

He-CF₄ 및 He-CClF₃ 系の 氣液相平衡 : II. 液相*

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Gas-Liquid Phase Equilibria in the He-CF₄ and He-CClF₃ Systems: II. Liquid Phase*

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요 약

He 이 CF₄ 및 CClF₃ 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 보라도 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 値와 實驗値와는 實驗値의 55% 以內的 오차를 가지고 있었다.

Abstract

The Henry's law constants and partial molar volumes at infinite dilution for helium in CF₄ and CClF₃ have been extracted from the experimental phase equilibrium data¹⁾ using the Krichevsky-Kasarnovsky equation²⁾ 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 Herrington³⁾ 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.

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Extraction of H_2^∞ and \bar{V}_2^∞ 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 equation³⁾ can be derived as given below with the assumptions that the liquid solution is ideal and the change of \bar{V}_2^∞ with pressure is negligible.

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

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^∞ and \bar{V}_2^∞ 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 $\ln H_2^\infty$ and whose slope is equal to $\bar{V}_2^\infty/(RT)$. The only unknown in the graphical evaluation of H_2^∞ and \bar{V}_2^∞ 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.

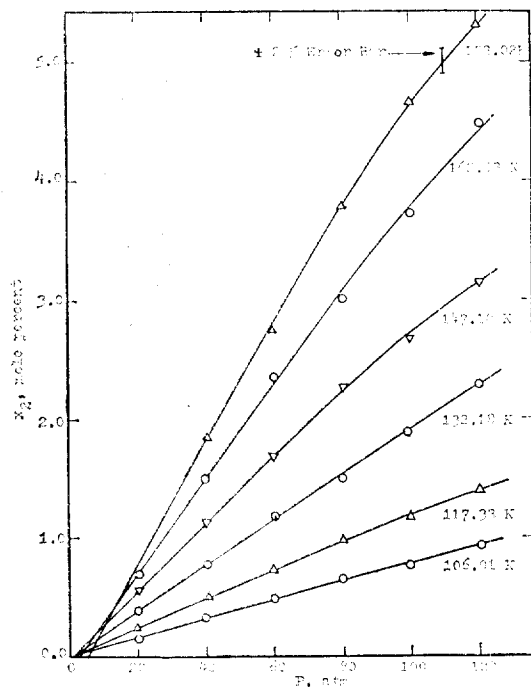


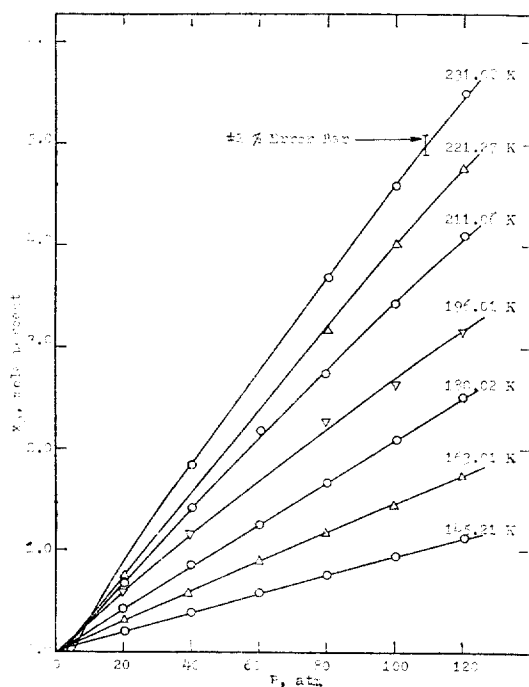
Fig. 1. Experimental solubility of He in liquid CF_4

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 paper¹⁾. 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.¹⁾ 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 CClF₃.

Since the virial coefficients used in evaluating Eq. (5) are not determined homogeneously but selected on the basis of best representation to the experimental data⁴⁾, 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,³⁰⁾ White, et al.,³¹⁾ Canfield, et al.,³²⁾ and Hoover, et al.,³³⁾ and all the other third virial coefficients were predicted using the method of Chueh and Prausnitz.³⁴⁾

Results and Discussion

The smoothed values of H_2^∞ and \bar{V}_2^∞ presented in Tables 1 and 2 were obtained from the smooth curves which represent the extracted values of H_2^∞ and \bar{V}_2^∞ 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^∞ and \bar{V}_2^∞ were available in the literature for the systems of He-CF₄

and He-CClF₃, 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^∞ is much greater than that of H_2^∞ . This is because in the systems of this work a small percent change of H_2^∞ produces a large percent change in the slope of the $\ln(f_2^G/x_2)$ vs. $(P-P_{01})$ curve which determines \bar{V}_2^∞ .

A good summary of the H_2^∞ and \bar{V}_2^∞ values for the helium binary systems is given recently by Garber⁵⁾. In his paper, he has compared H_2^∞ and \bar{V}_2^∞ 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^∞ and \bar{V}_2^∞ values, indicating the highest solubility of helium in the liquid nitrogen. In this work, the values of H_2^∞ in the He-CF₄ and He-CClF₃ systems have been found to be even smaller than those in the He-N₂ system; the H_2^∞ value at $T_{R1}=0.75$ for the He-CF₄ system is 1920 atm and that for the He-CClF₃ system 1960 atm, compared with H_2^∞ of 2120 atm for the He-N₂ system at the same reduced temperature. Although no attempt has been made to account for this high solubility of He in the liquid CF₄ and CClF₃, this is probably due to the anomalous solvent behavior of fluorochemicals. The values of \bar{V}_2^∞ in the helium-hydrocarbon systems studied by Garber⁵⁾ are all above 30cc/gm-mole at $T_{R1}=0.75$, the smallest being 30.7cc/gm-mole in the He-CH₄ system. This value is comparable to the values of \bar{V}_2^∞ in the He-CF₄ and He-CClF₃ systems, which are 27.8 and 31.1 cc/gm-mole, respectively.

Theoretical Prediction of H_2^∞ and \bar{V}_2^∞

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^∞ , and for the prediction of partial molar volume at infinite dilution, \bar{V}_2^∞ . Miller and Prausnitz⁶⁾, using the free volume theory^{7,8)}, 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^∞ and \bar{V}_2^∞ for the He-CF₄ System

T, K	H_2^∞ , atm		\bar{V}_2^∞ , 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^∞ and \bar{V}_2^∞ for the He-CClF₃ System

T, K	H_2^∞ , atm		\bar{V}_2^∞ , 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^{9,10)} for the calculation of H_2^∞ and \bar{V}_2^∞ has been presented by Pierotti^{11,12)} and used by Heck¹³⁾ and Garber⁵⁾. Very recently, Preston and Prausnitz¹⁴⁾ have shown a generalized thermodynamic expression for Henry's law constant based on the statistical mechanics of dilute liquid solutions. Snider and Herrington²⁾ 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 Herrington²⁾ 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^∞ and \bar{V}_2^∞ . This method which is based on first principles, is basically similar to that given by Pierotti^{11,12,15)} 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

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

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

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^{9,10)} and later from the solution of the Percus-Yevick equation for the hard sphere model.^{16,17)} Since this hard sphere model does not take into account configurational internal energy, it cannot represent satisfactorily a real liquid.

Longuet-Higgins and Wisdom¹⁸⁾ 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 Herrington²⁾ 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 Herrington²⁾ have also applied this equation for the calculation of H_2^∞ and \bar{V}_2^∞ 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, Staveley¹⁹⁾ 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, H₂-N₂, and He-CH₄ and proved that this method predicts excellent values of H_2^∞ and \bar{V}_2^∞ .

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

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

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

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

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^∞ must be forced to agree with Eq. (11).

Staveley¹⁹⁾ 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-CF₄ and He-CClF₃ 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)	ΔH_V (cal/gm-mole)	P (atm)	v_{01} (cc/gm-mole)
He	4.215 ²⁴⁾	19.4 ²⁴⁾	1.0	32.05 ²⁵⁾
CF ₄	145.12 ²⁶⁾	2823.6 ²⁷⁾	1.0	54.88 ²⁸⁾
CClF ₃	191.75 ²⁹⁾	3705.6*	1.0	68.67 ²⁶⁾

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

Table 4. Parameters for the method of Snider and Herrington

	r (Å)	$a_1 \times 10^{56}$ (erg cc/molecule)	$a_{12} \times 10^{37}$ (erg cc/molecule)
He	2.143		
CF ₄	4.219	1.606	4.651
CClF ₃	4.542	2.635	3.106

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

	T, K	v, cc/gm-mole		Percent
		Experimental	Calculated using Eq. (10)	Difference
CF ₄	106.01	48.69 ²⁸⁾	47.42	2.6
	117.33	50.21	49.44	1.5
	132.18	52.43	52.26	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 ₃ 145.21	61.85 ²⁹⁾	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^∞ data to Eq. (11). In this sense, the method of Snider and Herrington for the prediction of H_2^∞ 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^∞ and \bar{V}_2^∞

Figures 3 through 6 show comparisons of the calculated and experimental values of H_2^∞ and \bar{V}_2^∞ for the He-CF₄ and He-CClF₃ systems. As can be seen in Figs. 3 and 4, the predicted values of H_2^∞ are lower than the smoothed experimental values of H_2^∞ 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 CF₄ and CClF₃. The smoothed experimental values of \bar{V}_2^∞ presented in Tables 1 and 2 are compared in Fig. 5 and 6 with the predicted values of \bar{V}_2^∞ . 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 Herrington²⁾ 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

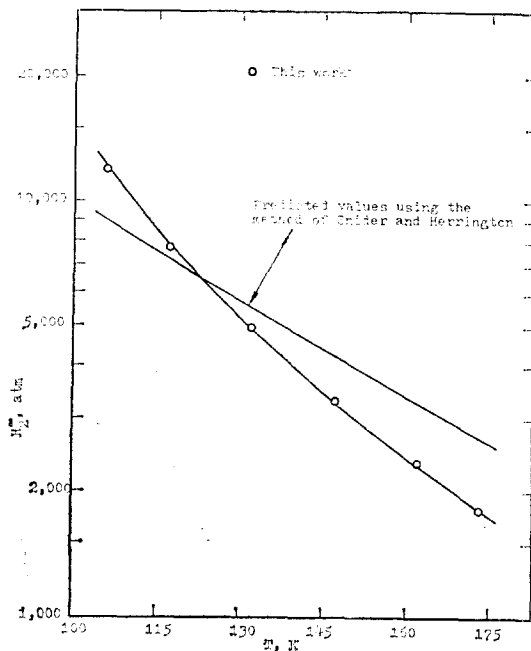


Fig. 3. Comparison of theoretical and experimental H_2^∞ for the He-CF₄ system

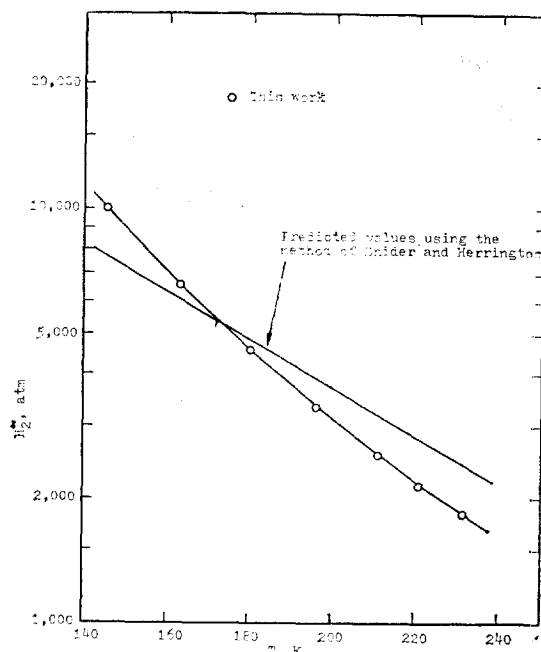


Fig. 4. Comparison of theoretical and Experimental H_2^∞ for the He-CClF₃ system

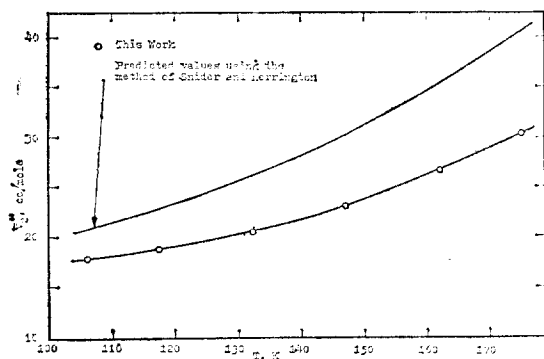


Fig. 5. Comparison of theoretical and experimental \bar{V}_2^∞ for the He-CF₄ system.

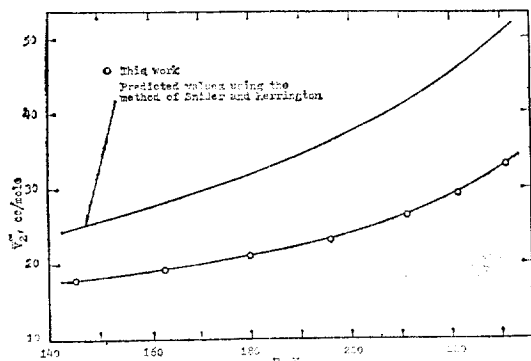


Fig. 6. Comparison of theoretical and experimental \bar{V}_2^∞ for the He-CClF₃ system.

in this work and the molar volumes of liquid CF₄ and CClF₃ 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, Staveley¹⁹⁾ has applied the method of Snider and Herrington²⁾ for the calculation of H_2^∞ and \bar{V}_2^∞ for the systems of Ne-Ar, H₂-N₂, He-CH₄, and He-H₂, and shown that the predicted values of H_2^∞ and \bar{V}_2^∞ are in quite satisfactory agreement with the experimental values except for the He-H₂ system, for which the predicted H_2^∞ value seriously exceeds the experimental value. This is, as Staveley¹⁹⁾ stated, probably due to the quantum effects for both compo-

nents, 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^∞ and \bar{V}_2^∞ values for the helium binary systems of this work with reasonable accuracy.

As stated by Snider and Herrington²⁾, 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 gases²⁰⁾ 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 Prausnitz²¹⁾ and Sherwood and Prausnitz²²⁾ 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 Brandt²³⁾ 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 CF₄ and CClF₃, strongly supports the use of the method of Snider and Herrington²⁾ for the calculation of the H_2^∞ and \bar{V}_2^∞ values for the He-CF₄ and He-CClF₃ systems.

Conclusions

The He-CF₄ and He-CClF₃ systems of this work

give the smallest H_2^∞ and \bar{V}_2^∞ values at a given reduced temperature of all helium binary systems investigated so far, indicating the highest solubility of helium in the two liquids, CF_4 and CClF_3 .

The method of Snider and Herrington²⁾ has been successfully applied to predict the H_2^∞ and \bar{V}_2^∞ values for the $\text{He}-\text{CF}_4$ and $\text{He}-\text{CClF}_3$ systems. Considering the simplicity of this method, this method is excellent in representing H_2^∞ and \bar{V}_2^∞ 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 $= 1.38054 \times 10^{-16} \text{ erg/K}$.
- n number of gm moles.
- P total absolute pressure
- R gas law constant $= 0.0820537 \text{ atm} \cdot \text{liter/gm mole} \cdot \text{K}$
- 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.
- μ chemical potential.
- ξ see Eq. (8).
- π $= 3.14159$
- ρ number density of fluid molecules, see Eq. (9).
- z see Eq. (7).

Subscripts

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

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