Pressure Dependence of Liquid Vapor Pressure: An Improved Gibbs Prediction

Parsafar, Gholam Abbas^{*+}***; Moeini, Vahid and Najafi, Bijan***
Isfahan University of Technology Isfahan, Zip code 84154, I. R. Iran

ABSTRACT: *A new model for the vapor phase of a pressurized liquid called "the cluster model" which is originally introduced in this work, along with an accurate equation of state for the liquid phase called the LIR, is used to derive an accurate equation for the vapor pressure of liquid as a function of external pressure. The chemical potential of both phases have been found to be in good agreement with experiment. The calculated vapor pressure is compared with the Gibbs prediction. We have found that the Gibbs prediction is accurate at low external pressures and is reasonable at moderate pressures, but has a significant deviation at high external pressures. The calculated vapor pressure is used to obtain the vaporization enthalpy in terms of the external pressure. The physical interpretations for pressure dependence of both the vapor pressure and enthalpy of vaporization are also given. Compared to the temperature dependence, the pressure dependence of vapor pressure is insignificant.*

KEY WORDS: *Equation of state, LIR, Liquids, Vapor pressure*

INTRODUCTION

The history of the vapor pressure is old, and its temperature dependence is fully understood via the Clausius-Clapeyron equation. Its pressure dependence is rather convoluted, due to the fact that the vapor pressure of a pressurized liquid does not behave like an ordinary gas, and therefore its thermodynamic state depends on the external pressure on the liquid as well.

The first attempt to calculate the vapor pressure of a pressurized liquid was made by Gibbs [1], using the fact that at equilibrium the chemical potential of both phases must be equal; $\mu(l)= \mu(g)$, where μ is the chemical potential. Therefore, for any change that preserves equilibrium, the change in $\mu(l)$ must be equal to the change in $\mu(g)$, i.e. $d\mu(g)= d\mu(l)$. At constant temperature, when the pressure p on the liquid is increased by dp, the vapor pressure p^* must increase, in such a way that

$$\nu dp = \nu^* dp^* \qquad (1)$$

where dp^* is the change in the vapor pressure p^* of the liquid, ν and ν^* are the molar volume of the liquid and vapor, respectively. Gibbs treated the vapor as a perfect gas, i.e.

$$d\mu(g)= \frac{RTdp^*}{p^*} \qquad (2)$$

---

* *To whom correspondence should be addressed.*

+ *E-mail: parsafar@cc.iut.ac.ir*

1021-9986/2001/1/37 7/$/2.70

and by equating the two changes in the chemical potentials, one finds that $RTd\ln p^* = \nu dp$, which may be written as,

$$RT\left(\frac{\partial \ln p^*}{\partial p}\right)_T = \nu \tag{3a}$$

Eq. (3a) known as the Poynting equation. Integration of Eq. 3a at constant temperature gives the following result:

$$RT\int_{p_1^*}^{p_2^*} \frac{dp^*}{p^*} = \int_{p}^{p+\Delta p} \nu d\rho \tag{3b}$$

where p_1^* is the vapor pressure when there is no additional pressure acting on the liquid, which is equal to the pressure experienced by the liquid, p , and p_2^* is the vapor pressure when there is an additional pressure Δp on the liquid. Gibbs also assumed that the molar volume of the liquid is independent of the applied pressure on the liquid and obtained,

$$RT \ln \frac{p_2^*}{p_1^*} = \nu\Delta p \tag{4}$$

This equation shows the increase of the vapor pressure with the increment of the external pressure on the liquid.

The two assumptions made in deriving Eq. (4) are not valid over a wide range of external pressures, since (i) the molar volume of the liquid is pressure dependent and (ii) the vapor cannot be treated as a perfect gas. The main purpose of this work is to derive a more accurate equation by which the vapor pressure may be calculated over a wide range of external pressures. To undertake such a derivation, one must modify the two mentioned assumptions. Thus we may first calculate the chemical potential of the liquid experiencing an external pressure, and then calculate that for the vapor. Equating these two quantities, we may obtain an accurate expression, from which the vapor pressure of the liquid under an external pressure can be calculated.

Chemical potential of liquids

In this section we want to calculate the chemical potential of a liquid, $\mu(l)$, without assuming that volume is pressure independent. In order to take into account the pressure dependence of the liquid volume, an accurate equation of state for dense fluids is needed.

One of the recent and accurate equations of state which can be applied for all types of dense fluids has been derived by Parsafar and Mason [2-4], which is called the LIR (abbreviated for the Linear Isotherm Regularity). The LIR is stated as:

$$(Z - 1)v^2 = A + B\rho^2 \tag{5}$$

where A and B are temperature dependent parameters, and defined as,

$$A = A_2 - \frac{A_1}{RT} \tag{6}$$

and

$$B = \frac{B_1}{RT} \tag{7}$$

Z is the compressibility factor and $\nu = 1/\rho$ is the molar volume. Since the LIR is valid for a wide temperature range, specifically $T < 2T_B$, where T_B is the Boyle temperature of the fluid, therefore, it is applicable to all temperatures of interest in work, since the equilibrium between two phases exists only when $T < T_c$.

The change in the chemical potential of the liquid, $\Delta\mu$, is given as,

$$\Delta\mu = \int_{p}^{p+\Delta p} \frac{dp}{\rho} \tag{8}$$

which by applying the LIR (Eq. 5), one gets

$$\Delta\mu = RT\left\{\frac{3}{2}A(\rho_2^2 - \rho_1^2) + \frac{5}{4}B(\rho_2^4 - \rho_1^4) + \ln\frac{\rho_2}{\rho_1}\right\} \tag{9}$$

In order to check the validity of this equation, Eq. (9) may be written as,

$$\frac{\mu}{RT} - \ln(\rho/\rho^\circ) = \rho^2\left[\frac{3A}{2}\right] + \rho^4\left[\frac{5B}{4}\right] + \text{constant} \tag{10}$$

where $\rho^\circ = 1$ mole. dm^{-3}, according to which $\mu/RT - \ln(\rho/\rho^\circ)$ versus ρ^2 is a quadratic function. For this purpose, the experimental data of argon [5] have been used to plot $\mu/RT - \ln(\rho/\rho^\circ)$ against ρ^2, the results is shown in Fig. 1. As shown, the experimental points are fitted on a quadratic function very well.

Chemical potential of vapor

It is evident that the external pressure is applied solely on the surface of the liquid and the vapor may experience a much lower pressure than the surface of

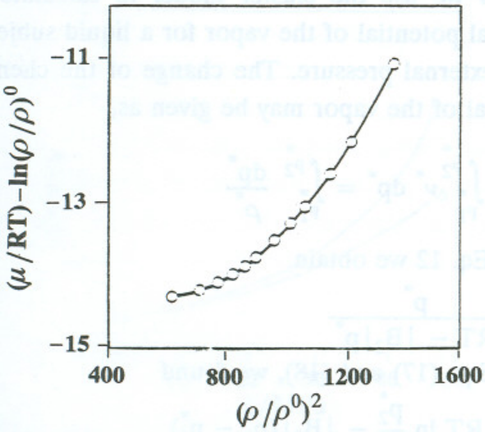

Fig. 1: Test of Eq. (10), as predicted by the LIR, for Ar. The density, ρ, is in terms of mol.L^{-1}

the liquid. However, the vapor remains at equilibrium with the liquid. Even though the supersaturated vapor (SV) exists at low temperatures and high pressures, no condensation occurs. If the external pressure is removed, the SV will be condensed, as much as the pressure is reduced to the vapor pressure (VP). In other words, SV is not a stable phase in the absence of the external pressure. Due to the fact that the external pressure prevents the condensation of the SV, therefore the thermodynamic state of the SV depends on the external pressure on the liquid, as well as the ordinary variables, like density (or temperature). Due to the absence of any condensation, we may postulate that there is no attraction among the particles in the SV (note that condensation arises from attractions). In the absence of any attraction, the perfect gas model seems to be appropriate for describing the SV. However, one must bear in mind that the SV is denser than the VP, and we may expect that the probability of cluster formation is more probable in the SV (by cluster we mean dimers, trimers, ... in the vapor without any attraction among them).

In order to include the effect of cluster formation on pressure, we may use the virial coefficients of the vapor. The abundance of monomer, dimer, ... clusters may be related to the absolute values of the first, second,... coefficients of the virial equation of state, respectively (This conclusion is in accordance with the Dalton's partial pressure law. Note that the minus and plus signs are attributed to the net attractive and repulsive interactions, respectively.). For example, the number of dimers is related to $[B_2]\rho^*$ of the virial expansion, where B_2 is the second virial coefficient of the vapor. Let us initially assume that the vapor consists of monomer and dimer clusters only, then, the fraction of particles as dimer is given by α_d, where :

$$\alpha_d = \frac{|B_2|\rho^*}{1+|B_2|\rho^*} \tag{11}$$

Of course $1/(1+|B_2|\rho^*)$ is the fraction for monomer. The following equilibrium may be considered in the vapor,

$$\underset{1-2\alpha_d}{2A} \rightleftharpoons \underset{\alpha_d}{A_2}$$

where A stands for the monomer. According to the cluster model, the vapor pressure can be calculated as,

$$p^* = \rho^*(1-\alpha_d)RT = \rho^*\,RT\left[1-\frac{B_2\rho^*}{1+|B_2|\rho^*}\right] \tag{12}$$

where ρ^* is the monomer density and $\rho^*(1-\alpha_d)$ is the effective particle density of the vapor. As expected, the formation of clusters will reduce the vapor pressure.

Now suppose that the trimer clusters are also formed in the vapor, then the following equilibria may be considered:

$$2A \rightleftharpoons A_2$$

and

$$3A \rightleftharpoons A_3$$

The monomer fraction is equal to $1-\alpha_d-2\alpha_t$, where α_d and α_t are the fraction of dimer and trimer clusters in the vapor, respectively, which are given by,

$$\alpha_d = \frac{|B_2|\rho^*}{1+|B_2|\rho^*+|B_3|\rho^{*2}} \tag{13}$$

and

$$\alpha_t = \frac{|B_3|\rho^{*2}}{1+|B_2|\rho^*+|B_3|\rho^{*2}} \tag{14}$$

where B_3 is the third virial coefficient. The vapor pressure is then given as,

$$p^* = \rho^*\,RT\left(\frac{1-|B_3|\rho^{*2}}{1+|B_2|\rho^*+|B_3|\rho^{*2}}\right) \tag{15}$$

Using the same argument, we may calculate the vapor pressure if larger clusters are also taken into account. For example, if tetramer clusters are also formed, the vapor pressure can be obtained as,

$$p^* = \rho^* RT\left(\frac{1 - |B_3|\rho^{*2} - 2|B_4|\rho^{*3}}{1 + |B_2|\rho^* + |B_3|\rho^{*2} + |B_4|\rho^{*3}}\right) \quad (16)$$

where B_4 is the fourth virial coefficient.

In order to test the accuracy of the cluster model, we have used the model to calculate the vapor pressure of water at different temperatures. the calculated results are compared with experiment data [6] in Table 1. The calculations are based on the cluster model with the maximum size of monomer (or perfect gas model), dimer (Eq. 12), trimer (Eq. 15), and tetramer (Eq. 16). As shown in Table 1, Eq. 12 is adequate at all temperatures, except in the vicinity of the critical temperature. In other words, the assumption of existence of molecules in vapor either as monomer or dimer clusters is sufficient, except for temperatures close to T_c. Such an assumption is reasonable due to the fact that the vapor density is high at temperatures close to T_c, and therefore the formation of larger clusters are more probable.

Table 1: The experimental vapor pressure of water (p_{exp}^*) at given temperatures compared with the calculated values, using the perfect gas model, p_1^*, and the cluster model with the maximum cluster size of 2,3, and 4 which is shown by p_2^*, p_3^*, and p_4^* respectively. All vapor pressures are in MPa units. The values of virial coefficients are taken from reference 7.

T/K	$^a p_{exp}^*$	p_1^*	p_2^*	p_3^*	p_4^*
313.15	0.0074	0.0074	0.0074		
333.15	0.0199	0.0200	0.0199		
353.15	0.0474	0.0478	0.0472		
373.15	0.101	0.103	0.101		
393.15	0.199	0.203	0.199		
413.15	0.361	0.375	0.362		
433.15	0.618	0.651	0.620		
453.15	1.003	1.079	1.003		
473.15	1.555	1.717	1.581		
493.15	2.320	2.647	2.377		
513.15	3.348	3.971	3.436	3.397	
533.15	4.694	5.839	4.955	4.887	
597.15	11.90	19.48	13.96	13.42	11.90

^{a}Reference 6

Now we use the cluster model to calculate the chemical potential of the vapor for a liquid subjected to an external pressure. The change of the chemical potential of the vapor may be given as,

$$\Delta\mu^g = \int_{p_1^*}^{p_2^*} v^* \, dp^* = \int_{p_1^*}^{p_2^*} \frac{dp^*}{\rho^*} \quad (17)$$

Using Eq. 12 we obtain,

$$\rho^* = \frac{p^*}{RT - |B_2|p^*} \quad (18)$$

using Eqs. (17) and (18), we found

$$\Delta\mu^g = RT \ln \frac{p_2^*}{p_1^*} - |B_2|(p_2^* - p_1^*) \quad (19)$$

As it was mentioned before, including the cluster with a maximum size of dimer is enough for all temperatures, except in the vicinity of T_c.

Calculation of vapor pressure

At equilibrium, the chemical potential of the liquid under external pressure has to be equal to that of the vapor. Using Eqs. (9) and (19) gives,

$$RT\left[\frac{3}{2}(\rho_2^2 - \rho_1^2) + \frac{5}{2} B(\rho_2^4 - \rho_1^4) + \ln \frac{\rho_2}{\rho_1}\right] = RT \ln \frac{p_2^*}{p_1^*} - |B_2|(p_2^* - p_1^*) \quad (20)$$

where p_1^* and p_2^* are the vapor pressure of the liquid with density ρ_1 and ρ_2, respectively. A and B are the LIR parameters (Eq. 5) and B_2 is the second virial coefficient of the vapor.

From practical point of view, knowing the molar density of the liquid at the normal boiling point (at which vapor pressure, $p_1^* = 0.1$ MPa) enables us to calculate the vapor pressure at any applied external pressure. Eq. (5) can be used to calculate the liquid density, ρ_2, at any given applied pressure and temperature. The results given by Eq. (20) are compared with those given by Eq. (4) in Fig. 2 for H_2O at 393.15 K. Even though, the results are the same for low external pressures, however, the deviation becomes significant at high external pressures.

It must also be noted that Eq. (20) may not be used for cases that the vapor density is high, especially in the vicinity of T_c, where the formation of trimer and tetramer clusters are more probable.

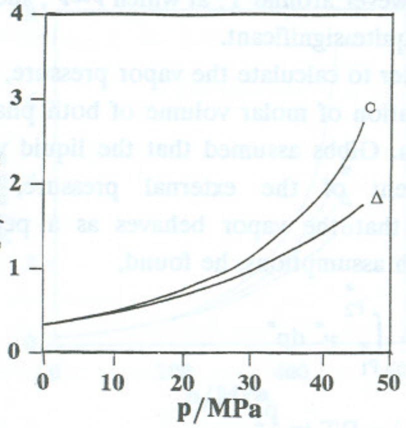

Fig. 2: Calculated vapor pressure of H_2O at 393.15 K in terms of the external pressure by the Gibbs prediction, Eq. (4)(Δ), and the cluster model, Eq. (20)(○).

Pressure dependence of vaporization enthalpy

The enthalpy of vaporization of a liquid under an external pressure, ΔH_{vap}, can be obtained by plotting the logarithm of the vapor pressure of the liquid (using Eq. 20) versus $1/T$. At any applied external pressure, ΔH_{vap}, can be calculated using the slope of such a plot. The logarithm of the calculated vapor pressure of water versus $1/T$ at some given external pressure is plotted in Fig. 3 in the temperature range of 393 K – 473 K. The linearity of such plots may be justified by the Clausius-Clapeyron equation, such a linearity is, almost true from the triple point up to critical temperature [8],

$$\ln p^* = -\frac{\Delta H_{vap}}{R}\frac{1}{T} + \text{constant} \tag{21}$$

which is derived, assuming that: (i) ΔH_{vap} is independent of both T and p, (ii) the molar volume of liquid is negligible with respect to that of the vapor, which is assumed to be an ideal gas. Such assumptions are not valid, especially around T_c, where the temperature dependence of ΔH_{vap} and of $\Delta\nu_{vap}$ are remarkable. However, there is some compensation of errors, in such a way that Eq. (21) is found to be valid from the triple point to critical temperature.

As far as we know the pressure dependence of ΔH_{vap} has not been investigated before. Eq. (21) along with Fig. 3 have been used to calculate ΔH_{vap} with respect to p for water which is shown in Fig. 4. As shown for pressure range of 1-300 MPa, the variation of ΔH_{vap} is less than 10%. The important point is that ΔH_{vap} versus p goes through a minimum, which may be justified thermodynamically.

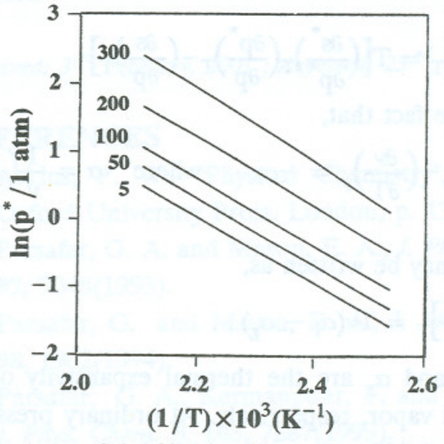

Fig. 3: A test of the Clausius-Clapeyron equation for water at given external pressures, using Eq. (20) (the numbers show the pressure in MPa).

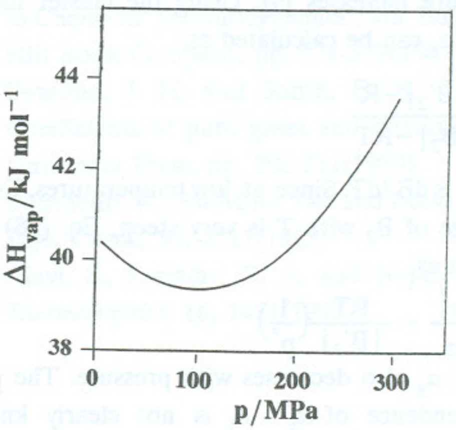

Fig. 4: The enthalpy of vaporization of water as a function of the external pressure, p.

Thermodynamically, the pressure dependence of ΔH_{vap} at constant temperature is given by,

$$\left[\frac{\partial(\Delta H_{vap})}{\partial p}\right]_T = \left[\left(\frac{\partial s^*}{\partial p^*}\right) - \left(\frac{\partial s}{\partial p}\right)_T\right] + \nu^*\left(\frac{\partial p^*}{\partial p}\right)_T - \nu \tag{22}$$

where s^* denotes the molar entropy of the vapor, (Note that $\Delta H_{vap} = H_g - H_l$ and $dH = \nu dp + TdS$). At equilibrium,

$$\left(\frac{\partial p^*}{\partial p}\right)_T = \frac{\nu}{\nu^*} \tag{23}$$

and, therefore, Eq. (22) reduces to

$$\left[\frac{\partial(\Delta H_{vap})}{\partial p}\right]_T = T\left[\left(\frac{\partial s^*}{\partial p}\right)_T - \left(\frac{\partial s}{\partial p}\right)_T\right] \tag{24}$$

or,

$$\left[\frac{\partial(\Delta H_{vap})}{\partial p}\right]_T = T\left[\left(\frac{\partial s^*}{\partial p^*}\right)_T\left(\frac{\partial p^*}{\partial p}\right)_T-\left(\frac{\partial s}{\partial p}\right)_T\right] \qquad (25)$$

Due to the fact that,

$$\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial \nu}{\partial T}\right)_p = -\alpha\nu \quad \text{where} \quad \alpha = \frac{1}{\nu}\left(\frac{\partial \nu}{\partial T}\right)_p \qquad (26)$$

Eq. (25) may be written as,

$$\left[\frac{\partial(\Delta H_{vap})}{\partial p}\right]_T = T\nu(\alpha_l - \alpha_g) \qquad (27)$$

where α_l and α_g are the thermal expansivity of the liquid and vapor, respectively. At ordinary pressures, $\alpha_l < \alpha_g$ and ΔH_{vap} decreases with the increment of p which is in accordance with Fig. 4.

The thermal expansivity of fluids decreases when the pressure increases [9]. Using the cluster model, Eq. (12), α_g can be calculated as,

$$\alpha_g = \frac{p^*|B'_2| - R}{p^*|B_2| - RT} \qquad (28)$$

where B'_2 is dB/dT. Since at low temperatures, $T<T_c$, the change of B_2 with T is very steep, Eq. (28) may be written as,

$$\frac{1}{\alpha_g} = \frac{|B_2|}{B'_2} - \frac{RT}{|B'_2|}\left(\frac{1}{p^*}\right) \qquad (29)$$

Therefore α_g also decreases with pressure. The pressure dependence of α_g - α_l is not clearly known. However, at ordinary pressures where $\alpha_l<\alpha_g$ we may except from Eq. 27 ΔH_{vap} reduces with the pressure, which is in accordance with Fig. 4. It seems from this figure that the decreasing rate of α_g with pressure is greater than that of α_l. In such a case, ΔH_{vap} must go through a minimum when pressure increases.

CONCLUSIONS

Although the vapor pressure of liquids increase when an external pressure is applied on the liquid surface at constant temperature, the increment is not significant except near T_c. At equilibrium, we have,

$$\frac{dp^*}{dp} = \frac{\nu}{\nu^*} \qquad (30)$$

Except near T_c , $v<<v^*$, then the change of the vapor pressure with the external pressure is very small. As noted before, this increase is about 10 percent for water when p increases by as much as 300 MPa. However around T_c at which $\nu\approx\nu^*$, such dependence is quite significant.

In order to calculate the vapor pressure, the pressure variation of molar volume of both phases must be known. Gibbs assumed that the liquid volume is independent of the external pressure, he also assumed that the vapor behaves as a perfect gas. With such assumptions, he found,

$$\int_{p_1}^{p_2} \nu dp = \int_{p_1^*}^{p_2^*} \nu^* dp^* \qquad (31)$$

or,

$$\nu(p_2 - p_1) = RT \ln \frac{p_2^*}{p_1^*} \qquad (32)$$

We here investigate first the effect of liquid volume correction and then the effect of supersaturated volume correction on the vapor pressure individually as follows:

i) Correction of liquid volume

If we use the actual volume of the liquid (i.e. from LIR, Eq. 5), the value of integral on the left hand side of Eq. (31) decreases and therefore p_2^* must also be less than that of the Gibbs equation (Eq. 4).

ii) Correction of supersaturated volume

In order to correct the pressure dependence of the vapor volume, we have used the cluster model, from which (in the simplest case),

$$\nu^* = \frac{RT}{p^*} - |B_2| \qquad (33)$$

Such a correction reduces the value of ν^* (compare to the perfect gas). In a given pressure range, in order for Eq. (31) to be valid, the pressure range of integration, $p_2^* - p_1^*$, must be increased (compare to the Gibbs, Eq. 4), therefore p_2^* must increase.

The above conclusions are in accordance with the results shown in Fig. 5 for H_2O at 393 K. When ν and ν^* are simultaneously corrected (by the LIR and the cluster model, respectively) the calculated result is compared with those in which the individual corrections are taken into account (Fig. 5). In summary, the following conclusions may be drawn:

1) The correction made for the vapor volume is more important than that for the liquid phase.

2) Gibbs prediction, Eq. (4), is accurate at low pres-

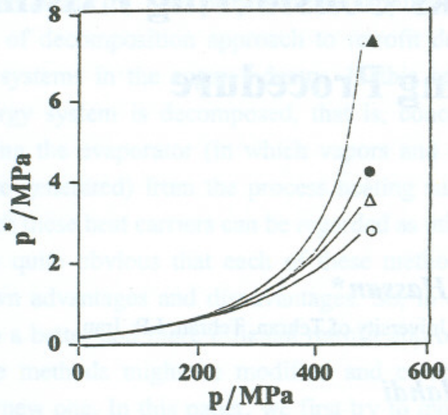

Fig. 5: Variation of the vapor pressure of H_2O at 393 K versus p, given by the Gibbs prediction (Δ), LIR for the correction of liquid volume (○), the cluster model for correction of vapor volume (▲), and for both corrections (●).

sures and is reasonable at moderate pressures, in which some compensation of errors occurs. However, the result given by Eq. (4) has significant deviations at high (external) pressures.

Acknowledgement

We wish to acknowledge the Research Council of Isfahan University of Technology for the financial support.

Received: 3rd February, 2001 ; Accepted: 23rd, April, 2001

REFERENCES

[1] Atkins, P. W., "Physical Chemistry", 4th Ed., Oxford University Press, London, p. 139(1990).

[2] Parsafar, G. A. and Mason, E. A., *J. Phys. Chem.*, **97**, 9048(1993).

[3] Parsafar, G. and Mason, E. A., *J. Phys. Chem.*, **98**, 1962(1994).

[4] Parsafar, G. A., Kermanpour, F. and Najafi, B., *J. Phys. Chem. B*, **103**, 7287(1999).

[5] Stewart, R. B. and Jacobsen, R. T., *J. Phys. Chem. Ref. Data*, **18**, 639(1989).

[6] Smith, J. M. and Van Ness, H. C., "Introduction to Chemical Thermodynamics", 4th Ed., McGraw-Hill Book Company, pp. 574-579(1987).

[7] Dymond, J. H. and Smith, E. B., "The Virial Coefficients of pure gases and mixtures", Oxford University Press, pp. 208-211(1980).

[8] Boushehri, A., Fu-Ming Tao and Mason, E. A., *J. Phys. Chem.*, **97**, 2711(1993).

[9] Alavi, S., Parsafar, G. A. and Najafi, B., *Int. J. Thermophysics*, **16**, 1421(1995).