Gas-Liquid Phase Equilibria in the He-CF$_4$ and He-CClF$_3$ Systems. I. Gas Phase

Yo Kil Yoon

Korea Military Academy

W. T. Ziegler

School of Chemical Engineering

Georgia Institute of Technology

요 약

低溫 高壓下에 있는 He-CF$_4$ 및 He-CClF$_3$ 系內에서의 氣體, 液體間의 平衡狀態가 實驗 및 理論的으로 硏究되었다. 氣體上의 組成을 예측하기 위해 氣相의 平衡組成에 對한 完全한 熱力學的 關係式을 획득하고 몇가지 理論的인 model 을 시험했다. 그중 Lennard-Jones(6-12) classical potential function 과 mixture energy parameter 의 幾何學的 mixing rule 에 보정상수를 사용한 Kihara potential function 에 基本을 둔 virial 狀態 方程式이 가장 만족할만한 결과를 보여 주었다.

Abstract

The gas-liquid phase equilibria at low temperatures and high pressures have been studied both experimentally and theoretically for the helium-carbon tetrafluoride and helium-chlorotrifluoromethane systems. An exact thermodynamic expression for the gas phase equilibrium composition was obtained for the prediction of the gas phase composition.

Of the various theoretical models used for the evaluation of this expression, the virial equation of state based on the Lennard-Jones (6-12) classical potential function and the Kihara potential function with a correction to the geometric mixing rule for its mixture energy parameter gave quite satisfactory prediction of the gas phase compositions.

Introduction

Knowledge of phase equilibria is fundamental to the understanding of separation processes and other chemical engineering operations. During the last fifteen years, extensive experimental measurements have been made of two phase equilibrium in binary systems. Comparison of these measurements with the results of theoretical calculations has been made possible with the availability of electronic digital computers which made practical the solution of the complicated thermodynamic relations involved in these theoretical calculations.

The purpose of this research has been to obtain the experimental phase equilibrium data and to test various theoretical models for the prediction of phase equilibrium compositions of pressurized binary systems, in which one component is below its critical temperature

and the other is well above its critical temperature. Low concentrations of the gas in the condensed phase and activity coefficients near unity are the characteristics of such systems.

The enhancement factor, $\phi = \dfrac{Py_1}{P_{o1}}$, has long been used by many investigators in describing the nonideality of the gas phase in equilibium with liquid or solid phase. (This enhancement factor can also be viewed as the ratio of the actual mole fraction y_1 to the ideal mole fraction $y_1^0 = P_{o1}/P$ in the gas phase.) Since an exact thermodynamic expression for the enhancement factor is derivalbe, the ability of the theoretical models for the prediction of gas phase equilibria can be readily tested simply by calculating the enhancement factors using those theoretical models with an assumption of ideal solution for the condensed phase and comparing these calculated enhancement factors with experimental values.

Experimental Apparatus and Procedure

The single-pass flow type phase equilibrium apparatus designed and built by Kirk[1] was used for the determination of the gas and liquid phase compositions together with two gas chromatographs. Detailed description of this apparatus is given by Kirk[1], Mullins[2], and Garber[3].

The phase equilibrium cell whose internal volume and height are 46 cc and 9 in., respectively, consists of an approximately cylindrical 9.5 pound copper body closed at both ends with threaded monel plugs sealed with soft solder. The cell is surrounded by a larger copper body which serves the function of a cryostat. A liquid nitrogen reservoir which provides the refrigeration for the cell is suspended beneath the copper cryostat. The entire assembly is suspended in an evacuated cylindrical container filled with an evacuated powder insulation containing metal flakes (Linde CS-5). The refrigeration of the cell is provided by transferring liquid nitrogen by means of a small tube from the reservoir to an annular space between the cell and the copper block cryostat surrounding the cell. The pressure inside the reservoir is maintained a little above atmospheric pressure by means of a differential pressure regulator. This facilitates controlling the rate of refriger-

ation by simply adjusting the throttling valve in the vent line, which increases or decreases the rate of transfer of liquid nitrogen.

The primary thermometer used for temperature measurements of the cell is a capsule-type platinum resistance thermometer manufactured by Leeds and Northrup Company and has been calibrated by the National Bureau of Standards on the International Practical Temperature Scale of 1948 (IPTS-48) above 90.18 K. All temperatures in this work were converted from IPTS-48 to IPTS-68 and are reported on the Kalvin scale. Considering the temperature gradients along the cell and the cell temperature fluctuation, the uncertainty of temperature measurements was estimated to be ±0.03 K.

At first, the annular space between the copper cryostat and the insulation container is evacuated with a mechanical pump, while at the same time flushing out the equilibrium cell with helium gas to remove all impurities in it. The next step is to reduce the temperature of the cell using liquid nitrogen down to approximately the operating temperature, and then the pressure of the system is set using the pressure regulating valve, measuring the resulting gas flow rate. Right after this, a known amount of the liquid component is introduced into the equilibrium cell and this cell temperature is adjusted to the desired value. Establishing the equilibrium conditions, gas and liquid samples are continuously withdrawn and analyzed using two gas chromatographs.

Helium used in this work was obtained from the Air Reduction Company and had a quoted purity of 99.997 percent. Carbon tetrafluoride and chlorotrifluoromethane were supplied by E. I. de Pont de Nemours & Company, Inc. with a claimed purity of 99.9 percent. The argon used as a carrier gas for liquid analysis was perchased from the American Cryogenics, Inc. and its quoted purity was 99.999 percent. These materials were used without further purification.

Experimental Results and Discussion

Six isotherms in the gas-liquid region were studied for the helium-carbon tetrafluoride system and those

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for the gas phase are shown in Figure 1 except 147.10 K isotherm. The curvesa re smoothly drawn by eye through the experimental points so that the curves intersect the abscissa at the values of pressure equal to the vapor pressures of carbon tetrafluoride at given temperatures.

Seven isotherms in the gas-liquid region for the helium-chlorotrifluoromethane system are shown for the gas phase as a plot of enhancement factor vs pressure in Figure 2 except two isotherms, 180. 02 and 211. 00 K. The exprimental error in the gas phase analysis for the helium-carbon tetrafluoride system was estimated to be ±2 percent of the stated analysis and for the helium-chlorotrifluoromethane system ±3. 5 percrnt. These error ranges are also shown in Figures 1 and 2. In Figure 3, the smoothed enhancement factors obtained from Figures 1 and 2 are plotted agaist 1000/T for given pressures.

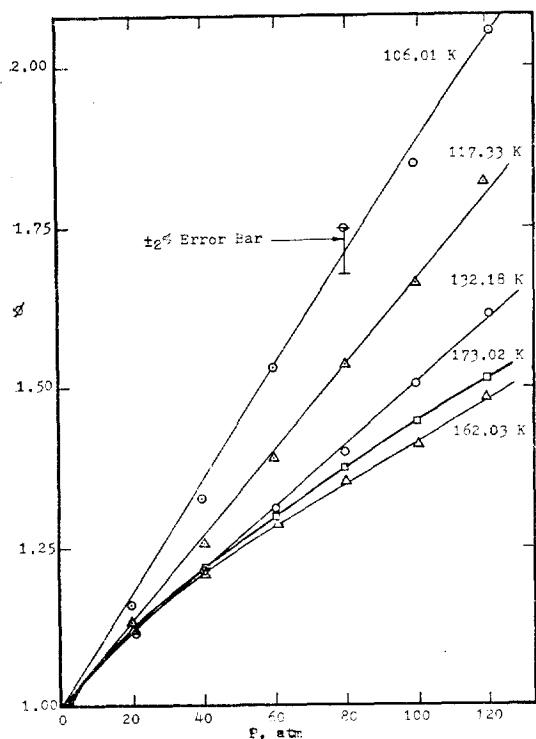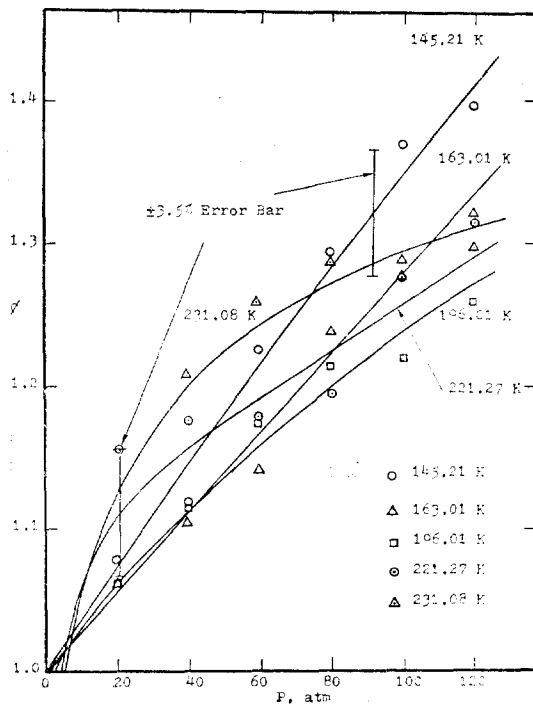Since no experimental phase equilibrium data were available for the systems of this work, no direct com-

Fig. 2. Experimental Enhancement Factors of Chlorotrifluoromethane in Helium.

Fig. 3. Experimental Enhancent Factors along Isobars.

Fig. 1. Experimental Enhancement Factors of Carbon Tetrafluoride in Helium.

parison could be made. However, the results are discussed in relation to those of similar binary systems. In most helium binary systems with light hydrocarbons, [1,4,5,6,7,8,9,10,11] the enhancement factors have been shown to be usually between one and two in the gas-liquid region at pressures up to 120 atm., and those in the helium-saturated hydrocarbon systems are greater than those in the corresponding unsaturated hydrocarbon systems[5,7] at the same pressures and reduced temperatures. Liu[12] has also shown that the enhancement factors in the helium-carbon dioxide system are smaller than those in other helium binary systems such as helium-argon, [13] -oxygen, [14] -nitrogen, [15] and -methane[16] systems; the maximum enhancement factors at pressures up to 120 atm in the latter systems are not much greater than two. In other words, the helium binary systems involving nonpolar spherical molecules generally give greater enhancement factors than those with less spherical molecules. These interesting facts are also true in the systems studied in this work as shown in Figures 1 and 2. Thus, the behavior of these helium-halogen-substituted methane systems is not much different from other helium binary systems.

Figure 3 shows the general trend of the enhancement factor isobars in the helium-carbon tetrafluoride and helium-chlorotrifluoromethane systems. As the temperature increases, the enhancement factors at the constant pressure decrease and then after passing a minimum point at around the normal boiling point of condensed component(145.12 K for CF_4[17] and 191.75 K for $CClF_3$[18]), the enhancement factors begin to increase with increasing temperature. This phenomenon was first noted by Hiza and Duncan[7] in their study of the helium-ethane system.

Figure 3 clearly shows these minimum points on the isobar curves and their shift to the higher temperature as the pressure increases. The lowest isobar curve in Figure 3 is extended with dotted line so that after passing a maximum point it crosses the abscissa at the temperature at which the vapor pressure of carbon tetrafluoride is 20 atm.

Calculation of Enhancement Factors

To predict the enhancement factors, that is, to cal-

culate ϕ without experimental value of y_1 in Equation (1), an exact thermodynamic expression for the enhancement factor is necessary.

$$\phi = \frac{Py_1}{P_{01}} \tag{1}$$

For the gas-liquid equilibrium in a binary system at the temperature T and pressure P, the chemical potential of the condensible component 1 in every phase must be equal, that is,

$$\mu_1^L(P, T, x_1) = \mu_1^G(P, T, y_1) \tag{2}$$

From Equation (2) the following expression for the enhancement factor can be obtained.

$$\ln \phi = \ln \frac{Py_1}{P_{01}} = \ln \frac{PV_m}{P_{01}V_{01}} + \frac{1}{RT}\int_{P_{01}}^{P} v_1 dP + \frac{1}{RT} \int_{V_{01}}^{\infty}\left[\left(\frac{\partial P}{\partial n_1}\right)_{V_1, T} - \frac{RT}{V_1}\right]dV_1 - \frac{1}{RT}\int_{V_m}^{\infty}\left[\left(\frac{\partial P}{\partial n_1}\right)_{V_m, T, n_2} - \frac{RT}{V_m}\right]dV_m + \ln(\gamma_1' x_1)$$

Assuming ideal solution for liquid phase and using a generalized correlation for the compressibilities of normal liquids given by Chueh and Prausnitz[9] for the evaluation of the liquid molar volumes and the virial equation of state truncated after the third virial coefficient, Equation (3) can be written as follows.

$$\ln \phi = \frac{v_{01}}{8.5RT}\left[\left\{1 + 9\beta^S(P - P_{01})\right\}^{\frac{8}{9}} - 1\right] + \frac{2B_{11}}{V_{01}} + \frac{3C_{111}}{2V_{01}^2} - \ln Z_{01} - \frac{2(y_1B_{11} + y_2B_{12})}{V_m} + \ln Z_m + \ln x_1 - \frac{3(y_1^2C_{111} + 2y_1y_2C_{112} + y_2^2C_{122})}{2V_m^2} \tag{4}$$

This equation is the working equation used for the prediction of the enhancement factor in the gas-liquid region of this work.

Several theoretical models used in this work for the evaluation of the virial coefficients are given in the following.

LJCL Model

Hirschfelder, et al. [20] have calculated the second and third virial coefficients based on the Lennard-Jones (6-12) classical potential function. LJCL model uses these virial coefficients for the calculation of Equation (4).

KIH Model

In evaluating Equation (4) for the KIH model, the expression for the second virial coefficient based on the Kihara [2,22] core potential function is used. The

third virial coefficient for this model is estimated using a correlation for the reduced third virial coefficient shown by Chueh and Prausnitz[23].

KIHCK12 and KIHEK12

These models are essentially the same as KIH except that the geometric mixing rule for the energy parameter requires a correction factor, K_{12}[7] in evaluating the interaction virial coefficient. Recently Hiza and Duncan[7] have reported an numerical correlation for K_{12} of simple binary gas mixtures as follows.

$$(U_o)_{12} = (1 - K_{12})(U_{o1}U_{o2})^{\frac{1}{2}} \tag{5}$$

$$K_{12} = 0.17(I_v - I_c)^{\frac{1}{2}} \ln\left(\frac{I_v}{I_c}\right) \tag{6}$$

Using Equation (6), K_{12} can be evaluated from the ionization potentials of the two components. The KIH model with this predicted K_{12} for the geometrice mixing rule for the energy parameter is called KIHCK12, and when K_{12} which is evaluated so as to fit the experimental interaction second virial coefficient data is used, it is designated as KIHEK12.

Comparison of Predicted and Experimental Enhancement Factors

For the prediction of enhancement factors for the helium-carbon tetrafluoride and helium-chlorotrifluorome thane systems, four theoretical models, LJCL, KIH, KIHCK12, and KIHEK12, have been studied. The required physical properties in predicting the enhancement factors using these models are given in Table 1. One representative isotherm for each system has been selected and presented for comparison in Figures 4 and 5.

In the prediction of enhancement factors at low pressures, where the third virial coefficients are insignificant, the B_{12} values play an important role within the same group of theoretical models such as KIH, KIHCK12, and KIHEK12 since the pure second virial coeffcents are identical in all the models. As can be seen in Figures 4 and 5, the two isotherms are best represented by the KIHEK12 and LJCL models, particularly at low pressures, which predicted the B_{12} values closest to the experimental values; the experimental B_{12} values were also extracted[24] from the phase equilibrium data of this work using Equation (4) and compared with the calculated values but are not shown

in this paper.

Table 1. Physical Properties for He, CF₄, and CClF₃

Component / Physical properties	He	CF₄	CClF₃
Ionization potential (eV)	24.46[25]	15.0[26]	12.91[27]
Calculated K_{12}		0.28	0.37
Experimental K_{12}**		0.06 (106—173K)	0.25 (145—231K)
P_c(atm)		36.96[17]	38.19[18]
V_c (cc/gm·mole)	37.5[23]	140.65[17]	180.81[18]
T_c(K)	10.47[23]	227.53[17]	302.00[18]
LJCL(6-12)			
ϵ/k(K)	6.96[2]	151.5[28]	This work 185.8
b_o(cc/gm·mole)	22.9[2]	134.7[28]	This work 220.7
KIHARA			
U_o (K)	9.927[29]	289.7[28]	This work 404.4
ρ_o(Å)	2.921[29]	3.232[28]	This work 3.367

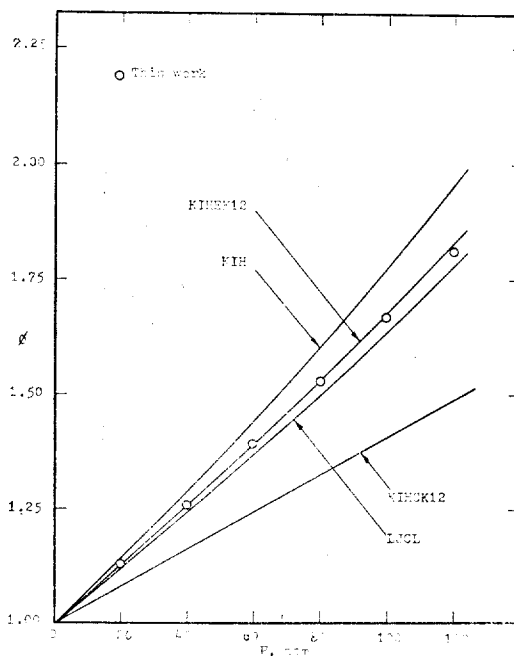** These values represent an average value over the specified temperature range

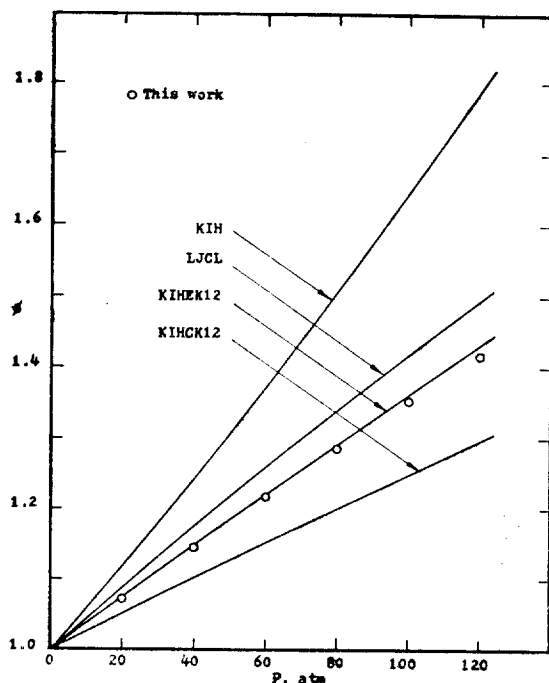Fig. 4. Theoretical and Experimental Enhancement Factors in the He-CF₄ System at 117.33 K.

Fig. 5. Theoretical and Experimental Enhancement Factors in the He-CClF₃ System at 145. 21 K.

For both of the helium binary systems considered here, the KIH model predicts larger enhancement factors at all the temperatures than not only the other Kihara models, KIHCK12 and KIHEK12, but also LJCL model. This can be expected since, first, the K_{12} factor is always positive and this positive value of K_{12} increases the B_{12} values which contribute negatively to the enhancement factors, and second, B_{12} values of the KIH model are greater than those of the LJCL model.

Unlike other helium binary gas mixtures, the K_{12} values calculated using Equation (6) are quite different from the experimentally determined K_{12} values. This difference produced a considerable difference in the predicted enhancement factors. From these results, it is concluded that the correlation for the K_{12} factor given by Hiza and Duncan[7] is inadequate for the helium-carbon tetrafluoride and helium-chlorotrifluoromethane systems.

Of all theoretical models considered, except the KIHEK12 model which has been adjusted to agree with the experimental enhancement factors, the LJCL model predicts most satisfactorily the enhancement factors for both systems, although the agreement of its predicted values with experimental data is poor at the highest isotherms. Since y_1 is much smaller than unity and V_m is very small compared with V_{o1} in Equation (4), the effect of B_{12} on the enhancement factors at low temperatures is much greater than B_{11}. Thus, the agreement of the B_{12} values predicted by the LJCL model with the experimental B_{12} values can easily account for this trend.

Some investigators[3,5,7,10] have experimentally shown that the enhancement factors in the helium binary systems decrease along an isobar with increasing temperature and then increase with increasing temperature, thereby generating a minimum point in the enhancement factor isobars. Recently, Garber[3] has pointed out that this minimum in the enhancement factor isobars is rather general in the helium binary systems and seems to be unique to these systems. The enhancement factor isobars shown in Figure 3 show this minimum as can be expected. This phenomenon is more pronounced at the higher isobars where the third virial coefficients are important. All theoretical models used in this work also exhibit this minimum in their isobars. In other words, the prediction of enhancement factors using these various theoretical models can be at least qualitatively satisfactory.

Conclusion

From the experimental results and enhancement factor calculation, the following conclusion can be drawn.

1. As has been shown by other investigators, the helium binary systems of this work have also shown the minimum point on their enhancement factor isobars both experimentally determined and theoretically calculated, demonstrating again the uniqueness of this phenomenon to the helium binary systems.

2. The theoretical model which can predict the B_{12} values accurately predicts generally the better enhancement factors.

3. Accordingly, the KIHEK12 model is the best in predicting the enhancement factors in both helium binary systems considered here. The LJCL model is generally satisfactory in he prediction of the enhancement factors compared with other theoretical models.

4. The correlation of Hiza and Duncan[7] has to be improved or new correlation is necessary for the correction factor, K_{12}, to the geometric mixing rule for the Kihara energy parameter for the helium-carbon tetrafluoride and helium-chlorotrifluoromethane systems.

m; gas mixture.

v; volatile component.

Superscripts

G; gas.

L; liquid.

Nomenclature

B, second virial coneffcient.

B_{12}; interaction second virial coefficient.

C; third virial coefficient.

e/k; energy parameter in Lennard-Jnes (6—12) intermolecular potential function.

I; ionization potential.

K_{12}; constant repesenting the deviation from the Kihara potential geometric mean of the characteristic energy parameters of components 1 and 2.

n; number of gm moles.

P; total absolute pressure.

R; gas law constant=0.0820537 atm-liter/gm·mole·K

T; temperature, K.

T_c; critical temperarature.

U_o; minimum energy of the Kihara potential function.

U_o/k; energy parameter in Kihara (6—12) model.

V; molar volume of gas.

V_c; critical molar volume.

v; molar volume of liquid phase.

x; mole fraction in the condensed phase.

y; mole fraction in the gas phase.

y^o; ideal mole fraction in the gas phase.

Z; compressibility factor.

β^s; isothermal compressibility for the pure component at sautration.

γ; activity coneffcient of component 1 in liquid solutions referred to the pure liquid component at the saturation temperature and pressure.

μ; chemical potential.

φ_o; shortest distance between molecular cores at minimum potential energy.

ϕ; enhancement factor.

Subscripts

1; condensible component.

01; gas at its normal vapor pressure.

2; helium.

c; condensible component.

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