

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

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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 et 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 chem-

ical 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 CH₂ and CH₃ groups in normal alkanes were determined from second virial coefficient data for pure C₂-n-C₈ alkanes, and parameters for CH₄ 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

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second virial coefficient data of pure alkanes presented by Tsouopoulos et al. [1989] and Tsouopoulos 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, O₂ and H₂), 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 (F₂, Cl₂, CS₂, H₂S, NO, and N₂O). 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]:

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

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:

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

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

$$F_s(Z) = -\frac{s}{12} \sum_{j=1}^{\infty} \frac{2^j}{j!} Z^{(j/2 + s/12)} \Gamma\left(\frac{6j-s}{12}\right) \quad (3)$$

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

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

where M is the molecular weight (g mol⁻¹), T is the Kelvin temperature, $T^* = kT/\varepsilon$, σ is in \AA , and viscosity η is in micropoise. The quantity Ω_η is the collision integral for viscosity and depends on the choice of intermolecular potential. And the Ω_η 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]:

$$\frac{1}{\eta_{mix}} = \frac{X_\eta + Y_\eta}{1 + Z_\eta} \quad (5)$$

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

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

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

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

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

$$\eta_{12} = 26.693 \frac{\sqrt{2M_1M_2T}}{\sigma_{12}^2 \Omega_\eta(T_{12}^*)} \quad (9)$$

Finally, the quantity Ω_D is the collision integral for diffusivity and, like Ω_η , 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_η 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]:

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

where D_{12} is in cm² 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

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

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 α_{He-He} , β_{He-He} and a_{He-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-Margardt 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 |

^aTaken from Oh and Campbell [1997].

^bTaken 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, 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] | | | | | |
| | | | | | 23 | 2.3 | 3.3 | [c] | | | | | |
| Neon | 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] | | | | | | | | | | |
| Krypton | 23 | 4.5 | 4.2 | [c] | 23 | 1.7 | 0.6 | [c] | | | | | |
| | | | | | 12 | 33.2 | 37.4 | [e] | | | | | |
| | | | | | 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.

^aDymond and Smith [1980]. ^bStephan and Lucas [1979]. ^cKestin et al. [1984]. ^dPrausnitz et al. [1999]. ^eByrne et al. [1968]. ^fLide [1995]. ^gKestin and Yata [1968]. ^hKestin et al. [1971]. ⁱKestin et al. [1970]. ^jKestin and Ro [1974]. ^kKestin and Ro [1982]. ^lHellemans et al. [1972]. ^mKestin et al. [1972a]. ⁿKestin et al. [1972b]. ^oKestin et al. [1972c]. ^pKestin et al. [1972d]. ^qKalelkar 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 $\text{cm}^3 \text{mol}^{-1}$ for second virial coefficients and RMSD_r (root mean square deviation, relative) in % for viscosities, respectively, and are defined by

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

$$\text{RMSD}_r = \sqrt{\frac{1}{n} \sum_{i=1}^n \left(\frac{\eta_{\text{calc},i} - \eta_{\text{exp},i}}{\eta_{\text{exp},i}} \right)^2} \quad (22)$$

Included in Table 2 is a comparison of the proposed method to other two corresponding states methods: the Tsionopoulos 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 Tsionopoulos: average RMSD values of $2.0 \text{ cm}^3 \text{ mol}^{-1}$ and $6.9 \text{ cm}^3 \text{ mol}^{-1}$ were obtained by the present method and the Tsionopoulos correlation, respectively. Especially for the neon gas with its experimental uncertainty of $\pm 1.0 \text{ cm}^3 \text{ mol}^{-1}$ 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 ($1.5 \text{ cm}^3 \text{ mol}^{-1}$) is somewhat higher than that of Tsionopoulos correlation ($1.2 \text{ cm}^3 \text{ mol}^{-1}$). 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 Tsionopoulos correlation for pure gases:

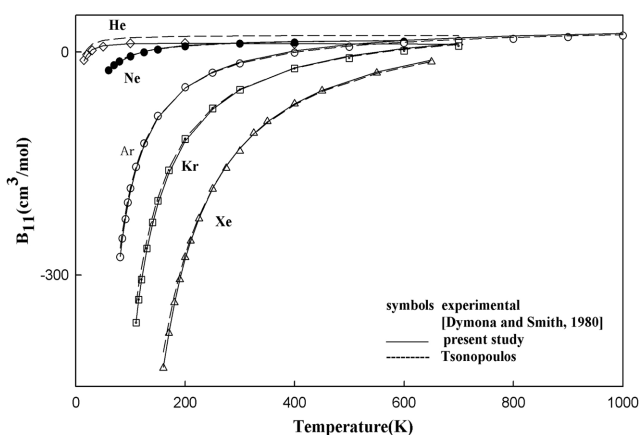


Fig. 1. Comparison of experimental and regressed second virial coefficients for pure noble gases (He, Ne, Ar, Kr and Xe).

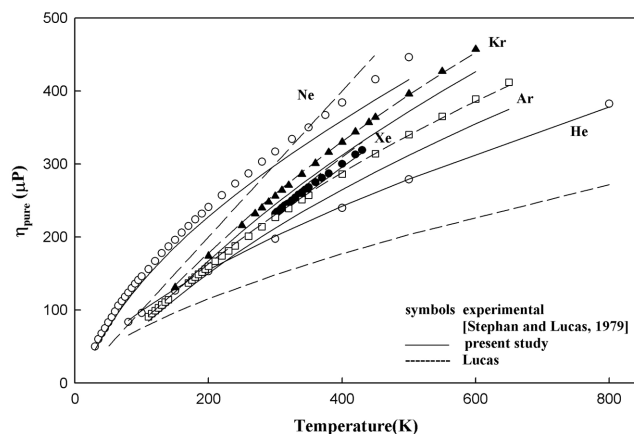


Fig. 2. Comparison of experimental and regressed viscosities for pure noble gases (He, Ne, Ar, Kr and Xe).

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

Also shown in Table 2 are resulting deviations between the experimental and calculated viscosities from parameter estimations. The average RMSD_r 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 Kestin 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 $\% \text{RMSD}_r$ value for all 324 data points of all pure gases, 2.4% and 5.9% by the present study and the Lucas method, respectively.

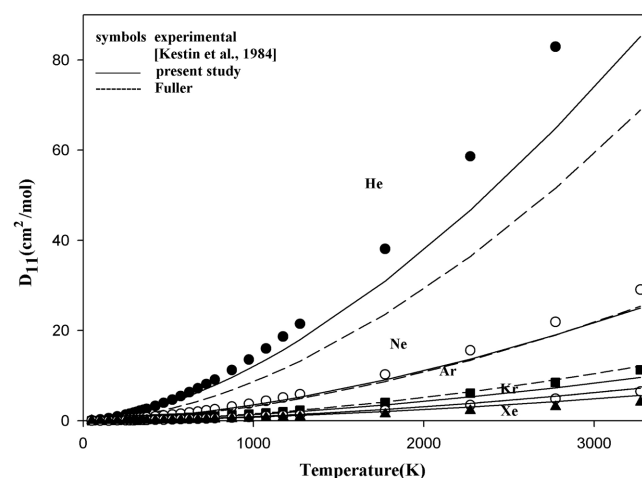
As mentioned earlier, using the Chapman and Enskog theory [1970], the proposed group contribution concept based on the Kihara intermolecular potential function can be extended to predict other transport properties of the dilute gas state as well. Here, the possibility of applying the model to diffusivities 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 average RMSD_r 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 | |

^aNumber of data points for self diffusion coefficients.

^aKestin 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 $k_{j,gc}$ 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, $k_{j,gc}$) 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 | Tsonopoulos | |
| | | ($K_{j,gc}=0$) | ($K_{12}=0$) | |
| 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.

^aKestin et al. [1984].

^bDymond 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 $\text{cm}^3 \text{mol}^{-1}$ 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 $1.4 \text{ cm}^3 \text{mol}^{-1}$ deviation difference for Kr-Xe mixture between $5.9 \text{ cm}^3 \text{mol}^{-1}$ for the present study and $4.6 \text{ cm}^3 \text{mol}^{-1}$ 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 %RMSD_r value for each type of mixture, the present study provides better agreement between

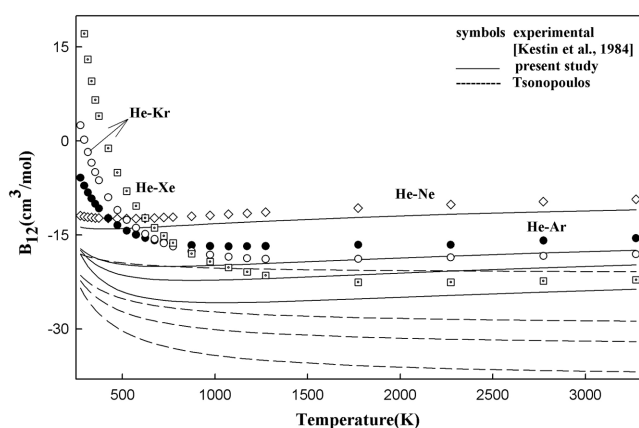


Fig. 4. Comparison of experimental and predicted second virial cross coefficients for helium gas mixtures (He-Ar, He-Kr and He-Xe).

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 | |

^aKestin et al. [1984]. ^bThornton and Baker [1962]. ^cKestin and Nagashima [1964]. ^dReitveld et al. [1959]. ^eIwasaki and Kestin [1963]. ^fKestin et al. [1972d]. ^gReitveld et al. [1953]. ^hKalelkar and Kestin [1970]. ⁱThornton [1960a]. ^jKestin and Kobayashi [1966]. ^kThornton [1960b]. ^lKestin et al. [1970]. ^mReitveld et al. [1956]. ⁿKestin et al. [1972b].

measured and predicted mixture viscosities than the Lucas method for helium mixtures: 6.9 %RMSD_r by the present model and 13.2 %RMSD_r 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 %RMSD_r by the present model and the Lucas method, respectively; for argon mixtures, 9.3 and

3.7 %RMSD_r by the present model and the Lucas method, respectively; for krypton mixture, 5.9 and 3.9 %RMSD_r 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

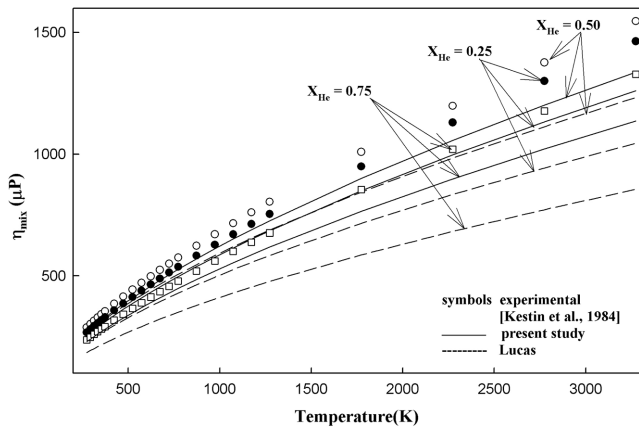


Fig. 5. Comparison of experimental and predicted mixture viscosities for noble gas mixture (He-Ne).

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 | |

^aKestin et al. [1984], ^bvan Heijningen [1968], ^cKestin et al. [1972d], ^dHolsenv and Strunk [1964], ^eSeager et al. [1963], ^fStrehlow [1953], ^gStrehlow [1959], ^hChapman and Cowling [1970], ⁱLide [1995], ^jPoling et al. [2000], ^kSaxena and Mason [1959], ^lFuller et al. [1966], ^mKalelkar and Kestin [1970], ⁿThornton [1960], ^oKestin et al. [1972b], ^pHumphreys and Mason [1970].

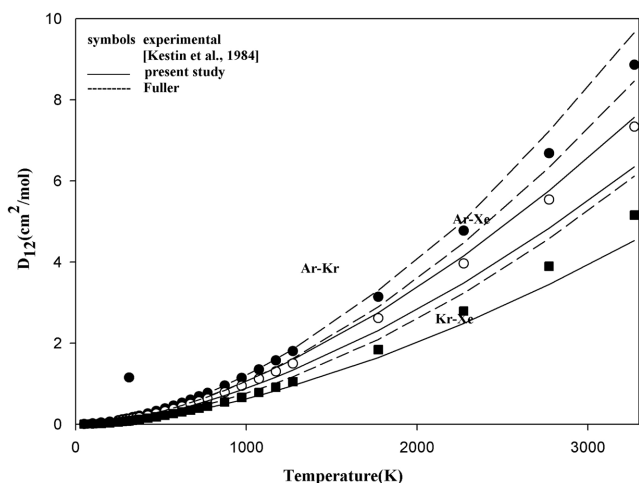


Fig. 6. Comparison of experimental and predicted binary diffusion coefficients for noble gas mixtures (Ar-Kr, Ar-Xe, Kr-Xe).

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

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NOMENCLATURE

- a : core radius [Δ]
- a^* : reduced core radius, $2a/(\sigma - 2a)$
- B : second virial coefficient [$\text{cm}^3 \text{mol}^{-1}$]
- D : diffusion coefficient [$\text{cm}^2 \text{sec}^{-1}$]
- 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 [$\text{cm}^3 \text{mol}^{-1}$]
- %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 [$\text{cm}^3 \text{mol}^{-1}$]
- 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 [JK]
- 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

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