11.555	22.618	0.20556	0.041906	0.35725

Binary Parameter (Equation (13))

	$k_{12}^{BM}$	$k_{12}^{CS}$
Neon/Argon	0.12	0.13
Argon/Neopentane	0.12	0.14
Methane/ <u>n</u> -Decane	0.	0.02
Hydrogen/ <u>n</u> -Hexane	0.03	0.13

<sup>7</sup>For the temperature dependence of van der Waals covolume parameter  $b$  for hydrogen see Equation (17).

Table 2

T (K)	H <sup>exp</sup> (bar)	H <sup>BM</sup> (%-Dev)	H <sup>CS</sup> (%-Dev)
83.91	1118	8.5	3.9
86.11	1067	8.7	4.6
87.45	1021	10.6	6.7

Table 3

T (K)	P (bar)	$\rho^{\text{exp}}$ (mol/l)	$\rho^{\text{BM}}$ (%-Dev)	$\rho^{\text{CS}}$ (%-Dev)
110.8	100.7	31.7	0.	0.6
110.8	180.7	32.3	0.6	1.2
121.4	192.4	28.1	2.1	3.2

Table 4

T (K)	P (bar)	$\rho^{\text{exp}}$ (mol/l)	$\rho^{\text{BM}}$ (%-Dev)	$\rho^{\text{CS}}$ (%-Dev)
323.2	96.53	9.7	-4.5	-2.9
323.2	164.0	10.7	-5.6	-3.7
323.2	242.5	11.8	-7.6	-5.1

Table 5

T (K)	P (bar)	$\rho^{\text{exp}}$ (mol/l)	$\rho^{\text{RM}}$ (Z-Dev)	$\rho^{\text{CS}}$ (Z-Dev)
310.9	6.89	5.19	11.95	20.04
310.9	206.8	8.89	7.09	15.19
310.9	362.0	13.0	-5.38	-9.23
510.9	13.79	3.89	1.52	3.08
510.9	103.4	4.81	1.66	7.69
510.9	189.6	5.59	2.50	9.09

Table 6

T (K)	P (bar)	$\rho^{\text{exp}}$ (mol/l)	$\rho^{\text{RM}}$ (Z-Dev)	$\rho^{\text{CS}}$ (Z-Dev)
277.6	68.95	8.09	8.41	16.69
277.6	275.8	8.95	10.95	27.37
277.6	689.5	11.33	6.35	24.18
477.6	68.95	5.38	-6.13	-3.53
477.6	206.8	6.51	-1.08	4.45
477.6	344.7	7.78	1.67	6.43



**List of Figure Captions:**

**Figure 1:** Compressibility factor for an equimolar binary hard-sphere mixture.

**Figure 2:** Calculated and experimental vapor-liquid equilibria for neon/argon at 129.93 K.

**Figure 3:** Calculated and experimental vapor-liquid equilibria for argon/neopentane at 323.15 K.

**Figure 4:** Calculated and experimental vapor-liquid equilibria for methane/n-decane at 310.93 and 510.93 K.

**Figure 5:** Predicted and experimental Henry's constants for methane in n-decane.

**Figure 6:** Calculated and experimental vapor-liquid equilibria for hydrogen/n-hexane at 277.59 K.

**Figure 7:** Predicted and experimental Henry's constants for hydrogen in n-hexane

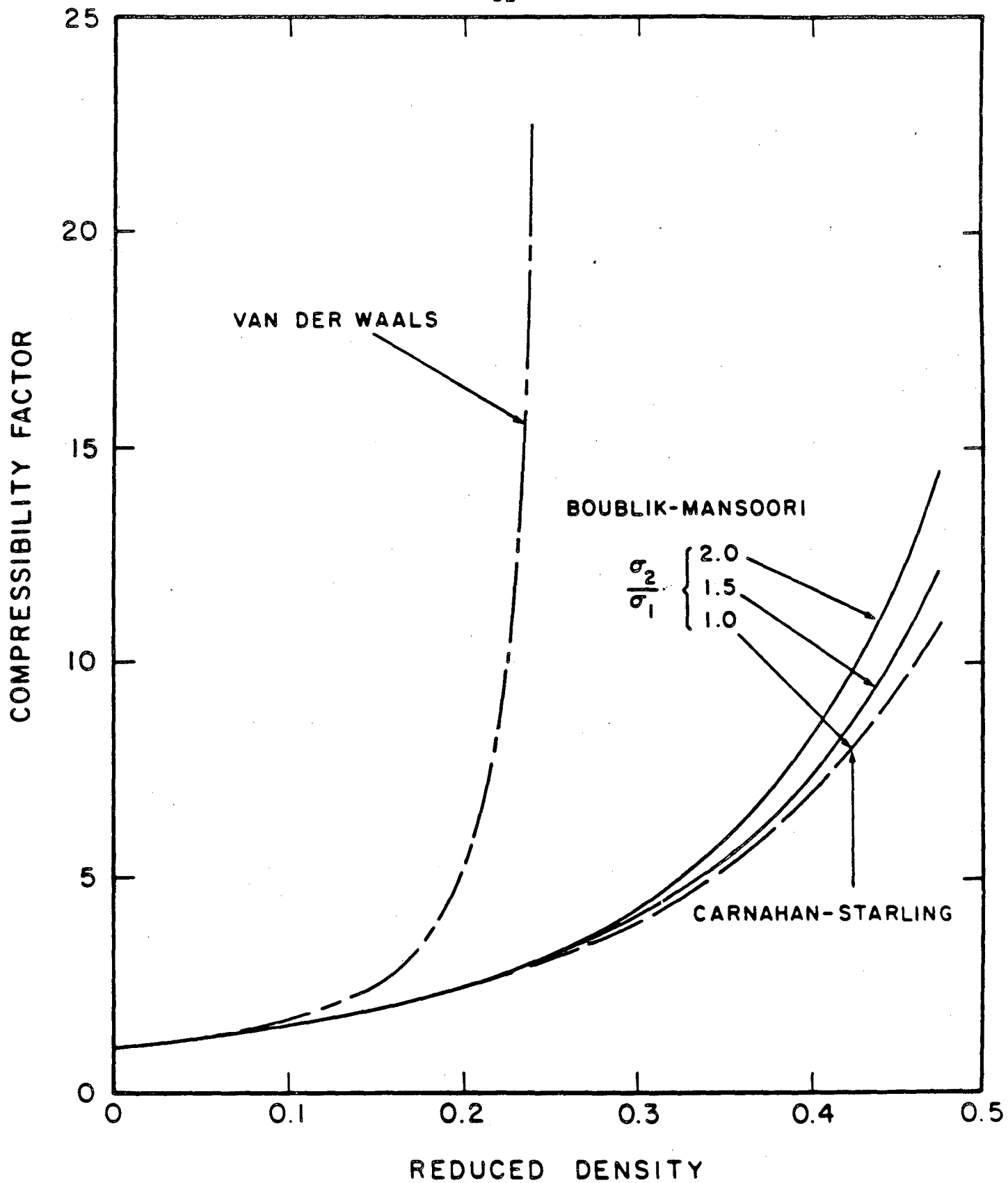
**Figure 8:** Henry's constants  $H_{1,2}$  for Solute 1 in Solvent 2 for Lennard-Jones (6,12) molecules. (Adapted from Shing and Gubbins, 1982)

**Figure 9:** Calculated and experimental vapor-liquid equilibria for hydrogen/n-hexane at 277.59 K. Effect of combining rule for van der Waals

covolume cross-coefficient  $b_{12}$

**Figure 10:** Calculated and experimental vapor-liquid equilibria for methane/n-decane at 310.93 K. Effect of Prigogine parameter  $3c$ .

**Figure 11:** Predicted and experimental Henry's constants for methane in n-decane.



$$\frac{\pi N_A}{6} \rho \sum_i \sum_j x_i x_j \left( \frac{\sigma_i + \sigma_j}{2} \right)^3$$

Figure 1

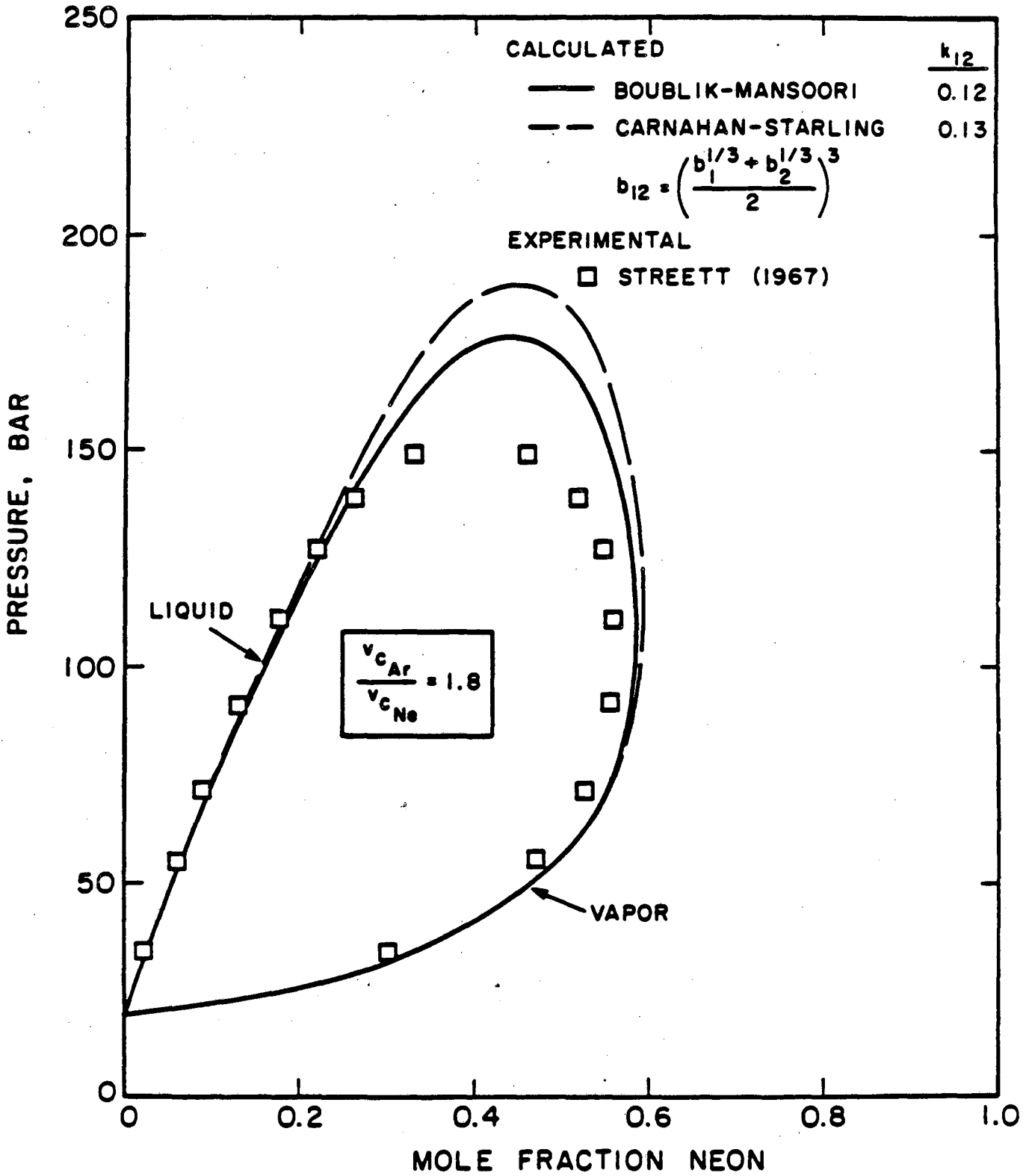


Figure 2

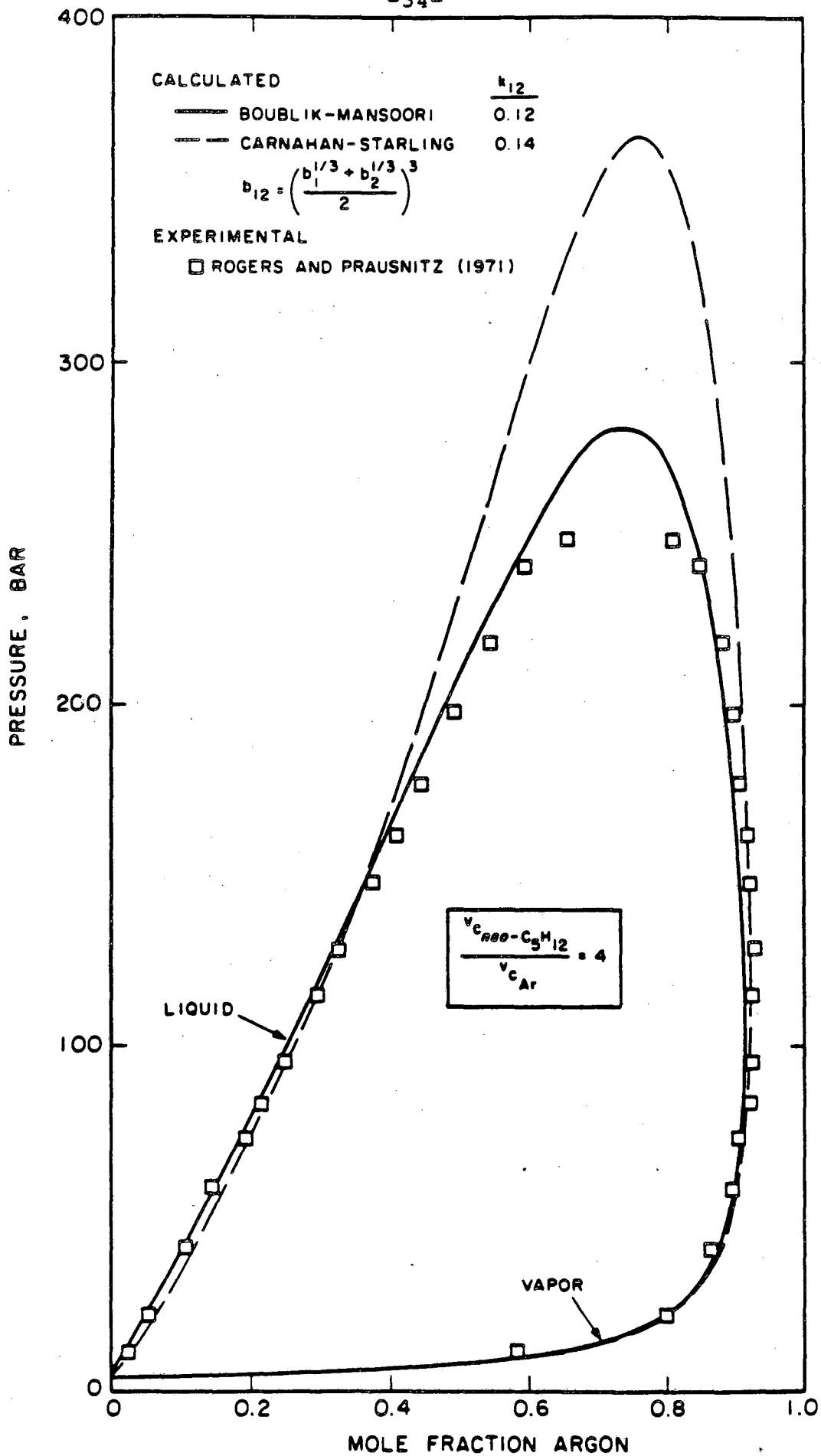


Figure 3

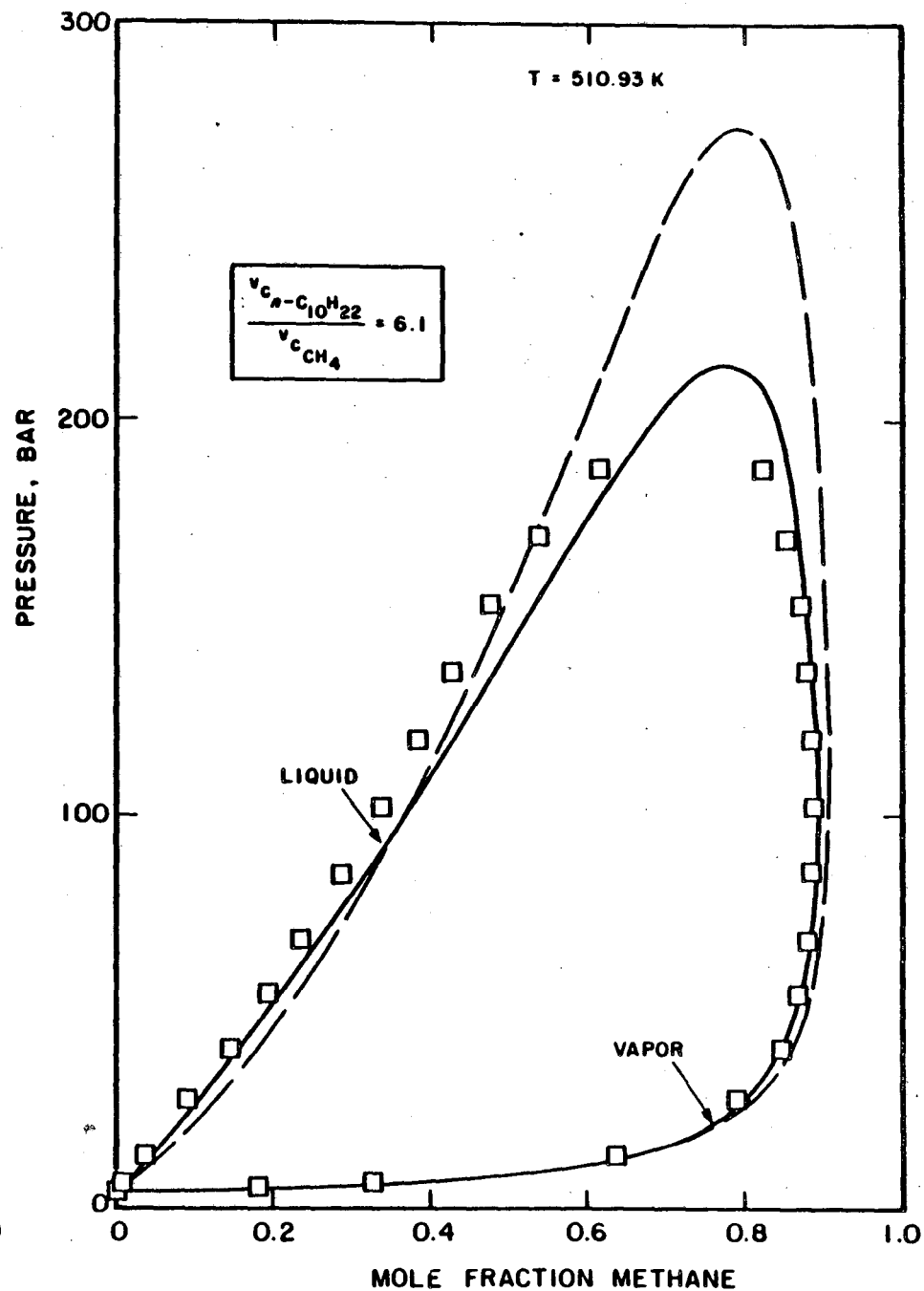
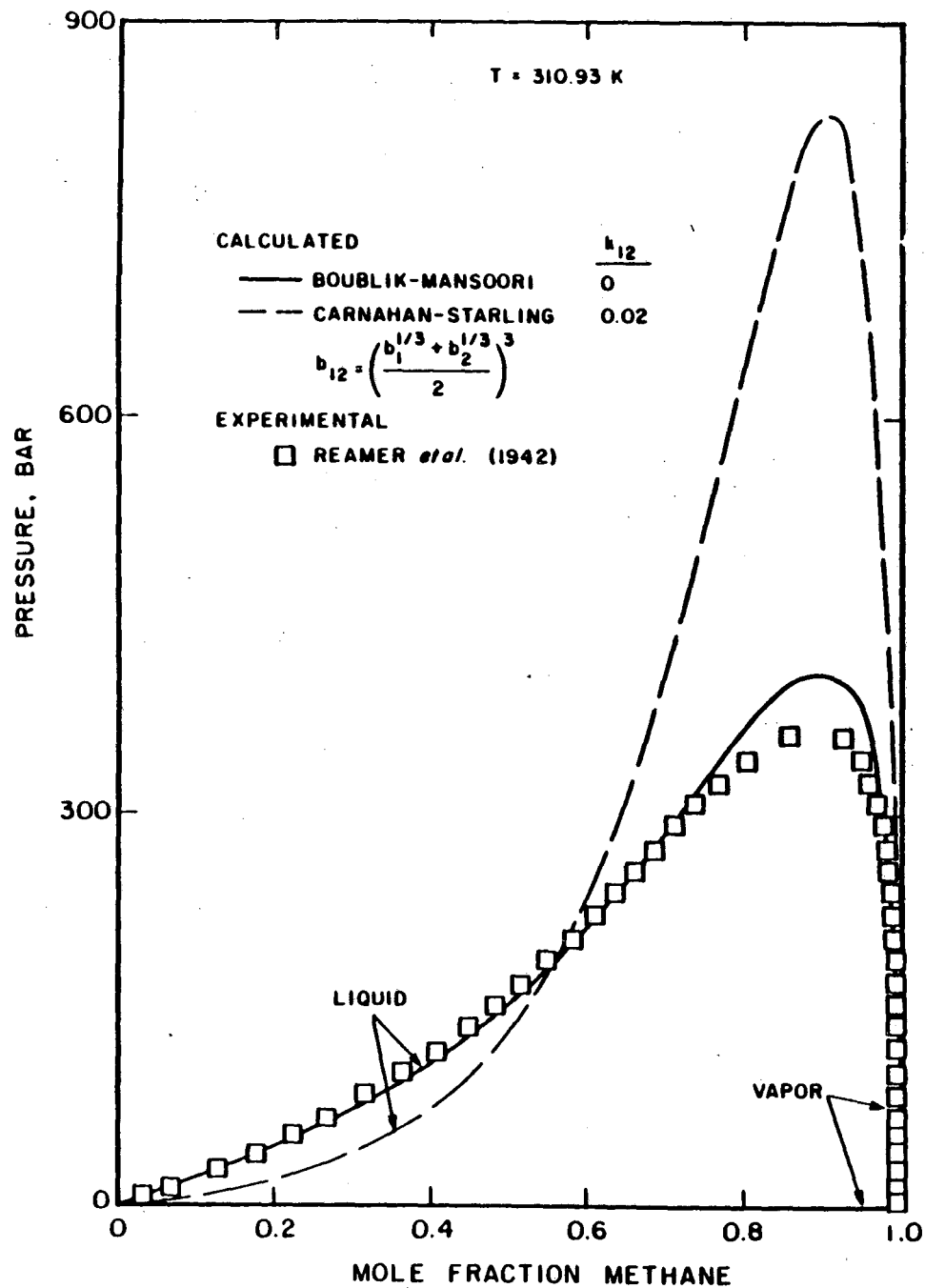


Figure 4

HENRY'S CONSTANT, BAR

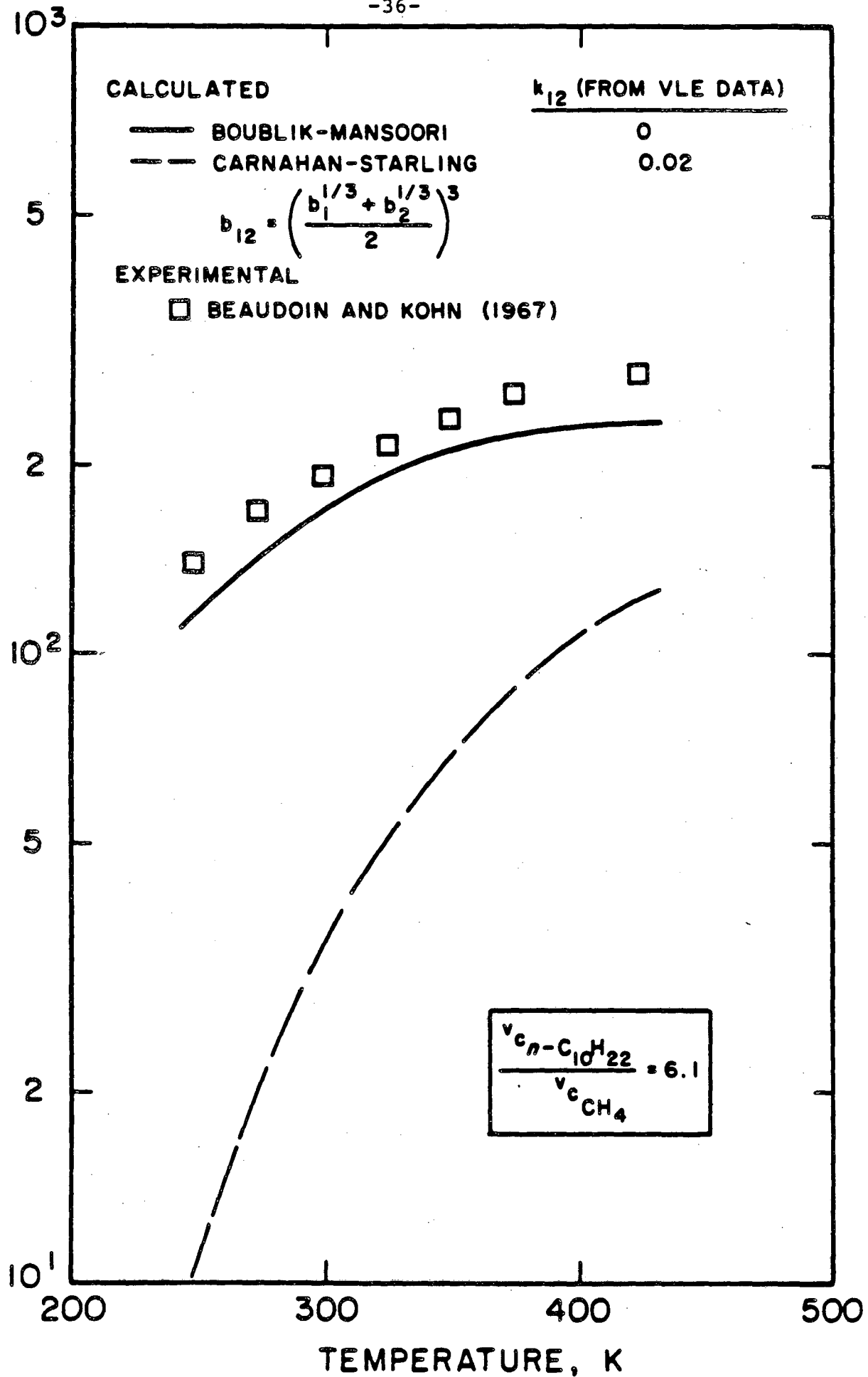


Figure 5

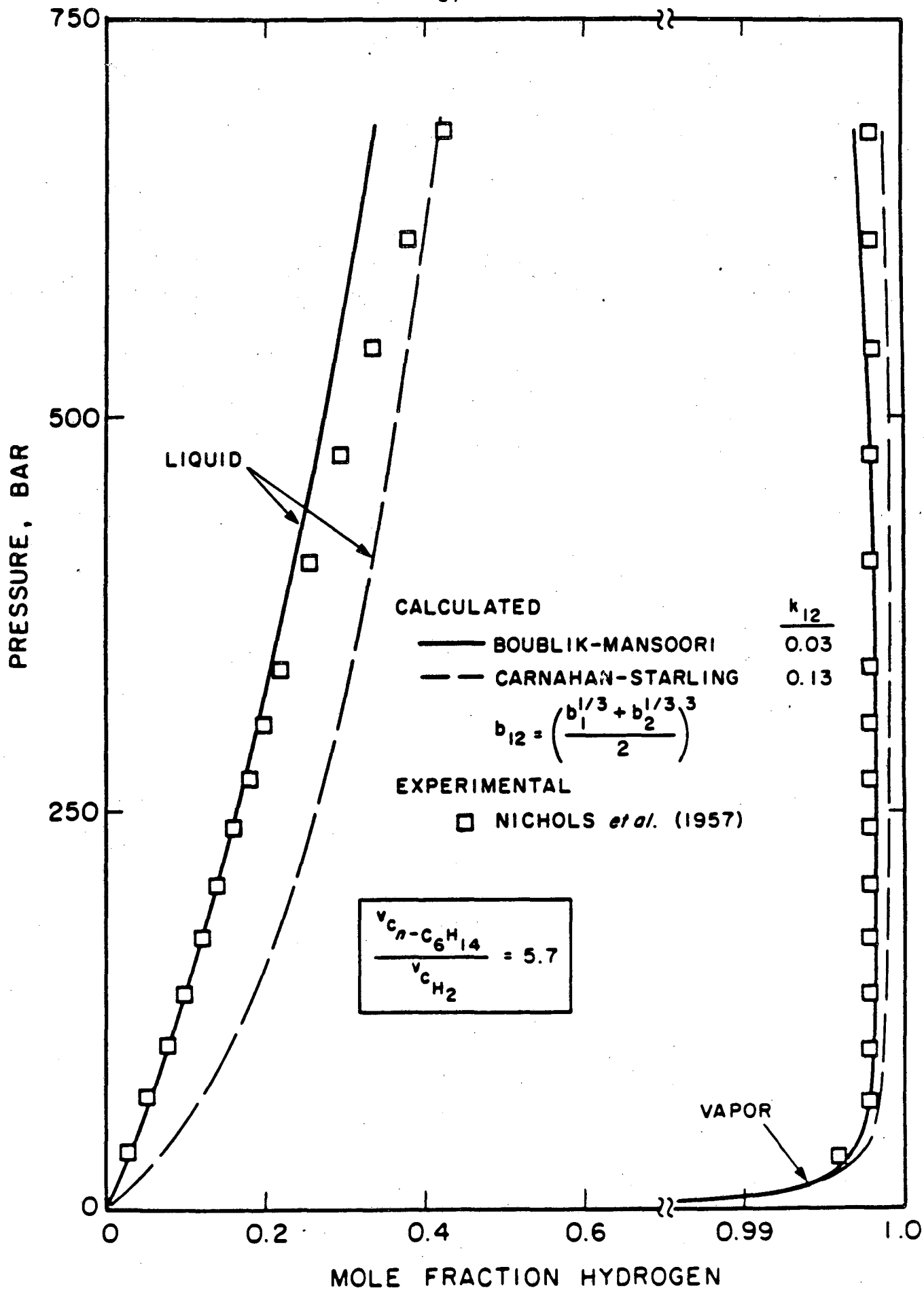
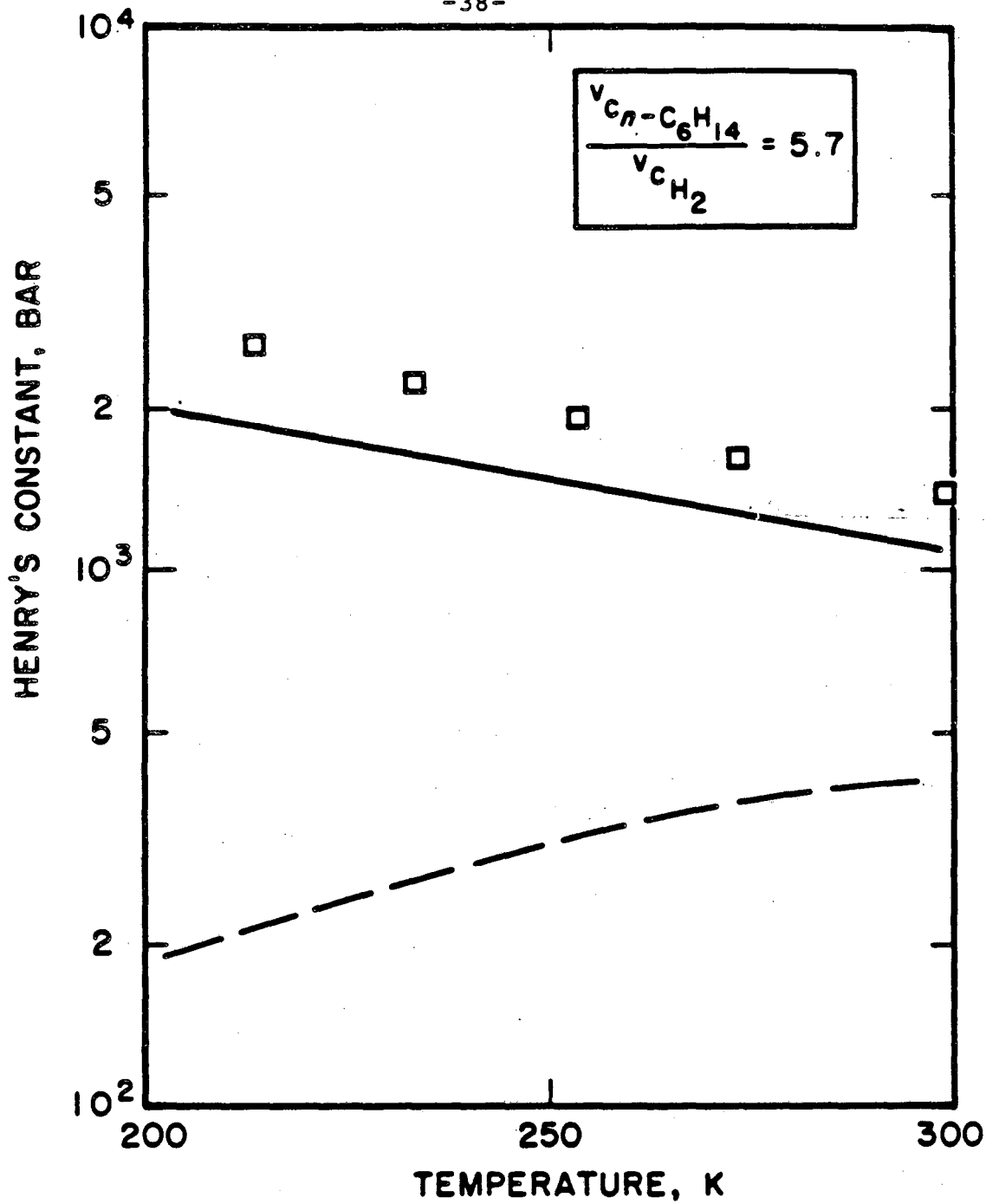


Figure 6





CALCULATED

- BOUBLIK-MANSOORI
- - - CARNAHAN-STARLING

$$b_{12} = \left( \frac{b_1^{1/3} + b_2^{1/3}}{2} \right)^3$$

$k_{12}$  (FROM VLE DATA)

- 0.03
- 0.13

EXPERIMENTAL

- KATAYAMA AND NITTA (1976)

Figure 7

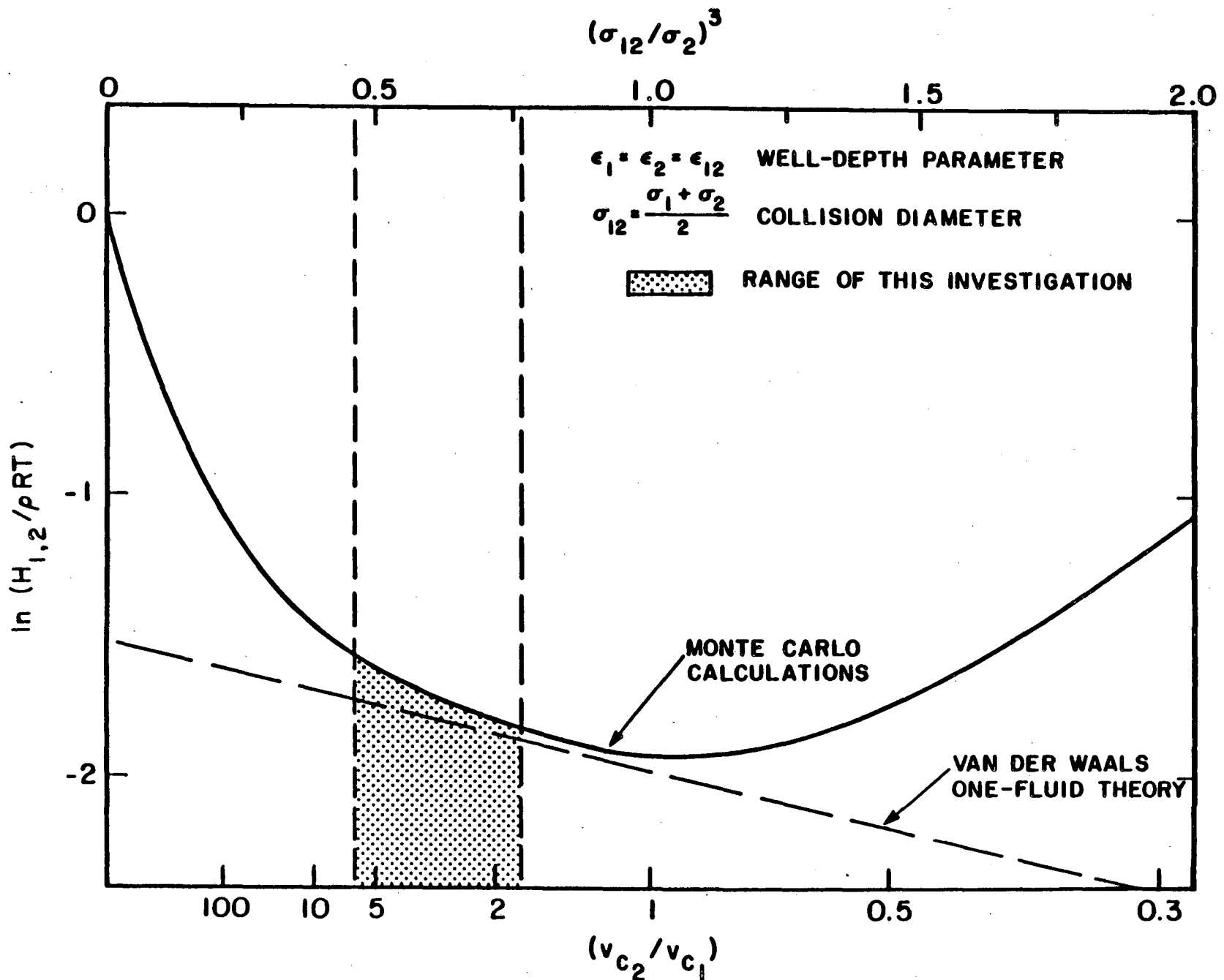


Figure 8

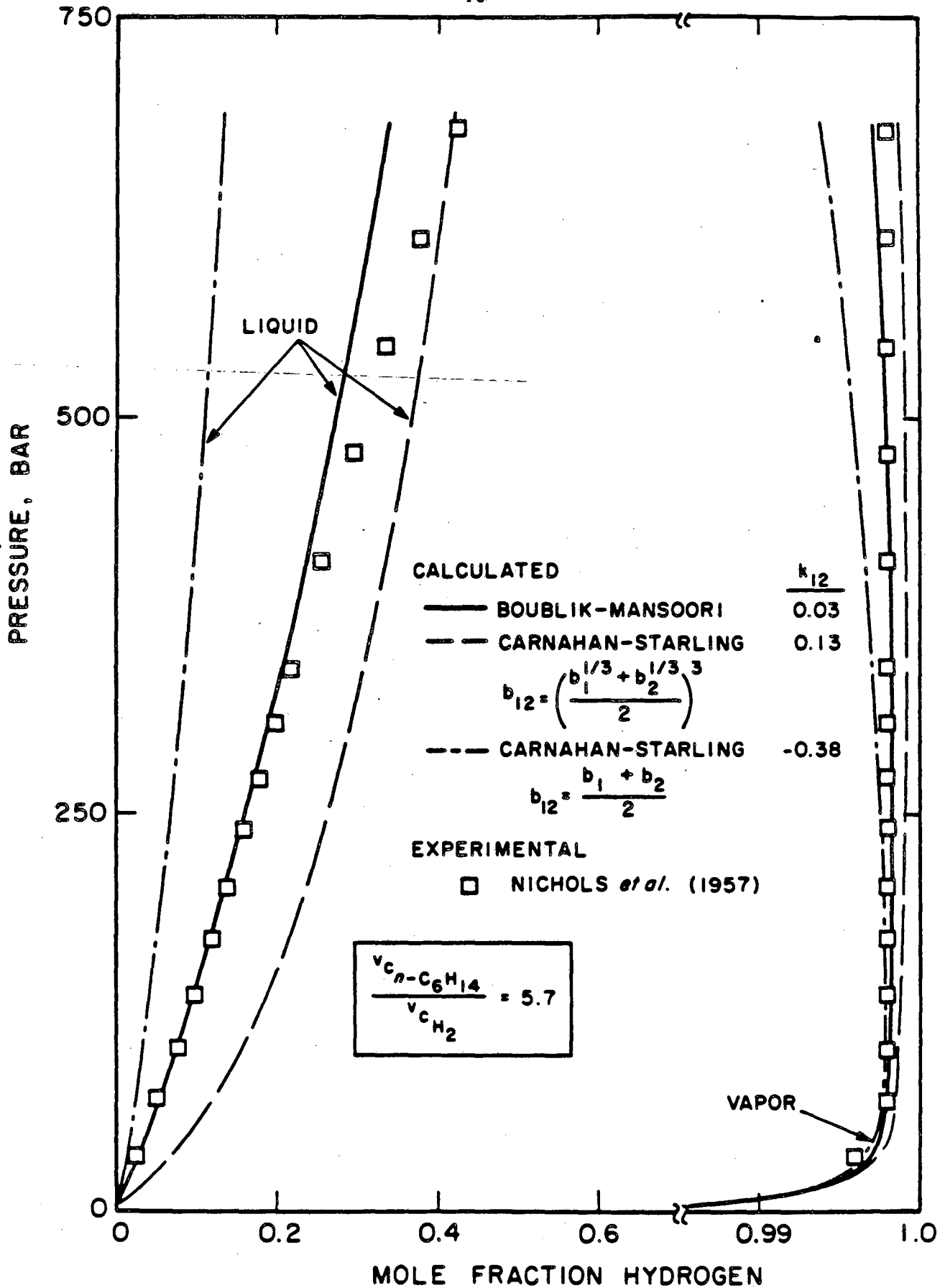


Figure 9

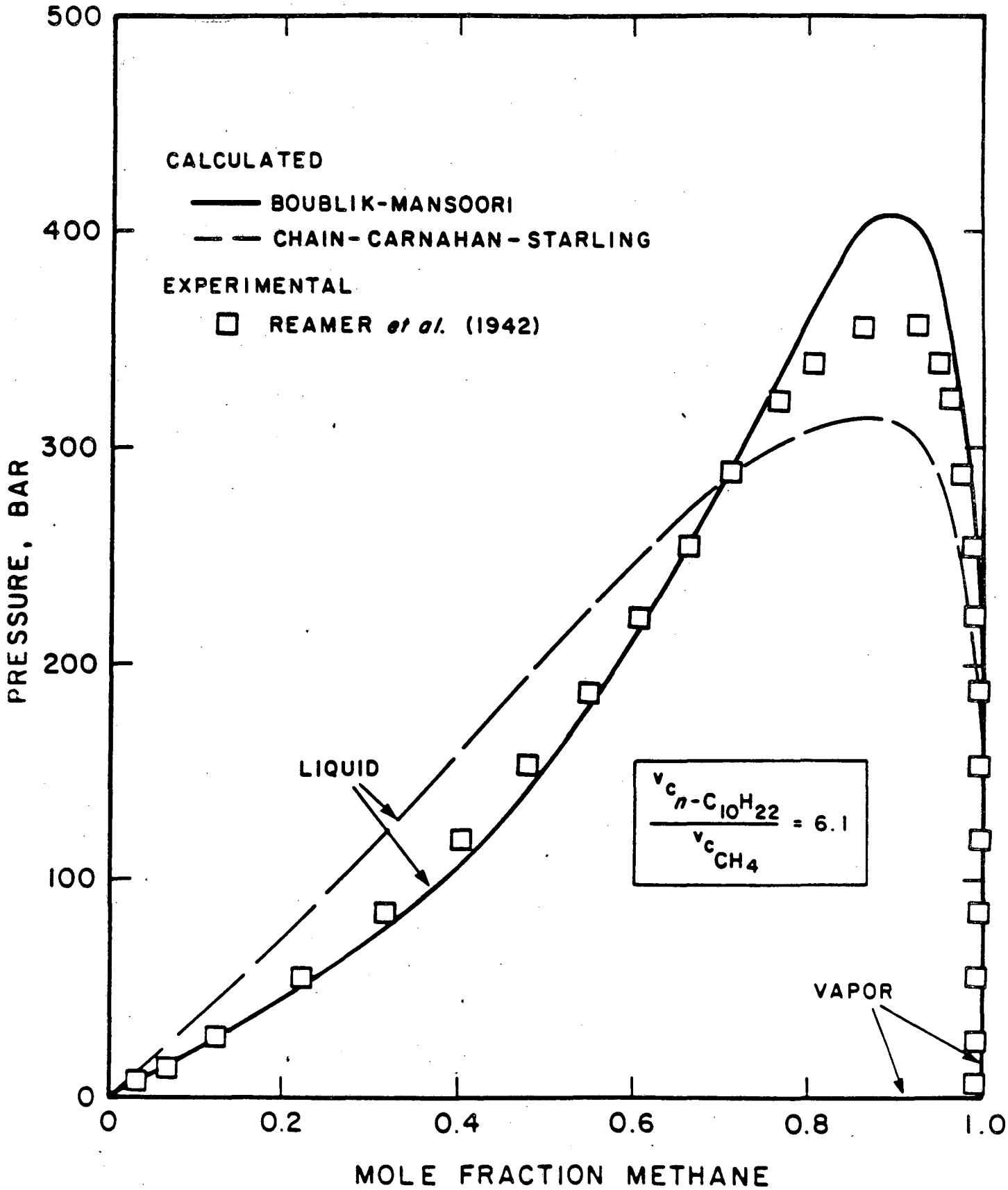
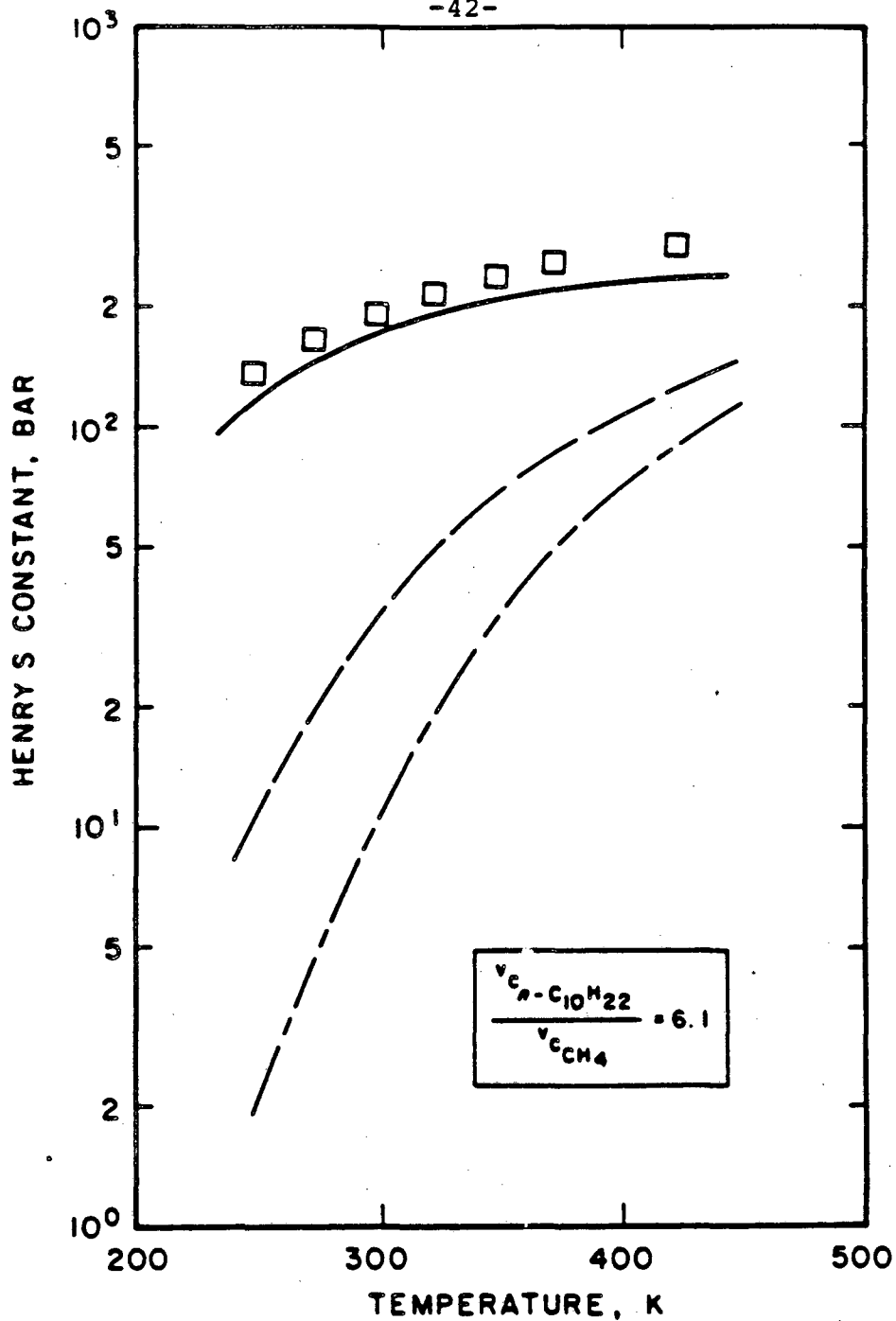


Figure 10



CALCULATED

- BOUBLIK - MANSOORI
- - - CARNAHAN - STARLING  

$$b_{12} = \left( \frac{b_1^{1/3} + b_2^{1/3}}{2} \right)^3$$
- - - VAN DER WAALS  

$$b_{12} = \left( \frac{b_1^{1/3} + b_2^{1/3}}{2} \right)^3$$

$k_{12}$  (FROM VLE DATA)

- 0
- 0.02
- 0.11

EXPERIMENTAL

- BEAUDOIN AND KOHN (1967)

Figure 11

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