

An extension of the group contribution method for estimating thermodynamic and transport properties. Part IV. Noble gas mixtures with polyatomic gases

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Abstract—Earlier work on the group contribution method applied to Kihara potentials is extended to noble-polyatomic gas mixtures for the calculation of second virial cross coefficients, mixture viscosities and binary diffusion coefficients of dilute gas state using a single set of gas group parameters. Previously estimated parameter values for pure gas groups by our work [Oh, 2005; Oh and Sim, 2002; Oh and Park, 2005] were used. Assuming that noble-polyatomic gas mixtures examined are chemically dissimilar, a group binary interaction coefficient, $k_{ij,gc}$, was assigned to each interaction between noble-polyatomic gas groups, and 25 group binary interaction parameter values ($k_{He-H_2,gc}$, $k_{He-N_2,gc}$, $k_{He-CO,gc}$, $k_{He-CO_2,gc}$, $k_{He-O_2,gc}$, $k_{He-NO,gc}$, $k_{He-N_2O,gc}$; $k_{Ne-H_2,gc}$, $k_{Ne-N_2,gc}$, $k_{Ne-CO,gc}$, $k_{Ne-CO_2,gc}$, $k_{Ne-O_2,gc}$; $k_{Ar-H_2,gc}$, $k_{Ar-N_2,gc}$, $k_{Ar-CO,gc}$, $k_{Ar-CO_2,gc}$, $k_{Kr-O_2,gc}$; $k_{Kr-H_2,gc}$, $k_{Kr-N_2,gc}$, $k_{Kr-CO,gc}$, $k_{Ar-CO_2,gc}$; $k_{Xe-H_2,gc}$, $k_{Xe-N_2,gc}$, $k_{Xe-CO,gc}$, $k_{Xe-CO_2,gc}$) were determined by fitting second virial cross coefficients data. Application of the model shows that second virial cross coefficient data are represented with good results comparable to values predicted by means of the corresponding states correlation. Reliability of the model for mixture viscosity predictions is proved by comparison with the Lucas method. And prediction results of binary diffusion coefficients are in excellent agreement with literature data and compared well with values obtained by means of the Fuller method. Improvements of the group contribution model are observed when group binary interaction coefficients are adopted for mixture property predictions.

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

INTRODUCTION

A group contribution concept was first applied to the spherical core potential of Kihara [1978] 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-nC₈ 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 Cowling, 1970] can be proved.

Previous works [Oh, 1989; Oh and Campbell, 1997] proved the feasibility of applying the group contribution method to simultaneous representation of second virial coefficients, viscosity and diffusion coefficients 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 step for parameter estimations. With addition of group binary interaction coefficients, the model was extended to chemically dissimi-

lar mixtures of N₂- and CO₂-hydrocarbons, with success.

A set of functional group parameters for pure alkanes was re-evaluated by Oh and Sim [2002] with revised recommendations of 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 applied to the Kihara potential was repeated for calculating second virial coefficients, dilute gas viscosities and binary diffusion coefficients of normal and branched alkanes, alkenes, N₂ and CO₂. And applications were extended to industrially important pure linear gases (CO, O₂ and H₂), as well as to its mixtures with favorable results. Later, extensions of the group contribution method were made to polyatomic gases (F₂, Cl₂, CS₂, H₂S, NO, and N₂O) by Oh and Park [2005] and to noble gases (He, Ne, Ar, Kr and Xe) by Oh [2005] with good results, in which simple fluids of this type were also assumed to consist of a single functional group, namely gas group.

In this work, the group contribution method using the spherical core Kihara potentials is extended to a variety of mixtures of noble gases and polyatomic gases. According to the characteristics of the group contribution concepts between molecules, mixture properties (second virial cross coefficients, dilute gas mixture viscosities and diffusion coefficients) are calculated by using parameter values estimated in advance by our previous studies.

The scope of this work is to show that the feasibility of the group contribution model using parameters determined from information of pure components is proved with success for mixture property calculations, and that improvement of the model is observed by taking group binary interaction coefficients into account for the calculations

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of the chemically dissimilar mixture properties.

RESULTS AND DISCUSSION

An advantage of the group contribution concepts is that mixture properties can be calculated by using a single set of gas group parameters obtained from information of pure compounds without additional parameters. Gas group parameters determined by reducing second virial coefficient and viscosity data for pure gases together were used to calculate second virial cross coefficients and mixture viscosities, and to calculate binary diffusion coefficients, not used in data regression steps, were calculated in an analogous way as well.

As a part of systematic program of our researches, application of the group contribution method was extended to noble gas (He, Ne, Ar, Kr and Xe) mixtures with polyatomic gas (H_2 , N_2 , CO , CO_2 , O_2 , NO and N_2O), and of which pure gas group parameters (α_{ij} , β_{ij} and a_{ij}^*) were evaluated in advance by our previous work. Parameter values for noble gas groups (He, Ne, Ar, Kr and Xe) determined by Oh [2005], for polyatomic gas groups (H_2 , N_2 , CO , CO_2 and O_2) by Oh and Sim [2002], and for polyatomic gas groups (NO and N_2O) by Oh and Park [2005] were used to calculate mixture properties in this work. It is mentioned that all pure gases examined here were assumed to consist of a single functional group, called a gas group.

Oh and Campbell [1997] proved that calculations of thermody-

Table 1. Group binary interaction coefficients $k_{j,gc}$ between unlike functional groups

| | He | Ne | Ar | Kr | Xe |
|--------|---------|---------|---------|---------|---------|
| H_2 | 0.17813 | 0.14096 | 0.11620 | 0.14316 | 0.25656 |
| N_2 | 0.03451 | 0.10828 | 0.01229 | 0.65009 | 0.08697 |
| CO | 0.04478 | 0.15016 | 0.08843 | 0.02599 | 0.42911 |
| CO_2 | 0.22615 | 0.21968 | 0.09848 | 0.10385 | 0.11181 |
| O_2 | 0.00089 | 0.08596 | 0.05086 | - | - |
| NO | 0.18373 | - | - | - | - |
| N_2O | 0.42667 | - | - | - | - |

namic and transport properties based on the group contribution concepts have been improved by using the group binary interaction coefficient $k_{j,gc}$ for the case of chemically dissimilar mixtures. Assuming that all noble gas mixtures with polyatomic gas studied here are chemically dissimilar, structural effects can be compensated by adding an additional parameter (a group binary interaction coefficient, $k_{j,gc}$) assigned to each interaction between noble-polyatomic gas groups. Values of $k_{j,gc}$ were determined by fitting second virial cross coefficients B_{12} data of noble-polyatomic gas mixtures to within the observed uncertainties.

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 supplied to data re-

Table 2. Deviations between experimental and predicted second virial cross coefficients for noble gas - polyatomic gas mixtures

| Mixtures | Number of points | Average RMSD in B (cm ³ mol ⁻¹) | | | | Data source |
|-------------------|---------------------|--|--------------------------------|----------------------|----------------------|-------------|
| | | Present study | | Tsonopoulos | | |
| | | (K _{<i>ij,gc</i>} =0) | (K _{<i>ij,gc</i>} ≠0) | (K ₁₂ ≠0) | (K ₁₂ =0) | |
| Helium | | | | | | |
| - hydrogen | 18 | 8.7 | 4.5 | 6.9 | 6.9 | [a; #1-7] |
| | 9 | 8.4 | 4.1 | 6.5 | 6.5 | [b] |
| - nitrogen | 27 | 3.6 | 3.4 | 5.2 | 5.2 | [a; #1-10] |
| | 6 | 2.3 | 2.0 | 5.1 | 5.2 | [b] |
| - carbon monoxide | 6 | 4.3 | 4.2 | 5.0 | 5.1 | [b] |
| - carbon dioxide | 15 | 6.8 | 5.1 | 2.9 | 3.0 | [a; #1-7] |
| | 6 | 6.7 | 5.8 | 4.2 | 4.4 | [b] |
| - oxygen | 1 | 2.7 | 2.0 | 7.1 | 1.8 | [a; #2] |
| | 6 | 1.6 | 1.4 | 6.0 | 6.0 | [b] |
| - nitric oxide | 5 | 4.1 | 2.1 | 4.8 | 4.8 | [b] |
| - nitrous oxide | 4 | 5.8 | 1.7 | 2.9 | 3.1 | [b] |
| Avg. | 103 | 5.5 | 3.7 | 5.2 | 5.2 | |
| Neon | | | | | | |
| - hydrogen | 14 | 3.8 | 1.3 | 1.5 | 1.5 | [a; #1-2] |
| | 5 | 2.3 | 0.6 | 0.7 | 0.7 | [b] |
| - nitrogen | 10 | 6.8 | 2.4 | 6.6 | 5.8 | [a; #1-3] |
| | 8 | 5.6 | 1.6 | 5.5 | 4.6 | [b] |
| - carbon monoxide | 5 | 5.7 | 0.9 | 5.4 | 4.4 | [b] |
| - carbon dioxide | 6 | 13.8 | 4.5 | 11.0 | 9.9 | [b] |
| - oxygen | 1 | 13.6 | 4.4 | 13.2 | 11.9 | [a; #1] |
| | 9 | 5.0 | 1.8 | 4.9 | 4.2 | [b] |
| Avg. | 57 | 6.1 | 1.9 | 5.0 | 4.4 | |

Table 2. Continued

| Mixtures | Number of points | Average RMSD in B (cm ³ mol ⁻¹) | | | | Data source |
|-------------------|------------------|--|-------------------------|----------------------|----------------------|---------------------|
| | | Present study | | Tsonopoulos | | |
| | | (K _{ij,gc} =0) | (K _{ij,gc} ≠0) | (K ₁₂ ≠0) | (K ₁₂ =0) | |
| Argon | | | | | | |
| - hydrogen | 22 | 6.6 | 3.4 | 4.1 | 4.2 | [a; #1-4] |
| | 6 | 10.0 | 1.9 | 8.2 | 8.3 | [b] |
| - nitrogen | 32 | 4.2 | 4.2 | 3.4 | 3.4 | [a; #1-5] |
| | 3 | 1.6 | 2.3 | 0.5 | 0.6 | [c] |
| | 9 | 3.5 | 3.2 | 2.6 | 2.5 | [b] |
| - carbon monoxide | 12 | 2.5 | 2.6 | 7.4 | 2.4 | [a; #1-2] |
| | 6 | 2.2 | 2.0 | 1.9 | 1.8 | [b] |
| - carbon dioxide | 22 | 10.1 | 5.4 | 8.2 | 7.9 | [a; #1, 3, 4, 6, 7] |
| | 7 | 9.0 | 7.0 | 6.3 | 6.0 | [d] |
| | 6 | 12.7 | 1.5 | 10.2 | 9.9 | [b] |
| - oxygen | 1 | 1.5 | 3.2 | 11.3 | 11.3 | [a; #1] |
| | 6 | 8.5 | 3.7 | 7.1 | 7.1 | [b] |
| Avg. | 132 | 6.3 | 3.8 | 5.4 | 4.9 | |
| Krypton | | | | | | |
| - hydrogen | 8 | 7.2 | 2.5 | 4.6 | 4.8 | [b] |
| - nitrogen | 6 | 89.0 | 14.2 | 86.2 | 86.2 | [b] |
| - carbon monoxide | 5 | 5.8 | 1.1 | 3.9 | 3.9 | [b] |
| - carbon dioxide | 5 | 21.0 | 2.2 | 15.4 | 15.4 | [b] |
| Avg. | 24 | 30.2 | 5.1 | 26.6 | 26.6 | |
| Xenon | | | | | | |
| - hydrogen | 16 | 78.2 | 30.5 | 28.0 | 28.0 | [a; #1-3] |
| | 9 | 34.9 | 4.3 | 2.8 | 2.3 | [b] |
| - nitrogen | 4 | 16.8 | 0.2 | 70.2 | 64.8 | [b] |
| - carbon monoxide | 2 | 14.4 | 4.8 | 13.0 | 12.4 | [b] |
| - carbon dioxide | 5 | 116.3 | 3.2 | 98.1 | 28.7 | [b] |
| Avg. | 36 | 84.0 | 15.4 | 35.3 | 24.9 | |
| Overall | 400 | 13.7 | 4.1 | 7.9 | 7.4 | |

*Number of data points for second virial cross coefficient.

**Number of data points for mixture viscosity. #Reference number of data compiled.

^aDymond and Smith [1980]. ^bDymond et al. [2003]. ^cNhu and Deiters [1996]. ^dSchramm and Muller [1982].

gression for the determination of group binary interaction coefficients, and to all subsequent calculations and evaluations. 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. In all, 25 parameter values of group binary interaction coefficients ($k_{He-H_2,gc}$, $k_{He-N_2,gc}$, $k_{He-CO,gc}$, $k_{He-CO_2,gc}$, $k_{He-O_2,gc}$, $k_{He-NO,gc}$, $k_{He-N_2O,gc}$, $k_{Ne-H_2,gc}$, $k_{Ne-N_2,gc}$, $k_{Ne-CO,gc}$, $k_{Ne-CO_2,gc}$, $k_{Ne-O_2,gc}$, $k_{Ar-H_2,gc}$, $k_{Ar-N_2,gc}$, $k_{Ar-CO,gc}$, $k_{Ar-CO_2,gc}$, $k_{Kr-H_2,gc}$, $k_{Kr-N_2,gc}$, $k_{Kr-CO,gc}$, $k_{Kr-CO_2,gc}$, $k_{Xe-H_2,gc}$, $k_{Xe-N_2,gc}$, $k_{Xe-CO,gc}$, $k_{Xe-CO_2,gc}$) for noble-polyatomic gas mixtures available in the literature are presented in Table 1. As expected, all $k_{ij,gc}$ values estimated in this way turned out to be between zero and unity, indicating that parameter values for $k_{He-O_2,gc}$ and $k_{Ar-CO,gc}$ are too close to zero caused by the 95% confidence regions of these parameters break zero. Unrealistic-looking values for these two interactions may be due either to uncertainties in the data or to propagation of

the uncertainties in previously determined parameter values, as indicated by Oh [1989].

Resulting deviations between measured and calculated second virial coefficient data are given in Table 2, where RMSD (root mean square deviation) in cm³ mol⁻¹ for second virial coefficients and RMSD_r (root mean square deviation, relative) in % for transport properties (viscosities and diffusion coefficients), respectively, and were defined by Oh [2005].

In order to check out the improvement of the model by a usage of the group binary interaction coefficients, also included in this table is a column showing the result of assuming that $k_{ij,gc}$ is equal to zero. For a comparison to both methods, also included in Table 2 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 this type. Results of the Tsonopoulos method with the assumption that $k_{12}=0$ are also presented in Table 2. This table indicates

that based on the average RMSD in $\text{cm}^3 \text{mol}^{-1}$ for each type of mixture the present method is remarkably improved by taking group binary interaction coefficients into account for all types of noble-polyatomic gas mixtures, while the corresponding correlations do not show appreciable enhancements with k_{12} values obtained.

Compared to both methods with the use of interaction coefficients ($k_{ij,gc}$ or k_{12}) for the calculations of second virial cross coefficients, the proposed model is observed to compare very well with the corresponding correlation of Tsonopoulos: overall RMSD values of $4.1 \text{ cm}^3 \text{mol}^{-1}$ and $7.4 \text{ cm}^3 \text{mol}^{-1}$ were obtained by the present method and the Tsonopoulos method, respectively, for all 400 data points. And it is noted that the present study is less reliable than Tsonopoulos' correlations on mixtures of He-CO₂, Ar-N₂ and Xe-H₂. Here, it is believed that one point of B_{12} data for He-, Ne-, and Ar-O₂ mixtures compiled by Dymond and Smith [1980] might be unrealistic for the right comparison. Fig. 1 shows the comparison of observed and predicted second virial cross coefficients for noble-polyatomic gas

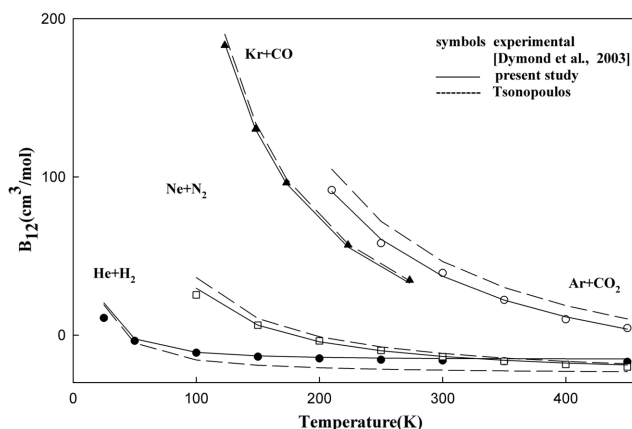


Fig. 1. Comparison of observed and predicted second virial cross coefficients for noble gas mixtures with polyatomic gas (He-H₂, Ne-N₂, Ar-CO₂ and Kr-CO).

Table 3. Deviations between experimental and predicted mixture viscosities for noble gas - polyatomic gas mixtures

| Mixtures | Number of points | Average RMSD _r in η (%) | | | Data source |
|-------------------|---------------------|---|-------------------------|-----------------|----------------|
| | | Present study | | Lucas Method | |
| | | (K _{ij,gc} =0) | (K _{ij,gc} ≠0) | | |
| Helium | | | | | |
| - hydrogen | 18 | 1.7 | 1.5 | 25.5 | [a] |
| - nitrogen | 14 | 1.2 | 1.3 | 8.7 | [b] |
| | 32 | 1.2 | 0.8 | 12.6 | [c] |
| - carbon monoxide | 10 | 1.6 | 0.7 | 8.5 | [d] |
| - carbon dioxide | 56 | 1.8 | 1.7 | 11.8 | [e] |
| - oxygen | 13 | 2.2 | 2.2 | 15.3 | [a] |
| Avg. | 143 | 1.6 | 1.2 | 13.5 | |
| Neon | | | | | |
| - nitrogen | 32 | 4.3 | 3.7 | 21.0 | [f] |
| - carbon monoxide | 10 | 5.7 | 4.5 | 7.9 | [d] |
| - carbon dioxide | 36 | 6.8 | 2.9 | 1.2 | [e] |
| Avg. | 78 | 5.6 | 3.4 | 10.2 | |
| Argon | | | | | |
| - nitrogen | 24 | 4.7 | 4.4 | 1.4 | [g] |
| - carbon monoxide | 10 | 5.4 | 5.5 | 7.9 | [d] |
| - carbon dioxide | 12 | 12.5 | 12.5 | 12.7 | [b] |
| | 28 | 6.7 | 5.6 | 2.1 | [e] |
| - nitrous oxide | 10 | 3.8 | 2.4 | 3.4 | [h] |
| Avg. | 84 | 6.3 | 5.9 | 4.3 | |
| Krypton | | | | | |
| - nitrogen | 24 | 5.3 | 3.0 | 1.2 | [g] |
| - carbon monoxide | 24 | 1.8 | 1.5 | 2.3 | [i] |
| - carbon dioxide | 6 | 7.5 | 5.6 | 3.2 | [a] |
| Avg. | 54 | 4.0 | 2.6 | 1.9 | |
| Xenon | | | | | |
| - carbon monoxide | 24 | 3.9 | 1.6 | 35.6 | [i] |
| Avg. | 24 | 3.9 | 1.6 | 35.6 | |
| Overall | 383 | 4.0 | 3.0 | 11.1 | |

^aKestin and Yata [1968]. ^bKestin et al. [1966]. ^cKestin et al. [1972a]. ^dHaghighi et al. [2002]. ^eKestin and Ro [1974].

^fKestin et al. [1972b]. ^gHelleman et al. [1972]. ^hKestin and Ro [1982]. ⁱKestin et al. [1984].

mixtures (He-H_2 , Ne-N_2 , Ar-CO_2 , and Kr-CO), in which the present study is believed to yield better representations than the Tsionopoulos method.

Then, mixture viscosity data measured by several other researchers referenced in Table 3 were next predicted by using gas 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 three types of mixtures (Ar-CO , Ar-CO_2 and Kr-CO_2) by the proposed model and for most types of mixtures by the Lucas method [Lucas, 1980]. Prediction results of mixture viscosities for noble gas mixtures with polyatomic gas are presented in Table 3, in which RMSD_r (root mean square deviation, relative) in % for mixture viscosities, and were defined by Oh [2005].

Based on the average % RMSD_r values for each type of mixture, the present study provides better agreement between measured and predicted mixture viscosities than the Lucas method for all kinds of noble gas mixtures: as for total 383 data points available in the literature, overall 3.0% RMSD_r (4.0% RMSD_r with the assumption of $k_{ij,gc}=0$) by the present model and 11.1% RMSD_r by the Lucas method. It is also noted that with the use of group binary interaction coefficients the reliability of the group contribution method was enhanced markedly. However, as shown in Table 3, the Lucas method proves to be more reliable than the proposed model for the other five types of mixtures (Ne-CO_2 , Ar-N_2 , Ar-CO_2 , Kr-N_2 , and Kr-CO_2).

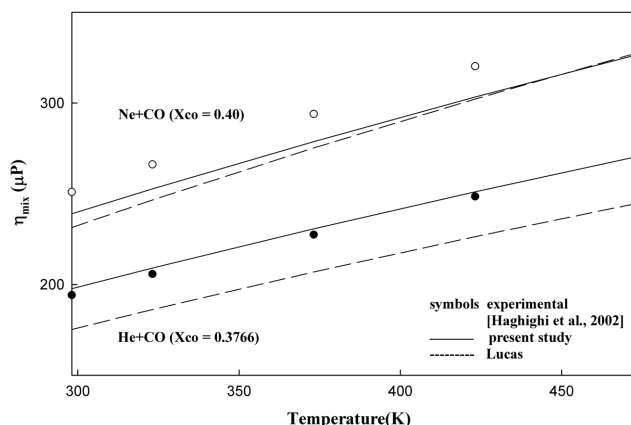


Fig. 2. Comparison of observed and predicted mixture viscosities for noble gas mixtures with polyatomic gas (He-CO and Ne-CO).

Fig. 2 shows a comparison of observed and predicted mixture viscosities for two different types of CO mixtures with He and Ne at a given mole fraction of CO. Also included for comparison in Fig. 2 are results from the Lucas method.

As mentioned by Oh and Campbell [1997], using the Chapman and Enskog theory, the proposed group contribution concept based on the Kihara intermolecular potential function can be practically extended to predict other transport properties of dilute gas state as

Table 4. Deviations between experimental and predicted binary diffusion coefficients

| Mixtures | Number of points | Average RMSD_r in D (%) | | | Data source |
|-------------------|------------------|----------------------------------|-----------------------|---------------|-------------|
| | | Present study | | Fuller et al. | |
| | | ($K_{ij,gc}=0$) | ($K_{ij,gc}\neq 0$) | | |
| Helium | | | | | |
| - hydrogen | 2 | 1.8 | 0.2 | 14.7 | [b] |
| | 7 | 5.8 | 4.6 | 14.1 | [c] |
| - nitrogen | 12 | 4.7 | 4.5 | 14.6 | [d] |
| | 4 | 8.0 | 7.6 | 16.3 | [e] |
| | 7 | 3.0 | 3.2 | 13.1 | [f] |
| | 7 | 3.3 | 2.9 | 17.5 | [c] |
| | 8 | 3.2 | 2.8 | 13.4 | [h] |
| - carbon monoxide | 7 | 1.6 | 2.2 | 15.3 | [i] |
| | 10 | 1.3 | 0.8 | 17.2 | [k] |
| | 7 | 3.7 | 3.1 | 18.3 | [c] |
| - carbon dioxide | 3 | 1.1 | 5.4 | 11.7 | [k] |
| | 8 | 1.8 | 5.6 | 9.7 | [f] |
| | 7 | 5.0 | 0.3 | 8.0 | [i] |
| | 2 | 1.7 | 2.3 | 12.5 | [g] |
| | 5 | 10.3 | 14.9 | 14.9 | [c] |
| | 11 | 1.6 | 5.5 | 10.2 | [d] |
| | 11 | 5.4 | 9.7 | 8.1 | [l] |
| - oxygen | 6 | 3.4 | 3.6 | 14.2 | |
| | 2 | 2.4 | 2.1 | 12.5 | [b] |
| | 2 | 1.9 | 1.6 | 13.9 | [a] |
| | 7 | 1.5 | 1.5 | 10.3 | [d] |
| Avg. | 135 | 3.5 | 4.3 | 13.2 | |

Table 4. Continued

| Mixtures | Number of points | Average RMSD _r in D (%) | | | Data source |
|-------------------|---------------------|------------------------------------|-------------------------|---------------|----------------|
| | | Present study | | Fuller et al. | |
| | | (K _{ij,gc} =0) | (K _{ij,gc} ≠0) | | |
| Neon | | | | | |
| - hydrogen | 7 | 10.7 | 8.6 | 10.9 | [c] |
| - nitrogen | 6 | 7.1 | 5.4 | 7.4 | [m] |
| - carbon monoxide | 10 | 8.5 | 6.5 | 13.9 | [j] |
| - carbon dioxide | 6 | 11.7 | 6.4 | 8.4 | [c] |
| | 10 | 28.6 | 24.2 | 26.6 | [n] |
| Avg. | 39 | 14.3 | 11.2 | 14.7 | |
| Argon | | | | | |
| - hydrogen | 6 | 15.1 | 12.6 | 32.2 | [c] |
| | 2 | 19.2 | 16.8 | 8.7 | [g] |
| | 3 | 18.8 | 16.9 | 11.2 | [d] |
| - nitrogen | 6 | 6.3 | 5.2 | 4.8 | [c] |
| | 6 | 7.4 | 6.3 | 4.0 | [o] |
| | 6 | 6.7 | 5.7 | 4.7 | [p] |
| - carbon monoxide | 6 | 6.7 | 6.1 | 4.2 | [c] |
| | 10 | 10.2 | 10.4 | 0.9 | [j] |
| - carbon dioxide | 2 | 10.3 | 6.9 | 12.8 | [k] |
| | 6 | 17.0 | 13.7 | 6.9 | [c] |
| - oxygen | 6 | 4.9 | 2.8 | 9.5 | [c] |
| - nitrous oxide | 5 | 6.1 | 3.5 | 14.4 | [q] |
| Avg. | 64 | 9.4 | 8.3 | 8.7 | |
| Krypton | | | | | |
| - hydrogen | 7 | 11.4 | 8.2 | 1.8 | [c] |
| - nitrogen | 6 | 18.7 | 4.4 | 9.7 | [c] |
| | 6 | 13.9 | 6.7 | 7.0 | [o] |
| | 6 | 16.5 | 16.5 | 8.7 | [p] |
| - carbon monoxide | 24 | 6.6 | 6.0 | 8.4 | [n] |
| | 6 | 5.4 | 4.7 | 8.6 | [c] |
| - carbon dioxide | 3 | 10.8 | 6.7 | 17.9 | [b] |
| Avg. | 58 | 10.3 | 7.2 | 8.2 | |
| Xenon | | | | | |
| - hydrogen | 6 | 9.6 | 3.4 | 9.0 | [c] |
| - nitrogen | 6 | 4.2 | 2.7 | 20.4 | [c] |
| - carbon monoxide | 24 | 5.5 | 5.2 | 14.3 | [n] |
| Avg. | 36 | 6.0 | 4.5 | 14.4 | |
| Overall | 332 | 7.4 | 6.4 | 11.8 | |

^aGiddings and Seager [1962].^bKestin and Yata [1968].^cLide [1995].^dFuller et al. [1966].^eWalker and Westenberg [1958].^fSeager et al. [1963].^gPoling et al. [2000].^hKestin et al. [1972a].ⁱGavril et al. [2004].^jHaghighi [2002].^kHolsen and Strunk [1964].^lSaxena and Mason [1959].^mKestin et al. [1972b].ⁿTrengove et al. [1984].^oHellemans et al. [1972].^pMason and Marrero [1970].^qKestin and Ro [1982].

well. Here, the feasibility of applying the model to diffusivities, not used in parameter estimations, was examined in this stage. With a set of gas group parameters evaluated in advance, binary diffusion coefficients of noble gas mixtures with polyatomic gas observed by a number of researchers were predicted. Their resulting deviations between experimental and predicted binary diffusion coefficients are presented in Table 4, in which RMSD_r (root mean square

deviation, relative) is in % for binary diffusion coefficients, and was expressed by Oh [2005].

Based on the average %RMSD_r values for each type of mixtures, except for the cases of Ar mixtures, the present study provides better agreement between measured and predicted mixture viscosities than the Fuller method for all kinds of noble gas mixtures: as for total 332 data points available in the literature, overall

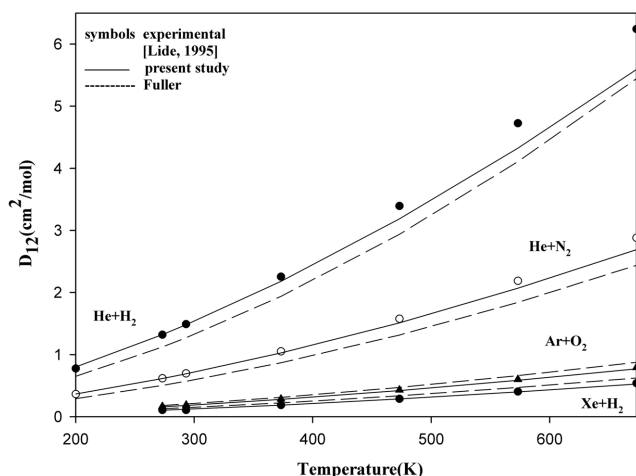


Fig. 3. Comparison of observed and predicted binary diffusion coefficients for noble gas mixtures with polyatomic gas (He-H_2 , He-N_2 , Ar-O_2 and Xe-H_2).

6.4%RMSDr (7.4%RMSDr with the assumption of $k_{ji,gc}=0$) by the present model and 11.8%RMSDr by the Fuller method. As shown in Table 4, when assuming that $k_{ji,gc}$ is not equal to zero, the accuracy of the group contribution method was not improved appreciably. That reason may be that the parameter value of the group binary interaction coefficients $k_{ji,gc}$ was estimated from information on second virial cross coefficients, not from binary diffusion coefficients. Therefore, as shown in Table 3, the Fuller method proves to be more reliable than the proposed model for Ar-H_2 , Ar-N_2 , Ar-CO_2 , and Kr-H_2 mixtures. However, it is believed that binary diffusion coefficients predictions by both methods are fitted to within experimental uncertainties of approximately 6 to 7%. Comparison of the observed and predicted binary diffusion coefficients for noble gas mixtures with polyatomic gas (He-H_2 , He-N_2 , Ar-O_2 and Xe-H_2) is presented in Fig. 3.

CONCLUSIONS

The group contribution method has been extended to noble gas mixtures with polyatomic gas for the estimation of second virial cross coefficients, mixture viscosities and binary diffusion coefficients by using a single set of parameters, which values were determined for noble gas groups (He , Ne , Ar , Kr and Xe) by Oh [2005], for polyatomic gas groups (H_2 , N_2 , CO , CO_2 and O_2) by Oh and Sim [2002], and for polyatomic gas groups (NO and N_2O) by Oh and Park [2005]. With the assumption that noble-polyatomic gas mixtures studied here are chemically dissimilar, a group binary interaction coefficient was assigned to each interaction between noble-polyatomic gas groups, and 25 new group binary interaction parameters ($k_{\text{He-H}_2,gc}$, $k_{\text{He-N}_2,gc}$, $k_{\text{He-CO},gc}$, $k_{\text{He-CO}_2,gc}$, $k_{\text{He-O}_2,gc}$, $k_{\text{He-NO},gc}$, $k_{\text{He-N}_2\text{O},gc}$; $k_{\text{Ne-H}_2,gc}$, $k_{\text{Ne-N}_2,gc}$, $k_{\text{Ne-CO},gc}$, $k_{\text{Ne-CO}_2,gc}$, $k_{\text{Ne-O}_2,gc}$; $k_{\text{Ar-H}_2,gc}$, $k_{\text{Ar-N}_2,gc}$; $k_{\text{Ar-CO},gc}$, $k_{\text{Ar-CO}_2,gc}$; $k_{\text{Kr-O}_2,gc}$; $k_{\text{Kr-H}_2,gc}$, $k_{\text{Kr-N}_2,gc}$, $k_{\text{Kr-CO},gc}$, $k_{\text{Ar-CO}_2,gc}$; $k_{\text{Xe-H}_2,gc}$, $k_{\text{Xe-N}_2,gc}$, $k_{\text{Xe-CO},gc}$, $k_{\text{Xe-CO}_2,gc}$) are estimated by reducing second virial cross coefficient data available in the literature.

Application of the model shows that second virial cross 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 mixture viscosity predictions is also proved by comparison with the Lucas method as well. The characteristic nature of the group contribution concept makes possible diffusivity predictions as well, not supplied to the parameter estimation steps. Prediction results of binary diffusion coefficients are in excellent agreement with the observed data and compare well with results obtained by the Fuller method. Extension of the model to mixtures of this type shows that by taking group binary interaction coefficients into account, improvement of the model was found to provide better results, for all mixture properties (second virial cross coefficient, mixture properties and binary diffusion coefficients), than those obtained by the assumption that $k_{ji,gc}$ is equal to zero.

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

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