

## An Extension of the Group Contribution Method for Estimating Thermodynamic and Transport Properties Part II. Polyatomic Gases (F<sub>2</sub>, Cl<sub>2</sub>, CS<sub>2</sub>, H<sub>2</sub>S, NO and N<sub>2</sub>O)

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**Abstract**—Earlier work on the group contribution method applied to the Kihara potential is extended to polyatomic gases for the calculation of second virial coefficients, viscosities and diffusivities of dilute gases with a single set of gas group parameters. Functional group parameters are evaluated from the simultaneous regression of second virial coefficient and viscosity data of pure gases. Parameters for gas groups (F<sub>2</sub>, Cl<sub>2</sub>, CS<sub>2</sub>, H<sub>2</sub>S, NO, and N<sub>2</sub>O) are found to provide good predictions of second virial cross coefficients, mixture viscosities and binary diffusion coefficients of gas-gas mixtures. Application of the model shows that second virial coefficient data can be represented with good results comparable to the values by means of the corresponding states model. The reliability of the present model in viscosity predictions is proved by comparison with the Lucas method. Predictions of binary diffusion coefficients are in excellent agreement with experimental data and compare well with values obtained by means of the Fuller method.

Key words: Theory, Group Contribution, Kihara Potential, 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 workers [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 methods 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 the prediction of thermodynamic properties and dilute gas transport properties. Here, a single set of parameters, appearing in an intermolecular potential function, is assigned to interactions 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 ap-

plicable with only information of both functional groups and van der Waals volume in molecules. 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<sub>2</sub> and CH<sub>3</sub> groups in normal alkanes were determined from second virial coefficient data for pure C<sub>2</sub>-n-C<sub>8</sub> alkanes, and parameters for CH<sub>4</sub> groups were determined from second virial coefficient for pure methane. Then these parameters were 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, it showed the possibility of predicting dilute gas transport properties (viscosities and diffusion coefficients) as well using Chapman and Enskog theory [Chapman and Cowing, 1939].

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. 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 nitro-

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gen- and carbon dioxide-hydrocarbons, with success.

In the previous work [Oh and Sim, 2002], a set of functional group parameters for pure alkanes were re-evaluated 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 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 (carbon monoxide, oxygen and hydrogen), as well as to mixtures of these gases with reliable calculations and predictions of second virial cross coefficients and mixture viscosities.

In this paper, extension of the group contribution method is made to polyatomic gases (fluorine, chlorine, carbon disulfide, hydrogen sulfide, nitric oxide and nitrous oxide). Applicability of the method based on the spherical core potential of Kihara [1978] is tested by assuming that all compounds studied here were to consist of a single functional group. It is considered for simple fluids examined here that use of the group contribution concept is not reasonable. Simultaneous regression of second virial coefficient and viscosity data for pure gases was done for the determination of functional group parameters. The scope of this work is to examine the possibility of applying this characteristic feature of the group contribution method to the simultaneous representation of second virial coefficients, dilute gas viscosities and diffusion coefficients with a single set of group parameters. Values of the collision integrals for viscosity and diffusion ( $\Omega_V$  and  $\Omega_D$ ) for Kihara potentials, required for the Chapman and Enskog theory, were tabulated in Oh [1989].

## GROUP CONTRIBUTION MODEL

The expression for group contribution rules for functional group parameters appearing in Kihara potential function was given in the previous paper [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  $\epsilon_{12}$  and  $\sigma_{12}$  are

$$\epsilon_{12}\sigma_{12}^3 = \sum \sum N_{i1}N_{j2}\epsilon_{ij}\sigma_{ij}^3 \quad (1)$$

and

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

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,  $\epsilon_{12}$  and  $\sigma_{12}$  are the well depth and collision diameter for interactions between molecules 1 and 2, and  $\epsilon_{ij}$  and  $\sigma_{ij}$  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:

$$a_{11}^* = \sum N_{ii}a_{ii}^* \quad (3)$$

and

$$a_{22}^* = \sum N_{j2}a_{jj}^* \quad (4)$$

followed by

$$a_{12} = \frac{a_{11} + a_{22}}{2} \quad (5)$$

where

$$a_{ii} = \frac{\sigma_{ii}a_{ii}^*}{2(1+a_{ii}^*)} \quad (6)$$

with an analogous expression for  $a_{22}$ .

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

$$\epsilon_{ii} = \alpha_{ii} + \frac{\beta_{ii}}{T} \quad (7)$$

$$\sigma_{ii} = \xi V_{vdw,ii}^{1/3} \quad (8)$$

where  $\alpha_{ii}$  and  $\beta_{ii}$  are group parameters,  $\xi$  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 polyatomic gases. The reciprocal temperature term in Eq. (7) 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.

$$\epsilon_{ij} = (1 - k_{ij,gc})\sqrt{\epsilon_{ii}\epsilon_{jj}} \quad (9)$$

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

, 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  $\xi$ , application of the model requires parameter values ( $\alpha_{ii}$ ,  $\beta_{ii}$ , and  $a_{ii}^*$ ) for each functional group  $i$  within molecules 1 and 2. In order to extend the model to gas-gas and hydrocarbon-gas mixtures examined here, values of group binary interaction coefficient  $k_{ij,gc}$  for each interactions between intermolecular groups  $i$  and  $j$  might be required for better predictions.

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, the group contribution method was extended to polyatomic gases ( $F_2$ ,  $Cl_2$ ,  $CS_2$ ,  $H_2S$ ,  $NO$ , and  $N_2O$ ). Functional group parameters  $\alpha_{ii}$ ,  $\beta_{ii}$  and  $a_{ii}^*$  were

**Table 1. Properties of the functional groups examined in this study (universal van der Waals volume constant=1.3692<sup>a</sup>)**

Group	$V_{vdw, ii}^b$	$a_{ii}^*$	$\alpha_{ii}$	$\beta_{ii}$
F <sub>2</sub>	14.2	0.2199	147.48	-
Cl <sub>2</sub>	24.1	0.4716	555.85	-
CS <sub>2</sub>	31.2	0.3194	713.21	-
H <sub>2</sub> S	18.0	0.9478	657.13	-
NO	13.9	0.1534	160.49	2089.2
N <sub>2</sub> O	18.9	0.0529	178.18	2794.5

<sup>a</sup>taken from Oh and Campbell [1997].<sup>b</sup>taken from Bondi [1964].

evaluated by regressing second virial coefficient and viscosity data of pure gases together, in which all gases studied here were assumed to consist of a single functional group. As shown in Eq. (8), values of van der Waals volume for gases required were taken from Bondi [1964]. The universal van der Waals volume constant  $\xi$  evaluated in the previous paper [Oh and Sim, 2002] was used in the data regressions for the determination of function group parameters for pure gases, and in all subsequent calculations and evaluations.

Second virial coefficient data for pure gases were taken from several references: Dymond and Smith [1980] for F<sub>2</sub>, Cl<sub>2</sub>, CS<sub>2</sub>, and H<sub>2</sub>S; Boushehri et al. [1987] for NO and N<sub>2</sub>O. And pure viscosity data required for the parameter estimation were obtained from several references: Stephan and Lucas [1979] for F<sub>2</sub>; Trautz and Ruf [1939] for Cl<sub>2</sub>; Titani [1933] for CS<sub>2</sub>; Schuil [1939] for H<sub>2</sub>S; Boushehri et al. [1987] for NO and N<sub>2</sub>O.

Gas group parameter values ( $a_{ii}^*$ ,  $\alpha_{ii}$  and  $\beta_{ii}$ ) for pure gases (F<sub>2</sub>, Cl<sub>2</sub>, CS<sub>2</sub>, H<sub>2</sub>S, NO and N<sub>2</sub>O) examined are shown in Table 1 and the sources of data used to obtain them are indicated in Table 2. The potential well depth for gas groups (F<sub>2</sub>, Cl<sub>2</sub>, CS<sub>2</sub>, and H<sub>2</sub>S) were regarded to be independent of temperature. Regression results proved it, as expected for essentially symmetric molecules. However, the temperature dependence of the potential well depth for other gases (NO and N<sub>2</sub>O) turned out to be considered to account for non-sphericity of the molecule, as proved by regression results. Values of the reduced core radius for all compound examined here are between 0 and 1, proving that by using Kihara spherical core potential [Kihara, 1978] the application of the present model to these polyatomic gases was made well.

As shown in Table 2, resulting deviations between experimental and calculated data from data regression are presented by the RMSD (root mean square deviation) values in cm<sup>3</sup> mol<sup>-1</sup> for second virial coefficients and by the %RMSDr (percent relative root mean square deviation, relative) values for viscosities. Also included in Table 2 are the references for second virial coefficients and viscosity data for pure gases. A comparison was made with the corresponding correlation [Tsonopoulos, 1974] on the calculation of second virial coefficients, and with the Lucas method [Lucas, 1980] on the calculation of viscosities.

Overall average RMSD values of second virial coefficients for six pure gases examined are 2.1 cm<sup>3</sup> mol<sup>-1</sup> and 8.8 cm<sup>3</sup> mol<sup>-1</sup> for the proposed method and the Tsonopoulos correlation, respectively, indicating that the proposed model is in excellent agreement with the experimental data and compares very well with the Tsonopoulos correlation. As for the second virial coefficient calculations for

**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 <sup>3</sup> mol <sup>-1</sup> )		Data source	Number of points*	Average RMSDr in $\eta$ (%)		Data source
		Present study	Tsonopoulos			Present study	Lucas	
<i>Regression results:</i>								
Flourine	45	0.7	3.0	[a]	28	0.6	7.8	[c]
Chlorine	13	2.9	6.0	[a]	6	1.7	8.1	[d]
Carbon disulfide	9	2.4	46.9	[a]	6	2.9	3.6	[e]
Hyrogen sulfide	6	1.5	15.1	[a]	3	4.2	15.3	[f]
Nitric oxide	27	3.1	9.0	[b]	27	2.2	5.5	[b]
Nitrous oxide	24	3.1	5.0	[b]	24	0.6	4.2	[b]
Overall	124	2.1	8.8	94	1.4	6.2		
<i>Prediction results:</i>								
Carbon disulfide	-	-	4	3.9	3.4	[f]		
Hyrogen sulfide	8	2.8	6.7	[g]	-	-		
Nitric oxide	32	16.2	18.7	[a, h]	47	5.8	6.2	[f, i, j, k]
Nitrous oxide	10	9.8	4.0	[h]	77	3.1	3.6	[i, j, l, m-t]

\*Number of data points for second virial coefficient.

<sup>a</sup>Dymond and Smith [1980].<sup>b</sup>Boushehri et al. [1987].<sup>c</sup>Stephan and Lucas [1979].<sup>d</sup>Trautz and Ruf [1934].<sup>e</sup>Titani [1933].<sup>f</sup>Schuil [1939].<sup>g</sup>Khouri and Robinson [1971].<sup>h</sup>Lide [1995].<sup>i</sup>Clifford et al. [1981].<sup>j</sup>Johnston and McClosky [1940].<sup>k</sup>Ellis and Raw [1959].<sup>l</sup>Fisher [1909].<sup>m</sup>Trautz and Kurz [1931].<sup>n</sup>Raw and Ellis [1958].

\*\*Number of data points for viscosity.

<sup>a</sup>Chakraborti and Gray [1965].<sup>b</sup>Harris et al. [1979].<sup>c</sup>Kestin and Wakeham [1979].<sup>d</sup>Takahashi et al. [1996].<sup>e</sup>Kestin and Ro [1982].<sup>f</sup>Vogel [1914].

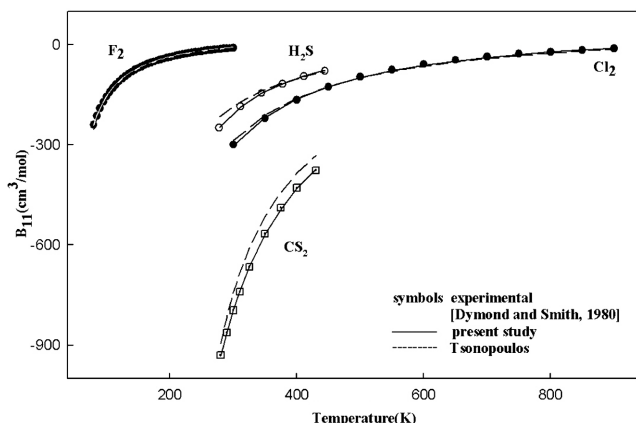


Fig. 1. Comparison of experimental and predicted second virial coefficients for pure gases ( $F_2$ ,  $Cl_2$ ,  $CS_2$  and  $H_2S$ ).

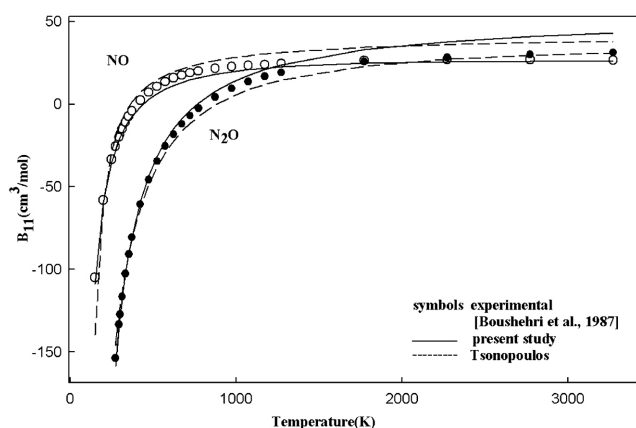


Fig. 2. Comparison of experimental and predicted second virial coefficients for pure gases ( $NO$  and  $N_2O$ ).

pure  $CS_2$  and  $H_2S$  gas, deviation values obtained by the Tsonopoulos correlation ( $46.9 \text{ cm}^3 \text{ mol}^{-1}$  and  $15.1 \text{ cm}^3 \text{ mol}^{-1}$ , respectively), are extremely higher than those of the present model ( $2.4 \text{ cm}^3 \text{ mol}^{-1}$  and  $1.5 \text{ cm}^3 \text{ mol}^{-1}$ , respectively). Dymond and Smith [1980] mention that experimental uncertainties of the  $CS_2$  gas are between  $\pm 15$  and  $30 \text{ cm}^3 \text{ mol}^{-1}$  and the reliability of the experimental data for  $H_2S$  gas is quite low. A comparison of the measured and predicted second virial coefficients for pure gases ( $F_2$ ,  $Cl_2$ ,  $CS_2$ , and  $H_2S$ ) and gases ( $NO$  and  $N_2O$ ) are presented in Fig. 1 and Fig. 2, respectively.

Resulting deviations from parameter estimation for pure gases between measured and calculated viscosity data are shown in Table 2; the overall 1.4% RMSDr value obtained by the method compares well with 6.2% RMSDr by means of the Lucas method. The present study is more reliable than the Lucas method, on the whole, and provides better viscosity predictions within the experimental uncertainties (3 to 5%) for all gases than those from the Lucas method, whose lowest deviation is between 3.6% (carbon disulfide) to 15.3% (hydrogen sulfide). Comparisons of the experimental and predicted viscosities for pure gases ( $F_2$ ,  $Cl_2$ ,  $CS_2$ , and  $H_2S$ ) and gases ( $NO$  and  $N_2O$ ) are made in Fig. 3 and Fig. 4, respectively.

Second virial coefficient and viscosity data, not supplied to the parameter estimation procedure, were then calculated with group parameter values determined in advance. As for the second virial

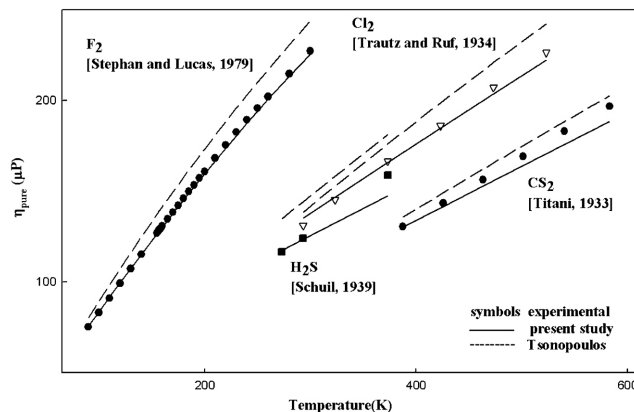


Fig. 3. Comparison of experimental and predicted viscosities for pure gases ( $F_2$ ,  $Cl_2$ ,  $CS_2$  and  $H_2S$ ).

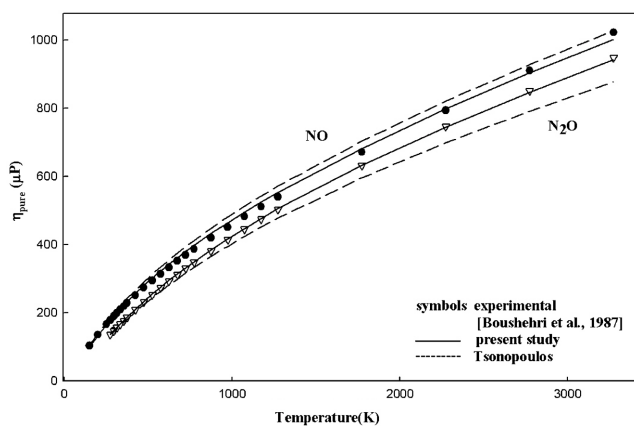


Fig. 4. Comparison of experimental and predicted viscosities for pure gases ( $NO$  and  $N_2O$ ).

coefficient ( $H_2S$ ,  $NO$  and  $N_2O$ ) and viscosity ( $CS_2$ ,  $NO$  and  $N_2O$ ) calculations, both methods are shown to be favorably comparable to each other. It is noted that resulting deviations from regressions are quite smaller than those of calculations for  $NO$  and  $N_2O$  gases. The reason is that the data used for calculations were obtained from different types of experimental measurements by several researchers, which experimental uncertainties are relatively larger.

## 2. Gas-gas Mixtures

An advantage of the group contribution method is that mixture properties can be predicted by using parameter values obtained from properties of pure compounds without additional parameters. Group parameter values, evaluated by means of the simultaneous regression of second virial coefficient and viscosity data for pure gases, were then used to predict second virial cross coefficients and mixture viscosities for gas-gas mixtures. Binary diffusion coefficients for gas-gas mixtures, which data were not supplied to data regression for the estimations of group parameters, can be estimated by using gas group parameters, since the group contribution method is based on the intermolecular potential function.

By the nature of the model, group binary interaction coefficients  $k_{ij,gc}$  were added for better calculations to mixtures consisting of chemically dissimilar compounds, as mentioned in the previous work [Oh and Campbell, 1997]. A single group binary interaction coefficient

**Table 3. Deviations between experimental and calculated second virial cross coefficients**

Mixtures	Number of points	Average RMSD in B (cm <sup>3</sup> mol <sup>-1</sup> )		Data source
		Present study (K <sub>ij,gc</sub> =0)	Tsonopoulos (K <sub>12</sub> =0)	
<i>Gas-gas mixtures</i>				
Carbon disulfide				
- carbon dioxide	1	3.4	5.8	[a]
- hydrogen	1	22.7	48.6	[a]
- nitrogen	1	28.6	38.5	[a]

<sup>a</sup>Dymond and Smith [1980].

**Table 4. Deviations between experimental and calculated mixture viscosities**

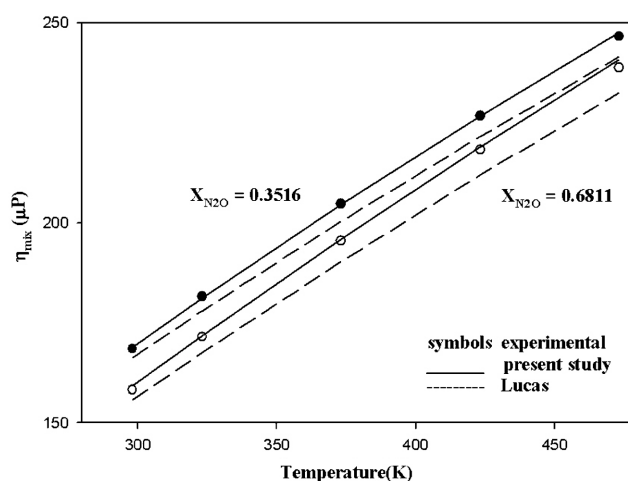
Mixtures	Number of points	Average RMSDr in $\eta$ (%)		Data source
		Present study ( $K_{ji,gc}=0$ )	Lucas	
<i>Gas-gas mixtures</i>				
Nitrous oxide				
- nitrogen	10	0.5	2.4	[a]
- hydrogen	16	3.3	8.5	[b]
- carbon dioxide	25	1.8	6.3	[a, b]
<i>Overall</i>	42	2.0	6.2	

<sup>a</sup>Kestin and Ro [1982]. <sup>b</sup>Trautz and Kurz [1931].

cient, required for every possible interaction between gas and gas groups, was determined by reducing second virial cross coefficient data for mixtures of gas *i* and gas *j*, along with universal van der Waals volume constant value (1.3627) evaluated by Oh and Sim [2002]. However, in this work,  $k_{ij,gc}$  values for all interactions between all compounds (diatomic or simple polyatomic gases) studied here were assumed to be zero. One second virial cross coefficient data point is available in the literature [Dymond and Smith, 1980] for each three carbon disulfide mixtures, such that group binary interaction coefficient  $k_{ij,gc}$  for  $\text{CS}_2$  mixture was not considered here. No second virial cross coefficient data other than ones shown in Table 3 are available for gas-gas mixtures. It is noted that the use of  $k_{ij,gc}$  for polyatomic gas-hydrocarbon mixtures is out of scope of this work.

Resulting deviations between observed and calculated second virial cross coefficient data for gas-gas mixtures are presented in Table 3. Also included for comparison in Table 3 are results from the corresponding states correlation. The Tsonopoulos correlation may require a value for the binary interaction coefficient  $k_{12}$  when extended to second virial cross coefficients for gas-gas mixtures of different type; however,  $k_{12}$  is assumed to be zero for equivalent comparisons. With zero value of  $k_{ij,gc}$  or  $K_{12}$ , the proposed method yields deviation values (3.4, 22.7 and 22.7  $\text{cm}^3 \text{mol}^{-1}$ ), while Tsonopoulos correlation obtains 5.8, 48.6 and 38.5  $\text{cm}^3 \text{mol}^{-1}$ , respectively, in order shown in Table 3. It is mentioned here that more data points are needed to compare the reliability of both models reasonably.

For mixture viscosity calculations, no data other than nitrous oxide mixtures were available. As shown in Table 4, the present study with the assumption of  $k_{ij,gc}=0$  provides a less resulting RMSDr value (2.0%) than the Lucas method (6.2%), showing that the present method is more reliable for the calculations of mixture viscosities for nitrous oxide mixtures with nitrogen, hydrogen and carbon

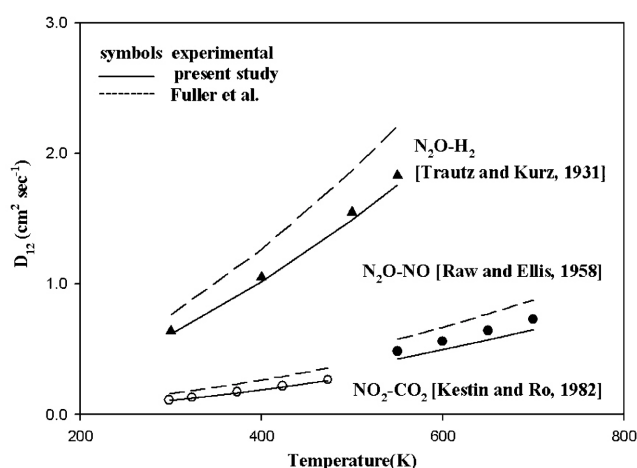
**Fig. 5. Comparison of experimental and predicted mixture viscosities for  $\text{N}_2\text{O}$  and  $\text{N}_2$  mixtures.**

dioxide. The comparison of experimental and calculated viscosities for nitrous oxide-nitrogen mixture at two different mole fractions of  $\text{N}_2\text{O}$  is shown in Fig. 5.

Deviations between measured and predicted properties are given for binary diffusion coefficients in Table 5. Also included for comparison are resulting deviations obtained from the corresponding states method by Fuller et al. [1966]. Higher deviations from the proposed model than those of the Fuller method were found for  $\text{NO}$ -gas mixtures, while the model shows better agreements between measured and predicted binary diffusion coefficients for  $\text{CS}_2$ -gas and  $\text{N}_2\text{O}$ -gas mixtures: on the whole, it can be said that for binary diffusion coefficient predictions the comparison of the present method is made well with the Fuller method, showing that overall %

**Table 5. Deviations between experimental and calculated binary diffusion coefficients**

Mixtures	Number of points	Average RMSDr in D (%)		Data source
		Present study ( $K_{ij,gc}=0$ )	Fuller et al.	
<i>Gas-gas mixtures</i>				
Carbon disulfide				
- carbon dioxide	1	8.1	85.4	[a]
Nitric oxide				
- nitrogen	3	7.6	7.0	[b, c]
- hydrogen	1	6.0	5.4	[d]
Nitrous oxide				
- nitric oxide	4	1.1	19.7	[e, f, g]
- hydrogen	6	0.5	20.8	[c, d, h]
- carbon dioxide	22	6.1	35.8	[a, i-o]
- nitrogen	5	1.0	21.5	[n]
Overall	42	4.4	28.8	

<sup>a</sup>Reid et al. [1987].<sup>f</sup>Ellis and Raw [1959].<sup>k</sup>Wall and Kidder [1946].<sup>b</sup>Trautz and Muller [1935].<sup>g</sup>Hawksworth et al. [1962].<sup>h</sup>Howard [1930].<sup>c</sup>Trautz and Sorg [1931].<sup>h</sup>Chapman and Cowling [1939].<sup>m</sup>Trautz and Kurz [1931].<sup>d</sup>Klemec [1923].<sup>i</sup>Amdur et al. [1952].<sup>n</sup>Kestin and Ro [1982].<sup>e</sup>Raw and Ellis [1958].<sup>j</sup>Boardman and Wild [1937].<sup>o</sup>Lide [1995].**Fig. 6. Comparison of experimental and predicted binary diffusion coefficients for mixture of  $N_2O$  with gases ( $H_2$ ,  $NO$  and  $CO_2$ ).**

RMSDr values resulted from the present model and the Fuller method are 3.4% and 28.8%, respectively. Comparison of experimental and predicted binary diffusion coefficients for mixtures of nitrous oxide with hydrogen, nitric oxide and carbon dioxide is shown in Fig. 6 with data sources.

## CONCLUSIONS

The group contribution method in the previous work [Oh and Sim, 2002] for the calculation of second virial coefficients, viscosities and diffusion coefficients has been extended to polyatomic gases. All compounds examined here were assumed to consist of a single gas group, not functional groups in molecules. Gas group parameters were obtained from the simultaneous regression of second virial

coefficient and viscosity data for pure gas. New group parameter values for pure gases ( $F_2$ ,  $Cl_2$ ,  $CS_2$ ,  $H_2S$ ,  $NO$ , and  $N_2O$ ) were reported.

Group binary interaction coefficients for chemically dissimilar mixtures of compounds could not be estimated since no second virial cross coefficient data other than  $H_2S$ -ethane mixture [Dymond and Smith, 1980] are available in the literature, such that group binary interaction coefficients for each interaction between gas-gas examined here were assumed to be zero.

Application of the model shows that second virial coefficient data can be represented with results comparable to those obtained by the corresponding states method [Tsonopoulos, 1974]. The accuracy of the model in viscosity predictions is comparable to the Lucas method [1980]. The characteristic feature of the group contribution method makes possible diffusivity predictions as well, which data were not used in parameter estimations. The reliability of the model in diffusion coefficient predictions is evaluated nicely by comparison with the Fuller method [1966].

A strong advantage of the 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 this 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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## NOMENCLATURE

- a : core radius [angstrom]  
 $a^*$  : 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  
 $k_{ij,gc}$  : groupbinaryinteractioncoefficientforinteractionsbetween  
 intermolecular functional groups  $i$  and  $j$   
 $N_{i1}$  : number of groups  $i$  in molecule 1  
 $N_{j2}$  : number of groups  $j$  in molecule 2  
 $P$  : pressure [atm]  
 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 [ $kT/\epsilon$ ]  
 $V$  : volume [ $\text{cm}^3$ ]  
 $V_{vdw,ii}$  : van der Waals volume of group  $i$  [ $\text{cm}^3 \text{mol}^{-1}$ ]  
 $x$  : mole fraction

### Greek Letters

$\alpha$  : functional group parameter for potential well depth [J]  
 $\beta$  : functional group parameter for potential well depth [J K]  
 $\epsilon$  : potential well depth [J]  
 $\eta$  : viscosity [ $\mu\text{P}$ ]  
 $\xi$  : universal van der Waals volume constant (1.3627) in Eq. (8)  
 $\sigma$  : collision diameter [angstrom]  
 $\Omega_v$  : collision integral for viscosity  
 $\Omega_D$  : collision integral for diffusivity

### Subscripts

$1, 11$  : property of molecule 1  
 $2, 22$  : property of molecule 2  
 $12$  : interaction property for molecules 1 and 2  
 $ij$  : interaction property for intermolecular groups  $i$  and  $j$   
 $C$  : critical property  
 $GAS$  : property of gas group  
 $gc$  : property of group binary interaction coefficient  
 $F2$  : property of  $F_2$  gas group  
 $Cl2$  : property of  $Cl_2$  gas group  
 $CS2$  : property of  $CS_2$  gas group  
 $H2S$  : property of  $H_2S$  gas group  
 $NO$  : property of  $NO$  gas group  
 $N2O$  : property of  $N_2O$  gas group

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