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CALCULATION OF THERMODYNAMIC PROPERTIES OF FLUIDS USING A NEW EQUATION OF STATE

Parsafar, Gh.*
Kermanpour, F.
Department of Chemistry, Isfahan University of Technology,
Isfahan, Iran.

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ABSTRACT : *Using the Lennard - Jones (12-6) potential, a new equation of state is obtained that can predict properties of both gases and liquids relatively well. This equation of state is given as* $(Z\text{-}a)V^2 = (A/V^2) - B$ *, where Z is the compressibility factor, A and B are constants, and a is an adjustable parameter that depends on the temperature, volume and the nature of the fluid, and its expression depends upon the fluid status. In this paper, appropriate expressions for argon are given for a, in the liquid region when* $0.6 < T_r < 1$*, and in the gaseous region when* $1.1 < T_r < 4$*. This expressions can be used for other fluids as well. Using this equation of state the thermodynamic quantities such as entropy, enthalpy, Gibbs free energy and isothermal compressibility factor of the liquid are calculated. The calculated results differ only a few percent (< 10)from the experimental results.*

Compared with Redlich - Kwong, Bendict - Webb - Rubin, and Peng- Robinson equations of state, the new equation yield results that are comparable in the case of gaseous fluids, and better by nearly a factor of 2 for liquids.

KEY WORDS : *Equation of state, Thermodynamic properties of Ar.*

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* Corresponding author

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INTRODUCTION :

Having an equation of state for a fluid, as a function of its temperature, pressure and volume which holds in a wide range of temperature and density, is an important problem which has been investigated by two different approaches: empirical and theoretical (by statistical mechanics). Among empirical (or semi – empirical) are those given by *Van der Waals* [1], *Dieterici* [2], *Berthelot* [3], *Benedict Webb - Rubin* [4], *Redlich - Kwong* [5] and *Beattie - Bridgman* [6], equations of state. And among those via statistical mechanics are the virial equation of state [7], and those obtained from the radial distribution function [8] and the perturbation theories [9]. With regard to the temperature and pressure ranges and the variety of compounds for which the equation of state is applicable, the most successful empirical equations of state are the *Benedict - Webb - Rubin* (with eight adjustable parameters) and the *Redlich - Kwong* equations of state (with two adjustable parameters).

The most famous equation of state obtained by using statistical mechanics is the virial equation of state. This equation had already been introduced by *Onnes* empirically [10]. The virial expansion is generally a convergent series, but at very high densities, the series becomes divergent [11].

In principle, the radial distribution function theory is based on the many – body nature of the fluid. In this theory, the pair correlation function or the radial distribution function, g(r), plays the key role. This function shows the distribution of molecules around a given molecule, in terms of r, the distance from that molecule. If the potential between molecules of the fluids is assumed to be pairwise additive, then all thermodynamic quantities of the system, including pressure, can be obtained in terms of g(r) [7]. A notable point is that, the radial distribution function can be determined by x– ray diffraction studies [12]. However, because of the complexity of the results obtained by using the radial distribution function, the use of such results is limited.

In the perturbation theories, a liquid is considered as a system of particles, which a strong repulsion potential, and an attractive potential which acts as a small perturbation. Such point of view for the liquid structure, was originated during *Van der Waals*, times. He was the first one to focus attention on the different roles played by the short – range intermolecular repulsive forces and the long – range intermolecular attractive forces, in determining the structure and dynamics of fluids. The *Van der Waals* equation of state may be easily obtained by the use of statistical mechanical perturbation theory, and the results obtained may even not have the limitations of the *Van der Waals* equation [13]. The perturbation theory is a convenient theory that can numerically predict the critical point and properties of fluid at the high densities, and at the present time forms an active field of research.

The hole theory, has been propounded in the 1930's to study the properties of fluids [14]. Recently, an equation of state has been presented that, is based on hole theory which is applicable to liquids except in the neighbourhood of the critical point [15]. Our goal in the present paper is to extend this equation of state in such a way as to make it useful in the neighbourhood of the critical point and even for the gaseous fluids.

THEORETICAL BASIS :

Deriving the equation of state

By using statistical mechanics, an expression is obtained for the entropy of liquid, in ref. [15], which is compared with:

$$dS = C_v \, d \ln T + \left(\frac{\partial S}{\partial V} \right)_T dV \qquad (1)$$

to obtain an expression for $\theta_l = N/M$ in terms of T (N is the number of fluid particles and M is the total available sites for them). In this reference, it is suggested that for liquids, the second term on the right hand side of Eq.(1) can be discarded in comparison with the first term, since the volume dependence of the entropy of liquid is negligible in comparison with its temperature dependence (note that the volume change of liquid is small, except around its critical point). Because of this approximation, the equation of state which is presented in that reference is not applicable to liquids, in the neighbourhood of the critical point, and to gases (almost under any condition). If we integrate Eq. (1), assuming C_v is temperature independent, the following result will be obtained:

$$S = C_v \ln T + g(T,V) + \text{constant} \qquad (2)$$

where:

$$g(T,V) = \int \left(\frac{\partial S}{\partial V} \right)_T dV \qquad (3)$$

The internal energy of a fluid can be obtained from the sum of the kinetic energy and the intermolecular potential of molecules. If we use the pairwise additive approximation for the intermolecular potential and if we assume that each molecule interacts only with its nearest neighbours, and C is the average number of the nearest neighbours for each molecule, the total internal energy of the fluid can be written as:

$$U = \frac{3}{2} NkT + \frac{NC}{2} U_{12} \qquad (4)$$

where N is the number of particles of the fluid and U_{12} is the potential energy between two neighbouring molecules. In right hand of Eq. (4), the first term indicates the total kinetic energy and the second term the total potential energy of the fluid. If the potential between a pair of molecules obeys the *Lennard - Jones (12-6)* potential function, then Eq. (4) can be written as:

$$U = \frac{3}{2} NkT + \frac{NC}{2} \left(\frac{A_1}{V^4} - \frac{B_1}{V^2} \right) \qquad (5)$$

where V is the volume of the fluid and A_1 and B_1 depend on the molecular parameters. By having U and S, the *Helmholtz* free energy can be obtained as:

$$A = \frac{3}{2} NkT + \frac{NC}{2} \left(\frac{A_1}{V^4} - \frac{B_1}{V^2} \right) - T \{ C_v \ln T + g(T,V) + \text{constant} \} \qquad (6)$$

Noting that:

$P = -(\partial A / \partial V)_T$

the pressure can be obtained as:

$$P = \frac{NC}{2} \left(\frac{4A_1}{V^5} - \frac{2B_1}{V^3} \right) + T \left(\frac{\partial g}{\partial V} \right)_T \qquad (7)$$

or:

$$P = \frac{RT}{V} \left\{ \frac{NC}{2} \left(\frac{4A_1/RT}{V^4} - \frac{2B_1/RT}{V^2} \right) + \frac{V}{R} \left(\frac{\partial g}{\partial V} \right)_T \right\} \qquad (8)$$

Eq. (8) can be reduced as:

$$[Z - a(T,V)]V^2 = \frac{A_2}{V^2} - B_2 \qquad (9)$$

where:

$A_2 = 2A_1NC/RT$

$B_2 = B_1NC/RT$

and Z is the compressibility factor of the fluid and the parameter a is defined as fllows:

$$a(T,V) = \frac{V}{R} \left(\frac{\partial g}{\partial V} \right)_T \qquad (10)$$

Like any equation of state with two parameters, (if a becames constant) A_2 and B_2 can be written in terms of the critical constants of the fluid, by applying the critical point conditions, and then the equation of state is converted to the reduced form as:

$$P_r = \frac{3}{8} \left(\frac{1}{V_r^5} \right) - \frac{5}{4} \left(\frac{1}{V_r^3} \right) + \frac{aT_r}{Z_c} \left(\frac{1}{V_r} \right) \qquad (11)$$

To derive Eq. (11), we rearrange Eq. (9) in the following form:

$$P = \frac{A_3}{V^5} - \frac{B_3}{V^3} + \frac{aRT}{V} \qquad (12)$$

where:

$$A_3 = A_2RT \qquad (13)$$

$$B_3 = B_2RT \qquad (14)$$

and by comparing Eq. (3) with Eq. (10), we get a as:

$$a = \frac{V}{R} \left(\frac{\partial S}{\partial V} \right)_T \qquad (15)$$

Note that a depends on T and V. For the moment, however, we consider a is constant in order to obtain A_3 and B_3 parameters in terms of the critical constants. By considering a as an adjustable parameter, this approximation will be then corrected. Therefore, for now we have;

$$\left(\frac{\partial P}{\partial V}\right)_{T_c} = -\frac{5A_3}{V^6} + \frac{3B_3}{V^4} - \frac{aRT}{V^2} = 0 \tag{16}$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c = T} = \frac{30A_3}{V^7} - \frac{12B_3}{V^5} + \frac{2aRT}{V^3} = 0 \tag{17}$$

Simultaneous solution of Eqs. (16) and (17), along with :

$$P_c = \frac{A_3}{V_c^5} + \frac{B_3}{V_c^3} + \frac{a_cRT_c}{V_c} \tag{18}$$

gives A_3 and B_3, if $T = T_c$, $V = V_c$, and $a = a_c$ are substituted into above equations:

$$A_3 = \frac{1}{5} Ra_cT_cV_c^4 \tag{19}$$

$$B_3 = \frac{2}{3} Ra_cT_cV_c^2 \tag{20}$$

$$a_c = \frac{15}{8} Z_c \tag{21}$$

Substitution of a_c, from Eq. (21), into Eqs. (19) and (20), gives A_3 and B_3 in terms of the critical constants as:

$$A_3 = \frac{3}{8} RZ_cT_cV_c^4 \tag{22}$$

$$B_3 = \frac{5}{4} RZ_cT_cV_c^2 \tag{23}$$

Substitution of A_3 and B_3 from Eqs. (22) and (23) into the equation of state (Eq. 12), and dividing both side of the resulting equation by P_c, reduces Eq. (12) to Eq. (11). The other forms of Eq. (11) are:

$$a = Z - \frac{Z_c}{T_rV_r^2}\left(\frac{3}{8V_r^2} - \frac{5}{4}\right) \tag{24}$$

$$(Z - a)V_r^2 = \frac{3Z_c}{8T_r}\left(\frac{1}{V_r^2}\right) - \frac{5Z_c}{4T_r} \tag{25}$$

Calculation of the adjustable parameter a for liquids

In order to study the equation of state obtained, we have to have the parameter a. We consider this parameter as an adjustable parameter, and attempt to give an appropriate mathematical function for it. The value of a can be calculated by using Eq. (24) and having Z at a given T_r and P_r and the value of Z_c for the fluid. The *Lee and Kesler's* tables [16] are used for such calculation. In these tables, the quantities of $Z^{(0)}$ and $Z^{(1)}$ are given at various reduced temperatures and pressures in the ranges of $0.3 < T_r < 4$ and $0.01 < P_r < 10$. $Z^{(0)}$ and $Z^{(1)}$ are related to Z and the acentric factor ,ω, as:

$$Z = Z^{(0)} + \omega Z^{(1)} \tag{26}$$

The value of the acentric factor ,ω, depends on the given fluid. Whenever the geometry of the molecule deviates from the spherical and groups belonging to the molecule are more complicated, the value of the acentric factor is larger. The value of ω, is taken from ref. [17]. It is clear that by having the value of Z at any given T_r and P_r , the value of V_r for a fluid may be calculated as:

$$V = \frac{ZRT}{P} = \frac{ZRT_cT_r}{P_cP_r} \tag{27}$$

$$V_r = \frac{V}{V_c}$$

Thus, the value of a for any given fluid can be calculated at any given T_r and V_r by using the experimental data. Now, we want to obtain a mathematical expression for a in terms of T_r and V_r, by using the thermodynamic equations and such data. From Eq. (15), we substitute $(\partial S/\partial V)_T$ into Eq. (1) to obtain the following result:

$$dS = \frac{C_v}{T} dT + \frac{Ra}{V} dV \tag{28}$$

Since dS is an exact differential, we have:

$$\frac{1}{T}\left(\frac{\partial C_v}{\partial V}\right)_T = \frac{R}{V}\left(\frac{\partial a}{\partial T}\right)_V \tag{29}$$

Since C_v is almost independent of temperature for liquids, not in a wide range of temperature [18], then:

$$\frac{1}{T}\frac{\partial C_v}{\partial V} = \frac{1}{T}\frac{dC_v}{dV} \tag{30}$$

This means that the left side of Eq. (29) is an exact differential. Therefore, Eq. (29) can be written as:

$$R\left(\frac{\partial a}{\partial \ln T}\right)_V = \frac{dC_v}{d\ln V} \tag{31}$$

Which at constant V becomes:

$$\frac{da}{d\ln T} = \frac{1}{R}\frac{dC_v}{d\ln V} \tag{32}$$

Since C_v does not depend on T, the right hand of Eq. (32) is a function of V only, we may then write:

$$\frac{1}{R}\frac{dC_v}{d\ln V} = f(V) \tag{33}$$

Eq. (32) may then reduced to:

$$\frac{da}{d\ln T} = F(V) \tag{34}$$

We integrate both sides of this equation at constant volume to obtain the following result:

$$a = f(V)\ln T + \text{constant} \tag{35}$$

It is obvious that the constant is a function of V, therefore the final result in terms of the reduced variables is as the following:

$$a = h(V_r) + f(V_r)\ln T_r \tag{36}$$

This means that a for liquids is linear in terms of $\ln T_r$. In order to evaluate this result, the calculated values of a are plotted against $\ln T_r$ in Fig. 1, in the temperature range of $0.8 < T_r < 1$, for the liquid argon at some given values of $P_r(V_r)$, in which its linearity is obvious. Fig. 1 is used to derive an appropriate expressions for $h(V_r)$ and $f(V_r)$ functions. The intercepts of these lines give $h(V_r)$and their slopes give $f(V_r)$. The results of such calculations are listed in Table 1. By using the data given in the Table 1, mathematical expressions for $h(V_r)$ and $f(V_r)$ in terms of V_r, can be obtained. For this purpose, an appropriate software was used and the mathematical expressions obtained were as follows:

$$f(V_r) = 17.318 - 26.717\ V_r \tag{37}$$

$$h(V_r) = 1.843 - 13.887\ V_r^2 + 23.000V_r^4 + 48.000V_r^6 - 64.000\ V_r^8 \tag{38}$$

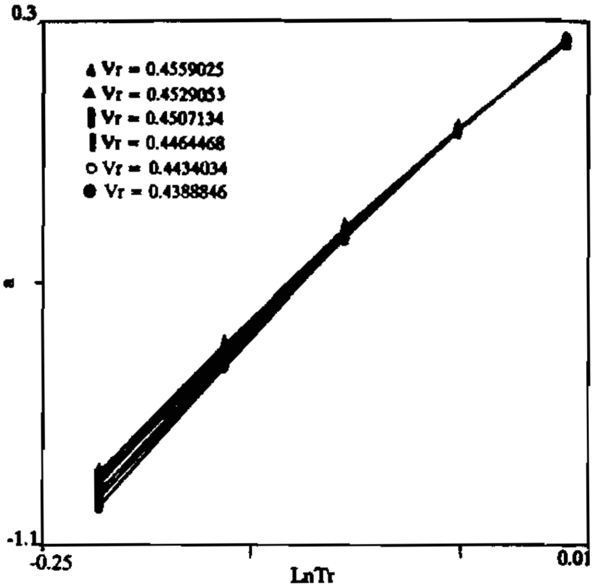

Fig. 1: The adjustable parameter a versus $\ln T_r$ for liquid Ar, at some given values of V_r

Table 1: The intercepts, $h(V_r)$, and slopes, $f(V_r)$, of the lines given in Fig. 1 for liquid Ar.

V_r	$h(V_r)$	$f(V_r)$	Max.Error
0.4559025	0.2620605	5.137312	2.3011e-2
0.4529058	0.2634809	5.217581	2.3777e-2
0.4507134	0.2648305	5.276571	2.4338e-2
0.4464468	0.2682128	5.391295	2.5394e-2
0.4434034	0.2712342	5.472501	2.6090e-2
0.4388846	0.2766630	5.591181	2.7610e-2

However, it is predicted that if the temperature range is taken to be wide, Eq. (36) is no longer applicable, because C_v will have a considerable temperature dependence (Fig. 12–1 in ref. [14]). To investigate this prediction, a is plotted againts $\ln T_r$ in Fig. 2, in the range of $0.6 < T_r < 1$ for some given values of $P_r(V_r)$, for liquid argon. As it is expected, the curves are nonlinear. In order to find an appropriate mathematical expression for a in a wide range of

Table 2: The coefficients of the polynomial $a=C_0 + C_1 \ln T_r + ... + C_5(\ln T_r)^5$ for the curves given in Fig. 2 for liquid Ar.

V_r	C_o	C_1	C_2	C_3	C_4	C_5
0.361	-4.358	15.270	-21.970	32.634	-45.160	32.861
0.392	-4.181	14.479	-15.843	7.415	0.263	2.176
0.422	-4.010	13.725	-10.098	-16.002	42.091	-25.892
0.451	-3.843	12.977	-4.296	-39.911	85.209	-55.027
0.480	-3.674	12.241	1.251	-62.365	125.024	-81.592
0.512	-3.489	11.419	7.592	-88.375	171.829	13.131
0.545	-3.300	10.583	14.022	-114.782	219.118	-144.928
0.573	-3.144	9.882	19.453	-137.063	259.358	-172.126
0.613	-2.915	8.866	27.282	-169.172	316.928	-210.938
0.643	-2.743	8.103	33.153	-193.254	360.106	-240.033

temperature, we consider a as a polynomial in terms of $\ln T_r$:

$$a = \sum_{i=0}^{n} C_i(\ln T_r)^i \tag{39}$$

The best fit with the experimental data, is obtained for n=5:

$$a = C_0 + C_1 \ln T_r + C_2(\ln T_r)^2 + ... + C_5(\ln T_r)^5 \tag{40}$$

where the C_i coefficients depend on the volume. Indeed, Eq. (36) is a truncated form of Eq. (40), in which the third and higher terms have been neglected. The values of the coefficients are listed in Table 2, for some given values of volume. Using data given in Table 2, appropriate mathematical functions could be obtained for the C_is. The result obtained is as follows:

$$C_i = a_i + b_i V_r \tag{41}$$

where:

i	0	1	2	3	4	5
a_i	-0.305	11.080	24.500	152.400	379.700	356.600
b_i	1.193	-15.620	-66.310	-358.900	-965.500	-913.800

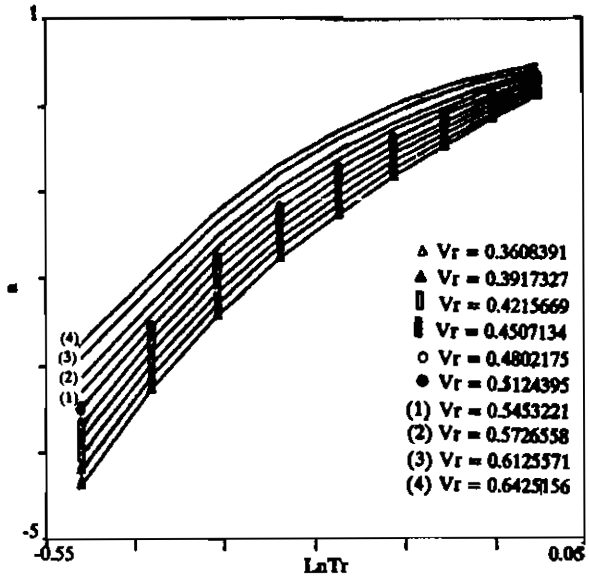

Fig. 2 : The adjustable parameter a versus $\ln T_r$ for liquid Ar, in the temperature range of $0.6 < T_r < 1$

Calculation of thermodynamic quantities for liquids

Now, having the adjustable parameter a, we can obtain expressions for the thermodynamic functions. By suing Eq. (10) and Eqs. (36) or (39) and (40) for a, the g function can be obtained for the ranges of $0.8 < T_r < 1$ and $0.6 < T_r < 1$, respectively, as:

$$g(T,V) = R \int a \frac{dV}{V} \qquad (42)$$

or:

$$g(T_r, V_r) = R \int a \frac{dV_r}{V_r} \qquad (43)$$

$$g(T_r, V_r) = R \{1.843 \ln V_r - 6.943 V_r^2 + 5.750V_r^4 + 8.000V_r^6 - 8.000V_r^8 + (17.318 \ln V_r - 26.717V_r) \ln T_r\}, \quad 0.8 < T_r < 1 \qquad (44)$$

$$g(T_r, V_r) = R \{\sum_{i=0}^{5} (a_i \ln V_r) + b_i V_r)(\ln T_r)^i\}, \quad 0.6 < T_r < 1 \qquad (45)$$

where the a_i and b_i have the same values given in Eq. (41). By using Eq. (6) and related equations for A_2, B_2, A_3 and B_3, ($A_2 = 2A_1NC / RT$, $B_2 = B_1NC/RT$, $A_3 = A_2RT$, $B_3 = B_2RT$ and Eqs. 22 and 23), the *Helmholtz* free energy can be related to g as:

$$A = RT_c \{ \frac{3Z_c}{32} (\frac{1}{V_r^4}) - \frac{5Z_c}{8} (\frac{1}{V_r^2}) - \frac{T_r}{R} g(T_r, V_r)\} + C(T) \qquad (46)$$

The integration constant of Eq. (43) and the other temperature dependent terms are included in the C(T) constant.

By using the equation of state (Eq. 12) and:

$$(\frac{\partial P}{\partial T})_V = (\frac{\partial S}{\partial V})_T \qquad (47)$$

the entropy can be obtained as:

$$S = g(T_r, V_r) + N(T_r, V_r) + C(T) \qquad (48)$$

where $g(T_r, V_r)$ is defined in Eq. (43) and the $N(T_r, V_r)$ expression is as:

$$N(T_r, V_r) = R \int T_r (\frac{\partial a}{\partial T_r})_{V_r} \frac{dV_r}{V_r} \qquad (49)$$

By using Eqs. (36 – 38) for the temperature range of $0.8 < T_r < 1$, we will have the following result for N:

$$N(T_r, V_r) = R(17.318 \ln V_r - 26.717 V_r) \qquad (50)$$

and for the temperature range of $0.6 < T_r < 1$, by using Eqs. (39) and (40) for a, we shall have:

$$N(T_r, V_r) = R \sum_{i=0}^{5} i(a_i \ln V_r + b_i V_r)(\ln T_r)^{i-1} \qquad (51)$$

The enthalpy can be calculated by having A, S and P. The results, in terms of $g(T_r, V_r)$ and $N(T_r, V_r)$ functions, are as the following:

$$H = A + TS + PV = RT_c \{ \frac{15Z_c}{32} (\frac{1}{V_r^4}) - \frac{15Z_c}{8} (\frac{1}{V_r^2}) + T_r[a + \frac{N(T_r, V_r)}{R}]\} + C(T) \qquad (52)$$

and, finally, the *Gibbs* free energy, G, can be calculated by having H and S,

$$G = RT_c \{ \frac{15Z_c}{32} (\frac{1}{V_r^4}) - \frac{15Z_c}{8} (\frac{1}{V_r^2}) + T_r[a - \frac{g(T_r, V_r)}{R}]\} + C(T) \qquad (53)$$

The isothermal compressibility of a fluid can be obtained as:

$$k = -V (\frac{\partial P}{\partial V})_T \qquad (54)$$

if we replace P from Eq. (12) into Eq. (54), we get:

$$k = P_c \{P_r + \frac{3}{2} (\frac{1}{V_r^5}) - \frac{5}{2} (\frac{1}{V_r^3}) - \frac{T_r}{Z_c} X\} \qquad (55)$$

where:

$$X = (\frac{\partial a}{\partial V_r})_{T_r} \qquad (56)$$

for the temperature range of $0.8 < T_r < 1$, by using Eqs. (36 − 38) for a, we have:

$$X = -27.773V_r + 92.000V_r^3 + 288.000V_r^5 - 512.000V_r^7 - 26.717\ \ln T_r \qquad (57)$$

and for the temperature range of $0.6 < T_r < 1$, by using Eqs. (39) and (40) for a, we get :

$$X = \sum_{i=0}^{5} b_i(\ln T_r)^i \qquad (58)$$

The results obtained for the thermodynamic quantities, by using Eqs. (43 − 53), are listed in Tables 3 and 4. The constant values in these equations, C(T), are chosen so that the best agreement is obtained with the experimental data in the whole range. The experimental values are taken from ref. [19]. In these tables, the experimental and calculated values, are also compared and the percent of their differences are listed. The values for the isothermal compressibility of liquid, are calculated by using Eqs. (55), (57) and (58), which are listed in Table 5. The experimental values are taken from ref. [20].

Table 3: Comparison of the experimental and theoretical thermodynamic quantities for liquid argon.*

T = 120 (K)									
P (atm)	S_r (J/m.K)	S_c (J/m.K)	RDS	H_r (J/m)	H_c (J/m)	RDH	G_r (J/m)	G_c (J/m)	RDG
15	69.71	69.12	0.85	4621	4559	1.34	−3744	−3735	0.24
20	69.58	69.01	0.81	4630	4564	1.43	−3720	−3718	0.05
25	69.45	68.91	0.78	4639	4570	1.50	−3695	−3700	0.12
30	69.32	68.80	0.75	4647	4576	1.54	−3671	−3681	0.26
40	69.06	68.59	0.68	4664	4589	1.61	−3623	−3642	0.51
50	68.81	68.37	0.64	4677	4605	1.55	−3580	−3600	0.55
60	68.56	68.26	0.44	4688	4613	1.59	−3539	−3578	1.09
70	68.32	68.03	0.42	4697	4632	1.38	−3501	−3532	0.87
80	68.08	67.92	0.24	4706	4642	1.35	−3464	−3508	1.28
100	67.62	67.57	0.07	4723	4677	0.98	−3391	−3432	1.19
120	67.19	67.33	0.21	4740	4702	0.79	−3323	−3377	1.65
140	66.79	66.97	0.27	4757	4764	0.23	−3258	−3290	0.99
160	66.41	66.59	0.27	4774	4796	0.45	−3195	−3195	0.00
180	66.06	66.34	0.42	4790	4832	0.88	−3137	−3128	0.30
200	65.73	66.21	0.72	4806	4852	0.95	−3082	−3093	0.37
300	64.09	65.12	1.61	4878	5036	3.23	−2813	−2779	1.21
500	61.38	63.02	2.67	5055	5502	8.85	−2311	−2060	10.84

* S_r , H_r , G_r [19] and the calculated values, S_c , H_c and G_c (calculated by using Eqs. 36-38, 44, 50, 52 and 53)and the percent differences for entropy, RDS, enthalpy, RDH and *Gibbs* free energy, RDG, for the liquid Ar. The constants of integration for the entropy, enthalpy and *Gibbs* free energy are equal to 256 $J.\ mol^{-1}.\ K^{-1}$ 30506 $J.mol^{-1}$ and -228 $J.mol^{-1}$, respectively.

Table 4: Comparison of the experimental and theoretical thermodynamic quantities for liquid argon.*

T = 120 (K)									
P (atm)	S_r (J/m.K)	S_c (J/m.K)	RDS	H_r (J/m)	H_c (J/m)	RDH	G_r (J/m)	G_c (J/m)	RDG
15	69.71	69.62	0.13	4621	4596	0.53	−3744	−3758	0.38
20	69.58	69.48	0.15	4630	4599	0.66	−3720	−3738	0.50
25	69.45	69.33	0.17	4639	4603	0.79	−3695	−3717	0.61
30	69.32	69.19	0.19	4647	4606	0.88	−3671	−3696	0.68
40	69.06	68.90	0.24	4664	4615	1.05	−3623	−3652	0.80
50	68.81	68.60	0.30	4677	4626	1.09	−3580	−3606	0.73
60	68.56	68.45	0.16	4688	4632	1.19	−3539	−3582	1.22
70	68.32	68.15	0.24	4697	4646	1.09	−35.01	−3533	0.89
80	68.08	68.00	0.11	4706	4653	1.12	−3464	−3507	1.25
100	67.62	67.55	0.10	4723	4680	0.92	−3391	−3426	1.03
120	67.19	67.24	0.08	4740	4700	0.84	−3323	−3369	1.39
140	66.79	66.78	0.01	4757	4735	0.45	−3258	−3278	0.63
160	66.41	66.31	0.15	4774	4776	0.05	−3195	−3181	0.44
180	66.06	66.00	0.10	4790	4807	0.36	−3137	−3112	0.79
200	65.73	65.84	0.16	4806	4824	0.37	−3082	−3077	0.16
300	64.09	64.54	0.71	4878	4984	2.17	−2813	−2761	1.84
500	61.38	62.17	1.28	5055	5409	7.00	−2311	−2051	11.22

* S_r , H_r , G_r [19] and the calculated values, S_c , H_c , and G_c (obtained by using Eqs. 39-42, 45, 48, 51, 52 and 53) and the percent differences for entropy, RDS, enthalpy, RDH and *Gibbs* free energy, RDG, for the liquid Ar. The constants of integration for the entropy, enthalpy and *Gibbs* free energy are equal to 138 $J.mol^{-1}$. K^{-1} 16702 $J.mol^{-1}$ and 111 $J.mol^{-1}$, respectively.

Table 5 : Comparison of the experimental and theoretical values for isothermal compressibilities*

P(atm)	V_r	k(atm)	k_1(atm)	k_2(atm)	RDk_1	RDk_2
25	0.46485	1437.8	1545.9	1882.45	7	23.62
50	0.45746	1689.2	1887.1	2153.95	10.49	21.58
100	0.44569	2165.4	2492.2	2654.56	13.11	18.43
200	0.42882	3052.5	3525.5	3551.97	13.42	14.06
400	0.40695	4683.8	5264.6	5139.78	11.03	8.87
600	0.39221	6207.3	6794.4	6582.37	8.46	5.76

* The experimental isothermal compressibility, k, [20] and the calculated values obtained by using Eqs. 55 and 57, k_1, and by Eqs. 55 and 58, k_2, respectively and the percent deviations for k_1, RDk_1, and k_2, RDk_2, for liquid Kr at T = 170 K.

Calculation of the adjustable parameter a for gas

As stated, the fact that the temperature dependence of C_v of liquid is negligible, not in a wide range of temperature, we could obtain an appropriate expression for a. However, gases do not possess such a property. We then have to obtain an expression through other means for gases. For this purpose, a has to be considered as a function of V_r, in such a way that its behaviour becomes similar at different temperatures. From various studies that were performed in this regard, it was found that the function a/V_r in terms of V_r has similar behaviour at various temperatures, (Fig. 3). On the basis of this figure, the following general form is obtained for a/V_r:

$$\frac{a}{V_r} = \frac{A}{V_r^n} \tag{59}$$

Where A and n are two constants, whose values depend on the temperature. If we take the logarithm of both sides of Eq. (59), we will have:

$$\ln\left(\frac{a}{V_r}\right) = \ln A - n \ln V_r \tag{60}$$

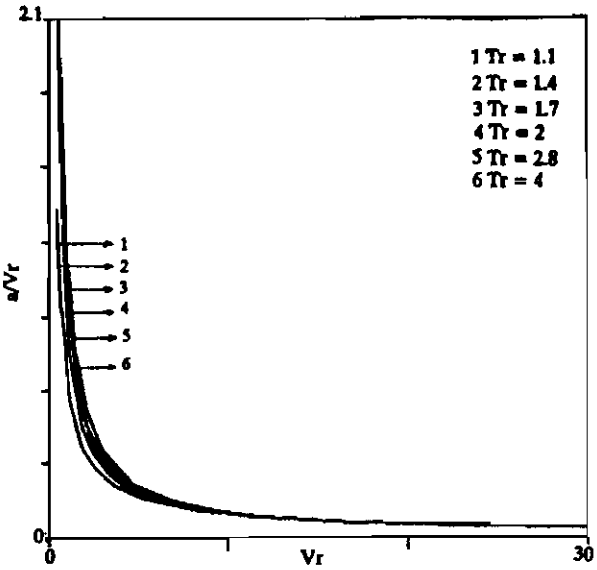

Fig. 3: Function a/V_r against V_r for gaseous Ar.

This means $\ln(a/V_r)$ versus $\ln V_r$ is a straight line for gaseous fluids. In order to evaluate this result, the calculated values of $\ln(a/V_r)$ is plotted versus $\ln V_r$ in Fig. 4, for the temperature range of $1.1 < T_r < 4$ (the data necessary for this calculation is taken from ref. [16]), in which the linearity of the curves are apparent. The values of A and n can be respectively obtained by using the intercepts and slopes of the lines drawn in Fig. 4, at various temperatures. The results obtained are listed in Table 6. By using the data given in Table 6, A and n can be obtained in terms of T_r. The following results are obtained:

$$A(T_r) = 2.60335 - 2.42252T_r + 1.32392T_r^2 - 0.30790T_r^3 + 0.02601T_r^4 - 0.87883T_r^{-6} - 0.02266T_r^{-8} \tag{61}$$

$$n(T_r) = -1.33023 + 0.54505T_r - 0.31547T_r^2 + 0.07650T_r^3 - 0.00667T_r^4 - 0.29309T_r^{-6} + 0.6344T_r^{-8} \tag{62}$$

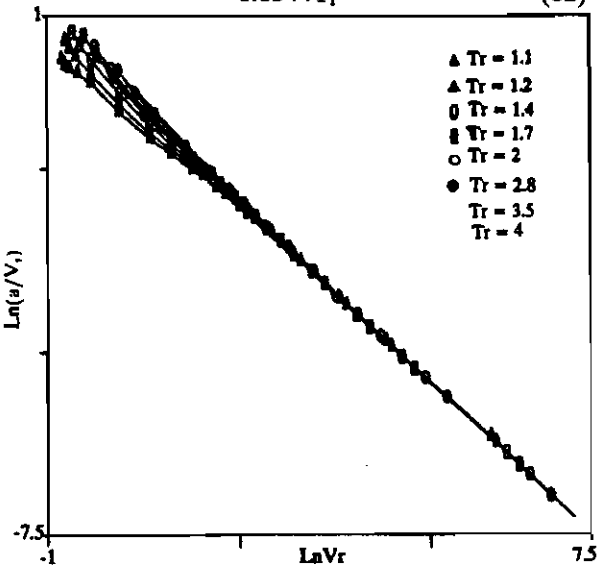

Fig. 4 : Function $\ln(a/V_r)$ againt $\ln V_r$ for gaseous Ar, in the range of $1.1 < T_r < 4$

Table 6 : The values of A and n which are obtained from the lines given in Fig. 4 for gaseous Ar.

T_r	$A(T_r)$	$n(T_r)$
1.1	0.6714	−0.9093
1.4	0.9486	−0.9983
1.7	1.0345	−1.0160
2	1.0690	−1.0200
2.8	1.0979	−1.0220
3.5	1.1014	−1.0210
4	1.1001	−1.0200

Calculation of the thermodynamic quantities for gas

Similar to the calculations performed in the previous section for the liquids, the thermodynamic properties of gases can also be calculated by using Eqs. (59), (61) and (62) for a. In order to calculate the thermodynamic properties of a gaseous fluid, in addition to the a function, we must have the $g(T_r, V_r)$ and $N(T_r, V_r)$, as well, which are given as:

$$g(T_r, V_r) = RA(T_r)\,\frac{V_r^{n(T_r)+1}}{n(T_r)+1} \tag{63}$$

$$N(T_r, V_r) = R\,[T_r\,\frac{A'(T_r)}{n(T_r)+1}\,V_r^{n(T_r)+1} + T_rAT_rn'(T_r)\,\{\frac{V_r^{n(T_r)+1}}{n(T_r)+1}\ln V_r - \frac{V_r^{n(T_r)+1}}{[n(T_r)+1]^2}\}] \tag{64}$$

where:

$$A'(T_r) = \frac{dA(T_r)}{dT_r} = -2.42252 + 2.64784T_r - 0.92370T_r^2 + 0.10404T_r^3 + 5.27298T_r^{-7} + 0.18128T_r^{-9} \tag{65}$$

and:

$$n'(T_r) = \frac{dn(T_r)}{dT_r} = 0.54505 - 0.63094T_r + 0.22950T_r^2 - 0.02668T_r^3 + 1.75854T_r^{-7} - 5.07520T_r^{-9} \tag{66}$$

By substitution of Eqs. (59) through (66) into Eqs. (48), (52) and (53), the entropy, enthalpy and *Gibbs* free energy can be calculated. The results of such a calculation is given in Table 7. Again, the temperature dependent constants of Eqs. (48), (52) and (53), are chosen in such a way that the best fit with the experimental data, given in ref. [19], is obtained.

*Table 7 : Comparison of the experimental and theoretical thermodynamic quantities for argon gas**

T = 120 (K)

P (atm)	S_r (J/m.K)	S_c (J/m.K)	RDS	H_r (J/m)	H_c (J/m)	RDH	G_r (J/m)	G_c (J/m)	RDG
10	135.2	133.4	1.36	13886	13660	1.63	−26686	−26362	1.21
20	129.3	127.3	1.52	13813	13568	1.77	−24974	−24631	1.37
50	121.1	119.1	1.65	13598	13394	1.50	−27729	−22337	1.72
80	116.6	114.8	1.53	13386	13274	0.84	−21594	−21170	1.96
120	112.5	111.1	1.25	13115	13130	0.11	−20629	−20194	2.11
160	109.4	108.5	0.84	12867	12992	0.97	−19944	−19546	2.00
200	106.9	106.5	0.38	12656	12860	1.61	−19417	−19089	1.69
300	102.5	103.2	0.76	12310	12572	2.13	−18428	−18406	0.12
500	97.1	100.0	3.06	12068	12262	1.61	−17074	−17749	4.12
1000	90.4	97.0	7.27	12437	12448	0.09	−14680	−16643	13.37

* The experimental thermodynamic quantities S_r, H_r, G_r [19] and the calculated values, S_c, H_c and G_c (obtained by using Eqs. 43, 48, 49, 52, 53, 59 and 61-65)and the percent differences for the entropy, RDS, enthalpy, RDH, and the Gibbs free energy, RDG, for gaseous Ar. The constants of integration for entropy, enthalpy and Gibbs free energy are equal to -93039.09 $J.mol^{-1}.K^{-1}$, 2594480 $J.mol^{-1}$, and 1967252 $J.mol^{-1}$, respectively.

DISCUSSION AND CONCLUSIONS :

Results presented in Tables 3, 4 and 7 show, the equation of state presented in this paper, can predict well the thermodynamic quantities of liquid and gaseous fluids, in such a way that the deviations do not exceed two percent, except at very high pressures. The results listed in Tables. 8 and 9 also show that, the equation of state given in this paper, for liquids, predicts the pressure about two times more accurate than the *Redlich - Kwong, Benedict - Webb - Rubin* and *Peng- Robinson* equations of state, and for gases the precision of results are comparable with those given by two mentioned equations.

The other notable point is that, for gaseous fluids, the highest deviations for the pressure and the thermodynamic quantities are observed at high pressures (over 300 atm), in which $\ln(a/V_r)$does not linearly change with $\ln V_r$ (Fig. 4). This behaviour can be physically explained as follows. The equation of state presented in this paper, is obtained on the basis of the *Lennard-Jones (12-6)* potential and the pairwise additive approximation of the total potential. These approximations at high pressures lead to serious errors and it can be predicted that by using more

*Table 8 : Comparison of the experimental and theoretical values of pressure for liquid argon**

T = 120 (K)										
P(exp)	P_1	P_2	P (RK)	P (BWR)	P (PR)	RDP_1	RDP_2	RDP (RK)	RDP (BWR)	RDP (PR)
15	23	11	40	5	9	35	27	62	67	38
20	28	16	43	9	11	29	20	53	55	46
25	33	22	47	12	12	24	12	47	52	51
30	39	29	50	16	14	23	3	40	47	54
40	50	41	58	24	17	20	2	31	40	57
50	63	55	65	32	20	21	9	23	36	59
60	69	62	69	36	22	13	3	13	40	63
70	83	77	78	46	26	16	9	10	34	63
80	90	85	82	51	28	11	6	2	36	65
100	113	109	96	66	34	12	8	4	34	66
120	129	126	106	77	38	7	5	12	36	68
140	156	154	123	96	46	10	9	12	31	67
160	185	184	140	116	53	13	13	13	28	67
180	206	205	153	131	59	13	12	15	27	67
200	217	216	160	139	62	8	7	20	31	69
300	316	316	221	211	88	5	5	26	30	71
500	552	549	376	394	153	9	9	25	21	69

* The experimental values of pressure [19] , P_{exp}, and the calculated values obtained by using the equation of state presented in this paper, for the temperature ranges $0.8 < T_r < 1$, P_1, and $0.6 < T_r < 1$, P_2, and the calculated values by using the *Redlich - Kwong* equation of state, $P_{(RK)}$, the *Benedict - Webb - Rubin* equation of state, $P_{(BWR)}$, and the *Peng- Robinson* equation of state, $P_{(PR)}$, and the percent differences given by RDP_1, RDP_2 , $RDP_{(RK)}$, $RDP_{(BWR)}$, $RDP_{(PR)}$, respectively, for the liquid Ar at 120 K. The values of pressure are in atmosphere.

Table 9 : Comparison of the experimental and theoretical values of pressure for argon gas.*

P(exp)	P	P (RK)	P (BWR)	RDP	RDP (RK)	RDP (BWR)
10	10.1	10.0	10.0	0.57	0.02	0.03
20	20.2	20.0	20.0	0.97	0.12	0.14
50	51.0	49.8	49.8	1.98	0.30	0.35
80	81.9	79.7	79.6	2.40	0.39	0.46
120	122.4	119.7	119.5	1.97	0.28	0.38
160	160.5	159.8	159.7	0.29	0.10	0.20
200	195.0	200.2	200.0	2.48	0.08	0.02
300	264.0	299.4	299.9	11.98	0.20	0.03
500	359.5	487.2	493.2	28.11	2.57	1.36
1000	591.0	931.0	975.7	40.90	6.90	2.43
2000	1176.8	1839.3	1981.8	41.16	8.04	0.91

* The experimental values of pressure taken from [19], P_{exp} , and the calculated values obtained by using the equation of state pressented in this paper for the temperature range $1.1 < T_r < 4$, P, and the calculated values by using the *Redlich - Kwong* equation of state, $P_{(RK)}$, and the *Benedict - Webb- Rubin* equation of state, $P_{(BWR)}$, and the percent differences given by RDP, $RDP_{(RK)}$ and $RDP_{(BWR)}$, respectively, for the gaseous Ar. The values of pressure are in atmosphere.

realistic potential functions such as the *Aziz* potential [21] and also by using additional terms for the non – pairwise part of potential will improve the results (in this regard see chapter 12 of ref. [7]).

If the truncated virial equation:

$Z = 1 + B_2 / V$

is compared with the equation of state presented in this paper, at low pressures (in which $1/V_r^3$ and $1/V_r^5$) terms can be neglected), the adjustable parameter a is related to the second virial coefficient as:

$B_2 = (a - 1)V_r$

therefore, it is expected that the function $(a-1)V_r$ againts temperature has a behaviour similar to the second virial coefficient. Such an expectation can be seen in Fig. 5. However, because the maximum of the second virial coefficient occurs at T_r between 5 and 20 (Fig. 15–2 of ref. [7]), and the obtained equation of state is accurate in the range of $1.1 < T_r < 4$, no maximum is seen in Fig. 5.

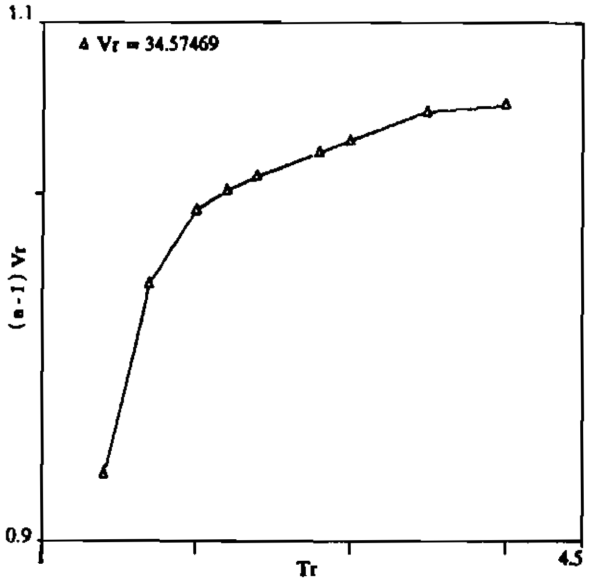

Fig. 5 : Function $(a-1)V_r$ versus T_r for gaseous Ar, the value of a is calculated from Eqs. 59, 61 and 62.

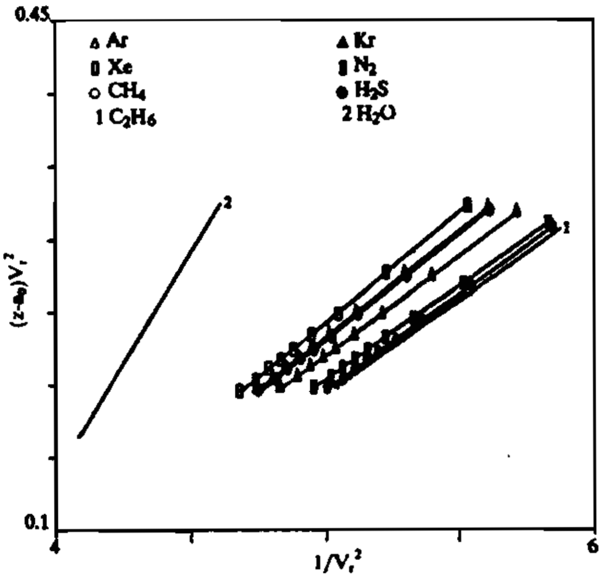

Fig.6 : $(z-a)V_r^2$ versus $1/V_r^2$ for various liquids at $T_r=0.8$

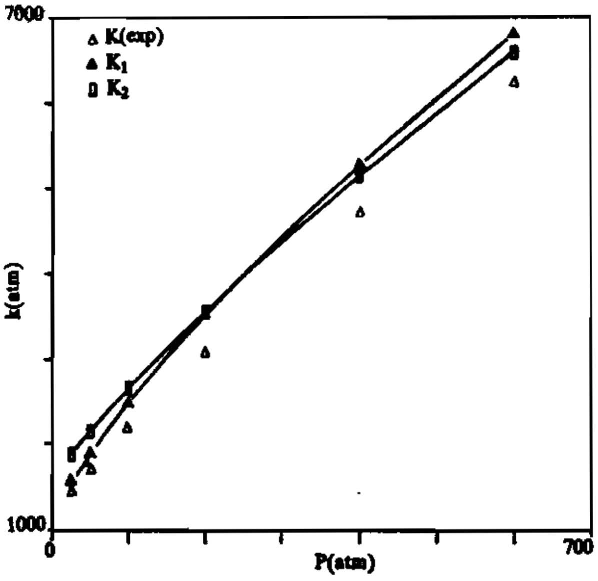

Fig. 7 : The experimental and calculated isothermal compressibility, k(exp), k_1 and k_2, for the liquid Kr at T=170 K. The necessary data are taken from Table 5.

Table 10 : Same as Table 8 for liquid propane at 300 K.

T = 300 (K)										
P(exp)	P_1	P_2	P (RK)	P (BWR)	P (PR)	RDP_1	RDP_2	RDP (RK)	RDP (BWR)	RDP (PR)
10	20	14	142	55	−19	50	29	93	82	152
15	26	21	150	65	−16	42	29	90	77	191
20	31	27	156	73	−14	35	26	87	73	171
25	38	35	165	85	−11	34	29	85	71	144
30	43	41	172	94	−9	30	27	83	68	128
35	47	45	176	100	−7	26	22	80	65	120
40	53	52	183	109	−4	25	23	78	63	111
50	63	63	196	126	0	21	21	75	60	99
60	74	75	209	144	5	19	20	71	58	91
70	86	87	222	163	10	19	20	69	57	85
80	94	95	231	175	14	15	16	65	54	83
90	107	109	246	196	19	16	17	63	54	79
100	115	117	256	209	23	13	15	61	52	77
150	160	164	308	284	42	6	8	51	47	72
200	202	206	358	355	61	0	3	44	44	70

According to Eq. (25), $(Z - a)V_r^2$ must be linear in terms of $1/V_r^2$ for the liquid fluids at each temperature. In order to evaluate the generality of the equation of state given in this paper, we have plotted this function for the various liquids: Kr, Xe, CH_4, CCl_4, SF_6, N_2, O_2, CO, C_2H_2, C_2H_4, CO_2, C_2H_6, C_3H_8, n− C_4H_{10}, n− C_5H_{12}, n− C_6H_{14}, n− C_7H_{16}, n− C_8H_{18},

H_2O, H_2S and NH_3 at $T_r = 0.8$, in which very good linearity is seen, some of the results are shown in Fig. 6. Also, using the obtained equation of state:

$$k = -V(\partial P/\partial V)_T$$

is plotted in terms of P in Fig. 7, for liquid Kr at T = 170 K, in which the behaviour is the same as that is expected, experimentally [22].

The pressure values given by the equations of state presented in this paper (P_1 and P_2), and those given by the *Redlich - Kwong, Benedict-Webb - Rubin* and *Peng - Robinson* equations of state are compaired with the experimental pressure (given in ref. [19]) in Table 10 for liquid propane at 300 K.

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