Korean J. Chem. Eng., **22**(6), 949-959 (2005)

An Extension of the Group Contribution Method for Estimating Thermodynamic and Transport Properties. Part III. Noble Gases

Seung-Kyo Oh†

Chemical and Biochemical Engineering Department, Kon-Yang University,
San 26, Naedong, Nonsan, Chungnam 320-711, Korea
(*Received 26 April 2005 • accepted 4 July 2005*)

Abstract–Earlier work on the group contribution method applied to the Kihara potential is extended to noble gases for the estimation of second virial coefficients, dilute gas viscosities and diffusivities with a single set of gas group parameters. Group parameters are determined when second virial coefficient and viscosity data of pure gases are satisfactorily fitted within the experimental uncertainties. Parameters for gas groups (He, Ne, Ar, Kr and Xe) are found to provide good predictions of mixture properties: second virial cross coefficients, mixture viscosities, and binary diffusion coefficients. Application of the model shows that second virial coefficient data are represented with good results comparable to the values by means of the corresponding states correlation. The reliability of the present model in viscosity predictions is proved by comparison with the Lucas method. Prediction results of diffusivity are in excellent agreement with literature data and compare well with values obtained by means of the Fuller method.

Key words: Theory, Group Contribution, Kihara Potential, Noble Gas, Second Virial Coefficient, Viscosity, Diffusivity

INTRODUCTION

A number of methods have been proposed for the prediction of second virial coefficients and dilute gas transport properties. Although most studies have focused on individual properties, a number of investigators [Dymond and Alder, 1969; O'Connell and Prausnitz, 1965; Tee et al., 1966] have used statistical mechanics and the kinetic theory of gases to represent both thermodynamic and transport properties with a single set of parameters, namely, those appearing in an intermolecular potential function. In one particularly interesting study of [Tee at al., 1966], the Lennard-Jones potential parameters were related to the critical properties and acentric factor. The result was a corresponding states correlation for simultaneous prediction of second virial coefficients and dilute gas viscosities for molecules ranging in shape from spherical to chains as long as n-heptane. However, two difficulties are faced in corresponding states calculations. First, critical properties and acentric factors may not be available for all of the compounds in question. Second, and perhaps more important, extension of corresponding states method to mixtures requires additional information, generally in the form of a binary interaction coefficient.

The group contribution concept has formed an alternative to the corresponding states framework for property calculations. Here, a single set of parameters is assigned to each interaction between intermolecular functional groups. An advantage of this method is that it does not require values for the critical properties and acentric factors, which may not be available for all of the compounds in question, and that it is applicable with only information of both functional group and van der Waals volume in molecule. Since the number of functional groups is much smaller than the number of possible chemical species, a relatively small number of group parameters can describe a large number of different mixtures. This concept forms the basis for the UNIFAC [Fredenslund et al., 1975] and ASOG [Derr and Deal, 1969] activity coefficient models and for the GPSCT [Jin et al., 1986] and GSPHCT [Georgeton and Teja, 1988] equations of state models.

A group contribution concept was applied to the Kihara potential functions for calculating second virial coefficients of pure gases and mixtures [Campbell, 1989]. Functional group parameters for CH_2 and CH_3 groups in normal alkanes were determined from second virial coefficient data for pure C_2-nC_8 alkanes, and parameters for CH_4 groups were determined from second virial coefficient for pure methane. These parameters were then used to predict, without additional parameters, second virial cross coefficients of alkane mixtures. The model was found to perform well, even for such asymmetric systems as methane-eicosane. Since the group contribution method is based on an intermolecular potential function, the possibility of predicting dilute gas transport properties (viscosities and diffusion coefficients) as well using the Chapman and Enskog theory [Chapman and Cowing, 1970] can be proved.

Previous works [Oh, 1989; Oh and Campbell, 1997] proved the feasibility of applying group contribution method to simultaneous representation of second virial coefficient, viscosity and diffusion coefficient of dilute gases with a single set of parameters. Parameter values for functional groups were estimated by regressing second virial coefficient and viscosity data for pure gases together. It was noted that diffusivity data were not supplied to data regression steps for parameter estimation. By introducing the concept of a group binary interaction coefficient, the model was extended to chemically dissimilar mixtures of nitrogen- and carbon dioxide-hydrocarbons, with success.

A set of functional group parameters for pure alkanes was re-evaluated by Oh and Sim [2002] with revised recommendations of

†To whom correspondence should be addressed.
E-mail: sunkist@konyang.ac.kr

second virial coefficient data of pure alkanes presented by Tsonopoulos et al. [1989] and Tsonopoulos and Dymond [1997] in order to improve the reliability of predictions. The group contribution method using Kihara potential was repeated for calculating second virial coefficients, dilute gas viscosities and binary diffusion coefficients of normal and branched alkanes, alkenes, nitrogen and carbon dioxide. And applications were extended to industrially important pure linear gases (CO, O_2 and H_2), as well as to mixtures of these gases with reliable calculations and predictions of second virial cross coefficients and mixture viscosities. Later, Oh and Park [2005] extended the group contribution method to polyatomic gases (F_2, Cl_2, CS_2, H_2S, NO, and N_2O). Assuming that all simple fluids examined consist of a single functional group, namely gas group, the method based on the spherical core potential of Kihara [1978] was approved with good results.

In this paper, as a continuation of our research, an extension of the group contribution concept using the spherical core Kihara potentials is made to noble gases (He, Ne, Ar, Kr and Xe). All noble gases studied here were regarded as a single functional group. Use of the group contribution concept for these types of simple fluids does not look practically realistic; however, simultaneous regression of second virial coefficient and viscosity data for pure gases was done for the estimation of gas group parameters. The scope of this work is to examine the possibility of applying this characteristic feature of the group contribution concepts to the simultaneous representation of second virial coefficients, dilute gas viscosities and diffusion coefficients with a single set of gas group parameters.

THEORY

The potential function used in this work is the spherical core potential of Kihara [1978]:

$$U = 4\varepsilon\left[\left(\frac{\sigma - 2a}{r - 2a}\right)^{12} - \left(\frac{\sigma - 2a}{r - 2a}\right)^{6}\right] \tag{1}$$

where U and r are, respectively, the potential energy and separation distance between molecules 1 and 2, σ is the collision diameter, ε is the well depth, and a is the hard core radius. Specification of the values for parameters (σ, ε, and a) allows calculation of a number of different gas properties as summarized below.

The expression of the second virial coefficient for the Kihara spherical core potential is given by:

$$B = \frac{2\pi N\sigma^3}{3(1+a^*)^3}[a^{*3} + 3(2)^{1/6}a^{*2}F_1(Z) + 3(2)^{1/3}a^*F_2(Z) + (2)^{1/2}F_3(Z)] \tag{2}$$

where $Z = \varepsilon/kT$, $a^* = 2a/(\sigma - 2a)$ and

$$F_s(Z) = -\frac{s}{12}\sum\frac{2^j}{j!}Z^{(j/2+s/12)}\Gamma\left(\frac{6j - s}{12}\right) \tag{3}$$

Second virial cross coefficients may be calculated from Eq. (2) by using ε_{12}, σ_{12}, and a^*_{12} for ε, σ, and a^* respectively.

Transport properties of dilute gases are calculated from Chapman-Enskog theory [1970]. Although the theory applies rigorously only to monatomic gases, it has been adopted (except for thermal conductivity) in a number of studies [Poling et al., 2000] of polyatomic gases. For a pure gas, the Chapman-Enskog expression for viscosity is

$$\eta = 26.693\frac{\sqrt{MT}}{\sigma^2\Omega_V(T^*)} \tag{4}$$

where M is the molecular weight (g mol^{-1}), T is the Kelvin temperature, $T^* = kT/\varepsilon$, σ is in Δ, and viscosity η is in micropoise. The quantity Ω_V is the collision integral for viscosity and depends on the choice of intermolecular potential. And the Ω_V values required for the Chapman and Enskog theory were tabulated in Oh [1989]. The composition dependence of viscosity for a binary gas mixture is given by Hirschfelder et al. [1954]:

$$\frac{1}{\eta_{mix}} = \frac{X_\eta + Y_\eta}{1 + Z_\eta} \tag{5}$$

where η_{mix} is the viscosity of the mixture and where

$$X_\eta = \frac{x_1^2}{\eta_1} + \frac{2x_1x_2}{\eta_{12}} + \frac{x_2^2}{\eta_2} \tag{6}$$

$$Y_\eta = \left(\frac{3\Omega_V}{5\Omega_D}\right)\left[\frac{x_1^2}{\eta_1}\right] \tag{7}$$

$$Z_\eta = \left(\frac{3\Omega_V}{5\Omega_D}\right)[x_1^2] \tag{8}$$

and where x_i, M_i, and η_i are the mole fraction, molecular weight and viscosity at the mixture temperature of gas i (i=1, 2), respectively. The quantity η_{12} is defined by

$$\eta_{12} = 26.693\frac{\sqrt{\frac{2M_1M_2T}{(M_1+M_2)}}}{\sigma_{12}^2\Omega_V(T^*_{12})} \tag{9}$$

Finally, the quantity Ω_D is the collision integral for diffusivity and, like Ω_V, depends on the choice of intermolecular potential. Values of the Ω_D for Kihara potentials required for the Chapman and Enskog theory were also tabulated in Oh [1989]. O'Connell [1988] prepared tables for the Kihara potential function in which Ω_V and Ω_D are given as functions of reduced properties $T^* = kT/\varepsilon$ and $\gamma^* = a^*/(1+a^*)$. Details about how these tables were used in the calculations described here are given in Oh and Campbell [1997].

The Chapman-Enskog expression for binary diffusion coefficients of dilute gas is by presented by Hirschfelder et al. [1954]:

$$D_{12} = 0.001858T^{3/2}\frac{\sqrt{\frac{(M_1+M_2)}{M_1M_2}}}{P\sigma_{12}^2\Omega_D(T^*_{12})} \tag{10}$$

where D_{12} is in cm^2 sec^{-1}, P is in atmosphere and T is in Kelvin. If molecules 1 and 2 are identical, Eq. (10) provides expression for the self-diffusivity.

GROUP CONTRIBUTION MODEL

The expression of group contribution rules for functional group parameters appearing in Kihara potentials was given in previous work [Oh and Campbell, 1997]. For better understanding, however, it is necessary to describe it briefly.

Group contribution rules for the spherical core Kihara potential parameters are written for the general case of non-identical molecules 1 and 2. Calculations for pure gases are made by setting molecule 2 identical to molecule 1. The rules for ε_{12} and σ_{12} are

$$\varepsilon_{12}\sigma_{12}^3 = \sum\sum N_{i1}N_{j2}\varepsilon_{ij}\sigma_{ij}^3 \quad (11)$$

and

$$\sigma_{12} = \frac{(\sum N_{i1}\sigma_{ii}^3)^{1/3} + (\sum N_{j2}\sigma_{jj}^3)^{1/3}}{2} \quad (12)$$

where N_{i1} is the number of functional groups of type i in molecule 1, N_{j2} is the number of functional groups of type j in molecule 2, ε_{12} and σ_{12} are the well depth and collision diameter for interactions between molecules 1 and 2, and ε_{ij} and σ_{ij} are the well depth and the collision diameter for interactions between intermolecular groups i and j, respectively. This rule for the Kihara potential is also required for the core radius a_{12}, where the group additivity of the reduced core radii is assumed:

$$a_{11}^* = \sum N_{i1}a_{ii}^* \quad (13)$$

and

$$a_{22}^* = \sum N_{j2}a_{jj}^* \quad (14)$$

followed by

$$a_{12} = \frac{a_{11} + a_{22}}{2} \quad (15)$$

where

$$a_{11} = \frac{\sigma_{11}a_{11}^*}{2(1 + a_{11}^*)} \quad (16)$$

with an analogous expression for a_{22}.

The rules given above express ε_{12}, σ_{12} and a_{12} in terms of group interaction parameters ε_{ij} and σ_{ij} and group core parameters a_{ii}. For interactions between two identical groups i, we assume

$$\varepsilon_{ii} = \alpha_{ii} + \frac{\beta_{ii}}{T} \quad (17)$$

$$\sigma_{ii} = \xi V_{vdw,ii}^{1/3} \quad (18)$$

where α_{ii} and β_{ii} are group parameters, ξ is an undetermined universal van der Waals volume constant, and $V_{vdw,ii}$ is the van der Waals volume for functional group i as tabulated by Bondi [1964]. The Kihara potential function is spherically symmetric, and is applied here to noble gases. The reciprocal temperature term in Eq. (17) is used as a rough way of accounting for nonsphericity of the molecule, as suggested by Campbell [1989].

For mixtures of chemically dissimilar substances such as hydrocarbon-gas, the Lorentz-Berthelot combining rules for intermolecular interactions between unlike groups i and j were assumed as follows:

$$\varepsilon_{ij} = (1 - k_{ij,gc})\sqrt{\varepsilon_{ii}\varepsilon_{jj}} \quad (19)$$

$$\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2 \quad (20)$$

where $k_{ij,gc}$ is a group binary interaction coefficient defined in analogy with the binary interaction coefficient k_{12} of the corresponding state calculations.

In addition to the value of universal van der Waals volume constant ξ, parameter values (α_{ii}, β_{ii}, and a_{ii}^*) for each functional group i within molecules 1 and 2 are required for the application of the model. To extend the model to mixtures of noble gases examined here, values of group binary interaction coefficient $k_{ij,gc}$ for each interactions between intermolecular groups i and j (or gas groups i and j in this work) might be assumed to be zero since mixtures of noble gases studied here are symmetric.

Although the group contribution model contains a number of parameters, it is practically applicable to pure gases, and as well as to a variety of mixtures. Hence, group parameter values may often be determined from data for pure substances. Data used for the group parameter evaluations and for predictions of thermodynamic properties and dilute gas transport properties of pure gases and mixtures are discussed in the following section.

RESULTS AND DISCUSSION

1. Pure Gases

As a part of the systematic program of our researches, application of the group contribution method was extended to noble gases (He, Ne, Ar, Kr and Xe), and of which gas group parameters (α_{ii}, β_{ii} and a_{ii}^*) were evaluated from the simultaneous regression of second virial coefficient and viscosity data of the pure compound, in which noble gases examined here were assumed to consist of a single functional group. For instance, parameter values of $\alpha_{He\text{-}He}$, $\beta_{He\text{-}He}$ and $a_{He\text{-}He}^*$ for the He group were determined from second virial coefficient and viscosity data of pure helium gas. Group parameters for other four groups were evaluated in an analogous manner. Values of van der Waals volume tabulated by Bondi [1964] and the universal value of the van der Waals volume constant ξ (1.3692) evaluated by Oh and Campbell [1997] were used in data regression for the determination of group parameters for pure gases, and in all subsequent calculations and evaluations.

All second virial coefficient data were taken from a critical compilation of Dymond and Smith [1980]. However, they indicated that the agreement between the various set of data for the second virial coefficient of helium is good down to temperature 15 K. Therefore, in this work, second virial coefficient data below this temperature showing a significant discrepancy among the results of several observers were excluded for the evaluation of group parameters for the He group. And pure viscosity data for the parameter determination were all taken from Stephan and Lucas [1979]. Non-linear least square parameter estimation subroutine based on the Levenberg-Marguardt algorithm supplied by IMSL STAT/library [1994] was used in this data regression, in which each data point was weighted by its estimated experimental uncertainty taken from the corresponding Refs.

Resulting parameters values (a_{ii}^*, α_{ii} and β_{ii}) for He, Ne, Ar, Kr,

Table 1. Properties of the functional groups examined in this study (universal van der Waals volume constant=1.3692[a])

Group	$V_{vdw,ii}$[b]	a_{ii}^*	α_{ii}	β_{ii}
He	6.92	0.03324	7.4986	-
Ne	9.21	0.01846	36.486	-
Ar	16.76	0.10556	134.473	-
Kr	20.80	0.03499	167.802	986.2193
Xe	25.43	0.09557	255.841	1,558.0337

[a]Taken from Oh and Campbell [1997].
[b]Taken from Bondi [1964].

Table 2. Deviations between experimental second virial coefficients and viscosities, and those calculated using group parameters examined in this study

Compound	Number of points*	Average RMSD in B ($cm^3\ mol^{-1}$)		Data source	Number of points**	Average $RMSD_r$ in η (%)		Data source
		Present study	Tsonopoulos			Present study	Lucas	
Regression results:								
Helium	8	0.8	9.2	[a]	9	2.2	25.7	[b]
Neon	10	1.5	1.2	[a]	36	6.7	2.8	[b]
Argon	18	2.8	4.5	[a]	30	6.7	1.7	[b]
Krypton	14	2.4	10.5	[a]	19	5.1	1.2	[b]
Zenon	16	1.6	8.0	[a]	23	2.4	2.5	[b]
Avg.	66	2.0	6.9		117	5.2	4.0	
Prediction results:								
Helium	23	0.7	12.5	[c]	23	1.5	6.5	[c]
					6	0.8	26.5	[f]
					1	0.8	26.2	[g]
					1	0.1	25.7	[h]
					8	1.5	30.7	[j]
					8	1.5	30.5	[m]
					8	1.5	30.7	[o]
					6	1.5	30.1	[p]
					9	1.5	31.3	[q]
Neon	23	2.3	3.3	[c]	23	2.0	0.9	[c]
	10	1.7	1.2	[d]	6	3.2	2.5	[f]
					8	3.0	1.8	[i]
					8	4.3	2.2	[j]
					8	3.2	2.2	[o]
					6	3.7	2.4	[p]
					8	3.2	2.3	[m]
Argon	23	5.2	3.9	[c]	23	1.9	0.7	[c]
	18	2.0	6.1	[e]	6	5.9	9.5	[f]
					1	6.0	1.3	[h]
					8	3.0	1.5	[i]
					7	3.1	1.3	[j]
					5	3.3	0.8	[k]
					6	4.0	1.4	[l]
					9	2.9	1.9	[q]
					8	3.0	1.5	[o]
					7	2.5	1.5	[n]
Krypton	23	4.5	4.2	[c]	23	1.7	0.6	[c]
	12	33.2	37.4	[e]	2	3.8	1.1	[g]
					6	2.7	0.8	[f]
					8	2.7	0.6	[i]
					6	3.1	0.6	[l]
					9	2.7	0.7	[q]
					8	2.5	0.6	[o]
					8	2.8	0.6	[n]
Zenon	23	5.4	4.7	[c]	23	1.4	0.6	[c]
					6	2.2	2.0	[f]
					8	2.1	1.4	[o]
Avg.	155	5.6	7.8		324	2.4	5.9	

*Number of data points for second virial coefficient. **Number of data points for viscosity.

[a]Dymond and Smith [1980]. [b]Stephan and Lucas [1979]. [c]Kestin et al. [1984]. [d]Prausnitz et al. [1999]. [e]Byrne et al. [1968]. [f]Lide [1995]. [g]Kestin and Yata [1968]. [h]Kestin et al. [1971]. [i]Kestin et al. [1970]. [j]Kestin and Ro [1974]. [k]Kestin and Ro [1982]. [l]Hellemans et al. [1972]. [m]Kestin et al. [1972a]. [n]Kestin et al. [1972b]. [o]Kestin et al. [1972c]. [p]Kestin et al. [1972d]. [q]Kalelkar and Kestin [1970].

and Xe gas groups from data regressions are shown in Table 1, and the data sources used to obtain them are indicated in Table 2. The 95% confidence region of the parameter β_{ii} indicating temperature of the potential well depth for He, Ne and Ar groups was bracketed zero, so it was set to zero and the regression was repeated to obtain values of other parameters a_{ii}^* and α_{ii} giving better results.

Resulting deviations between measured and calculated second virial coefficient and viscosity data are given in Table 2, where RMSD (root mean square deviation) in $cm^3\ mol^{-1}$ for second virial coefficients and $RMSD_r$ (root mean square deviation, relative) in % for viscosities, respectively, and are defined by

$$RMSD = \frac{1}{n}\sqrt{\sum_{i=1}^{n}(B_{calc,i} - B_{exp,i})^2} \tag{21}$$

$$RMSD_r = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(\frac{\eta_{calc,i} - \eta_{exp,i}}{\eta_{exp,i}}\right)^2} \tag{22}$$

Included in Table 2 is a comparison of the proposed method to other two corresponding states methods: the Tsonopoulos correlation [1974] for second virial coefficients and the corresponding states method of Lucas [1980] for viscosities of dilute gas state. It is noted that corresponding states methods require the critical pressure and temperature of pure gas in question.

For the second virial coefficient calculations, the proposed model is observed to compare well with the corresponding correlation of Tsonopoulos: average RMSD values of 2.0 $cm^3\ mol^{-1}$ and 6.9 $cm^3\ mol^{-1}$ were obtained by the present method and the Tsonopoulos correlation, respectively. Especially for the neon gas with its experimental uncertainty of ±1.0 $cm^3\ mol^{-1}$ calculated by Kestin et al. [1984] in the temperature range 50-1,000 K, it is indicated that the deviation value obtained from the proposed model (1.5 $cm^3\ mol^{-1}$) is somewhat higher than that of Tsonopoulos correlation (1.2 $cm^3\ mol^{-1}$). A comparison of the experimental and regressed second virial coefficients for pure noble gases is presented in Fig. 1.

Next, second virial coefficient data measured by several researchers [Kestin et al., 1984; Prausnitz et al., 1999; Byrne, 1968], not used in data regressions, were next predicted by using group parameter values determined in advance. Based on average RMSD value for all 155 data points, the proposed method yields less resulting deviation than the Tsonopoulos correlation for pure gases:

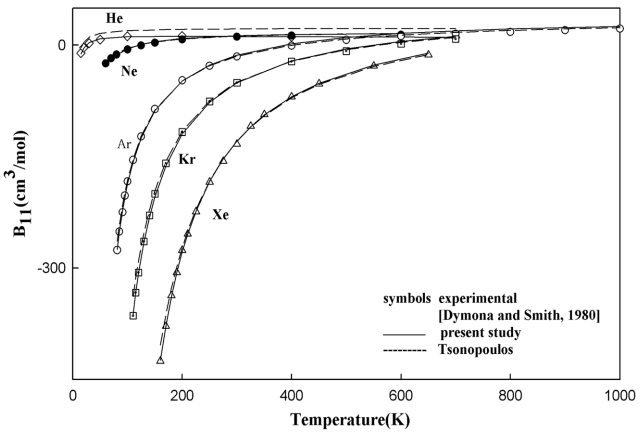

Fig. 1. Comparison of experimental and regressed second virial coefficients for pure noble gases (He, Ne, Ar, Kr and Xe).

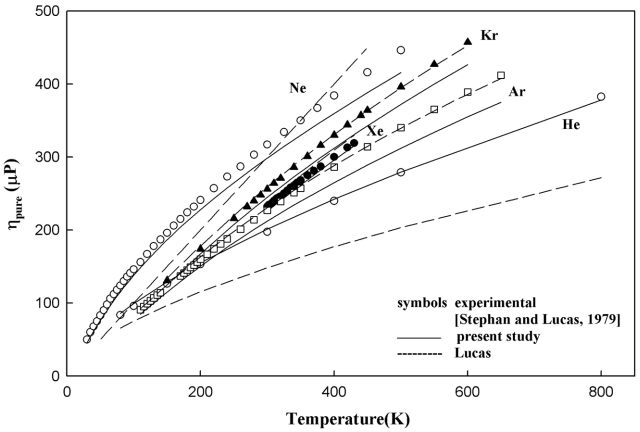

Fig. 2. Comparison of experimental and regressed viscosities for pure noble gases (He, Ne, Ar, Kr and Xe).

5.6 and 7.8 $cm^3\ mol^{-1}$ by the present study and the Tsonopoulos correlation, respectively.

Also shown in Table 2 are resulting deviations between the experimental and calculated viscosities from parameter estimations. The average RMSDr value of 5.2% obtained by the proposed method compares well with 4.0% by means of the Lucas method, indicating that the present study is less reliable than the Lucas method on the whole. The present study provides better viscosity predictions for He and Xe gases and fewer predictions for the other three gases (Ne, Ar and Kr) than those of the Lucas method. Comparisons of the measured and regressed viscosities for pure noble gases are shown in Fig. 2.

Then, viscosity data measured by several other researchers referenced in Table 2 were predicted by using group parameter values, showing that viscosity predictions of both methods are within what is commonly estimated to be experimental uncertainty (approximately 4 to 5%), except for two cases of argon gas by the proposed model and for all cases of helium gas and one case of argon gas by the Lucas method. It is believed here that one point of viscosity data observed by Ketin and Yata [1968] and Kestin et al. [1971] might be unrealistic for comparisons. In total, the present study is believed to yield better resulting deviations than those of the Lucas method for viscosity predictions of these types of data: on average %RMSDr value for all 324 data points of all pure gases, 2.4% and 5.9% by the present study and the Lucas method, respectively.

As mentioned earlier, using the Chapman and Enskog theory [1970], the proposed group contribution concept based on the Kihara intermolecular potential function can be extended to predict other transport properties of the dilute gas state as well. Here, the possibility of applying the model to diffusivities of noble gases, not used in data regression, was examined. With gas group parameters evaluated in advance, self diffusion coefficients of pure noble gases proposed by Kestin et al. [1984] were predicted and its resulting deviations are presented in Table 3. The proposed method shows less deviation between measured and predicted self diffusion coefficients for three gases (He, Ne and Xe) than the Fuller method, and both methods are comparable to each other for the Ar and Kr gases. The overage RMSDr value of 3.9% for all 115 data points obtained by the proposed method compares very well with 6.2% by means of

Table 3. Deviations between experimental self diffusivities and those calculated by using group parameters examined in this study

Compound	Number of points[a]	Average RMSD$_r$ in D (%)		Data source
		Present study	Fuller	
Prediction Results:				
Helium	23	3.0	8.3	[a]
Neon	23	2.1	4.4	[a]
Argon	23	2.1	0.6	[a]
Krypton	23	1.9	1.7	[a]
Zenon	23	10.5	16.0	[a]
Averall	115	3.9	6.2	

*Number of data points for self diffusion coefficients.
[a]Kestin et al. [1984].

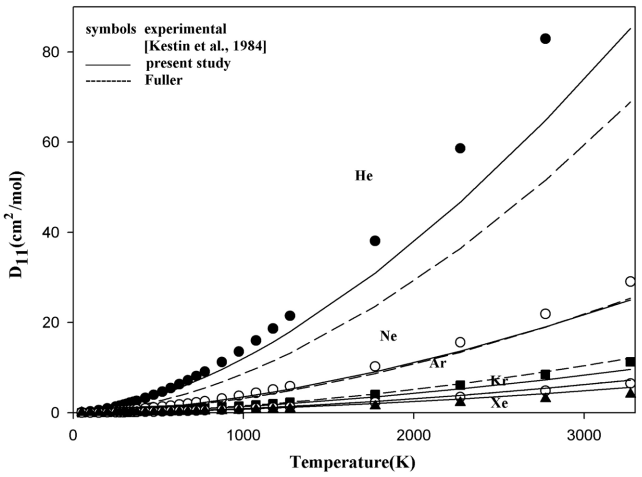

Fig. 3. Comparison of experimental and predicted self diffusion coefficients for pure noble gases (He, Ne, Ar, Kr and Xe).

the Fuller method, indicating that the present study provides less resulting deviation, within experimental error of approximately 5%. Fig. 3 presents comparisons of the experimental and predicted self diffusivities for pure noble gases.

2. Mixtures of Noble Gases

An advantage of the group contribution concepts is that mixture property calculations can be made by using gas group parameters obtained from properties of pure compounds without additional parameters. Gas group parameters determined by reducing the second virial coefficient and viscosity data for pure gases together were used to calculate second virial cross coefficients and mixture viscosities for mixtures of noble gases. Binary diffusion coefficients for noble gas mixtures were calculated in an analogous way as well.

As proved by Oh and Campbell [1997], calculations of thermodynamic and transport properties based on the group contribution concepts have been improved by using the group binary interaction coefficient $k_{ij,gc}$ only for the case of chemically dissimilar mixtures, for instance, hydrocarbon and diatomic gas mixture of C_3H_8 and N_2. However, in this work, all mixtures of noble gases studied here were assumed to be chemically similar; the additional parameter (gas group binary interaction coefficient, $k_{ij,gc}$) for interaction between gas groups i and j (or between molecules 1 and 2) was not

Table 4. Deviations between experimental and predicted second virial cross coefficients

Mixtures	Number of points	Average RMSD in B (cm^3 mol^{-1})		Data source
		Present study ($K_{ij,gc}$=0)	Tsonopoulos (K_{12}=0)	
Mixtures of noble gases				
Helium				
- Neon	23	1.6	8.1	[a]
	8	1.6	5.6	[b; #3]
- Argon	23	6.0	12.0	[a]
	6	0.6	5.2	[b; #3]
	8	0.9	3.6	[b; #4]
	3	0.4	3.9	[b; #5]
- Krypton	23	10.0	16.0	[a]
	6	10.4	3.3	[b; #1]
	3	3.9	0.9	[b; #2]
- Xenon	23	19.1	24.8	[a]
	4	15.0	8.3	[b; #1]
Avg.	130	7.7	12.1	
Neon				
- Argon	23	4.5	4.0	[a]
	8	6.9	4.5	[b; #2]
	5	5.9	2.7	[b; #3]
	7	3.3	3.0	[b; #4]
- Krypton	23	6.3	6.0	[a]
	7	28.2	22.7	[b; #2]
	5	8.1	6.6	[b; #3]
	7	3.2	3.9	[b; #4]
- Xenon	23	12.7	12.1	[a]
	5	15.3	15.0	[b; #1]
	7	8.2	9.0	[b; #2]
Avg.	120	8.7	7.8	
Argon				
- Krypton	23	5.2	4.3	[a]
	0	33.5	36.4	[b; #1]
	12	5.4	2.7	[b; #2]
	17	1.8	1.2	[b; #3]
	6	3.4	1.6	[b; #3]
- Xenon	23	7.2	5.7	[a]
	15	10.9	11.1	[b; #1]
	6	2.9	3.5	[b; #2]
Avg.	111	8.0	7.4	
Krypton				
- Xenon	23	3.1	4.4	[a]
	11	11.8	6.1	[b; #1]
	12	7.5	5.1	[b; #2]
	6	2.3	1.4	[b; #3]
Avg.	52	5.9	4.6	

*Number of data points for second virial coefficient.
**Number of data points for viscosity.
#Reference number of data compiled.
[a]Kestin et al. [1984].
[b]Dymond and Smith [1980].

adopted for the enhancement of mixture property calculations. However, estimation of $k_{ij,gc}$ for interactions between noble gas and noble gas groups was made to see just what their values are. As expected, all $k_{ij,gc}$ values estimated by regressing second virial cross coefficient data turned out to be negative, and which values are not presented in this paper.

Resulting deviations between measured and calculated second virial cross coefficient data for mixtures of noble gases are presented in Table 4. Also included for comparison in Table 4 are results from the corresponding states method of Tsonopoulos [1974], which requires a value for the binary interaction coefficient k_{12} when extended to second virial cross coefficients for mixtures of different types. However, in this study, k_{12} is assumed a priori to be zero for these types of mixtures. Based on the average RMSD in cm^3 mol^{-1} for each type of mixture, the proposed method is in better agreement with the observed and calculated second virial cross coefficients for helium mixtures and gives somewhat higher deviations for other types of mixtures: at most 1.4 cm^3 mol^{-1} deviation difference for Kr-Xe mixture between 5.9 cm^3 mol^{-1} for the present study and 4.6 cm^3 mol^{-1} for Tsonopoulos correlation. It might be said that both methods compare very well with each other.

Fig. 4 shows the comparison of experimental and predicted second virial cross coefficients for all types of helium mixtures (He-Ne, -Ar, He-Kr and He-Xe), in which the present method is in better agreements for He-Ne and He-Ar mixtures, and worse agreements between observed and predicted second virial cross coefficients for He-Kr and He-Xe mixtures than Tsonopoulos correlation. Biased results observed for all helium mixtures might be that reliability of the experimental data measured by Kestin et al. [1984] is in doubt. As size difference of molecules in mixture becomes larger, the resulting deviation goes higher. Therefore, it is recommended that application of the group contribution concepts using Kihara spherical core potential to this kind of mixture requires some modifications of accounting for size effects of the molecules. However, applicability of the method based on the spherical core potential of Kihara to noble gas mixtures was proved with good results.

Prediction results of mixture viscosities for noble gases are presented in Table 5. Based on the average %RMSDr value for each type of mixture, the present study provides better agreement between

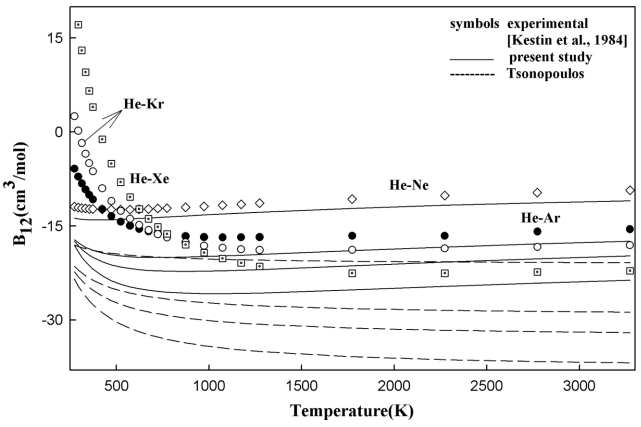

Fig. 4. Comparison of experimental and predicted second virial cross coefficients for helium gas mixtures (He-Ar, He-Kr and He-Xe).

Table 5. Deviations between experimental and predicted mixture viscosities

Mixtures	Number of points	Average $RMSD_r$ in η (%)		Data source
		Present study ($K_{ij,gc}$=0)	Lucas method	
Noble Gas - noble gas mixtures				
Helium				
- Neon	87	7.8	19.4	[a]
	9	4.5	15.6	[b]
	12	3.8	20.4	[c]
	20	6.9	16.9	[d]
	32	7.2	17.9	[f]
- Argon	87	6.2	13.6	[a]
	16	11.1	14.2	[e]
	13	3.6	11.6	[b]
	70	9.3	11.2	[g]
	40	5.8		[h]
- Krypton	87	5.7	9.8	[a]
	11	3.3	10.4	[i]
	19	13.4	12.6	[j]
	40	5.2	11.7	[h]
- Xenon	87	5.4	7.2	[a]
	12	1.9	10.2	[k]
Avg.	642	6.6	13.2	
Neon				
- Argon	87	7.6	4.5	[a]
	13	6.1	2.5	[e]
	12	28.6	36.5	[c]
	36	8.1	1.3	[h]
	36	7.8	3.3	[m]
- Krypton	87	7.3	4.6	[a]
	11	6.5	4.1	[i]
	32	8.0	5.2	[n]
- Xenon	87	13.2	11.5	[a]
	10	15.3	15.0	[i]
Avg.	411	9.5	6.8	
Argon				
- Krypton	87	7.9	3.5	[a]
	36	8.0	1.3	[l]
	11	4.7	2.4	[i]
- Xenon	87	11.7	4.8	[a]
	11	4.3	4.8	[i]
Avg.	232	9.3	3.7	
Krypton				
- Xenon	87	6.2	4.0	[a]
	11	3.9	3.0	[i]
Avg.	98	5.9	3.9	

[a]Kestin et al. [1984]. [b]Thornton and Baker [1962]. [c]Kestin and Nagashima [1964]. [d]Reitbeld et al. [1959]. [e]Iwasaki and Kestin [1963]. [f]Kestin et al. [1972d]. [g]Reitbeld et al. [1953]. [h]Kalelkar and Kestin [1970]. [i]Thornton [1960a]. [j]Kestin and Kobayashi [1966]. [k]Thornton [1960b]. [l]Kestin et al. [1970]. [m]Reitbeld et al. [1956]. [n]Kestin et al. [1972b].

measured and predicted mixture viscosities than the Lucas method for helium mixtures: 6.9 %RMSDr by the present model and 13.2 %RMSDr by the Lucas method. But for the other four types of mixtures the Lucas method proved to be more reliable the proposed model: for neon mixtures, 9.5 and 6.8 %RMSDr by the present model and the Lucas method, respectively; for argon mixtures, 9.3 and 3.7 %RMSDr by the present model and the Lucas method, respectively; for krypton mixture, 5.9 and 3.9 %RMSDr by the present model and the Lucas method, respectively. However, mixture viscosity predictions for helium and krypton mixtures by the present study are within or about experimental uncertainties of 5 to 7 absolute % deviations. Fig. 5 shows a comparison of experimental and predicted mixture viscosities for three different helium mole fractions of helium-neon mixtures. Also included for comparison

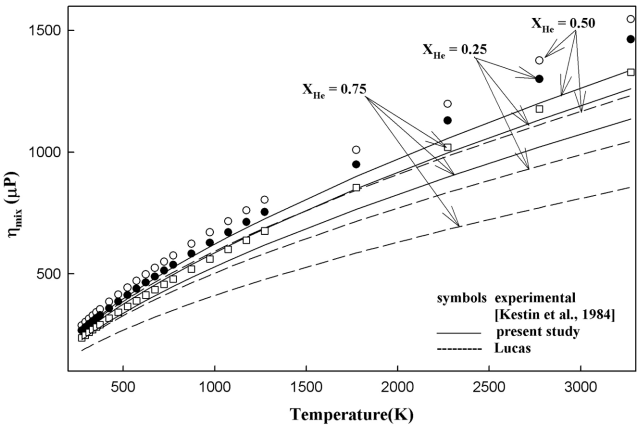

Fig. 5. Comparison of experimental and predicted mixture viscosities for noble gas mixture (He-Ne).

Table 6. Deviations between experimental and predicted binary diffusion coefficients

Mixtures	Number of points	Average $RMSD_r$ in D (%)		Data source
		Present study ($K_{ij,gc}$=0)	Fuller et al.	
Noble Gas - Noble Gas Mixtures				
Helium				
- Neon	29	8.6	30.5	[a]
	5	4.9	36.9	[b]
	6	9.6	31.2	[c]
- Argon	29	7.5	24.2	[a]
	3	2.7	22.0	[d]
	7	4.1	20.8	[e]
	3	7.6	24.6	[f]
	4	13.8	25.3	[g]
	1	4.8	24.8	[h]
	7	6.0	33.2	[i]
	2	9.8	26.7	[j]
	4	5.0	25.5	[b]
	13	17.3	25.5	[k]
	17	8.0	22.9	[l]
	8	11.0	23.9	[m]
- Krypton	29	6.6	19.1	[a]
	7	4.4	20.8	[i]
	4	16.7	30.2	[b]
	8	6.8	19.3	[m]
- Xenon	29	4.3	13.2	[a]
	7	2.1	15.2	[i]
	4	2.3	17.5	[b]
Avg.	226	7.5	22.9	

Table 6. Continued

Mixtures	Number of points	Average $RMSD_r$ in D (%)		Data source
		Present study ($K_{ij,gc}$=0)	Fuller et al.	
Neon				
- Argon	29	10.0	12.7	[a]
	7	9.6	12.8	[i]
	4	9.3	15.2	[b]
	8	10.1	13.8	[n]
	9	6.7	13.6	[l]
- Krypton	29	20.1	20.2	[a]
	7	10.3	13.2	[i]
	4	9.2	12.4	[b]
	4	7.0	12.1	[l]
	8	9.5	11.4	[o]
- Xenon	29	10.9	7.9	[a]
	7	9.9	8.6	[i]
	4	9.6	8.7	[b]
Avg.	149	11.8	13.0	
Argon				
- Krypton	29	18.8	21.7	[a]
	7	7.5	6.2	[i]
	1	8.8	3.4	[j]
	4	6.3	9.1	[b]
	8	5.9	22.6	[n]
	9	9.4	4.4	[l]
	8	10.1	1.9	[n]
- Xenon	29	20.4	48.7	[a]
	7	6.8	8.5	[i]
	2	9.5	9.3	[j]
	4	6.4	17.9	[b]
	4	7.1	14.2	[l]
Avg.	112	13.9	23.1	
Krypton				
- Xenon	29	8.1	23.8	[a]
	7	3.0	10.3	[i]
	4	5.4	26.6	[b]
Avg.	40	6.9	21.7	

[a]Kestin et al. [1984]. [b]van Heijningen [1968]. [c]Kestin et al. [1972d]. [d]Holsenv and Strunk [1964]. [e]Seager et al. [1963]. [f]Strehlow [1953]. [g]Strehlow [1959]. [h]Chapman and Cowling [1970]. [i]Lide [1995]. [j]Poling et al. [2000]. [k]Saxena and Mason [1959]. [l]Fuller et al. [1966]. [m]Kalelkar and Kestin [1970]. [n]Thornton [1960]. [o]Kestin et al. [1972b]. [p]Humphreys and Mason [1970].

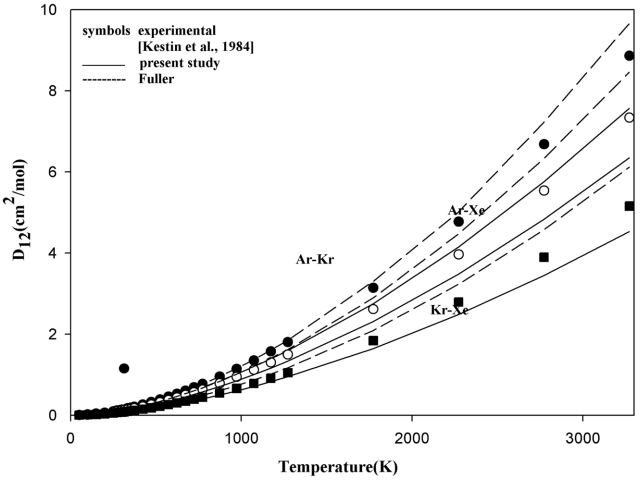

Fig. 6. Comparison of experimental and predicted binary diffusion coefficients for noble gas mixtures (Ar-Kr, Ar-Xe, Kr-Xe).

in Fig. 5 are results from the Lucas method.

Given in Table 6 are the resulting deviations between measured and predicted binary diffusion coefficients for noble gas mixtures. Included for comparison in Table 6 are results from the Fuller method. Based on the average %RMSDr value for each type of mixture, the present study is in quite better agreement between measured and predicted binary diffusion coefficients than the Lucas method for all four types of noble gas mixtures: for helium mixes of 226 points, 7.5 and 22.9 %RMSDr by the present model and the Lucas method, respectively; for neon mixtures of 149 points, 11.8 and 13.0 %RMSDr by the present model and the Lucas method, respectively; for argon mixtures of 112 points, 13.9 and 23.1 %RMSDr by the present model and the Lucas method, respectively; for krypton mixture of 40 points, 6.9 and 21.7 %RMSDr by the present model and the Lucas method, respectively. Comparison of experimental and predicted binary diffusion coefficients for neon-argon and krypton-xenon mixtures is shown in Fig. 6 and Fig. 7, respectively.

CONCLUSIONS

The group contribution method has been extended to noble gases for the estimation of second virial coefficients, viscosities and diffusion coefficients. Gas group parameters were obtained from the simultaneous regression of second virial coefficient and viscosity data for pure gases. All compounds examined here were assumed to consist of a single functional group, or a single gas group in a molecule. New gas group parameter values for He, Ne, Ar, Kr and Xe groups were reported.

For mixture property predictions, group binary interaction coefficients were not adopted for these types of symmetric mixtures of chemically similar compounds. Application of the model shows that second virial coefficient data can be represented with results comparable to those obtained by the corresponding states method. The accuracy of the model in viscosity predictions is comparable to the Lucas method. The characteristic feature of the group contribution method makes possible diffusivity predictions as well, which data were not supplied to the parameter estimation steps. The reliability of the model in diffusion coefficient predictions is evaluated nicely by comparison with the Fuller method.

A strong advantage of the method is that it is capable of representing several different properties with one set of group parameter values. Thus, data for one property may be used to predict a different property. On top of that, since this method does not require the critical properties and acentric factors, it may be used to predict properties of substances in question for which these data are not available.

ACKNOWLEDGMENT

This paper was supported by the Konyang University Research Fund, in 2005.

NOMENCLATURE

a : core radius [Δ]
a^* : reduced core radius, $2a/(\sigma - 2a)$
B : second virial coefficient [cm^3 mol^{-1}]
D : diffusion coefficient [cm^2 sec^{-1}]
k_{12} : binary interaction coefficient for Tsonopoulos correlation
$k_{ij,\,gc}$: group binary interaction coefficient for interactions between intermolecular functional groups i and j
M : molecular weight [gram mol^{-1}]
N : Avogadro's number
N_{i1} : number of groups i in molecule 1
N_{j2} : number of groups j in molecule 2
P : pressure [atm]
r : distance between molecular centers of molecules 1 and 2 [Δ]
RMSD : root mean square deviation [cm^3 mol^{-1}]
%RMSDr : percent relative root mean square deviation, relative [%]
T : temperature [K]
T^* : reduced temperature, kT/ε
V : volume [cm^3]
$V_{vdw,\,ii}$: van der Waals volume of group i [cm^3 mol^{-1}]
x : mole fraction
X_η : defined by Eq. (6)
Y_η : defined by Eq. (7)
Z_η : defined by Eq. (8)
Z : reciprocal reduced temperature, $1/T^* = \varepsilon/kT$

Greek Letters

α : functional group parameter for potential well depth [J]
β : functional group parameter for potential well depth [J K]
ε : potential well depth [J]
η : viscosity [μP]
ξ : universal van der Waals volume constant (1.3692) in Eq. (18)
σ : collision diameter [Δ]
Ω_V : collision integral for viscosity
Ω_D : collision integral for diffusivity

Subscripts

1,11 : property for molecule 1

2,22 : property for molecule 2
12 : interaction property for molecules 1 and 2
ij : interaction property for molecules i and j
C : critical property
GAS : property for gas group
gc : property for group binary interaction coefficient
He : property for He gas group
Ne : property for Ne gas group
Ar : property for Ar gas group
Kr : property for Kr gas group
Xe : property for Xe gas group
η : property for viscosity

REFERENCES

Bondi, A., "van der Waals Volumes and Radii," *J. Phys. Chem.*, **68**(3), 441 (1964).

Byrne, M. A., Jones, M. R. and Staveley, L. A. K., "Second Virial Coefficient of Argon, Krypton and Methane and their Binary Mixtures," *Trans. Faraday Soc.*, **64**, 1747 (1968).

Campbell, S. W., "Application of the Group Contribution Concept to the Kihara Potential for the Calculation of Second Virial Coefficients," *Fluid Phase Equilibria*, **47**, 47 (1989).

Chapman, S. and Cowling, T. G., *The Mathematical Theory of Nonuniform Gases*, 3rd ed., Cambridge University Press, New York (1970).

Derr, E. L. and Deal, C. H., "Analytical Solution of Groups: Correlation of Activity Coefficients Through Structural Group Parameters," *Inst. Chem. Eng. Symp. Ser.*, **32**, 44 (1969).

Dymond, J. H. and Alder, B. J., "Pair Potential for Argon," *J. Chem. Phys.*, **51**(1), 309 (1969).

Dymond, J. H. and Smith, E. B., *The Virial Coefficients of Pure Gases and Mixtures-A Critical Compilation*, Clarendon Press, Oxford (1980).

Fredenslund, A., Jones, R. L. and Prausnitz, J. M., "Group-contribution Estimation of Activity Coefficients in Nonideal Liquid Mixtures," *AIChE J.*, **21**(6), 1086 (1975).

Fuller, E. N., Schettler, P. D. and Giddings, J. C., "New Method for Prediction of Binary Gas-Phase Diffusion Coefficients," *Ind. Eng. Chem.*, **58**(5), 18 (1966).

Georgeton, G. K. and Teja, A. S., "A group Contribution Equation of State Based on the Simplified Perturbed Hard Chain Theory," *Ind. Eng. Chem. Res.*, **27**, 657 (1988).

Hellemans, J. M., Kestin, J. and Ro, S. T., "Viscosity of Binary Mixtures of Nitrogen with Argon and Krypton," *J. Chem. Phys.*, **57**(9), 4038 (1972).

Hirschfelder, J. O., Curtiss, C. F. and Bird, R. B., *Molecular Theory of Gases and Liquids*, Wiley, New York (1954)

Holsen, J. N. and Strunk, M. R., *Ind. Eng. Chem. Fund.*, **3**, 143, (1964).

Humphreys, A. E. and Mason, E. A., "Intermolecular Forces: Thermal Diffusion and Diffusion in Ar-Kr," *The Physics of Fluids*, **13**(1), 65 (1970).

IMSL, *IMSL STAT/LIBRARY: Regression*, IMSL, Houston (1994).

Iwasaki, H. and Kestin, J., "The Viscosity of Argon-Helium Mixtures," *Physica*, **29**, 1345 (1963).

Jin, G., Walsh, J. M. and Donahue, M. D., "A Group-contribution Correlation for Predicting Thermodynamic Properties with the Perturbed-Soft-Chain Theory," *Fluid Phase Equilibria*, **31**, 123 (1986).

Kalelkar, A. S. and Kestin, J., "Viscosity of He-Ar and He-Kr Binary Mixtures in the Temperature Range 25-700 °C," *J. Chem. Phys.*, **52**(8), 4248 (1970).

Kestin, J. and Nagashima, A., "Viscosity of Neon-Argon Mixtures at 20 °C and 30 °C," *J. Chem. Phys.*, **40**(12), 3648 (1964).

Kestin, J., Kobayashi, Y. and Wood, R. T., "The Viscosity of Four Binary, Gases Mixtures at 20 °C and 30 °C," *Physica*, **32**, 1065 (1966).

Kestin, J. and Yata, J., "Viscosity and Diffusion Coefficient of Six Binary Mixtures," *J. Chem. Phys.*, **49**(11), 4780 (1968).

Kestin, J., Wakeham, W. and Watanabe, K., "Viscosity, Thermal Conductivity, and Diffusion Coefficient of Ar-He and Ar-Kr Mixtures in the Temperature Range 25-700 °C," *J. Chem. Phys.*, **53**(10), 3773 (1970).

Kestin, J., Paykoc, E. E. and Sengers, J. V., "On the Density Expansion for Viscosity in Gases," *Physica*, **54**, 1 (1971).

Kestin, J., Ro, S. T. and Wakeham, W. A., "Viscosity of Binary Gasous Mixtures Helium-Nitrogen," *J. Chem. Phys.*, **56**(8), 4036 (1972a).

Kestin, J., Ro, S. T. and Wakeham, W. A., "Viscosity of Binary Gaseous Mixtures Neon-Krypton," *J. Chem. Phys.*, **56**(8), 4086 (1972b).

Kestin, J., Ro, S. T. and Wakeham, W. A., "Viscosity of the Noble Gases in the Temperature Range 25-7,900 °C," *J. Chem. Phys.*, **56**(8), 4119 (1972c).

Kestin, J., Ro, S. T. and Wakeham, W. A., "Viscosity of the Binary Mixtures He-Ne and He-N_2 in the Temperature Range 25-700 °C," *J. Chem. Phys.*, **56**(12), 5837 (1972d).

Kestin, J. and Ro, S. T., "The Viscosity of Nine Binary and Two Ternary Mixtures of Gases at Low Density," *Ber. Bunsen-Ges. Physik. Chem.*, **20**, 20 (1974).

Kestin, J. and Ro, S. T., "The Viscosity and Diffusion Coefficient of Binary Mixtures with Ar, N_2, CO_2," *Ber. Bunsen-Ges. Phys. Chem.*, **86**, 948 (1982).

Kestin, J., Knierim, K., Mason, E. A., Najafi, B., Ro, S. T. and Waldman, M., "Equilibrium and Transport Properties of the Noble Gases and Their Mixtures at Low Density," *J. Phys. Chem. Ref. Data*, **13**(1), 229 (1984).

Kihara, T., *Intermolecular Forces*, Wiley, New York (1978).

Lide, D. R., *Handbook of Chemistry and Physics*, 76th Ed., CRC Press (1995).

Lucas, K., *Phase Equilibria and Fluid Properties in the Chemical Industry*, Dechema, Frankfurt (1980).

O'Connell, J. P. and Prausnitz, J. M., *Advances in Thermophysical Properties at Extreme Temperatures and Pressures*, 3rd Symposium of Thermophysical Properties, ASME, New York (1965).

O'Connell, J. P., Personal Communication (1988).

Oh, S.-K., *A Group Interaction Model for Second Virial Coefficients of Pure Gases and Mixtures*, M.S. Thesis, University of S. Florida, Tampa (1989).

Oh, S.-K. and Campbell, S. W., "A Group Contribution Model for Thermodynamic and Transport Properties of Dilute Gases," *Fluid Phase Equilibria*, **129**, 69 (1997).

Oh, S.-K. and Sim, C.-H., "An Extension of the Group Contribution Model for Thermodynamic and Transport Properties of Dilute Gases," *Korean J. Chem. Eng.*, **19**, 843 (2002).

Oh, S.-K. and Park, K.-H., "An Extension of the Group Contribution Method for Estimating Thermodynamic and Transport Properties: Part II. Polyatomic Gases (F_2, Cl_2, CS_2, H_2S, NO and N_2O)," *Korean*

J. Chem. Eng., **22**, 268 (2005).

Poling, B. E., Prausnitz, J. M. and O'Connell, J. P., *The Properties of Gases and Liquids*, 5th ed., McGraw Hill, NY (2000).

Prausnitz, J. M., Lichtenthaler, R. N. and de Azevedo, E. G, *Molecular Thermodynamics of Fluid-Phase Equilibria*, 3rd ed., Prentice Hall (1999).

Rietveld, A. O., Van Itterbeek, A. and Van Den Berg, G. J., "Measurements on the Viscosity of Mixtures of Helium and Argon," *Physica*, **19**, 517 (1953).

Rietveld, A. O., Van Itterbeek, A. and Van Den Berg, G. J., "Measurements on the Viscosity of Mixtures of Neon ans Argon," *Physica*, **22**, 785 (1956).

Rietveld, A. O., Van Itterbeek, A. and Velds, C. A., "Viscosity of Binary Mixtures of Hydrogen Isotopes and Mixtures of Helium and Neon," *Physica*, **25**, 205 (1959).

Seager, S. L., Geertson, L. R., Giddings, J. C., "Temperature Dependence of Gas and Vapor Diffusion Coefficients," *J. Chem. Eng. Data*, **8**, 168 (1963).

Strehlow, R. A., *J. Chem. Eng. Data*, **21**, 2101 (1953).

Strehlow, R. A., *J. Chem. Eng. Data*, **31**, 519 (1959).

Saxena, S. C. and Mason, E. A., "Thermal Diffusion and the Approach to the State in Gases: II," *Mol. Phys.*, **2**, 379 (1959).

Stephan, K. and Lucas, K., *Viscosity of Dense Fluids*, Plenum Press, New York (1979).

Tee, L. S., Gotoh, S. and Stewart, W. E., "Molecular Parameters for Normal Fluids. Kihara Potential with Spherical Core," *Ind., Eng. Chem. Fund.*, **5**, 363 (1966).

Thornton, E. and Baker, W. A. D., "Viscosity and Thermal Conductivity of Binary Gas Mixtures: Argon-Neon, Argon-Helium and Neon-Helium," *Proc. Phys. Soc.*, **80**, 1171 (1962).

Thornton, E., "Viscosity and Thermal Conductivity of Binary Gas Mixtures: Krypton-Argon, Krypton-Neon and Krypton-Helium," *Proc. Phys. Soc.*, **77**, 1166 (1960a).

Thornton, E., "Viscosity and Thermal Conductivity of Binary Gas Mixtures: Xenon-Helium, Xenon-Neon and Xenon-Argon," *Proc. Phys. Soc.*, **76**, 104 (1960b).

Tsonopoulos, C., Dymond, J. M. and Szafranski, A. M., "Second Virial Coefficients of Normal Alkanes, Linear 1-Alkanols and Their Binaries," *Pure & Appl. Chem.*, **61**(6), 1387 (1989).

Tsonopoulos, C. and Dymond, J. H., "Second Virial Coefficients of Normal Alkanes, Linear 1-Alkanols (and Water), Alkyl Ethers, and Their Mixtures," *Fluid Phase Equilibria*, **133**, 11 (1997).

Tsonopoulos, C., "An Empirical Correlation of Second Virial Coefficients," *AIChE J.*, **20**(2), 263 (1974).

van Heijningen, R. J. J., Harpe, J. P. and Beenakker, J. J. M., "Determination of the Duffusion Coefficients of Binary Mixtures of the Noble Gases As a Function of Temperature and Concentration," *Physica*, **38**, 1 (1968).