Calculation of Molar Volume of Mixtures of Krypton with Argon and Xenon from the Statistical-Mechanical Based Equation of State¶

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In this paper, the analytical equation of state (EoS) proposed by Ihm-Song-Mason was applied to calculate molar volume of mixtures of krypton with argon and xenon. The pair interaction potential has been used to evaluate the second virial coefficients and the Ihm-Song-Mason equation of state (ISM-EoS) parameters (*i.e.*, α and b). The calculated values of aforesaid quantities were applied to predict the molar volumes for mixtures of krypton with argon and xenon. Agreement with experiment was excellent for both systems.

Key Words: Molar volume, Equation of state, Pair interaction potential, Statistical mechanics.

INTRODUCTION

The thermophysical properties of gases, such as the density, heat capacity, viscosity and thermal conductivity are important quantities in both science and engineering. Anyhow, volumetric properties are ubiquitous in chemical processes and form the building blocks of process designing. The importance of the volumetric properties of fluid in technology is maintained across the varied diversity. On the other hand, all of the thermodynamic properties of a fluid are encapsulated in the mathematical relationship between the fluid's pressure, volume and temperature-which is commonly called its "equation of state" (EoS)[1-4]. It is therefore hardly surprising what an ability to predict such equations of state accurately and with a minimum of empiricism has been highly delved in engineering applications[5-7]. An ability to understand equation of state on purely molecular level, using nothing more than information on intermolecular potentials and the tools of equilibrium statistical mechanics, would mean finally meeting a challenge posed over a century ago by van der Waals and would signify that one could, finally, claim some reasonable measure of understanding of at least the equilibrium properties of liquids and gases.

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Thermodynamics deals with the general principles and laws that govern the behaviour of matter and with the relationships between material properties. The origins of these laws and quantitative values for the properties are provided by statistical mechanics, which analyses the interaction of molecules and provides a detailed description of their behaviour. The thermodynamic properties of fluids are of continuing interest for theoretical and industrial applications. The requirement of industry for accurate values and estimation schemes of thermodynamic properties is increasing, because working fluids are often mixtures. The need for sufficient data to reliably estimate thermodynamic properties of mixtures remains today a major industrial problem. Measurements are costly and time consuming. Thus, it appears very useful to have methods for realistic evaluation of thermodynamic properties *via* equation of state (EoS).

Cubic and generalized van der Waals (vdW) EoS have been a subject of active research since van der Waals[8] proposed his famous EoS. During the intervening years, they played major role in the development of fluid state theories as well as in modeling fluid behaviour for practical purposes. The cubic and generalized EoS are not the most appropriate models for the accurate representation of pure-fluid properties, because they usually lake the necessary flexibility in some regions of the phase diagram. Also, they are not the most useful methods for understanding the properties of fluids from a microscopic perspective. For such purposes, their theoretical background is usually insufficiently rigorous. On the other hand, the empirical EoS involve many parameters and require extensive experimental data over wide ranges of pressure and temperature[2,3]. These empirical EoS are specific to a substance and their parameters lack of a physical meaning. An alternative approach is provided by semi-empirical equations. These EoS are widely used in engineering applications and require less experimental information to determine the parameters[2]. In many cases the semi-empirical EoS are modifications of the vdW EoS. One category of these EoS is cubic EoS. In contrast, the statistical-mechanically based EoS provides a physical understanding of the thermodynamic and is potentially of very accuracy. Hence, for prediction purposes, it may be preferable to use a statistical-mechanically sound basis EoS such as Ihm-Song-Mason (ISM) EoS[9]. This is a versatile equation with physically sound parameters, *i.e.*, having explicit significance in terms of molecular interactions[9].

For the last decade, a considerable progress has been made in theoretical understanding of single fluids and their mixtures. There are some efforts about EoS the associating fluids and fluids mixtures or statistical associating fluid theory (SAFT) EoS[10]. Besides the theoretical importance, the knowledge of physicochemical properties of multi-component mixtures are indispensable for many chemical process industries. Examples are all of the substances which are commonly used in industries where involved physicochemical processes to handle the single fluids and their mixtures. Physicochemical analysis method can be used for getting sound information for interaction between the components and the function of the binary interaction[11-18].

The thermodynamic studies of binary mixtures have attracted much attention of scientists and experimental data on a number of systems. As mentioned before, the Ihm-Song-Mason (ISM) EoS, which has been named as Mason EoS after death of Prof. Edward Allen Mason, have received outstanding attention[19-23]. The purpose of the present paper is not to review the all kinds of EoS. One can find the details of EoS elsewhere[1-4,10]. The main objective of the present research is to compute the molar volume of mixtures of krypton with argon and xenon using the statistical-mechanically sound basis EoS such as ISM EoS.

EXPERIMENTAL

The ISM EoS is obtained from the pressure equation *via* statistical-mechanical perturbation theory for mixtures. The pressure equation is as follow[24]:

$$P / k_B T = \rho - \rho^2 / 6 k_B T \int_0^\infty r U'(r) g(r) 4 \pi r^2 dr \tag{1}$$

where P is pressure, ρ is number density, $U' = \partial U / \partial r$, g(r) is radial (or pair) distribution function and the other symbols have their usual meaning.

The derived equation by ISM has the following form:

$$P / \rho k_B T = 1 + \rho \sum_{ij} x_i x_j ((B)_{ij} - \alpha_{ij}) F_{ij} + \rho \sum_{ij} x_i x_j \alpha_{ij} G_{ij} \tag{2}$$

where P is the pressure, x is the mole fraction, ρ is the molar densities, B is the second virial coefficient, α is a correction factor for the softness of the repulsive forces, G is the average pair distribution function at contact for hard convex bodies and $k_B T$ is the thermal energy per one molecule. The interaction second virial coefficient, B_{ij} and the parameters F_{ij}, G_{ij}, α and b are defined as:

$$B = 2\pi \int_0^\infty (1 - e^{-u(r)/k_B T}) r^2 dr \tag{3}$$

$$F_{ij} = \frac{1}{1-\eta} - (\frac{b_i b_j}{b_{ij}})^{1/3} \frac{\rho \sum_k x_k b_k^{2/3} (\delta_k + 1/4)}{(1-\eta)(1 + \rho \sum_k x_k b_k \delta_k)} \tag{4}$$

$$G_{ij} = \frac{1}{1-\eta} + (\frac{b_i b_j}{b_{ij}})^{1/3} \frac{\rho \sum_k x_k b_k^{2/3} (\lambda_k - 1/4)}{(1-\eta)(1 - \rho \sum_k x_k b_k \lambda_k)} \tag{5}$$

$$\eta \equiv \frac{\rho}{4} \sum_k x_k b_k \tag{6}$$

$$\alpha = 2\pi \int_0^{r_m} (1 - e^{-u^0(r)/k_B T}) r^2 dr \tag{7}$$

$$b = 2\pi \int_0^{r_m} (1 - [1 + u^0(r)/k_B T] - e^{-u^0(r)/k_B T}) r^2 dr \tag{8}$$

Here, b is a temperature-dependent parameter analogous to the van der Waals co-volume, λ is an adjustable parameter and $\delta = 0.22 \lambda$. The intermolecular potential is identified by the u(r) whereas the repulsive part, $u^0(r)$, has its usual meaning of decomposition of u(r) according to the Weeks-Chandler-Anderson[25,26] formulation of the thermodynamic perturbation theory[27]. The eqn. 1 been derived from the pressure equation in conjunction the assumption that the intermolecular potentials are pair-wise additive. The major feature of the ISM EoS is its sound statistical-mechanical basis.

The purpose of the present work is to find the second virial coefficients as well as the parameters α and b for pure components and their mixtures. The relation between parameters, B, α and b with the intermolecular potential have been given by the eqns. 3, 7 and 8. We have used the Lennard-Jones 12,6 (LJ 12,6) for the calculation of the interaction parameters of the ISM EoS. The LJ (12,6) has the familiar form:

$$U(r_{ij}) = 4\varepsilon_{ij}[(\sigma_{ij}/r_{ij})^{12} - (\sigma_{ij}/r_{ij})^6] \tag{9}$$

interaction parameters B_{ij}, α_{ij} and b_{ij} for $i \neq j$ correspond to a hypothetical single substance whose molecules interact according to a pair-wise ij potential. We have used the well-known combining rules relating the like and unlike parameters which have been called as 'Lorentz-Bertholet' rules, *viz.*:

$$\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2 \tag{10}$$

$$\varepsilon_{ij} = (\varepsilon_{ii}\varepsilon_{jj})^{1/2} \tag{11}$$

For i=j the parameters are those for pure substance 'i'. The mathematical expressions for B_{ij}, α_{ij} and b_{ij} are as the same as for pure fluids, but the intermolecular potential energy for pure substances should be replaced by the interaction potential for unlike molecules.

RESULTS AND DISCUSSION

We have used the LJ (12,6) pair intermolecular potentials[28] as input data to determine the cross second virial coefficients for mixtures of Kr-Ar and Kr-Xe. The calculated that appear in λ_k and b have been inserted to the eqn. 1. The values of λ_k values of eqns. 2 and 3 were found empirically from P-V-T data of pure dense components and are as follow: 0.42, 0.43 and 0.42 for argon, krypton and xenon, respectively. Knowing the temperature-dependent parameters; second virial coefficient, α and β, along with the value of λ, the ISM EoS for mixtures can be employed to predict P-V-T properties of the aforesaid mixtures. The calculated and experimental values of molar volume have been tabulated in Tables 1-8. The used values of the experimental molar volume are adopted from the Streett *et al.* for mixtures of krypton-xenon[29] and krypton-argon[30]. As it is clear from Figs. 1 and 2 the accuracy of our predicted values commensurate to the experimental data.

TABLE-1
CALCULATED AND EXPERIMENTAL VALUES OF MOLAR VOLUME FOR 0.485 Ar
+ 0.515 Kr. THE EXPERIMENTAL VALUES ARE TAKEN FROM Ref. [30]. DEVIATION
IS DEFINED AS Dev (%) = 100 ($V_{cal.}$ − $V_{Exp.}$) / $V_{Exp.}$

P (MPa)	$V_{Cal.}$ (cc/mol)	$V_{Exp.}$ (cc/mol)	Dev (%)
T = 129.32 K			
3.98	34.980	34.977	0.01
5.43	34.824	34.782	0.12
7.80	34.582	34.507	0.21
15.13	33.567	33.770	-0.60
21.47	33.174	33.250	-0.23
30.43	32.867	32.620	0.74
36.84	32.508	3.234	0.85
42.83	32.060	31.888	0.99
51.79	31.802	31.420	1.21
T = 134.32 K			
3.30	35.913	35.950	-0.10
7.68	35.363	35.314	0.14
10.41	35.053	34.959	0.27
24.21	33.811	33.614	0.58
30.57	33.359	33.133	0.68
37.25	34.942	34.680	0.80
46.90	32.418	32.128	0.90
52.65	32.142	31.831	0.97
59.95	31.823	31.488	1.06
65.37	31.605	31.252	1.13
T = 142.68 K			
4.49	38.515	37.426	2.91
7.80	37.466	36.831	1.72
14.52	37.028	35.735	3.61
22.01	35.033	34.857	0.50
28.53	34.385	34.152	0.58
29.10	34.385	34.152	0.68
36.98	33.780	33.552	0.68
43.62	33.338	33.084	0.76
50.55	32.928	32.644	0.87
58.13	32.529	32.240	0.89
64.75	32.216	31.928	0.90
71.23	31.935	31.621	0.99
79.43	31.611	31.276	1.07
84.60	31.422	31.073	1.23
91.50	33.185	30.815	1.20
105.97	30.744	30.330	1.36
128.04	30.175	29.694	1.62
150.65	29.690	29.141	1.68

P (MPa)	$V_{Cal.}$ (cc/mol)	$V_{Exp.}$ (cc/mol)	Dev (%)
T = 147.08 K			
6.11	40.102	38.101	5.25
8.22	39.283	37.594	4.49
13.58	38.108	36.626	4.04
16.71	36.260	36.147	0.31
17.03	36.219	36.103	0.32
24.23	35.379	35.223	0.44
30.63	34.759	34.565	0.56
35.94	34.311	36.116	0.57
44.76	33.668	33.447	0.66
52.07	33.209	32.980	0.69
57.37	32.909	32.661	0.76
67.65	32.391	32.130	0.81
71.51	32.215	31.945	0.84
78.67	31.911	31.623	0.91
94.25	31.333	31.002	1.06
104.46	31.004	30.650	1.15
109.42	30.856	30.484	1.22
114.25	30.718	30.333	1.27
120.45	30.550	30.145	1.34

TABLE-2
SAME AS TABLE-1 for 0.277 Ar + 0.723 Kr; T = 34.32 K

P (MPa)	$V_{Cal.}$ (cc/mol)	$V_{Exp.}$ (cc/mol)	Dev (%)
4.62	35.407	35.681	-0.76
8.74	35.017	35.249	-0.65
15.66	34.685	34.592	0.28
24.03	34.036	33.988	0.14
28.36	33.623	33.715	-0.27
36.29	33.055	33.241	0.56
44.70	32.687	32.810	-0.37
50.97	32.439	32.510	-0.21
59.31	32.139	32.146	0.02
66.97	31.887	31.842	0.14

TABLE-3
SAME AS TABLE-1 FOR 0.698 Ar + 0.302 Kr; T = 134.32 K

P (MPa)	$V_{Cal.}$ (cc/mol)	$V_{Exp.}$ (cc/mol)	Dev (%)
5.52	37.1247	35.881	3.46
16.43	35.2390	34.179	-0.65
21.82	34.5600	33.559	2.98
29.61	33.7510	33.827	2.81
36.43	33.1620	32.291	2.69
46.28	32.4510	31.639	2.56
50.56	32.1810	31.387	2.53
58.42	31.7340	30.959	2.50
64.48	31.4260	30.665	2.48
68.07	31.2550	30.508	2.45

TABLE-4
SAME AS TABLE-1 FOR 0.787 Ar + 0.213 Kr; 129.32 K

P (MPa)	$V_{Cal.}$ (cc/mol)	$V_{Exp.}$ (cc/mol)	Dev (%)
3.66	38.765	36.635	5.81
6.24	37.966	35.982	5.51
10.58	36.887	35.084	5.14
19.40	35.296	33.752	4.57
27.39	34.247	32.883	4.15
35.80	33.379	32.158	3.79
42.42	32.811	31.672	3.59
50.69	32.205	31.134	3.44
58.95	31.687	30.667	3.32
66.68	31.262	30.281	3.24
76.60	30.784	29.843	3.15

TABLE-5
CALCULATED AND EXPERIMENTAL VALUES OF MOLAR VOLUME FOR
0.556 Kr + 0.444 Xe. THE EXPERIMENTAL VALUES ARE ADOPTED FROM
[Ref. 29]. DEVIATION IS DEFINED AS Dev % = 100 $(V_{cal.} - V_{Exp.}) / V_{Exp.}$

P (MPa)	$V_{Cal.}$ (cc/mol)	$V_{Exp.}$ (cc/mol)	Dev (%)
T = 177.99 K			
8.12	43.323	43.360	-0.08
13.06	42.271	42.801	-0.18
40.50	40.371	40.413	-0.10
49.74	39.807	39.802	0.01
T = 185.00 K			
8.05	44.920	44.234	1.55
17.75	42.748	42.835	-0.20
38.43	40.886	40.860	0.06
59.80	39.559	39.455	0.26
T = 190.01 K			
6.10	45.239	45.274	-0.07
31.54	42.002	41.887	0.27
41.88	41.146	41.000	0.35
52.22	40.430	40.278	0.37
63.52	39.766	39.602	0.41
73.54	39.259	39.049	0.53

TABLE-6
SAME AS TABLE-2 FOR 0.546 Kr + 0.454 Xe; T = 195.03 K

P (MPa)	$V_{Cal.}$ (cc/mol)	$V_{Exp.}$ (cc/mol)	Dev (%)
5.90	48.408	46.149	4.89
22.99	44.473	43.307	2.69
27.63	42.642	42.832	-0.44
37.46	42.063	41.699	0.87
48.77	41.164	41.147	0.04

TABLE-7
SAME AS TABLE-2 FOR 0.319 Kr + 0.681 Xe; T = 190.01 K

P (MPa)	$V_{Cal.}$ (cc/mol)	$V_{Exp.}$ (cc/mol)	Dev (%)
7.60	46.875	45.488	3.04
10.86	46.434	45.083	2.99
17.75	45.618	44.265	3.05
31.54	44.320	42.999	3.07
41.88	43.262	42.238	2.42
52.22	42.888	41.584	3.13
62.56	42.318	41.011	3.18
73.59	41.786	40.406	3.41

TABLE-8
SAME AS TABLE-2 FOR 0.707 Kr + 0.293 Xe; T = 190.01 K

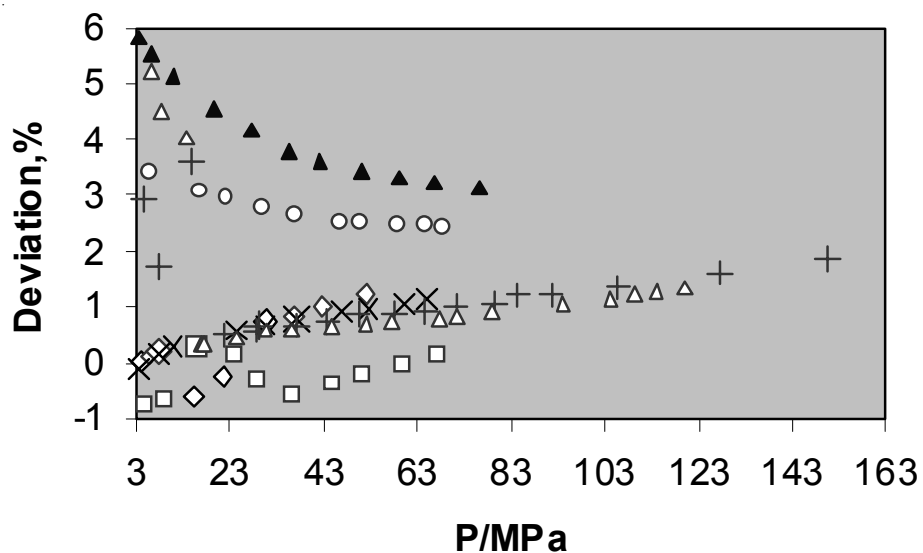| P (MPa)	$V_{Cal.}$ (cc/mol)	$V_{Exp.}$ (cc/mol)	Dev (%)
12.10	43.130	43.838	-1.63
18.99	42.074	42.764	-1.61
34.15	40.357	40.931	-1.40
73.58	37.676	38.104	-1.12

Fig. 1.   Deviation $[100(V_{Cal.}-V_{Exp.})/V_{Exp.}]$ plot for the molar volume of 0.485Ar + 0.515Kr
(◇) at 129.32K; 0.277Ar + 0.723Kr (□), 0.485Ar + 0.515Kr (×), 0.698Ar + 0.302Kr
(○) and 0.787Ar + 0213Kr (▲) at 134.32K; 0.485Ar + 0.515Kr (+) at 142.68K;
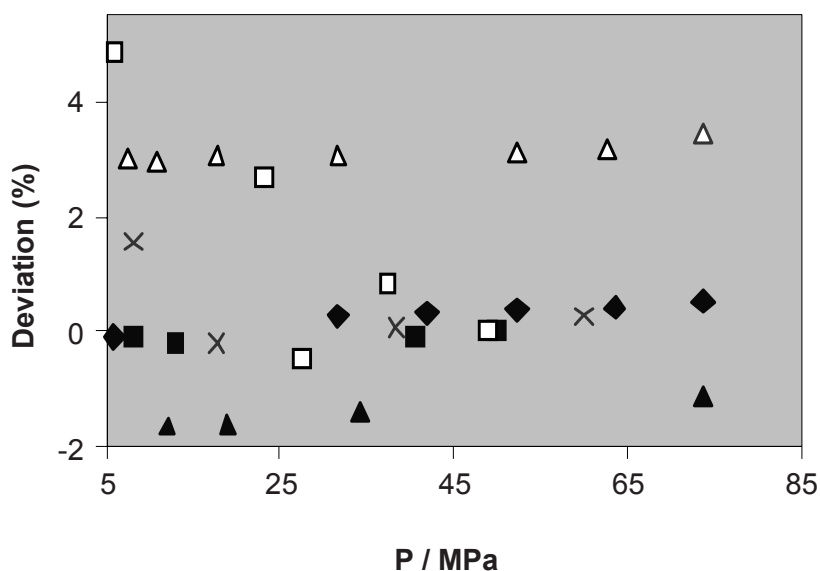0.485Ar + 0.515Kr (△) at 147.08K

Fig. 2. Same as Fig. 1 for 0.556Kr + 0.444Xe (■) at 179.99K; 0.556Kr+0.444Xe
(×) at 185.00 K; 0.319Kr + 0.681Xe (△), 0.556Kr + 0.444Xe (◆) and
0.707Kr + 0.293Xe (▲) at 190.01 K; 0.546Kr + 0.454Xe (□) at 195.03 K

Symbols:
α = Attraction term.
λ = Adjustable parameter of EoS.
B = Second virial coefficient.
b = Temperature-dependent parameter analogous to the van der Waals co-volume.
P = Pressure.
k_B = Boltzmann constant.
T = Absolute temperature.
ρ = Density.
F_{ij} = Parameter of EoS.
G_{ij} = Parameter of EoS.
B_{ij} = interaction second virial coefficient.
x = mole fraction.

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