

An Extension of the Group Contribution Model for Thermodynamic and Transport Properties of Dilute Gases

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Abstract—Earlier work of the group contribution method presented by Oh and Campbell [Oh and Campbell, 1997] for prediction of second virial coefficients and dilute gas transport properties has been repeated with a new set of normal alkane second virial coefficient data (methane, ethane, propane, and normal pentane critically compiled by Dymond and Smith [1980], normal hexane recommended by Dymond et al. [1986], and the recommendation for normal butane, heptane and octane updated by Tsonopoulos and Dymond [1997]). This method has been extended to molecular linear gases (carbon monoxide, oxygen and hydrogen) and to alkanes-gases mixtures. The functional group parameters were revised from the simultaneous regression of second virial coefficient and viscosity data. Group parameters values (CH_0 , CH_1 , CH_2 , CH_3 , CH_4 , double-bonded CH_1 , double-bonded CH_2 , N_2 , and CO_2 groups) and 8 binary group interaction parameters ($k_{\text{N}_2\text{-CH}_0, \text{GC}}$, $k_{\text{N}_2\text{-CH}_1, \text{GC}}$, $k_{\text{N}_2\text{-CH}_2, \text{GC}}$, $k_{\text{N}_2\text{-CH}_3, \text{GC}}$; $k_{\text{CO}_2\text{-CH}_0, \text{GC}}$, $k_{\text{CO}_2\text{-CH}_1, \text{GC}}$, $k_{\text{CO}_2\text{-CH}_2, \text{GC}}$ and $k_{\text{CO}_2\text{-CH}_3, \text{GC}}$) were revised. New group parameter values are given for gases beyond those presented earlier (CO , O_2 and H_2) and 19 group binary interaction parameter values ($k_{\text{N}_2\text{-CH}_1\text{D}, \text{GC}}$, $k_{\text{N}_2\text{-CH}_2\text{D}, \text{GC}}$; $k_{\text{CO}_2\text{-CH}_1\text{D}, \text{GC}}$, $k_{\text{CO}_2\text{-CH}_2\text{D}, \text{GC}}$; $k_{\text{CO-CH}_1, \text{GC}}$, $k_{\text{CO-CH}_2, \text{GC}}$, $k_{\text{CO-CH}_3, \text{GC}}$, $k_{\text{CO-CH}_1\text{D}, \text{GC}}$, $k_{\text{CO-CH}_2\text{D}, \text{GC}}$; $k_{\text{O}_2\text{-CH}_0, \text{GC}}$, $k_{\text{O}_2\text{-CH}_1, \text{GC}}$, $k_{\text{O}_2\text{-CH}_2, \text{GC}}$, $k_{\text{O}_2\text{-CH}_3, \text{GC}}$; $k_{\text{H}_2\text{-CH}_0, \text{GC}}$, $k_{\text{H}_2\text{-CH}_1, \text{GC}}$, $k_{\text{H}_2\text{-CH}_2, \text{GC}}$, $k_{\text{H}_2\text{-CH}_3, \text{GC}}$, $k_{\text{H}_2\text{-CH}_1\text{D}, \text{GC}}$, $k_{\text{H}_2\text{-CH}_2\text{D}, \text{GC}}$) are presented for hydrocarbon mixtures with gases. Application of the model shows that second virial coefficient data can be represented with results comparable to those obtained by Oh and Campbell [1997] and by the corresponding states method of Tsonopoulos [1974]. The accuracy of the model in viscosity and diffusion coefficient predictions of dilute gases is comparable to the methods of Lucas [1980] and of the Fuller method [Fuller et al., 1966].

Key words: Theory, Group Contribution, Second Virial Coefficient, Viscosity, Diffusion Coefficient

INTRODUCTION

The group contribution concept becomes an alternative to the corresponding states framework for the prediction of second virial coefficients 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 applicable with only information of both functional group and van der Waals volume [Bondi, 1964] 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.

Campbell [1989] applied a group contribution concept to the Kihara potential function for second virial coefficients of pure gases and its mixture. Group parameters for alkane groups, obtained from second virial coefficient data for pure alkanes, were used to pre-

dict, 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. Based on an intermolecular potential function, the group contribution method is applicable to the calculation of dilute gas transport properties as well. Swelling models combined with group contribution models (UNIFAC, ASOG) was introduced to calculate the swelling equilibria of water(1)/poly(AM-SAS-AA)(2) systems [Kim et al., 2000].

Yeom et al. [2000] developed a semi-empirical equation of state for freely jointed square-well chain fluid adopting for the second and third virial coefficients for compressibility factor and the first two terms of the radial distribution function. Theories based on free-volume concepts have been developed to characterize the self and mutual diffusion coefficients of low molecular weight penetrants in rubbery and glassy polymer-solvent systems by Ramesh and Duda [2000]. Oh [1989] and Oh and Campbell [1997] proved the feasibility of applying the group contribution method to simultaneous representation of second virial coefficient, dilute gas viscosity and dilute gas diffusion coefficient. By introducing the concept of a binary group interaction coefficient, they extended the model to nitrogen- and carbon dioxide-alkane mixtures with success. Here, with the exception of n-hexane, second virial coefficient data from ethane through n-octane recommended by Dymond et al. [1986] were used for the evaluation of functional group parameters for alkanes.

In the mean time, the extensive 1986 analysis of Dymond et al. [1986] was extended to include recent data on C_4 - C_6 alkanes, and

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the recommendation for C₄-C₈ alkanes was updated by Tsonopoulos and Dymond [1997].

In this paper, as a continuation of the previous works on the application of the group contribution method to the intermolecular potentials, a set of functional group parameters for pure alkanes were re-evaluated with revised recommendations of pure alkane second virial coefficient data in order to improve the reliability of the predictions. Also, functional group parameters beyond those presented earlier are extended to industrially important linear molecular gases (carbon monoxide, oxygen and hydrogen), as well as to a variety of mixtures of these gases. As in the 1997 paper [Oh and Campbell, 1997], the group contribution concept applied to the Kihara intermolecular potential function was examined for normal and branched alkanes, alkenes, nitrogen and carbon dioxide.

The description for the second virial coefficient derived from the spherical core potential of Kihara [1978] and the Chapman and Enskog theory [Chapman and Cowling, 1939] for the viscosity and diffusivity of dilute gases is not made here, but a full description can be found either in the original paper [Campbell, 1989] or in 1997 extension [Oh, 1989]. Also, values of the collision integrals for viscosity and diffusion (Ω_v and Ω_D) for Kihara potential function, needed for the Chapman and Enskog theory, were tabulated in Oh and Campbell [1997].

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 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

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

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, 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 collision diameter for interactions between intermolecular groups i and j , respectively. This rule for the Kihara potentials is also required for the core radius a_{12} , where the group additivity of the reduced core radii is assumed:

$$a_{11}^* = \sum N_{i1}a_{ii}^* \quad (3)$$

and

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

followed by

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

where

$$a_{11} = \frac{\alpha_{11}a_{11}^*}{2(1+a_{11}^*)} \quad (6)$$

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

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

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

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 chain molecules. The reciprocal temperature term in Eq. (7) is used as a rough way of accounting for nonsphericity of the molecule [Campbell, 1989].

Finally, we assume the combining rules for interactions between unlike groups i and j such as normal alkane and nitrogen mixture.

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

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

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

In order to apply the group contribution model, values of α_{ii} , β_{ii} , and a_{ii}^* must be known for each functional group within molecules 1 and 2. The value of the constant ξ must also be known. Finally, values of the group interaction coefficient $k_{ij,gc}$ must be known for each interaction between intermolecular groups i and j .

Although the model contains a number of parameters, it is practically applicable to pure gases as well as mixtures. Hence, parameter values may often be determined from data for pure substances.

Table 1. Properties of the molecular groups examined in this study (universal van der Waals volume constant=1.3627)

Group	$V_{vdw,ii}^a$	a_{ii}^*	α_{ii}	β_{ii}
Hydrocarbons:				
CH ₀	3.33	0.1665	4.159	-
CH ₁	6.78	0.0362	43.23	-
CH ₂	10.23	0.0348	62.14	13025
CH ₃	13.67	0.1425	177.3	-
CH ₄	17.12	0.2261	217.1	-
Double-bonded CH ₁	8.47	-	45.59	18187
Double-bonded CH ₂	11.97	0.1715	166.9	-
Gas:				
N ₂	15.8	0.2950	150.3	-
CO ₂	19.7	0.1866	270.2	14594
CO	16.2	0.2527	150.7	-
O ₂	13.0	0.3373	186.5	-
H ₂	6.34	2.1698	133.3	-

^avan der Waals volumes $V_{vdw,ii}$ were taken from Bondi [1964].

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

Compound	Number of points ^a	Average RMSD in B (cm ³ mol ⁻¹)				Data source	Number of points ^b	RAD in η (%)			Data source
		Present study	Oh & Campbell	Tsonopoulos	Campbell			Present study	Oh & Campbell	Lucas	
<i>Normal alkanes</i>											
<u>A. Regression results:</u>											
Methane	28	2	3	3	1	[Dymond et al., 1986]	31	2.9	4.4	3.1	[Stephan and Lucas, 1979]
Ethane	22	7	8	5	3	[Dymond et al., 1986]	35	1.3	1.3	0.9	[Stephan and Lucas, 1979]
Propane	20	3	3	3	12	[Dymond et al., 1986]	29	2.2	2.6	3.6	[Stephan and Lucas, 1979]
n-butane	19	7	13	25	6	[Dymond et al., 1986]	32	1.8	2.5	1.7	[Stephan and Lucas, 1979]
n-pentane	16	4	9	6	18	[Dymond et al., 1986]	27	1.6	1.8	2.5	[Stephan and Lucas, 1979]
n-hexane	15	6	16	28	26	[Al-Bizreh and Wormald, 1978; Di Zio et al., 1966; Strein et al., 1971]	27	1.2	1.7	0.8	[Stephan and Lucas, 1979]
n-heptane	14	10	10	17	7	[Dymond et al., 1986]	20	3.4	3.0	3.4	[Stephan and Lucas, 1979]
n-octane	11	13	9	17	14	[Dymond et al., 1986]	23	5.3	5.2	4.1	[Stephan and Lucas, 1979]
Average		6	8	12	10			2.3	2.7	2.4	
<i>Branched alkanes</i>											
<u>A. Regression results:</u>											
2-methylpropane	11	11	24	28	37	[Das et al., 1973]	35	1.7	2.3	6.0	[Stephan and Lucas, 1979]
2-methylbutane	7	8	11	25	4	[Das et al., 1973]	9	2.4	2.0	3.5	[Vargaftik, 1975]
2,2-dimethylpropane	10	4	3	3	6	[Dymond and Smith, 1980]	4	4.7	2.4	2.3	[Lambert et al., 1955]
Average		8	13	18	18			2.1	2.3	5.2	
<u>B. Prediction results:</u>											
2-methylpentane	4	40	28	38	36	[Waddingston et al., 1949]					
3-methylpentane	4	39	41	56	30	[Waddingston et al., 1949]					
2,3-dimethylbuthane	5	20	52	65	23	[Waddingston et al., 1949]					
Average		32	41	54	28						
<i>Alkenes</i>											
<u>A. Regression results:</u>											
Ethylene	9	16	2	1	-	[Dymond and Smith, 1980]	21	0.9	1.5	0.7	[Stephan and Lucas, 1979]
Propylene	8	10	4	1	-	[Dymond and Smith, 1980]	29	0.9	0.6	1.8	[Stephan and Lucas, 1979]
cis-2-butene	5	21	16	33	-	[Dymond and Smith, 1980]					
trans-2-butene	5	8	12	25	-	[Dymond and Smith, 1980]					
but-1-ene	12	11	8	9	-	[Dymond and Smith, 1980]					
pent-1-ene	12	11	12	85	-	[Dymond and Smith, 1980]					
hep-1-ene	10	19	14	33	-	[Dymond and Smith, 1980]					
oct-1-ene	11	18	18	48	-	[Dymond and Smith, 1980]					
Average		14	11	29				0.9	1.0	1.4	

Table 2. Continued

Compound	Number of points ^a	Average RMSD in B (cm ³ mol ⁻¹)				Data source	Number of points ^b	RAD in η (%)			Data source
		Present study	Oh & Campbell	Tsonopoulos	Campbell			Present study	Oh & Campbell	Lucas	
<i>Gas</i>											
<u>A. Regression results:</u>											
Nitrogen	9	1.1	1.0	1.9	0.5	[Dymond and Smith, 1980]	33	1.4	2.1	0.7	[Stephan and Lucas, 1979]
Carbon dioxide	13	0.4	0.3	0.6	-	[Dymond and Smith, 1980]	25	2.0	1.8	2.5	[Stephan and Lucas, 1979]
Carbon monoxide	12	0.9	-	2.2	-	[Dymond and Smith, 1980]	16	1.2	-	1.7	[Stephan and Lucas, 1979]
Oxygen	11	2.0	-	4.2	-	[Dymond and Smith, 1980]	46	2.1	-	1.8	[Stephan and Lucas, 1979]
Hydrogen	5	0.4	-	4.3	-	[Dymond and Smith, 1980]	7	4.5	-	13.1	[Stephan and Lucas, 1979]
Average		1		2				1.9		2.3	

^aNumber of data points for second virial coefficient.^bNumber of data points for viscosity.

Table 3. Deviations between predicted and experimental second virial cross coefficients (hydrocarbons)

Mixtures	Number of points	Average RMSD in B (cm ³ mol ⁻¹)					Data source
		Present study	Oh & Campbell	Tsonopoulos correlation		Campbell	
				K ₁₂ =0	K ₁₂ ≠0		
<i>Normal - normal alkanes</i>							
Methane							
- ethane	16	3	-	1.7	0.6	-	[McElroy and Fang, 1994; Siebert and Knobler, 1983; Lotfi, 1987]
- n-butane	21	6	6	8	8	9	[Beattie et al., 1941; Dantzler et al., 1968; Wormald et al., 1979]
- n-hexane	10	10	12	26	9	7	[Dantzler et al., 1968; Wormald et al., 1979]
- n-octane	2	3	3	29	15	12	[Wormald et al., 1979]
- n-decane	4	61	53	119	28	36	[D'Avila et al., 1976]
- n-dodecane	12	42	29	116	4	5	[D'Avila et al., 1976]
- n-hexadecane	5	95	69	225	32	33	[Kaul and Prausnitz, 1978]
- n-eicosane	4	73	43	189	11	9	[Kaul and Prausnitz, 1978]
Ethane							
- n-butane	7	24	14	11	13	12	[Dantzler et al., 1968; Wormald et al., 1979]
- n-hexane	7	8	8	23	8	11	[Dantzler et al., 1968; Wormald et al., 1979]
- n-octane	2	6	2	41	10	16	[Wormald et al., 1979]
- n-hexadecane	3	83	31	308	25	39	[Daul and Prausnitz, 1978]
- n-eicosane	4	151	97	341	48	27	[Daul and Prausnitz, 1978]

Table 3. Continued

Mixtures	Number of points	Average RMSD in B (cm ³ mol ⁻¹)					Data source
		Present study	Oh & Campbell	Tsonopoulos correlation		Campbell	
				K ₁₂ =0	K ₁₂ ≠0		
Propane							
- n-hexane	7	5	4	23	5	6	[Dantzler et al., 1968; Wormald et al., 1979]
- n-heptane	3	13	12	12	15	13	[Wormald et al., 1979]
Butane							
- n-hexane	8	13	11	21	11	18	[Dantzler et al., 1968; Wormald et al., 1979]
- n-octane	3	6	6	20	12	9	[Wormald et al., 1979]
<i>Branched - normal alkanes</i>							
Methane							
- 2-methylpropane	7	7	6	10	6	5	[Gunn, 1958]
- 2-methylbutane	3	24	16	39	22	24	[Pecsok and Windsor, 1968; Mason and Eakin, 1961]
- 2-methylpentane	2	69	66	67	68	66	[Pecsok and Windsor, 1968]
- 2,2,5-trimethylhexane	4	35	37	124	53	38	[D’Avila et al., 1976]
- 2,2-dimethylpropane	36	20	16	32	14	13	[Strein et al.,1971; Hamann et al., 1955; Bellm et al., 1974; Baughman et al., 1975]
- 2,2-dimethylbutane	2	14	13	53	20	13	[Pecsok and Windsor, 1968]
- squalane	2	133	107	686	268	69	[Kaul and Prausnitz, 1978]
Ethane							
- squalane	2	265	219	1170	569	158	[Kaul and Prausnitz, 1978]
<i>Alkenes - normal alkanes</i>							
Ethylene							
- methane	18	5	8	11	10	-	[Mason and Eakin, 1961; McMath and Edmister, 1969; Lee and Edmister, 1970; Lee, 1976]
- n-hexadecane	3	75	74	297	11	-	[Kaul and Prausnitz, 1978]
Propylene							
- ethane	4	1	2	4	4	-	[Gunn, 1958]
- propane	1	18	19	13	14	-	[Mason and Eakin, 1961]
- n-butane	1	4	13	0.5	5	-	[Mason and Eakin, 1961]

Data used here for the functional group parameter evaluations and predictions of thermodynamic properties and dilute gas transport properties for pure gases and mixtures are discussed below.

RESULTS AND DISCUSSION

1. Normal Alkanes

For the determination of group parameters α_{ii} , β_{ii} and a_{ii}^* for the CH_2 and CH_3 groups, second virial coefficient and viscosity data of pure alkanes from ethane through n-octane were simultaneously regressed. The van der Waals volume constant ξ , evaluated in this regression, was used in all subsequent calculations and evaluations. It should also be noted that the group interaction parameter $k_{ij,gc}$ was assumed to be zero for all interactions between hydrocarbon groups. Methane was considered to consist of a single CH_4 group and parameters α_{ii} , β_{ii} and a_{ii}^* for the CH_4 group were evaluated from second virial coefficient and viscosity data for pure methane.

Tsonopoulos et al. [1989] made extensive analysis for C_4 - C_6 alkanes from earlier recommendation proposed by Dymond et al. [1986]. Subsequently, the 1989 re-analysis was updated for C_4 - C_8 alkanes by Tsonopoulos and Dymond [1997]. A more recent critical analysis of the data has been considered prior to this parameter estimation. Among C_4 - C_8 alkanes recommended by the 1997 analysis, data for n-pentane are determined to be less reliable than the previous ones from the preliminary regression results, and therefore second virial coefficient data for n-pentane were not replaced for better evaluations. Since the recommended values for normal hexane [Dymond et al., 1986] did not appear to us to be consistent with those of the other n-alkanes, smoothed values proposed by Tsonopoulos et al. [1989] were used instead. Consequently, data for only four alkanes (methane, ethane, propane and pentane), recommended by the compilation of Dymond et al. [1986], were equivalent to those used in the previous work [Oh and Campbell, 1997]. All viscosity data used here were taken from Stephan and Lucas [1979].

The parameter β_{ii} for the CH_4 group was assumed a priori to be zero since methane molecules are essentially spherical. The 95 percent confidence region for β_{ii} of the CH_3 group bracketed zero so it was set to zero and the regression was repeated to obtain values of the other parameters.

The group parameters were obtained using a non-linear least square parameter estimation program based on the Levenberg-Marquardt algorithm supplied by IMSL stat library. Each data point was weighted by its estimated experimental uncertainty.

Resulting parameter values for the CH_2 , CH_3 and CH_4 groups are given in Table 1 and the sources of data used are indicated in Table 2. Resulting deviations between experimental and calculated second virial coefficients and viscosities for n-alkanes up to n-octane, along with previous work of the author, are given in Table 2. Also included is a comparison of the present model to the Tsonopoulos correlation for second virial coefficient [Tsonopoulos, 1974] and the Lucas method for dilute gas viscosity [Lucas, 1980], which require the critical temperature and pressure of the pure species in question. The results from Campbell [1989] listed in Table 2 are the same group contribution model applied here except that parameters were obtained only from second virial coefficient data. The prediction results obtained here are also compared to those of both Oh and

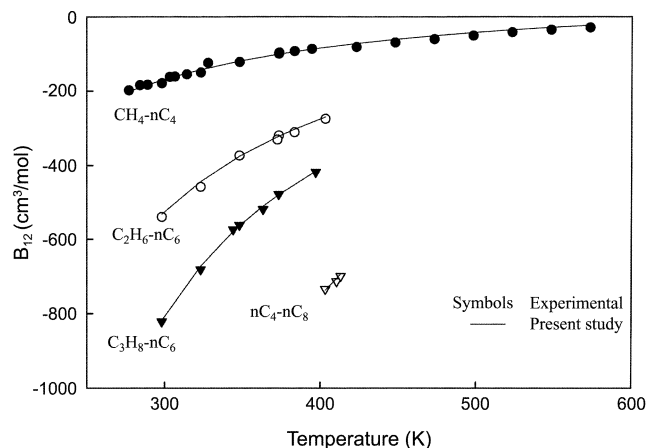


Fig. 1. Comparison of observed and predicted second virial cross coefficients of normal alkane+alkane mixtures.

Campbell [1997] and of Tsonopoulos, showing better predictions of average deviation of $6 \text{ cm}^3 \text{ mol}^{-1}$ than $8 \text{ cm}^3 \text{ mol}^{-1}$ and $12 \text{ cm}^3 \text{ mol}^{-1}$ on a RMS (root mean square) basis, respectively. For the predictions of viscosity of pure normal alkanes, resulting deviations of 2.3% in RAD (relative average deviation) basis is quite comparable to other two methods (Oh and Campbell [1997] and Lucas [1980]).

With the exception that a different set of second virial data for pure normal alkanes (normal butane, hexane, heptane and octane) is used in regression, both this method and the previous work [1997] are identical. The present study provides lower deviations for second virial coefficients because our previous works evaluated corresponding parameters from a slightly different data base.

An advantage of this group contribution method is that properties of alkane mixtures can be predicted by using the parameter values obtained from properties of pure substances. Comparisons between measured second virial cross coefficients and those predicted from the group contribution model are shown for several alkane-alkane systems in Fig. 1. Deviations between experimental and predicted values for alkane mixtures are given in Table 3, showing that the present work is somewhat worse than Oh and Campbell, which may be originated by the weight factors used in the parameter estimation procedure as an objective function. Weighting factors for different set of pure alkanes used in this study were calculated by the statistical analysis of the 95% confidence region for all observed values, while those used in Oh and Campbell are taken from the suggestion made by Dymond and Smith [1980].

Results from application of the Tsonopoulos correlation are included for comparison. The Tsonopoulos correlation requires a value of the binary interaction coefficient k_{12} when extended to second virial cross coefficients and two cases of this method are examined in Table 3: one in which k_{12} is assumed to be zero and one in which k_{12} is calculated as recommended for alkane-alkane mixtures by Chueh and Prausnitz [1967]:

$$k_{12} = 1 - \left[\frac{V_{c1}^{1/6} + V_{c2}^{1/6}}{V_{c1} + V_{c2}} \right]^3 \quad (11)$$

where V_{c1} and V_{c2} are the critical volumes of alkanes 1 and 2. More generally, this equation has been applied by Tarakad and Danner [1977] to systems in which both species were hydrocarbons.

The group contribution model does not require interaction coefficients for this type of symmetric mixture and it is observed, for mixtures where the size difference between two alkanes is small, to be comparable in accuracy to the Tsonopoulos correlation with binary interaction coefficients calculated from Eq. (11). As the size difference increases, the present study becomes somewhat less accurate than the Tsonopoulos correlation with $k_{12} \neq 0$, but is much more accurate than the Tsonopoulos correlation with $k_{12} = 0$.

The obtained group parameters were used next to predict transport properties for n-alkane mixtures. Relative percent deviations between measured and predicted values are given in Table 4 for viscosity and in Table 5 for diffusivity. Included for comparison in Table 4 are results from the Lucas method for mixture viscosity, and results from the method of Fuller et al. [1966] for diffusivity are included in Table 5, along with those obtained from Oh and Campbell [1997]. The method of Fuller et al. is a group contribution method

based on group additivity rather than group interactions. Slightly larger deviation between predicted and observed mixture viscosities than those of Oh and Campbell [1997] is yielded, but this method is still more attractive than the Lucas method. Predictions of binary diffusion coefficients are within what is commonly estimated to be experimental error. Comparisons of measured and predicted viscosities for alkane mixtures are shown in Fig. 2. Predicted self diffusivity of methane not included in parameter estimations is shown in Fig. 3, in order to demonstrate predictive capability of the group contribution method. Better agreement with both experimental data and predictions was found in this model, compared to those from Oh and Campbell [1997] and Fuller method [Fuller et al., 1966].

2. Branched Alkanes and Alkenes

The group contribution method was next extended to branched alkanes and alkenes. The CH_0 and CH_1 group parameters for branched alkanes and the double-bonded CH_1 and double-bonded CH_2 group

Table 4. Deviations between experimental and predicted mixture viscosities

Mixtures	Number of points	RAD in η (%)				Lucas	Data source
		Present study		Oh & Campbell			
		$K_{ij,gc}=0$	$K_{ij,gc}\neq 0$	$K_{ij,gc}=0$	$K_{ij,gc}\neq 0$		
<i>Normal - normal alkanes</i>							
Methane							
- ethane	28	1.9	-	1.1	-	3.2	[Trautz and Sorg, 1931]
- ethane	24	1.6	-	0.9	-	1.9	[Golubev, 1959]
- propane	20	2.5	-	1.4	-	3.6	[Trautz and Sorg, 1931]
- propane	24	2.7	-	1.5	-	4.3	[Golubev, 1959]
- propane	14	3.1	-	1.9	-	2.3	[Golubev and Petrov, 1953]
- propane	18	0.9	-	-	-	2.6	[Giddings et al., 1966]
- propane	12	2.6	-	-	-	3.7	[Bircher, 1943]
- butane	10	1.8	-	-	-	4.3	[Kestin and Yata, 1968]
Ethane							
- propane	20	1.2	-	0.8	-	3.4	[Trautz and Sorg, 1931]
- propane	24	0.9	-	0.6	-	3.1	[Golubev and Petrov, 1953]
<i>Alkenens - normal alkanes</i>							
Ethylene							
- ethane	12	2.1	-	1.7	-	0.7	[Golubev, 1959]
Propylene							
- ethane	9	4.6	-	0.4	-	2.9	[Golubev, 1959]
- propane	24	1.0	-	1.9	-	2.3	[Landolt-Bornstein, 1927]
<i>Gas - hydrocarbons</i>							
Nitrogen							
- methane	3	3.6	-	-	-	25.1	[Golubev and Petrov, 1953]
- n-heptane	4	3.1	4.2	2.4	3.4	6.7	[Golubev, 1959]
Carbon Dioxide							
- methane	10	3.3	-	-	-	27.8	[Kestin and Yata, 1968]
- propane	24	2.0	1.6	1.5	1.5	2.4	[Golubev and Petrov, 1953]
- propane	24	2.0	1.6	1.6	1.3	5.3	[Trautz and Sorg, 1931]
<i>Gas - gas</i>							
Nitrogen							
- carbon dioxide	5	4.2	-	-	-	0.8	[Kestin and Leidenfrost, 1959]
- hydrogen	5	2.9	-	-	-	23.1	[Pal and Barua, 1967; Trautz and Baumann, 1929]
- hydrogen	15	1.9	-	-	-	30.4	[Kestin and Yata, 1968]

Table 5. Deviations between predicted and experimental binary diffusion coefficients

Mixtures		Number of points	RAD in D (%)				Fuller	Data source
			Present study		Oh & Campbell			
			K _{ij,gc} =0	K _{ij,gc} ≠0	K _{ij,gc} =0	K _{ij,gc} ≠0		
Normal - normal alkanes								
Methane								
	- methane	5	5.9	-	7.3	-	13.8	[Weissman, 1974]
	- ethane	3	2.2	-	2.9	-	2.2	[Gotoh et al., 1974]
	- ethane	5	3.8	-	-	-	2.8	[Weissman, 1974; Wilke and Lee, 1955]
	- propane	4	0.8	-	1.7	-	2.2	[Gotoh et al., 1974]
	- propane	4	1.1	-	-	-	2.0	[Weissman, 1974]
	- n-butane	3	0.9	-	0.6	-	4.7	[Gotoh et al., 1974]
	- n-butane	2	2.6	-	-	-	10.1	[Kestin and Yata, 1968]
	- n-hexane	4	1.7	-	0.8	-	11.2	[Wilhelm and Battino, 1972]
	- n-heptane	5	2.2	-	1.9	-	10.6	[Wilhelm and Battino, 1972]
	- n-octane	5	2.4	-	1.9	-	12.9	[Wilhelm and Battino, 1972]
Ethane								
	- propane	8	15.2	-	6.8	-	16.5	[Weissman, 1974; Gotoh et al., 1974; Chen and Othmer, 1972]
	- n-butane	3	2.5	-	2.5	-	11.0	[Gotoh et al., 1974]
	- n-hexane	1	35.4	-	27.1	-	60.3	[Carmichael et al., 1955]
Propane								
	- n-butane	2	2.3	-	2.2	-	14.4	[Weissman, 1974]
n-heptane								
	- n-octane	2	63.8	-	-	-	116.8	[Weissman, 1974]
Branched alkanes								
Methane								
	- 2-methylpropane	3	2.6	-	2.8	-	2.7	[Chen and Othmer, 1972]
	- 2,2-dimethylpropane	3	2.0	-	2.7	-	6.0	[Gotoh et al., 1974]
	- 2-methylheptane	5	2.0	-	1.1	-	10.9	[Gotoh et al., 1974]
Ethane								
	- 2-methylpropane	3	5.0	-	4.6	-	5.0	[Gotoh et al., 1974]
	- 2,2-dimethylpropane	3	2.0	-	2.7	-	10.5	[Gotoh et al., 1974]
Propane								
	- 2-methylpropane	3	4.3	-	4.2	-	9.8	[Gotoh et al., 1974]
	- 2,2-dimethylpropane	3	2.7	-	2.9	-	12.9	[Gotoh et al., 1974]
n-butane								
	- 2,2-dimethylpropane	3	10.6	-	8.0	-	3.8	[Gotoh et al., 1974]
2-methylpropane								
	- 2,2-dimethylpropane	3	2.8	-	6.3	-	15.9	[Gotoh et al., 1974]
Alkenes								
Propylene								
	- propane	4	5.8	-	2.6	-	5.4	[Adzumi, 1937]

parameters for alkenes were evaluated by using the same approach as those for normal alkanes. Along with the universal van der Waals volume constant ξ previously evaluated, parameter values for the CH_2 and CH_3 functional groups were supplied to these regressions as inputs, providing different set of CH_0 , CH_1 , double-bonded CH_1 and double-bonded CH_2 group parameters.

Obtained group parameters values for the CH_0 , CH_1 , double-bond-

ed CH_1 and double-bonded CH_2 groups are shown in Table 1. The parameter β_{ii} value for the CH_0 groups and double-bonded CH_2 groups and a^* value for double-bonded CH_1 groups were found to be zero by the same reason as applied to the CH_3 functional group.

Resulting root mean square deviations between observed and calculated second virial coefficients and viscosities of pure alkenes and branched alkanes are given in Table 2. Several comparisons

Table 5. Continued

Mixtures	Number of points	RAD in D (%)						Data source
		Present study		Oh & Campbell		Fuller		
		$K_{ij,gc}=0$	$K_{ij,gc}\neq 0$	$K_{ij,gc}=0$	$K_{ij,gc}\neq 0$			
<i>Gas - hydrocarbons</i>								
Nitrogen								
- n-butane	4	3.7	0.9	5.0	2.0	2.0	[Gotoh et al., 1974]	
- n-heptane	4	4.4	0.7	5.5	1.4	2.4	[Fuller et al., 1966; McD. Cummings et al., 1955; McD. Cummings and Ubbelohde, 1955; Clarke and Ubbelohde, 1957]	
- n-octane	2	9.1	4.6	10.0	5.9	2.1	[McD. Cummings et al., 1955; McD. Cummings and Ubbelohde, 1955]	
- n-nonane	1	3.0	8.1	1.9	6.6	9.4	[McD. Cummings et al., 1955]	
- n-decane	1	6.8	12.2	5.0	5.3	7.2	[McD. Cummings and Ubbelohde, 1953]	
- n-dodecane	1	5.8	11.2	5.8	10.5	11.4	[McD. Cummings and Ubbelohde, 1953]	
- 2-methylpropane	1	5.4	6.8	-	-	10.1	[McD. Cummings and Ubbelohde, 1953]	
- 2,3-dimethylbutane	1	4.9	3.3	6.1	3.9	0.4	[McD. Cummings and Ubbelohde, 1953]	
- 2,4-dimethylpentane	1	3.8	1.6	4.9	2.4	1.5	[Clarke and Ubbelohde, 1957]	
- 2,2,4-trimethylpentane	3	5.3	3.9	6.7	5.5	1.1	[McD. Cummings and Ubbelohde, 1955]	
- 2,3,3-trimethylheptane	1	21.2	23.8	20.4	22.8	25.4	[McD. Cummings and Ubbelohde, 1955]	
Carbon Dioxide								
- methane	2	5.1	-	-	-	4.0	[Kestin and Yata, 1968]	
- propane	5	8.7	3.9	8.6	3.7	3.2	[Wall and Kidder, 1946]	
- propane	1	8.4	2.9	-	-	7.3	[Fuller et al., 1966]	
- propane	1	8.7	3.3	-	-	7.0	[Wilke and Lee, 1955]	
Oxygen								
- hexane	2	9.4	0.0	-	-	3.2	[Fuller et al., 1966; McD. Cummings and Ubbelohde, 1955]	
- octane	2	9.1	0.0	-	-	2.7	[Fuller et al., 1966; McD. Cummings and Ubbelohde, 1955]	
<i>Gas - gas</i>								
Nitrogen								
- carbon dioxide	1	12.4	-	-	-	3.0	[Walker and Westenberg, 1958]	
- carbon monoxide	1	7.5	-	-	-	4.2	[Amdur and Shuler, 1963]	
- hydrogen	2	3.0	-	-	-	3.2	[Kestin and Yata, 1968]	
- hydrogen	2	7.9	-	-	-	0.7	[Scott and Cox, 1960]	

between measured and predicted second virial coefficients for branched alkanes are also included in this table. Second virial coefficient and viscosity data for pure branched alkanes and alkenes are equivalent to those used in the previous work Oh and Campbell [1997]. It is indicated that the group contribution method is comparable to both the previous work and the Tsonopoulos [1974] method for second virial coefficient, and to the Lucas method [Lucas, 1980] for viscosity.

In order to show predictive capabilities, the obtained group parameters were next used to predict second virial cross coefficients, mixture viscosities, and binary diffusion coefficients for mixtures of normal and branched alkanes and mixtures of alkenes with normal alkanes. Table 3 shows deviations between predicted and observed second virial cross coefficients. The group contribution model is observed to be as accurate as the Tsonopoulos correlation with k_{12} evaluated from Eq. (11) and is almost identical to the results of

Oh and Campbell [1997].

As shown in Table 3, the results for mixtures of methane and ethane with squalane (2,6,10,15,19,23 hexamethyltetracosane) are of particular interest, showing the same comments as those in previous works. This comments point to an advantage of group contribution methods in which critical properties are not required as input data.

Deviations between measured and predicted properties are given for mixture viscosity in Table 4 and for binary diffusion coefficient in Table 5. Comparison with observed and calculated mixture viscosity for propylene-propane mixture was made in Fig. 4, while those of diffusion coefficients for methane-branched alkane mixtures were found in Fig. 5. In Fig. 4, calculated values by the Lucas method are higher than the observed data and those by Oh and Campbell are lower than the observed ones for all mole fractions of propane, showing the overall bias. And the present work is becoming worse

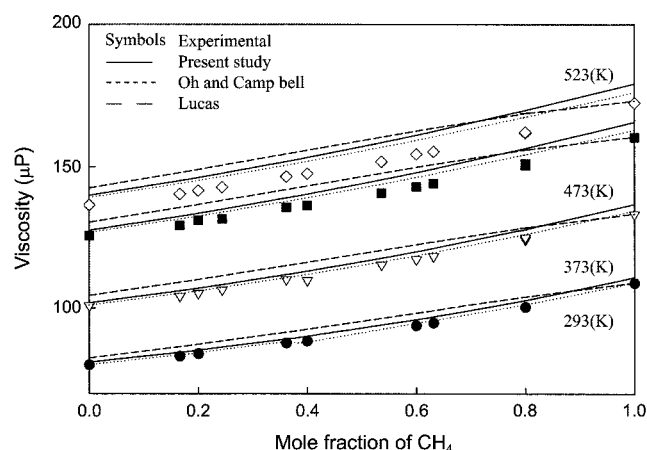


Fig. 2. Comparison of observed and predicted mixture viscosities of normal alkane+alkane mixtures.

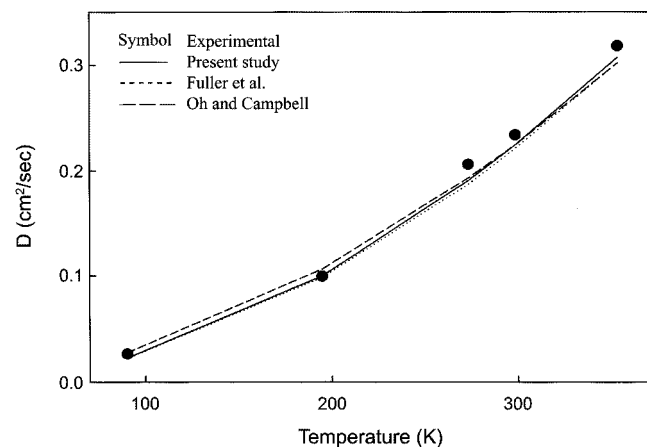


Fig. 3. Comparison of observed and predicted self diffusivity of methane.

as the mole fractions of propane increase.

Comparisons of observed viscosity data for pure propylene and propane, taken from Stephan and Lucas [1979] used in the parameter estimations and from Landolt-Bornstein [1927] used in the predictions of mixture viscosities, show that the observed values of pure propane by Landolt-Bornstein [1927] are about 2.0 [μP] higher than those by Stephan and Lucas [1979], while there is no inconsistency for pure propylene. And it is found that the group contribution method compares favorably to the Fuller method [Fuller et al., 1966] for binary diffusion coefficients, and that predictions of this method were comparable to those of Oh and Campbell, and quite better than

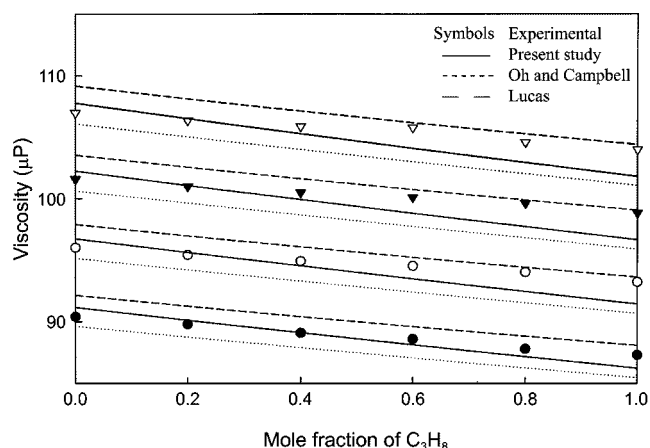


Fig. 4. Comparison of observed and predicted mixture viscosity for propylene+propane mixture.

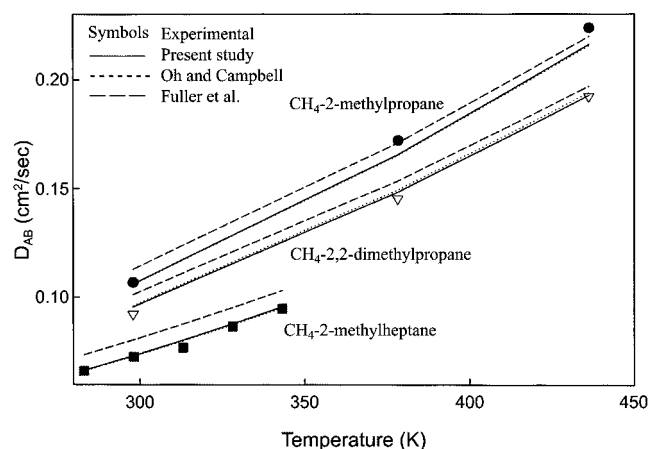


Fig. 5. Comparison of observed and predicted diffusion coefficients for methane-branched alkane mixtures.

those of the Lucas method [Lucas, 1980] for mixture viscosities.

3. Linear Molecular Gases

Here, as a part of systematic program of research on linear molecular gases (N_2 , CO_2 , CO , O_2 , and H_2), functional group parameters and group interaction coefficients for these gases were evaluated by the group contribution model. It is noted here that carbon dioxide and nitrogen were considered in our previous work.

Regarding to consist of a single group for all gases, parameters for these five gas groups were obtained by using second virial coefficient and viscosity data of gas, all of which data were taken from Dymond and Smith [1980]. The evaluated parameter values are

Table 6. Group binary interaction coefficients ($K_{gc,ij}$)

	CH_2	CH_3	CH_0	CH_1	DB- CH_1	DB- CH_2
N_2	0.18120714	0.01184874	0.22094482	0.238548	0.32771862	0.11860204
CO_2	0.18195991	0.11083865	6.8084972	1.1681387	0.34242607	0.35155945
CO	0.14037653	0.01998343	-	-0.4399703	0.40309055	0.27761217
O_2	0.16278568	0.00703636	0.32451504	0.0792222	-	-
H_2	0.2461055	0.2769978	0.22331828	0.04371495	0.020958786	0.40811768

also included in Table 1. With the exception of carbon dioxide, the potential well depth for all gas groups was assumed independent of temperature since the molecule is essentially spherical. Regression results proved it, as expected. Table 2 presents resulting deviations between calculated and experimental second virial coefficients and viscosities for five gases (pure nitrogen, carbon dioxide, carbon monoxide, oxygen, and hydrogen). As shown in Table 2, average root mean square deviation of second virial coefficients for five pure gases was $1 \text{ cm}^3 \text{ mol}^{-1}$ and $2 \text{ cm}^3 \text{ mol}^{-1}$ for this method and for Tsionopoulos, respectively. For the predictions of viscosity, percent relative average deviation between observed and pre-

dicted pure viscosities of linear molecular gases were 1.9% and 2.3% by this method and by Lucas, respectively, indicating that this work is more reliable than the Lucas method.

The obtained group parameters for gases were then used to predict second virial cross coefficients, mixture viscosities, and binary diffusion coefficients for gas-gas mixtures. It is assumed here that group binary interaction coefficients are equal to zero for all gas-gas mixtures. Resulting deviations between experimental data and predictions are shown in Tables 4, 5 and 7 for mixture viscosity and binary diffusion coefficient, and second virial cross coefficient, in order.

Table 7. Deviations between calculated and experimental second virial cross coefficients for gas-hydrocarbon and gas-gas mixtures

Mixtures	Number of points	Average RMSD in B (cm ³ mol ⁻¹)						Data source
		Present study		Oh & Campbell		Tsonopoulos		
		K _{ij,gc} =0	K _{ij,gc} ≠0	K _{ij,gc} =0	K _{ij,gc} ≠0	K _{ij} =0	K _{ij} ≠0	
<i>Nitrogen - normal alkanes</i>								
<u>A. Regression results:</u>								
- ethane	5	5	4	5	5	5	5	[Gunn, 1958]
- n-butane	6	16	5	16	4	20	6	[Gunn, 1958; Hicks and Young, 1968]
- n-pentane	5	25	7	24	7	33	17	[Hicks and Young, 1968; Young, 1968]
- n-hexane	14	33	9	31	10	46	20	[Hicks and Young, 1968; Young, 1968; Cruikshank et al., 1966; Letcher and Marsicano, 1974]
- n-heptane	2	33	2	31	3	50	15	[Young, 1968]
- n-octane	2	40	7	36	8	62	17	[Young, 1968]
- n-decane	6	56	5	48	6	88	20	[D'Avila et al., 1976; Prausnitz and Benson, 1959]
- n-dodecane	4	59	6	48	5	95	10	[D'Avila et al., 1976]
<u>B. Prediction results:</u>								
- methane	3	3	-	-	-	3	-	[Martin et al., 1982]
- methane	7	4	-	-	-	5	-	[Mason and Eakin, 1961; Roe, 1972]
- ethane	5	5	3	-	-	8	6	[Achtermann et al., 1991]
<i>Nitrogen - branched alkanes</i>								
<u>A. Regression results:</u>								
- 2,2-dimethylpropane	7	13	15	14	14	49	12	[Baughman et al., 1975]
- 2,2-dimethylpropane	7	19	14	-	-	62	34	[Baughman et al., 1975]
- 2,2-dimethylpropane	7	17	12	-	-	60	32	[Baughman et al., 1975]
- 2,2-dimethylbutane	5	27	18	29	22	66	19	[Cruikshank et al., 1966; Desty et al., 1962; Everett, 1965; Cruikshank et al., 1968]
- 2,2-dimethylpentane	2	41	54	40	50	38	41	[Desty et al., 1962; Gainey and Pecsok, 1970]
- 3,3-dimethylpentane	2	4	15	6	9	56	6	[Desty et al., 1962; Gainey and Pecsok, 1970]
- 2,2-dimethylhexane	1	13	37	12	32	43	33	[Gainey and Pecsok, 1970]
- 2,2,3,3-tetramethylbutane	1	18	24	17	15	64	9	[Gainey and Pecsok, 1970]
- 2-methylbutane	5	14	8	15	9	29	8	[Young, 1968; Desty et al., 1962; Gainey and Pecsok, 1970]
- 2-methylpentane	4	30	13	31	12	51	12	[Desty et al., 1962; Cruikshank et al., 1968; Gainey and Pecsok, 1970; Young, 1967]

Table 7. Continued

Mixtures	Number of points	Average RMSD in B (cm ³ mol ⁻¹)						Data source
		Present study		Oh & Campbell		Tsonopoulos		
		K _{ij,gc} =0	K _{ij,gc} ≠0	K _{ij,gc} =0	K _{ij,gc} ≠0	K _{ij} =0	K _{ij} ≠0	
- 3-methylpentane	2	25	3	26	3	55	3	[Desty et al., 1962; Gainey and Pecsok, 1970]
- 2,3-dimethylbutane	2	14	0.3	16	4	47	0	[Desty et al., 1962; Gainey and Pecsok, 1970]
- 2-methylhexane	2	29	4	29	6	57	7	[Desty et al., 1962; Gainey and Pecsok, 1970]
- 3-methylhexane	2	34	7	34	7	61	8	[Desty et al., 1962; Gainey and Pecsok, 1970]
- 3-ethylpentane	1	19	14	20	16	56	17	[Desty et al., 1962]
- 2,3-dimethylpentane	2	20	5	21	7	61	5	[Desty et al., 1962; Gainey and Pecsok, 1970]
- 2,4-dimethylpentane	4	25	7	27	7	38	7	[Desty et al., 1962; Cruikshank et al., 1968; Gainey and Pecsok, 1970; Uoung, 1967]
B. Prediction results:								
- 2,2,3-trimethylbutane	2	7	5	-	-	64	30	[Desty et al., 1962; Gainey and Pecsok, 1970]
- 2,2,4-trimethylpentane	2	33	19	-	-	88	48	[Prausnitz and Benson, 1959]
<i>Nitrogen - alkenes</i>								
A. Regression results:								
- ethylene	1	43	8	-	-	10	11	[Edwards and Roseveare, 1942]
- cis-pent-1,3-diene	1	59	2	-	-	22	8*†	[Letcher and Marsicano, 1974]
- n-pent-1-ene	1	22	50	-	-	57	40†	[Cruikshank et al., 1968]
- trans-pent-2-ene	1	75	13	-	-	31	15*†	[Letcher and Marsicano, 1974]
- trans-hexa-1,3-diene	5	60	13	-	-	21	8*†	[Letcher and Marsicano, 1974]
- trans-hexa-1,4-diene	2	53	21	-	-	30	12*‡	[Letcher and Marsicano, 1974]
- cis-hexa-1,3,5-triene	6	60	10	-	-	27	40*‡	[Letcher and Marsicano, 1974]
- hexa-1,5-diene	3	58	6	-	-	25	5*†	[Letcher and Marsicano, 1974]
- trans-hexa-2,4-diene	4	69	15	-	-	12	21*‡	[Letcher and Marsicano, 1974]
- n-hexa-1-ene	5	78	9	-	-	33	10	[Letcher and Marsicano, 1974; Cruikshank et al., 1968]
- trans-hexa-2-ene	2	76	12	-	-	39	16	[Letcher and Marsicano, 1974]
- trans-hexa-3-ene	3	76	7	-	-	40	15	[Letcher and Marsicano, 1974]
- n-hept-1-ene	2	87	13	-	-	42	13	[Young, 1968; Cruikshank et al., 1968]
<i>Carbon dioxide - normal alkanes</i>								
A. Regression results:								
- ethane	7	18	4	16	4	19	18	[Zaalishvili, 1956]
- propane	6	28	4	27	4	35	28	[Gunn, 1958]
- n-butane	4	32	4	31	4	45	31	[Gunn, 1958]
- n-pentane	2	102	26	98	28	142	96	[Massoudi and King, 1973; Sie et al., 1966]
- n-decane	2	164	14	139	14	335	120	[Prausnitz and Benson, 1959]

Higher deviations than those of Lucas were found for N₂-CO₂ mixture, while for N₂-CO₂ mixture excellent agreement was achieved for mixture viscosity predictions. Fig. 6 presents prediction results of mixture viscosity for N₂-H₂ mixtures, showing better predictions

than those from the Lucas method. Table 5 presents that resulting deviations from this method are worse than those of the Fuller method for binary diffusion coefficients. Prediction results of second virial cross coefficient for gas-gas mixtures, in the end of Table 7, show

Table 7. Continued

Mixtures	Number of points	Average RMSD in B (cm ³ mol ⁻¹)						Data source
		Present study		Oh & Campbell		Tsonopoulos		
		K _{ij,gc} =0	K _{ij,gc} ≠0	K _{ij,gc} =0	K _{ij,gc} ≠0	K _{ij} =0	K _{ij} ≠0	
<u>B. Prediction results:</u>								
- methane	2	10	-	-	-	8	-	[Brugge et al., 1989]
- methane	2	10	-	-	-	8	-	[Esper, 1987]
- methane	5	7	-	-	-	5	-	[McElroy et al., 1990]
- methane	3	10	-	-	-	8	-	[Martin et al., 1987]
- methane	1	18	-	-	-	16	-	[Mason and Eakin, 1961]
- ethane	1	20	8	-	-	23	21	[Jaeschke, 1987]
- ethane	1	20	7	-	-	24	21	[Jaeschke, 1988]
- ethane	2	23	7	-	-	27	24	[Brugge et al., 1989]
- ethane	5	17	10	-	-	22	20	[McElroy et al., 1990]
- ethane	1	22	6	-	-	25	23	[Weber, 1992]
- ethane	6	28	9	-	-	35	32	[Holste et al., 1982]
- propane	8	33	14	-	-	44	34	[McElroy et al., 1990]
<i>Carbon dioxide - branched alkanes</i>								
<u>A. Regression results:</u>								
- 2,2-dimethylbutane	1	167	26	183	24	283	212	[Desty et al., 1962]
- 2,2-dimethylpentane	1	191	12	165	13	298	196	[Desty et al., 1962]
- 3,3-dimethylpentane	1	186	9	168	10	312	206	[Desty et al., 1962]
- 2-methylbutane	1	185	36	168	34	219	173	[Desty et al., 1962]
- 2-methylpentane	1	170	37	189	35	271	191	[Desty et al., 1962]
- 3-methylpentane	1	193	32	184	30	268	190	[Desty et al., 1962]
- 2,3-dimethylbutane	1	189	13	205	12	283	189	[Desty et al., 1962]
- 2-methylhexane	1	173	15	188	13	305	189	[Desty et al., 1962]
- 3-methylhexane	1	169	11	184	9	298	189	[Desty et al., 1962]
- 3-ethylpentane	1	173	5	167	8	284	171	[Desty et al., 1962]
- 2,3-dimethylpentane	1	188	34	171	44	283	195	[Desty et al., 1962]
- 2,4-dimethylpentane	1	172	19	186	29	302	194	[Desty et al., 1962]
<u>B. Prediction results:</u>								
- 2,2,3-trimethylbutane	1	172	36	-	-	319	219	[Desty et al., 1962]
- 2,2,4-trimethylpentane	2	66	115	-	-	197	91	[Prausnitz and Benson, 1959]
<i>Carbon dioxide - alkenes</i>								
<u>A. Regression results:</u>								
- 1,3-butadiene	1	78	58	-	-	102	85	[Sie et al., 1966]
<i>Carbon monoxide - normal alkanes</i>								
<u>A. Regression results:</u>								
- propane	11	1	1	-	-	5	1	[McElroy and Moser, 1995]
- n-butane	2	4	1	-	-	10	2	[McElroy and Moser, 1995]
- n-butane	3	2	6	-	-	9	2	[McElroy, 1994]
- n-octane	7	22	5	-	-	40	7	[Everette et al., 1968; Connolly, 1964]
<u>B. Prediction results:</u>								
- methane	1	26	-	-	-	18	-	[Mason and Eakin, 1961]
- ethane	6	1	3	-	-	2	1	[McElory and Ababio, 1994]

comparability of both the present method and Tsonopoulos method. Presents prediction results of second virial cross coefficient for $\text{N}_2\text{-H}_2$ mixture are shown in Fig. 7 with those of the Tsonopoulos method.

4. Mixtures of Hydrocarbons with Linear Molecular Gases

As a continuation of our systematic research on asymmetric mixtures containing hydrocarbons with linear molecular gases (N_2 , CO_2 , CO , O_2 , and H_2), functional group parameters and group interac-

Table 7. Continued

Mixtures	Number of points	Average RMSD in B (cm ³ mol ⁻¹)						Data source
		Present study		Oh & Campbell		Tsonopoulos		
		K _{ij,gc} =0	K _{ij,gc} ≠0	K _{ij,gc} =0	K _{ij,gc} ≠0	K _{ij} =0	K _{ij} ≠0	
<i>Carbon monoxide - branched alkanes</i>								
<u>A. Regression results:</u>								
- 2-methylpropane	5	9	5	-	-	7	8	[McElroy and Moser, 1995; McElroy, 1994]
<i>Carbon monoxide - alkenes</i>								
<u>A. Regression results:</u>								
- ethylene	1	39	0.3	-	-	20	20	[Mason and Eakin, 1961]
- propylene	1	42	0.2	-	-	24	20	[Mason and Eakin, 1961]
<i>Oxygen - normal alkanes</i>								
<u>A. Regression results:</u>								
- n-pentane	1	13	10	-	-	10	19	[Desty et al., 1962]
- n-hexane	1	3	2	-	-	35	9	[Desty et al., 1962]
- n-heptane	1	10	6	-	-	52	9	[Desty et al., 1962]
<i>Oxygen - branched alkanes</i>								
<u>A. Regression results:</u>								
- 2,2-dimethylbutane	1	35	30	-	-	38	0	[Desty et al., 1962]
- 3,3-dimethylpentane	1	26	37	-	-	56	2	[Desty et al., 1962]
- 2-methylbutane	1	9	11	-	-	31	4	[Desty et al., 1962]
- 2-methylpentane	1	22	24	-	-	36	6	[Desty et al., 1962]
- 3-methylpentane	1	30	32	-	-	30	12	[Desty et al., 1962]
- 2,3-dimethylbutane	1	18	22	-	-	36	4	[Desty et al., 1962]
- 2-methylhexane	1	25	27	-	-	52	5	[Desty et al., 1962]
- 3-methylhexane	1	30	32	-	-	46	8	[Desty et al., 1962]
- 3-ethylpentane	1	26	28	-	-	52	5	[Desty et al., 1962]
- 2,3-dimethylpentane	1	17	20	-	-	56	4	[Desty et al., 1962]
- 2,4-dimethylpentane	1	15	18	-	-	54	0.2	[Desty et al., 1962]
<u>B. Prediction results:</u>								
- 2,2,3-trimethylbutane	1	26	23	-	-	57	7	[Desty et al., 1962]
<i>Hydrogen - normal alkanes</i>								
<u>A. Regression results:</u>								
- ethane	1	16	2	-	-	9	7	[Mason and Eakin, 1961]
- propane	1	18	2	-	-	8	4	[Mason and Eakin, 1961]
- n-butane	1	29	4	-	-	17	10	[Mason and Eakin, 1961]
- n-pentane	4	30	4	-	-	16	7	[Mason and Eakin, 1966; Cruikshank et al., 1996; Desty et al., 1962; Everett, 1965]
- n-hexane	2	33	3	-	-	17	4	[Cruikshank et al., 1966; Desty et al., 1962]
- n-octane	11	25	4	-	-	12	7	[Everette et al., 1968; Connelly, 1961]
<u>B. Prediction results:</u>								
- methane	1	5	-	-	-	0.3	-	[Mason and Eakin, 1961]
- methane	6	3	-	-	-	7	-	[Mueller et al., 1961]
- n-heptane	1	72	25	-	-	18	37	[Desty et al., 1962]
- n-decane	2	85	57	-	-	97	66	[Prausnitz and Benson, 1959]

tion coefficients for such mixtures were evaluated by the group contribution model. Up to this point, the group interaction coefficients $k_{ij,gc}$ were assumed to zero for all hydrocarbon mixtures, as indicated by Eq. (9). This assumption would not be expected to apply

when one of the compounds in the mixture is not a hydrocarbon. In this event, a group binary interaction coefficient is required for every possible interaction between a hydrocarbon and a non-hydrocarbon group.

Table 7. Continued

Mixtures	Number of points	Average RMSD in B (cm ³ mol ⁻¹)						Data source
		Present study		Oh & Campbell		Tsonopoulos		
		K _{ij,gc} =0	K _{ij,gc} ≠0	K _{ij,gc} =0	K _{ij,gc} ≠0	K _{ij} =0	K _{ij} ≠0	
<i>Hydrogen - branched alkanes</i>								
<u>A. Regression results:</u>								
- 2,2-dimethylbutane	2	34	8	-	-	31	19	[Cruikshank et al., 1966; Desty et al., 1962]
- 2,2-dimethylpentane	1	9	33	-	-	3	15	[Desty et al., 1962]
- 3,3-dimethylpentane	1	14	31	-	-	7	10	[Desty et al., 1962]
- 2-methylbutane	1	42	17	-	-	35	25	[Desty et al., 1962]
- 2-methylpentane	1	14	15	-	-	6	8	[Desty et al., 1962]
- 3-methylpentane	1	24	5	-	-	17	3	[Desty et al., 1962]
- 2,3-dimethylbutane	1	17	3	-	-	23	10	[Desty et al., 1962]
- 2-methylhexane	1	23	17	-	-	18	36	[Desty et al., 1962]
- 3-methylhexane	1	8	17	-	-	15	32	[Desty et al., 1962]
- 3-ethylpentane	1	5	42	-	-	18	35	[Desty et al., 1962]
- 2,3-dimethylpentane	1	2	39	-	-	12	4	[Desty et al., 1962]
- 2,4-dimethylpentane	1	13	43	-	-	11	6	[Desty et al., 1962]
<u>B. Prediction results:</u>								
- 2,2,3-trimethylbutane	1	0.3	29	-	-	12	4	[Desty et al., 1962]
- 2,2,4-trimethylpentane	4	22	21	-	-	38	24	[Prausnitz and Benson, 1959; Everette et al., 1968]
<i>Hydrogen - alkenes</i>								
<u>A. Regression results:</u>								
- ethylene	1	27	8	-	-	11	10	[Mason and Eakin, 1961]
- propylene	1	37	17	-	-	16	13	[Mason and Eakin, 1961]
- n-pent-1-ene	1	10	17	-	-	13	22	[Cruikshank et al., 1968]
- n-hex-1-ene	1	21	10	-	-	4	16	[Cruikshank et al., 1968]
- n-hept-1-ene	1	38	2	-	-	10	6	[Cruikshank et al., 1968]
<i>Gas - gas</i>								
<i>Nitrogen</i>								
- carbon dioxide	2	2.2	-	-	-	0.8	-	[Brugge et al., 1989]
- carbon dioxide	2	2.3	-	-	-	0.8	-	[Esper, 1987]
- carbon dioxide	1	3.9	-	-	-	7.3	-	[Edwards and Roseveare, 1942]
- carbon dioxide	1	1.0	-	-	-	0.4	-	[Gorski and Miller, 1953]
- carbon dioxide	1	1.4	-	-	-	1.9	-	[Pfefferle et al., 1955]
- carbon dioxide	3	4.2	-	-	-	6.7	-	[Cottrell et al., 1956]
- carbon dioxide	1	4.7	-	-	-	1.2	-	[Mason and Eakin, 1961]
- carbon dioxide	5	1.2	-	-	-	3.6	-	[Gunn, 1958]
<i>Nitrogen</i>								
- oxygen	1	10.3	-	-	-	0.2	-	[Gorski and Miller, 1953]
- oxygen	3	1.6	-	-	-	0.7	-	[Martin et al., 1982]
<i>Nitrogen</i>								
- hydrogen	1	4.2	-	-	-	1.3	-	[Edwards and Roseveare, 1942]
- hydrogen	4	3.3	-	-	-	6.7	-	[Ostronov et al., 1967]
- hydrogen	11	2.7	-	-	-	3.3	-	[Zandbergen and Beenakker, 1967]
- hydrogen	8	3.8	-	-	-	3.3	-	[Brewer and Vaughn, 1969]
<i>Carbon dioxide</i>								
- oxygen	1	6.6	-	-	-	8.0	-	[Edwards and Roseveare, 1942]
- oxygen	1	6.3	-	-	-	4.9	-	[Gorski and Miller, 1953]
- oxygen	3	8.1	-	-	-	7.1	-	[Cottrell et al., 1956]
<i>Carbon dioxide</i>								
- hydrogen	3	2.9	-	-	-	9.3	-	[Cottrell et al., 1956]

*Critical properties were taken from [http://www.pirika.com/chem/TCPEE/TCPE.htm].

† Acentric factors were taken from [http://data-books.com/bussei_e/bs_index.html].

‡ Acentric factors were taken from [http://www.aist.go.jp/RIODB/db030/hy/estimate.html].

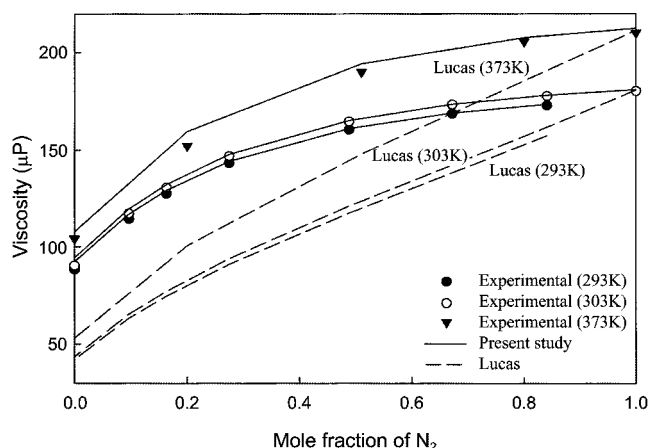


Fig. 6. Comparison of observed and predicted mixture viscosity for nitrogen-hydrogen mixture.

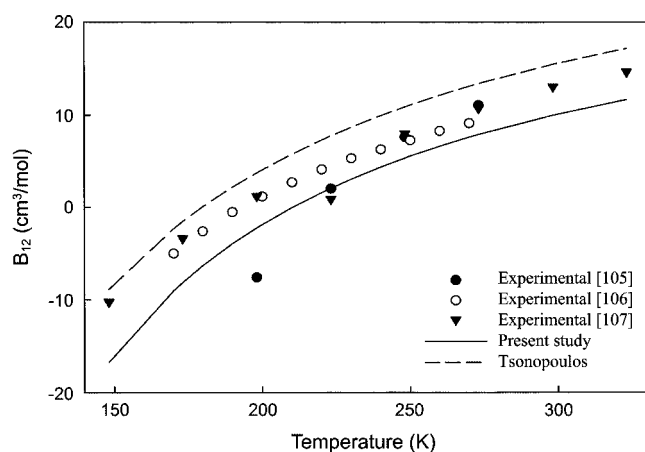


Fig. 7. Comparison of observed and predicted second virial cross coefficients for nitrogen-hydrogen mixture.

As mentioned earlier, the use of non-zero values of interaction coefficient between unlike functional groups is needed for better predictions. Values of the group interaction coefficient $k_{\text{GAS-GC}}$ were evaluated by regressing second virial cross coefficient data for alkane-gas mixtures. For instance, values of $k_{\text{N}_2\text{-CH}_2, \text{GC}}$ and $k_{\text{N}_2\text{-CH}_3, \text{GC}}$ were obtained from the experimental data for nitrogen-normal alkane mixtures. Using these obtained values, $k_{\text{GAS-CH}_1, \text{GC}}$ was next obtained from second virial cross coefficient data of gas-alkane mixture in which the alkane contained one or more CH_1 groups. Next, second virial cross coefficient data for gas-alkane mixtures in which the alkane contains one or more CH_0 groups were used to obtain the value of $k_{\text{GAS-CH}_0, \text{GC}}$. Finally, a similar procedure was followed for gas-alkene mixtures to evaluate $k_{\text{GAS-CH}_1\text{D}, \text{GC}}$ and $k_{\text{GAS-CH}_2\text{D}, \text{GC}}$ simultaneously, which were not examined in our previous work [1997].

With the exceptions of three cases in which no second virial cross coefficient data are available for $k_{\text{CO-CH}_0, \text{GC}}$, $k_{\text{O}_2\text{-DB-CH}_1, \text{GC}}$ and $k_{\text{O}_2\text{-DB-CH}_1, \text{GC}}$, 27 group binary interaction coefficients obtained in this manner are given in Table 6. It is expected that numerical values of the group interaction coefficients would vary from zero to unity. With the exceptions of $k_{\text{CO}_2\text{-CH}_0, \text{GC}}$, $k_{\text{CO}_2\text{-CH}_1, \text{GC}}$ and $k_{\text{O}_2\text{-CH}_1, \text{GC}}$, all values of

the group binary interaction coefficients satisfy this condition. The unrealistically out-bounded values for these three interactions may be due either to uncertainties in the data or to the propagation of uncertainties in previously determined parameter values, as indicated by Oh [1989], or to few data used for parameter estimation, for instance, only two points used for $k_{\text{O}_2\text{-CH}_1\text{D}, \text{GC}}$ and $k_{\text{O}_2\text{-CH}_2\text{D}, \text{GC}}$ in the same regression.

Resulting deviations between calculated and measured second virial cross coefficients of gas-hydrocarbon mixtures are given in Table 7. Also included in this table is one column indicating results of assuming that $k_{ij, \text{gc}}$ is equal to zero. As shown in Table 7, prediction results with non-zero values of binary interaction coefficient are superior to those with $k_{ij, \text{gc}}=0$ for all gas mixtures especially for gas-normal mixtures. But no appreciable improvements were found for mixtures of gas-branched alkane and gas-alkene, which may be due to the same reasons mentioned above.

In the event that binary interaction coefficients were assumed to non-zero, prediction results are comparable for both the group contribution method and the corresponding states method of Tsonopoulos. Results for the Tsonopoulos method with the assumption that $k_{12}=0$ are also given in Table 7. It is interesting to note that the group contribution method with $k_{ij, \text{gc}}=0$ has turned out to be a better predictor of second virial cross coefficients than the Tsonopoulos method with $k_{12}=0$. This is because $k_{ij, \text{gc}}$ in the group contribution model depends only on energetic interactions between groups i and j . It is assumed that values of binary interaction coefficients between methane-gas groups are zero. If critical properties and acentric factors needed for the Tsonopoulos method are not available, they must be estimated. For instance, critical properties for several alkenes indicated in Table 7 were estimated by the Joback method from the www site [http://www.pirilca.com/chem/TCPEE/crjp/joback.htm] and acentric factors for the corresponding alkanes were also obtained from the www site [http://data-books.com/bussei_e/bs_index.html] and [http://www.aist.go.jp/RIODB/db030/hy/estimate.html]. As for the case of $k_{12} \neq 0$ for all five gas mixtures, deviation between experimental data and predictions is almost identical to that obtained from the previous work. In order to show improved predictions with the assumption that the binary interaction coefficient is not zero, a comparison of predicted and measured mixture

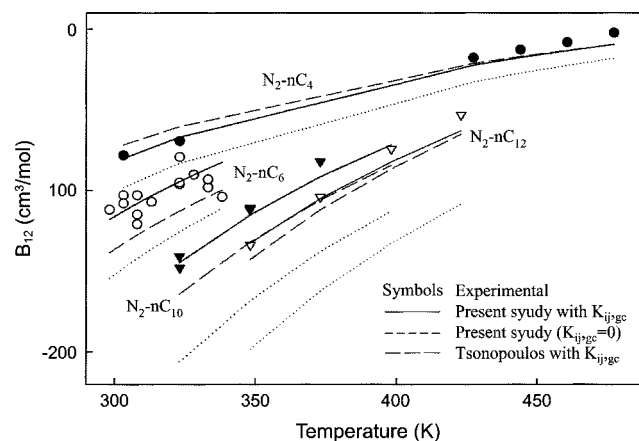


Fig. 8. Comparison of observed and predicted mixture viscosities for nitrogen-normal alkane mixtures.

viscosities is shown in Fig. 8 for nitrogen-normal alkane systems.

For the prediction of mixture viscosities and binary diffusion coefficients for mixtures of hydrocarbons (normal and branched alkanes and alkenes) with linear molecular gases, the group binary interaction coefficients given in Table 6 were used. Table 4 indicates that predicted and experimental mixture viscosities are in very good agreement, showing better predictions with non-zero values of binary interaction coefficient, and that accuracy of the group contribution method exceeds that of the corresponding states method of Lucas. In Table 5, binary diffusion coefficients were predicted with an accuracy, comparable to both the Fuller method and the previous work. No effect of binary interaction coefficient on predictions was found in mixtures of nitrogen and alkanes above n-octane and nitrogen-2,2,3-trimethylheptane mixture, which indicates that experimental data might be in doubt since both the previous work and the Fuller method yield similar results. But in mixtures of carbon dioxide, non-zero values of binary interaction coefficient improve predictions well.

CONCLUSIONS

The group contribution method proposed by Oh and Campbell [1997] for prediction of second virial coefficients and dilute gas transport properties has been repeated with a new set of normal alkane second virial coefficient data either from the recent data for normal C₆ by Dymond et al. [1986], or from the recommendation for C₄, C₇ and C₈ alkanes updated by Tsonopoulos and Dymond [1997]. This method has been extended to molecular linear gases (carbon monoxide, oxygen and hydrogen) and to mixtures of alkanes and those gases.

The functional group parameters are revised from the simultaneous regression of second virial coefficient and viscosity data. Group parameters values (CH₀, CH₁, CH₂, CH₃, CH₄, double-bonded CH₁, double-bonded CH₂, N₂, and CO₂ groups) and 8 binary group interaction parameters ($k_{N_2-CH_0, GC}$, $k_{N_2-CH_1, GC}$, $k_{N_2-CH_2, GC}$, $k_{N_2-CH_3, GC}$, $k_{CO_2-CH_0, GC}$, $k_{CO_2-CH_1, GC}$, $k_{CO_2-CH_2, GC}$ and $k_{CO_2-CH_3, GC}$) were revised.

New group parameter values are given for gases beyond those presented earlier (CO, O₂ and H₂) and 19 group binary interaction parameter values ($k_{N_2-CH_1D, GC}$, $k_{N_2-CH_2D, GC}$, $k_{CO_2-CH_1D, GC}$, $k_{CO_2-CH_2D, GC}$, $k_{CO-CH_1, GC}$, $k_{CO-CH_2, GC}$, $k_{CO-CH_3, GC}$, $k_{CO-CH_1D, GC}$, $k_{CO-CH_2D, GC}$, $k_{O_2-CH_0, GC}$, $k_{O_2-CH_1, GC}$, $k_{O_2-CH_2, GC}$, $k_{O_2-CH_3, GC}$, $k_{H_2-CH_0, GC}$, $k_{H_2-CH_1, GC}$, $k_{H_2-CH_2, GC}$, $k_{H_2-CH_3, GC}$, $k_{H_2-CH_1D, GC}$, $k_{H_2-CH_2D, GC}$) are presented for hydrocarbon mixtures with gases. Three group binary interaction parameter values ($k_{CO-CH_0, GC}$, $k_{O_2-CH_1D, GC}$ and $k_{O_2-CH_2D, GC}$) can not be estimated since no second virial cross coefficient data are available.

Application of the model shows that second virial coefficient data can be represented with results comparable to those obtained by Oh and Campbell [1997] and by the corresponding states method of Tsonopoulos [1974]. The accuracy of the model in viscosity and diffusion coefficient predictions is comparable to both methods of Lucas [1980] and of Fuller [Fuller et al., 1966], respectively.

Prediction results show that the accuracy of the model decreases as molecular size increases. This may be due to the fact that the Chapman-Enskog theory used here does not account for inelastic collisions which become more pronounced with increased number of groups in a molecule. It is also possible that the empirical modification used to extend the Kihara spherical core potential to chain molecules is not accurate as the length of the chain increases. It is

noted that values for the group interaction coefficients $k_{ij, gc}$ were sometimes physically unrealistic, which may be due to uncertainties in experimental data, or to the propagated errors of regression when parameter values were evaluated in advance. Although two of these interaction coefficients had unrealistic values, they were still predicted accurate property values.

A strong advantage of the method is that it is capable of representing several different properties with one set of 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 no data are available in the literature.

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NOMENCLATURE

a	: core radius [Å]
a*	: reduced core radius $[2a/(\sigma - 2a)]$
B	: second virial coefficient [cm ³ mol ⁻¹]
D	: diffusion coefficient [cm ² sec ⁻¹]
k ₁₂	: binary interaction coefficient for Tsonopoulos method
k _{ij, gc}	: group binary interaction coefficient for interactions between intermolecular groups i and j
n	: number of data points
N _{i1}	: number of groups i in molecule 1
N _{j2}	: number of groups j in molecule 2
P	: pressure [atm]

RAD(%): relative average deviation (%), $\frac{100}{n} \sqrt{\sum_{i=1}^n \left(\frac{\eta_{exp,i} - \eta_{cal,i}}{\eta_{exp,i}} \right)^2}$

RMSE: root mean square deviation, $\sqrt{\frac{\sum_{i=1}^n (B_{exp,i} - B_{cal,i})^2}{n}}$

T	: temperature [K]
T*	: reduced temperature, kT/ϵ
V	: molar volume [cm ³ mol ⁻¹]
V _{vdw, ii}	: van der Waals volume of group i [cm ³ mol ⁻¹]
x	: mole fraction

Greek Letters

α	: functional group well depth parameter [J]
β	: functional group well depth parameter [J K]
ε	: potential well depth [J]
η	: viscosity [μP]
ξ	: universal van der Waals volume constant (1.3627) in Eq. (18)
σ	: collision diameter [Å]
Ω _v	: collision integral for viscosity
Ω _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
- AB : interaction property for molecule A and B
- C : critical property
- CH1D : property of double-bonded CH1 group
- CH2D : property of double-bonded CH2 group
- GAS : property of gas group
- GC : property of binary interaction coefficient of group contribution
- mix : mixture property

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