

## He-CF<sub>4</sub> 및 He-CClF<sub>3</sub> 系の 氣液相平衡 : II. 液相\*

尹 汝 吉 · W. T. Ziegler

陸軍士官學校 Georgia Institute of Technology

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## Gas-Liquid Phase Equilibria in the He-CF<sub>4</sub> and He-CClF<sub>3</sub> Systems: II. Liquid Phase\*

Yo Kil Yoon and W. T. Ziegler

*Korea Military Academy, Seoul Korea  
 and*

*School of Chemical Engineering, Georgia Institute of Technology  
 Atlanta, Georgia, U. S. A.*

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### 요 약

He 이 CF<sub>4</sub> 및 CClF<sub>3</sub> 에 無限희석된 狀態下에서의 Henry's law Constant 와 Partial molar volume 을 Krichevsky-Kasarnovsky 式을 利用하여 相平衡實驗 data 로 부터 얻고 또한 理論的으로 計算하여 얻었다. 本 研究에서 취급한 系에서의 Henry's law constant 는 지금까지 研究된 어떤 helium 二成分系에서 보다는 제일 큰 事實이 發見되었다. 無限희석된 狀態下에서의 Henry's law constant 와 partial molar volume 을 추정하기 위해 Snider 와 Herrington 이 제시한 유체에 對한 hard sphere model 을 利用했다. 추정된 值와 實驗值와는 實驗值의 55% 以內의 오차를 가지고 있었다.

### Abstract

The Henry's law constants and partial molar volumes at infinite dilution for helium in CF<sub>4</sub> and CClF<sub>3</sub> have been extracted from the experimental phase equilibrium data<sup>1)</sup> using the Krichevsky-Kasarnovsky equation<sup>3)</sup> and also theoretically predicted. It has been found that the Henry's law constants for the systems considered in this work are larger than those for any other helium binary systems investigated so far at a given reduced temperature.

The hard sphere model of fluids as presented by Snider and Herrington<sup>2)</sup> has been used to predict the Henry's law constants and the partial molar volumes at infinite dilution. The predicted values agreed with the experimental values within at most 55% of the experimental values.

\* Part I: *Hwahak Konghak*, 12, (1974), 10.

## Extraction of $H_2^g$ and $\bar{V}_2^g$ from Experimental Phase Equilibrium Data

### Introduction

For a binary gas-liquid phase equilibrium system where the solubility of the gas and total pressure are small, the following relation can be written.

$$Py_2 = Hx_2 \quad (1)$$

This equation is widely known as the original Henry's law and is a special case of a more general thermodynamic formulation.

The conditions for the binary systems considered in this work are such that one component of a system (helium) is well above its critical temperature and the other component below its critical temperature, and that the two phases are in equilibrium. It is required from the latter that the chemical potential of the solute gas dissolved in the liquid phase be equal to the chemical potential of that species in the gas phase for a given temperature. Thus,

$$\mu_2^g(P, T, y_2) = \mu_2^l(P, T, x_2) \quad (2)$$

From Eq. (2) the Krichevsky-Kasarnovsky equation<sup>3)</sup> can be derived as given below with the assumptions that the liquid solution is ideal and the change of  $\bar{V}_2^g$  with pressure is negligible.

$$\ln \frac{f_2^g}{x_2} = \ln H_2^g(P_{01}, T) + \frac{\bar{V}_2^g(P - P_{01})}{RT} \quad (3)$$

This is the working equation that has been used in this study. It may be noted that Eq. (3) reduces to Eq. (1) if the system pressure is low and the last term in Eq. (3) is neglected, that is,  $P - P_{01} \rightarrow 0$ .

From Eq. (3), the values of  $H_2^g$  and  $\bar{V}_2^g$  can be extracted using experimental phase equilibrium data and an equation of state for the gas phase. A plot of  $\ln(f_2^g/x_2)$  vs.  $(P - P_{01})$  should give a straight line whose intercept at  $(P - P_{01}) = 0$  is equal to  $\ln H_2^g$  and whose slope is equal to  $\bar{V}_2^g/(RT)$ . The only unknown in the graphical evaluation of  $H_2^g$  and  $\bar{V}_2^g$  from Eq. (3) is the gas phase fugacity,  $f_2^g$ , since the values of  $x_2$  have already been obtained experimentally for the helium binary systems considered here. These

values are shown in Fig. 1 and 2 with the range of experimental error.

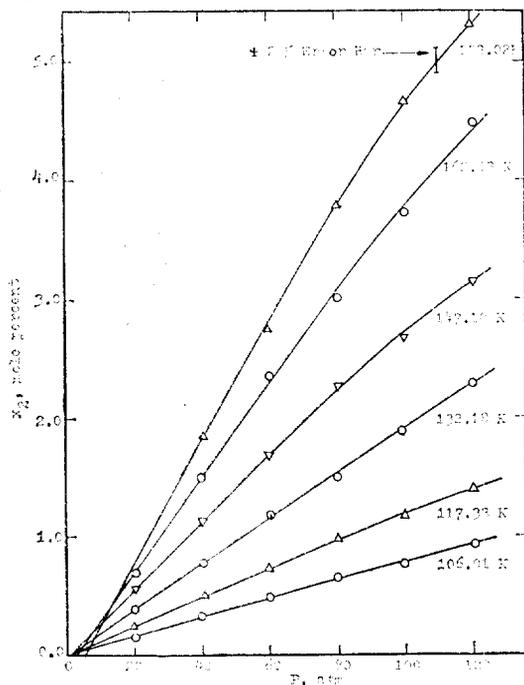


Fig. 1. Experimental solubility of He in liquid  $CF_4$

Choosing the standard state for the gas phase as an ideal gas at 1 atm, the following expression for  $f_2^g$  may be derived.

$$\ln f_2^g = -\frac{1}{RT} \int_V^{\infty} \left[ \left( \frac{\partial P}{\partial n_2} \right)_{V, T, n_1} - \frac{RT}{V} \right] dV - \ln \frac{V}{n_2 RT} \quad (4)$$

The evaluation of  $f_2^g$  from this equation requires an equation of state for the gas mixture as well as the composition of the gas phase, which has been experimentally determined for the systems of this work and whose values are presented in the form of enhancement factor (and hence  $y_1$ ) in the previous paper<sup>1)</sup>. The virial equation of state is used as an equation of state for the gas mixture since the necessary data for the virial coefficients have already been determined.<sup>1)</sup> After some algebraic manipulation, Eq. (5) is obtained from Eq. (4).

$$\ln \frac{f_2^g}{x_2} = -\frac{2(y_1 B_{12} + y_2 B_{22})}{V_m} + \frac{3(y_1^2 C_{112} + 2y_1 y_2 C_{122} + y_2^2 C_{222})}{2V_m^2} + \ln \frac{y_2 RT}{x_2 V_m} \quad (5)$$

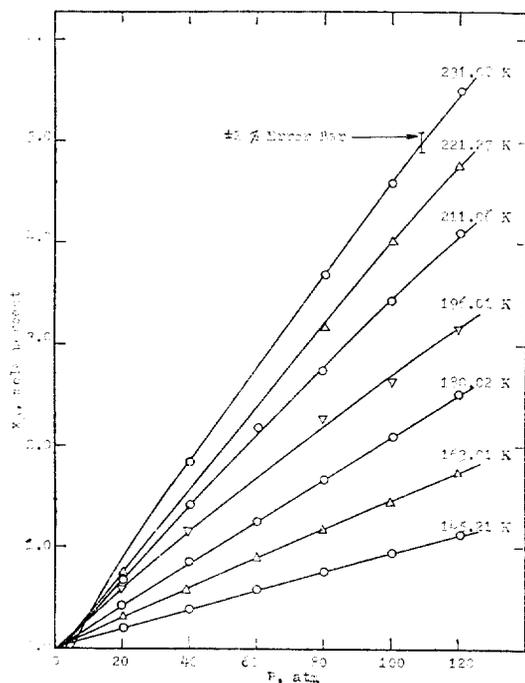


Fig. 2. Experimental solubility of He in liquid CClF<sub>3</sub>.

Since the virial coefficients used in evaluating Eq. (5) are not determined homogeneously but selected on the basis of best representation to the experimental data<sup>4)</sup>, the values of these virial coefficients have to be specified here in detail. The virial equation of state truncated after the third virial coefficient was used for the evaluation of  $V_m$ . The values of  $x_2$ ,  $y_1$ , and  $B_{12}$  used are those experimentally determined in this work. The values of  $C_{222}$  were graphically evaluated from the experimental data given by Keesom,<sup>30)</sup> White, et al.,<sup>31)</sup> Canfield, et al.,<sup>32)</sup> and Hoover, et al.,<sup>33)</sup> and all the other third virial coefficients were predicted using the method of Chueh and Prausnitz.<sup>34)</sup>

## Results and Discussion

The smoothed values of  $H_2^\infty$  and  $\bar{V}_2^\infty$  presented in Tables 1 and 2 were obtained from the smooth curves which represent the extracted values of  $H_2^\infty$  and  $\bar{V}_2^\infty$  from Eq. (3) using the phase equilibrium data of this work. Since these data are the only available data and no experimental values of  $H_2^\infty$  and  $\bar{V}_2^\infty$  were available in the literature for the systems of He-CF<sub>4</sub>

and He-CClF<sub>3</sub>, no comparison could be made. The error ranges shown in these tables are determined by varying the input data of  $y$  and  $x$  by the corresponding experimental errors.

As can be seen in Tables 1 and 2, the range of percent error of  $\bar{V}_2^\infty$  is much greater than that of  $H_2^\infty$ . This is because in the systems of this work a small percent change of  $H_2^\infty$  produces a large percent change in the slope of the  $\ln(f_2^G/x_2)$  vs.  $(P-P_0)$  curve which determines  $\bar{V}_2^\infty$ .

A good summary of the  $H_2^\infty$  and  $\bar{V}_2^\infty$  values for the helium binary systems is given recently by Garber<sup>5)</sup>. In his paper, he has compared  $H_2^\infty$  and  $\bar{V}_2^\infty$  for a number of helium binary systems at a reduced temperature ( $T_{R1}$ ) of 0.75. Of all the helium binary systems investigated by Garber the helium-nitrogen system gives the smallest  $H_2^\infty$  and  $\bar{V}_2^\infty$  values, indicating the highest solubility of helium in the liquid nitrogen. In this work, the values of  $H_2^\infty$  in the He-CF<sub>4</sub> and He-CClF<sub>3</sub> systems have been found to be even smaller than those in the He-N<sub>2</sub> system; the  $H_2^\infty$  value at  $T_{R1}=0.75$  for the He-CF<sub>4</sub> system is 1920 atm and that for the He-CClF<sub>3</sub> system 1960 atm, compared with  $H_2^\infty$  of 2120 atm for the He-N<sub>2</sub> system at the same reduced temperature. Although no attempt has been made to account for this high solubility of He in the liquid CF<sub>4</sub> and CClF<sub>3</sub>, this is probably due to the anomalous solvent behavior of fluorochemicals. The values of  $\bar{V}_2^\infty$  in the helium-hydrocarbon systems studied by Garber<sup>5)</sup> are all above 30cc/gm-mole at  $T_{R1}=0.75$ , the smallest being 30.7cc/gm-mole in the He-CH<sub>4</sub> system. This value is comparable to the values of  $\bar{V}_2^\infty$  in the He-CF<sub>4</sub> and He-CClF<sub>3</sub> systems, which are 27.8 and 31.1 cc/gm-mole, respectively.

## Theoretical Prediction of $H_2^\infty$ and $\bar{V}_2^\infty$

An examination of the literature has revealed several good methods for the prediction of the solubility of gas in a liquid phase in terms of Henry's law constant,  $H_2^\infty$ , and for the prediction of partial molar volume at infinite dilution,  $\bar{V}_2^\infty$ . Miller and Prausnitz<sup>6)</sup>, using the free volume theory<sup>7,8)</sup>, have presented a semi-empirical correlation for the prediction of the Henry's law constant for a high pressure system with one component well above its critical temperature. Another method

Table 1.  $H_2^\infty$  and  $\bar{V}_2^\infty$  for the He-CF<sub>4</sub> System

T, K	$H_2^\infty$ , atm		$\bar{V}_2^\infty$ , cc/gm-mole	
	From Eq. (3)	Smoothed	From Eq. (3)	Smoothed
106.01	11,830±287	11,840	18.2±1.5	17.9
117.33	7,723±140	7,715	20.2±1.5	18.9
132.18	4,949±75	4,975	19.3±1.5	20.6
147.10	3,308±60	3,310	24.1±1.7	23.1
162.03	2,336±51	2,345	25.6±2.1	26.6
173.02	1,812±33	1,810	30.5±2.1	30.3

Table 2.  $H_2^\infty$  and  $\bar{V}_2^\infty$  for the He-CClF<sub>3</sub> System

T, K	$H_2^\infty$ , atm		$\bar{V}_2^\infty$ , cc/gm-mole	
	From Eq. (3)	Smoothed	From Eq. (3)	Smoothed
145.21	10,037±327	10,000	18.4±3.2	17.9
163.01	6,516±179	6,550	18.2±3.6	19.3
180.02	4,537±148	4,570	20.7±3.9	21.1
196.01	3,314±122	3,340	25.7±4.8	23.3
211.06	2,599±87	2,540	25.5±4.8	26.5
221.27	2,191±76	2,160	28.0±5.0	29.3
231.08	1,808±66	1,830	34.8±6.0	33.2

based on the scaled particle theory<sup>9,10)</sup> for the calculation of  $H_2^\infty$  and  $\bar{V}_2^\infty$  has been presented by Pierotti<sup>11,12)</sup> and used by Heck<sup>13)</sup> and Garber<sup>5)</sup>. Very recently, Preston and Prausnitz<sup>14)</sup> have shown a generalized thermodynamic expression for Henry's law constant based on the statistical mechanics of dilute liquid solutions. Snider and Herrington<sup>2)</sup> have developed a method for the calculation of the excess thermodynamic functions of binary liquid mixtures and also for the problem of the solubility of gases in liquids by applying the hard sphere model for fluids.

Of the methods mentioned above, the method of Snider and Herrington<sup>2)</sup> was found to be most adequate to the systems of this work and has been used in the present investigation for the prediction of  $H_2^\infty$  and  $\bar{V}_2^\infty$ . This method which is based on first principles, is basically similar to that given by Pierotti<sup>11,12,15)</sup> except that the equation of state for the hard sphere fluid,

$$x(\xi) = \frac{P}{\rho k T} \quad (6)$$

was used in Pierotti's method, where

$$z(\xi) = \frac{(1+\xi+\xi^2)}{(1-\xi)^3} \quad (7)$$

$$\xi = \frac{\pi \bar{\rho}_r^3}{6} \quad (8)$$

and

$$\bar{\rho} = \frac{N_A}{v_{01}} \quad (9)$$

Equation (6), which is basically an approximation in closed form for the equation of state for the hard sphere fluid, was obtained first from the scaled particle theory<sup>9,10)</sup> and later from the solution of the Percus-Yevick equation for the hard sphere model.<sup>16,17)</sup> Since this hard sphere model does not take into account configurational internal energy, it cannot represent satisfactorily a real liquid.

Longuet-Higgins and Wisdom<sup>18)</sup> have proposed a simple liquid model which has a finite configurational internal energy. By assuming a field of uniform and negative potential energy for a fluid of hard spheres,

they have developed an equation of state for this model, which describes quite well the thermodynamic properties of argon at its triple point. This equation is

$$\frac{P}{\rho k T} = \chi(\xi) - \frac{a\bar{\rho}}{k T} \quad (10)$$

where  $a$  can be regarded as a measure of the strength of the attractive background potential. Equation (10) has been successfully applied to the pure liquids of small, nonpolar molecules. Snider and Herrington<sup>2)</sup> have generalized this equation to the case of binary mixtures and calculated the excess thermodynamic functions of binary mixtures composed of simple molecules. The agreement of their results with experimental data appears to be quite satisfactory.

Snider and Herrington<sup>2)</sup> have also applied this equation for the calculation of  $H_2^\infty$  and  $\bar{V}_2^\infty$  for a binary system in which component 1, a liquid solvent, is below its critical temperature and component 2, a gaseous solute, is well above its critical temperature. But, this case they concluded that the agreement with experiment was not good for neon-argon system. Later, Staveley<sup>19)</sup> pointed out that this disagreement was due to their choice of data for the neon-argon system and misinterpretation of these data. He has studied the systems of Ne-Ar, H<sub>2</sub>-N<sub>2</sub>, and He-CH<sub>4</sub> and proved that this method predicts excellent values of  $H_2^\infty$  and  $\bar{V}_2^\infty$ .

This method is described in detail in the following. The expressions used in this method are:

$$\ln \frac{H_2^\infty}{\bar{\rho} k T} = -\ln(1-\xi) + \xi \chi(\xi) \left( \frac{r_2}{r_1} \right)^3 + \frac{1}{2} \left( \frac{3\xi}{1-\xi} \right)^2 \left( \frac{r_2}{r_1} \right)^2 + \frac{3\xi}{1-\xi} \left[ \left( \frac{r_2}{r_1} \right)^2 + \frac{r_2}{r_1} \right] - \frac{2a_{12}\bar{\rho}}{k T} \quad (11)$$

$$\frac{\bar{\rho} \bar{V}_2^\infty}{N_A} = \frac{(1-\xi)^4}{2\xi^3 + 4\xi^2 + 4\xi - 1} w \quad (12)$$

$$w = \left( \frac{\xi}{1-\xi} \right) \left[ \frac{(1+2\xi)^2}{(1-\xi)^3} \left( \frac{r_2}{r_1} \right)^3 + 3 \frac{1+2\xi}{(1-\xi)^2} \left( \frac{r_2}{r_1} \right)^2 + \left( \frac{3}{(1-\xi)} \right) \left( \frac{r_2}{r_1} \right) + 1 \right] - \frac{2a_{12}\bar{\rho}}{k T} + 1 \quad (13)$$

The values of the hard sphere diameter  $r$  can be obtained from the boiling point data for pure components using either Eq. (14) or (15).

$$\frac{\Delta H_V}{N_A k T} = \ln \frac{P_0}{\bar{\rho} k T} - \ln(1-\xi) + \frac{3}{2} \xi \frac{2-\xi}{(1-\xi)^3} \quad (14)$$

$$\frac{\Delta H_V}{N_A k T} = \chi(\xi) + 1 - \frac{2P_0}{\bar{\rho} k T} \quad (15)$$

The last term in Eq. (15) is usually negligible except for very low-boiling liquids. Once  $r$  is determined, the parameter  $a$  can be calculated from Eq. (10) using the same boiling point data as was used in Eq. (14) or (15). In order to determine  $a_{12}$ , at least one experimental value of  $H_2^\infty$  must be forced to agree with Eq. (11).

Staveley<sup>19)</sup> pointed out in his paper that the value of  $r$  for helium calculated using Eq. (14) was much too small, whereas that from Eq. (15) was reasonable. Thus, the calculation of  $r$  in this work is restricted to Eq. (15). The values of  $r$  and  $a$  evaluated for the He-CF<sub>4</sub> and He-CClF<sub>3</sub> systems using the boiling point data in Table 3 are presented in Table 4 together

Table 3. Boiling point data for pure components

	T (K)	$\Delta H_V$ (cal/gm-mole)	P (atm)	$v_{01}$ (cc/gm-mole)
He	4.215 <sup>24)</sup>	19.4 <sup>24)</sup>	1.0	32.05 <sup>25)</sup>
CF <sub>4</sub>	145.12 <sup>26)</sup>	2823.6 <sup>27)</sup>	1.0	54.88 <sup>28)</sup>
CClF <sub>3</sub>	191.75 <sup>29)</sup>	3705.6*	1.0	68.67 <sup>26)</sup>

\*Value taken from the Handbook of Physics and Chemistry, 52nd ed. (1971)

Table 4. Parameters for the method of Snider and Herrington

	$r$ (Å)	$a_1 \times 10^{16}$ (erg cc/molecule)	$a_{12} \times 10^{17}$ (erg cc/molecule)
He	2.143		
CF <sub>4</sub>	4.219	1.606	4.651
CClF <sub>3</sub>	4.542	2.635	3.106

Table 5. Molar volumes of the pure liquid components at saturation

T, K	$v$ , cc/gm-mole		Percent Diffe- rence
	Experimental	Calculated using Eq. (10)	
CF <sub>4</sub>	106.01	48.69 <sup>28)</sup>	2.6
	117.33	50.21	1.5
	132.18	52.43	0.3

147.10	54.94	55.32	-0.7
162.03	57.80	58.69	-1.5
173.02	60.17	61.41	-2.1
CClF <sub>3</sub> 145.21	61.85 <sup>29)</sup>	60.14	2.8
163.01	64.20	63.22	1.5
180.02	66.73	66.37	0.6
196.01	69.41	69.54	-0.2
211.06	72.32	72.77	0.6
221.27	74.56	75.13	-0.8
231.08	76.99	77.52	-0.7

with  $a_{12}$  values. These  $a_{12}$  values have been determined by least-square fitting the experimental  $H_2^\infty$  data to Eq. (11). In this sense, the method of Snider and Herrington for the prediction of  $H_2^\infty$  can be said semi-empirical, though this method is firmly based on first principles. The experimental saturated liquid molar volumes given in Table 5 were used for the evaluation of  $\bar{v}$  which is  $N_A/v_{01}$ .

### Comparison of Predicted and Experimental $H_2^\infty$ and $\bar{V}_2^\infty$

Figures 3 through 6 show comparisons of the calculated and experimental values of  $H_2^\infty$  and  $\bar{V}_2^\infty$  for the He-CF<sub>4</sub> and He-CClF<sub>3</sub> systems. As can be seen in Figs. 3 and 4, the predicted values of  $H_2^\infty$  are lower than the smoothed experimental values of  $H_2^\infty$  given in Tables 1 and 2 at low temperatures by at most 20% and higher at high temperatures by at most 50%, giving the best agreement at around 20 to 25 K below normal boiling points of CF<sub>4</sub> and CClF<sub>3</sub>. The smoothed experimental values of  $\bar{V}_2^\infty$  presented in Tables 1 and 2 are compared in Fig. 5 and 6 with the predicted values of  $\bar{V}_2^\infty$ . In this case, the calculated values are consistently higher by 16 to 55% than the experimental values, the difference increasing with temperature.

Since the method of theoretical prediction is based on the equation of state for the hard sphere model, Eq. (10), Snider and Herrington<sup>2)</sup> have tested this equation by calculating molar volumes of pure components at the temperatures at which the mixtures were studied, using the parameters,  $r$  and  $a$ , extracted from the boiling point data of the pure components. This equation has also been tested

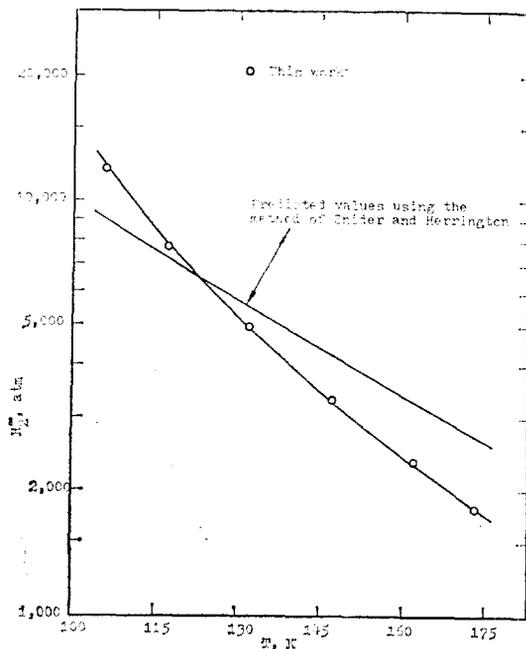


Fig. 3. Comparison of theoretical and experimental  $H_2^\infty$  for the He-CF<sub>4</sub> system

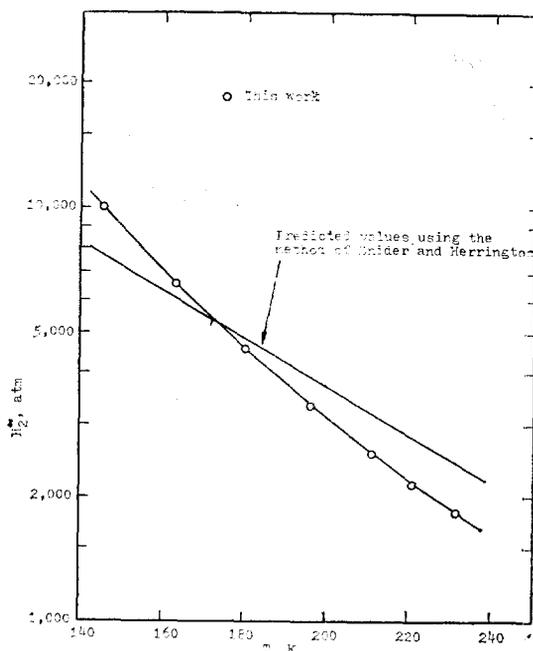


Fig. 4. Comparison of theoretical and Experimental  $H_2^\infty$  for the He-CClF<sub>3</sub> system

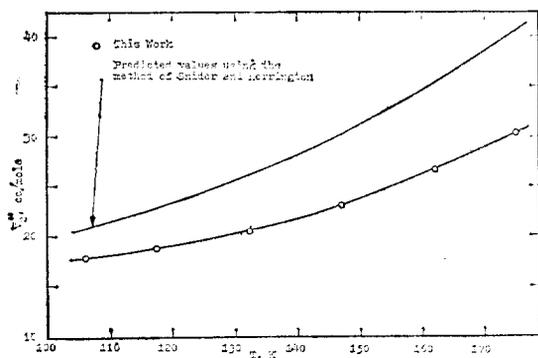


Fig. 5. Comparison of theoretical and experimental  $\bar{V}_2^\infty$  for the He-CF<sub>4</sub> system.

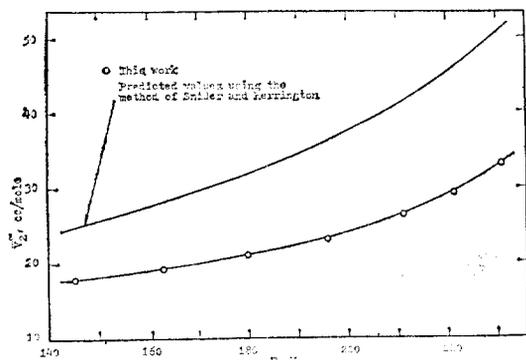


Fig. 6. Comparison of theoretical and experimental  $\bar{V}_2^\infty$  for the He-CClF<sub>3</sub> system.

in this work and the molar volumes of liquid CF<sub>4</sub> and CClF<sub>3</sub> are calculated at the temperatures of interest. These results are presented in Table 5 along with the experimental molar volumes. As shown in Table 5, Eq. (10) is quite satisfactory in representing the pure liquid molar volumes of these components over the temperature region of this work.

Recently, Staveley<sup>19)</sup> has applied the method of Snider and Herrington<sup>2)</sup> for the calculation of  $H_2^\infty$  and  $\bar{V}_2^\infty$  for the systems of Ne-Ar, H<sub>2</sub>-N<sub>2</sub>, He-CH<sub>4</sub>, and He-H<sub>2</sub>, and shown that the predicted values of  $H_2^\infty$  and  $\bar{V}_2^\infty$  are in quite satisfactory agreement with the experimental values except for the He-H<sub>2</sub> system, for which the predicted  $H_2^\infty$  value seriously exceeds the experimental value. This is, as Staveley<sup>19)</sup> stated, probably due to the quantum effects for both compon-

ents, which in turn suggest that this method may not be reliable for the binary systems in which both components exhibit quantum effects. The results presented in Figs. 3 through 6 show that this method generally represents the  $H_2^\infty$  and  $\bar{V}_2^\infty$  values for the helium binary systems of this work with reasonable accuracy.

As stated by Snider and Herrington<sup>2)</sup>, although this method was originally developed to describe the thermodynamic properties of the binary mixtures whose components are small, nonpolar spherical molecules, this method has been successfully used in reproducing experimental values of various thermodynamic quantities for the binary systems whose liquid components consist of nonspherical molecules such as oxygen, nitrogen, and carbon monoxide. They pointed out that this is so because these molecules as liquids very nearly obey the same equation of state as do the liquified rare gases<sup>20)</sup> and therefore can be treated as spherical molecules. They also pointed out that their method could not satisfactorily predict the experimental results for the larger molecules such as carbon tetrachloride and neopentane despite of their high symmetries.

O'Connell and Prausnitz<sup>21)</sup> and Sherwood and Prausnitz<sup>22)</sup> have shown that carbon tetrafluoride molecules can be treated as spherical molecules in the calculation of transport properties and second and third virial coefficients using Kihara potential. The nearly spherical or quasi-spherical nature of chlorotrifluoromethane molecules has been successfully used by Brandt<sup>23)</sup> for the calculation of intermolecular force constants from polarizabilities. Also, carbon tetrafluoride and chlorotrifluoromethane molecules are not so large as to behave like carbon tetrachloride or neopentane. The above discussion, together with the fact that Eq. (10) represents quite satisfactorily the molar volumes of the liquid CF<sub>4</sub> and CClF<sub>3</sub>, strongly supports the use of the method of Snider and Herrington<sup>2)</sup> for the calculation of the  $H_2^\infty$  and  $\bar{V}_2^\infty$  values for the He-CF<sub>4</sub> and He-CClF<sub>3</sub> systems.

## Conclusions

The He-CF<sub>4</sub> and He-CClF<sub>3</sub> systems of this work

give the smallest  $H_2^{\infty}$  and  $\bar{V}_2^{\infty}$  values at a given reduced temperature of all helium binary systems investigated so far, indicating the highest solubility of helium in the two liquids,  $\text{CF}_4$  and  $\text{CClF}_3$ .

The method of Snider and Herrington<sup>2)</sup> has been successfully applied to predict the  $H_2^{\infty}$  and  $\bar{V}_2^{\infty}$  values for the He- $\text{CF}_4$  and He- $\text{CClF}_3$  systems. Considering the simplicity of this method, this method is excellent in representing  $H_2^{\infty}$  and  $\bar{V}_2^{\infty}$  values for the binary systems of components whose molecules are small and either nonpolar or slightly polar.

The parameter  $a_{12}$  in Eq. (11) was found to be slightly dependent on temperature, though Snider and Herrington did not comment on this.

### Nomenclature

$a$	empirical parameter in the method of Snider and Herrington, Eq. (10).
$a_{12}$	empirical parameter in the method of Snider and Herrington, Eq. (11).
$B$	second virial coefficient.
$B_{12}$	interaction second virial coefficient.
$C$	third virial coefficient.
$f$	fugacity.
$H$	Henry's law constant.
$k$	Boltzman constant = $1.38054 \times 10^{-16}$ erg/K.
$n$	number of gm moles.
$P$	total absolute pressure
$R$	gas law constant = $0.0820537$ atm · liter/gm mole · K
$r$	hard sphere diameter.
$T$	temperature, K.
$V$	molar volume of gas.
$v$	molar volume of liquid.
$\bar{V}_i$	partial molar volume of component $i$ .
$w$	see Eq. (13).
$x$	mole fraction in the condensed phase.
$y$	mole fraction in the gas phase.
$\mu$	chemical potential.
$\xi$	see Eq. (8).
$\pi$	= $3.14159$
$\rho$	number density of fluid molecules, see Eq. (9).
$\lambda$	see Eq. (7).

Subscripts

1	condensable component
01	component 1 at its normal vapor pressure.
2	helium
$m$	gas mixture
	Superscripts
$\infty$	refers to infinite dilution.
$G$	gas
$L$	liquid

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