

The Angle-Averaged Pair-Potential Energy Function for Transport Properties of Polar-Nonpolar Gas Mixtures

by

Jae Ho Bae* and T. M. Reed, III**

*Department of Chemical Engineering
University of Florida
Gainesville, Florida*

極性 · 非極性 氣體混合物의 輸送特性에 關한 角平均 雙位置에너지 函數

플로리다 대학교 화학공학과

배 재 호 · 티 엠 리드, III

ABSTRACT

The angle-averaged 12-6-6 pair-potential energy function with temperature-dependent parameters, ϵ^* and γ^* , is applied to polar gas mixtures. The calculation is limited to binary mixtures of a polar and a nonpolar gas since there are no data available for polar-polar mixtures. With simple combining rules for unlike interaction the calculation of viscosity, diffusion, and thermal diffusion factor show very good agreements between experimental and calculated values, comparable to other models for polar or nonpolar molecules. The advantage of this model is that the conventional 12-6 Lennard-Jones integral tables are used with the temperature-dependent parameters.

Introduction

The angle-averaged pair potential energy function,

$$\langle \phi \rangle_{ij} = \epsilon_{ij}^0 \left[(\gamma_{ij}^0 / \gamma)^{12} - 2(\gamma_{ij}^0 / \gamma)^6 \right] - \left[2\mu_i^2 \mu_j^2 \beta / 3 + \mu_i^2 \alpha_j + \mu_j^2 \alpha_i \right] / \gamma^6 \quad (1)$$

has been used⁽¹⁾ successfully for correlating the trans-

port properties of polar molecules in the dilute gas phases. This potential, called the 12-6-6 model, contains the statistically weighted mean potential, averaged over relative molecular orientations, for the classical electrostatic dipole and dipole-induced dipole interaction, together with the Lennard-Jones 12-6 potential for the contributions of the dispersion force interactions. $\langle \phi \rangle_{ij}$ is the total weighted average mutual potential energy of the pair i, j . ϵ_{ij}^0 and γ_{ij}^0 are the constants characteristic of dispersion interaction, μ is the dipole moment, α is the mean polarizability, and $\beta = (kT)^{-1}$.

*Gulf Research & Development Company, P. O. Drawer 2038, Pittsburgh, Pa.

**Dept. of Chem. Eng., Univ. of Florida

Table I. Potential parameter and molecular constants for polar and nonpolar molecules

Molecules	$\epsilon^{\circ}/k., K$	$\gamma^{\circ}, \text{\AA}$	μ, debye	$\alpha, \text{\AA}^3$	$T_1, ^{\circ}K^*$	$T_2, ^{\circ}K^*$	Ref.
NH ₃	168.4	3.842	1.47	2.26	293.58	598.93	1
H ₂ O	200.1	3.439	1.85	1.49	873.16	1273.16	1
SO ₂	257.1	4.702	1.63	3.72	290.56	432.66	1
HCl	256.9	3.910	1.08	2.63	323.16	524.16	1
CH ₂ Cl ₂	352.6	5.464	1.57	6.48	295.2	582.6	1
C ₂ H ₅ OH	283.3	5.276	1.69	5.62	443.86	551.36	1
(CH ₃) ₂ CO	154.9	6.376	2.88	6.33	308.16	579.56	1
H ₂	37.0	3.287	—	0.79			3
N ₂	91.5	4.132		1.76			3
O ₂	113.0	3.853		1.60			3
CH ₄	144.0	4.261		2.60			3
C ₂ H ₄	205.0	4.750		4.26			3
CO ₂	190.0	4.485		2.65			3
CCl ₄	327.0	6.601		10.50			3
He	10.22	2.869		0.204			3
Ne	35.7	3.131		0.393			3
Ar	124.0	3.837		1.626			3

*Viscosities at these temperatures were used to evaluate the parameters $\epsilon^{\circ}/k.$ and γ° .

Table II Viscosities of binary mixtures

System	T ^o K	X polar*	$\eta \times 10^7$	calc.-expt. % dev.	Ref.	System	T ^o K	X polar*	$\eta \times 10^7$	calc.-expt. % dev.	Ref.		
NH ₃ +H ₂	293.16	0.9005	1003	-0.1	15				0.2920	2306	-0.4		
		0.7087	1045	-0.2					0.1111	2409	0.0		
		0.5177	1080	0.0					523.16	0.8883	2013	-3.8	
		0.2975	1088	+0.1						0.7147	2169	-2.7	
		0.2239	1073	+0.1						0.5638	2291	+1.8	
	373.16	0.1082	1013	+0.2	15				0.2920	2480	-0.8		
		0.9005	1335	+2.8					0.1111	2583	-0.4		
		0.7087	1361	+2.1					NH ₃ +O ₂	293.16	0.8755	1139	-0.3
		0.5177	1372	+1.3							0.7079	1343	-0.5
		0.2975	1338	+0.7							0.4786	1602	-0.1
	473.16	0.2239	1303	+0.3	15				0.2986	1783	0.0		
		0.1082	1207	+0.2					0.1351	1927	+0.2		
		0.9005	1726	+4.0					373.16	0.8755	1489	+2.1	
		0.7087	1730	+3.0						0.7079	1707	+1.0	
		0.5177	1711	+2.1						0.4786	1982	+0.5	
523.16	0.2975	1627	+1.1	15				0.2986	2174	+0.2			
	0.2239	1572	+0.8					0.1351	2329	+0.1			
	0.1082	1438	+0.4					473.16	0.8755	1896	+3.0		
	0.9005	1906	+4.4						0.7079	2123	+1.8		
	0.7087	1900	+3.43						0.4786	2409	+0.8		
NH ₃ +N ₂	293.16	0.5177	1865	+2.3	15				0.2986	2611	+0.3		
		0.2975	1756	+1.1					0.1351	2778	+0.2		
		0.2239	1690	+0.7					NH ₃ +CH ₄	287.66	0.9	990	-1.8
		0.1082	1438	+0.4							0.8	1019	-1.9
		0.9005	1906	+4.4							0.7	1043	-1.7
	373.16	0.7087	1730	+3.0	15				0.6	1063	-1.3		
		0.5177	1711	+2.1					0.5	1078	-1.2		
		0.2975	1627	+1.1					0.4	1087	-1.1		
		0.2239	1572	+0.8					0.3	1092	-1.2		
		0.1082	1438	+0.4					0.2	1090	-1.3		
	473.16	0.9005	1906	+4.4	15				0.1	1083	-1.5		
		0.7087	1730	+3.0					NH ₃ +C ₂ H ₄	293.16	0.8867	1013	+1.2
		0.5177	1711	+2.1							0.8071	1030	+1.7
		0.2975	1627	+1.1							0.6961	1047	+2.4
		0.2239	1572	+0.8					0.5172	1058	+2.7		
0.1082	1438	+0.4	0.2993	1049	+2.1								

*X=mole fraction

It was shown in reference 1 that the dispersion attraction constant $\epsilon^0\gamma^{06}$ obtained empirically from gas

Table I (Continued)

System	T °K	X polar*	$\eta \times 10^7$	calc. expt. %dev.	Ref.
HCl+H ₂	373.16	0.1096	1027	+1.2	15
		0.8867	1335	+3.2	
		0.8071	1342	+3.2	
		0.6961	1345	+3.1	
		0.5172	1338	+2.7	
		0.2993	1312	+1.6	
	473.16	0.1096	1277	+0.6	15
		0.8867	1712	+3.9	
		0.8071	1704	+3.4	
		0.6961	1689	+3.1	
		0.5172	1657	+2.2	
		0.2993	1609	+0.9	
	523.16	0.1096	1561	0.0	15
		0.8867	1886	+4.3	
		0.8071	1871	+3.7	
		0.6961	1848	+3.2	
		0.5172	1805	+2.3	
		0.2993	1747	+1.0	
	294.6	0.1096	1693	+0.2	17
		0.8220	1451	-0.7	
		0.7179	1459	-0.6	
		0.5042	1460	-0.7	
		0.2031	1331	-0.8	
		0.8220	1617	-0.6	
327.16	0.7179	1623	-0.6	17	
	0.5042	1614	-0.7		
	0.2031	1451	-1.4		
	0.8220	1839	-0.5		
	0.7179	1840	-0.8		
	0.5042	1816	-0.8		
372.16	0.2031	1607	-1.4	17	
	0.8417	2099	0.0		
	0.6989	2094	-0.5		
	0.5092	2057	+0.2		
	0.2409	1855	-0.6		
	0.8416	2307	-0.2		
473.16	0.6989	2296	-0.3	17	
	0.5092	2245	-0.7		
	0.2409	2008	-0.8		
	0.7947	2520	-0.3		
	0.6312	2489	-0.7		
	0.5178	2446	-0.3		
523.16	0.2991	2256	-1.1	17	
	0.9	1426	-2.3		
	0.8	1437	-2.4		
	0.7	1445	-2.6		
	0.6	1451	-2.7		
	0.5	1456	-2.9		
291.16	0.4	1459	-2.9	18	
	0.3	1460	-2.9		
	0.2	1459	-2.7		
	0.1	1457	-2.5		
	0.8215	1273	-1.5		
	0.5075	1333	-1.3		
290.16	0.2963	1346	-1.7	18	
	0.2286	1330	-1.0		

viscosity was essentially that required by the dispersion force theory of Mavroyannis and Stephen⁽²⁾ for

System	T °K	X polar*	$\eta \times 10^7$	calc. expt. %dev.	Ref.
HCl+CO ₂	318.16	0.1676	1294	-0.8	18
		0.8028	1409	-1.1	
		0.5075	1492	-0.9	
		0.2963	1464	-1.3	
		0.2286	1441	-0.8	
		0.1676	1397	-0.9	
	343.16	0.8028	1527	-0.5	18
		0.6999	1545	-0.8	
		0.6175	1559	-1.0	
		0.4823	1577	-0.6	
		0.2963	1568	-1.8	
		0.2306	1540	-0.7	
365.16	0.1676	1487	-0.9	18	
	0.1657	1485	-1.3		
	0.8028	1628	-0.3		
	0.6999	1646	-0.1		
	0.6175	1659	-1.0		
	0.4823	1674	-0.5		
397.16	0.2306	1624	-1.0	18	
	0.1676	1564	-0.6		
	0.1657	1562	-1.0		
	0.6760	1793	-0.2		
	0.4698	1813	-0.1		
	0.3265	1796	-0.3		
432.16	0.1636	1673	-0.7	18	
	0.6760	1946	+0.2		
	0.4698	1960	0.0		
	0.3265	1934	-0.4		
	0.1676	1797	-0.3		
	0.1512	1769	+1.2		
472.16	0.6760	2115	-0.1	18	
	0.4905	2123	+0.1		
	0.3265	2085	-0.6		
	0.1512	1893	-3.1		
	0.9	1262	-2.0		
	0.8	1289	-2.1		
288.96	0.7	1316	-1.6	16	
	0.6	1340	-1.7		
	0.5	1364	-1.4		
	0.4	1385	-1.6		
	0.3	1404	-1.7		
	0.2	1421	-1.8		
293.15	0.1	1434	-2.0	19	
	0.8425	987	-3.3		
	0.6985	989	-2.7		
	0.5014	988	-2.5		
	0.3114	985	-1.5		
	0.1484	981	-1.0		
353.16	0.6739	1196	-1.3	19	
	0.3649	1190	-0.1		
413.43	0.8485	1403	-1.5	19	
	0.7118	1401	-0.1		
	0.5264	1396	-1.1		
	0.2904	1387	+0.4		
	0.1261	1380	+0.9		

Table II. Diffusion coefficient of binary mixtures

System	T°K	D ₁₂	calc. -expt. % dev.	Ref.	System	T°K	D ₁₂	calc. expt. % dev.	Ref.			
H ₂ O+H ₂	293.11	0.828	-2.6	20	H ₂ O+C ₂ H ₄	352.26	0.331	-7.0	21			
	322.66	0.981	-3.0			307.76	0.186	-8.8				
	365.56	1.221	-1.0			328.46	0.211	-9.4				
	372.50	1.261	-1.6			52.56	0.241	-2.4				
	307.26	0.900	-11.8	21		H ₂ O+He	307.16	0.880		-2.4	21	
	328.56	1.013	-9.6	21			328.16	0.984		-2.7		
	352.66	1.147	-4.4				352.46	1.109		-1.1		
	307.16	0.900	-1.6	22			298.16	0.837		-7.8		
	H ₂ O+N ₂	328.66	1.014	+5.5			NH ₃ +H ₂	298.16		0.785	+0.3	4
		307.56	0.254	-0.8		21		328.16		0.927	-1.7	
328.56		0.287	-5.3		358.16	1.078		-1.4				
352.16		0.326	-9.2		263.0	0.630		+10.5				
328.96		0.288	-8.0	22	328.0	0.926		+2.9				
349.16		0.321	-9.3		395.0	1.276		-5.5				
H ₂ O+O ₂	308.06	0.258	-8.5	21	NH ₃ +N ₂	473.0	1.734	-6.3	4			
	328.96	0.292	-8.2			298.16	0.229	-4.3				
	352.36	0.331	-6.0			328.16	0.272	-4.6				
	400.00	0.417	-13.1	7		358.16	0.318	-3.0				
	500.00	0.621	-8.7			SO ₂ +H ₂	285.56	0.528		+0.6	25	
	700.00	1.118	-6.8				263.00	0.456		+6.0		
	900.00	1.718	-6.6				263.00	0.657		+7.7		
	1050.00	2.230	-6.7				473.00	1.272		+3.4		
	H ₂ O+CO ₂	296.11	0.175	+6.7		20	SO ₂ +N ₂	263.00		0.101	-2.9	24
		365.56	0.261	+5.2			SO ₂ +CO ₂	263.00		0.069	+7.8	24
372.54		0.270	+4.2		343.00	0.116	+7.4					
307.46		0.188	-6.9	21	473.00	0.212	+8.7					
328.56		0.213	+0.9		C ₂ H ₅ OH+H ₂	340.16	0.623	+6.3	20			
352.36		0.243	-0.8			C ₂ H ₅ OH+CO ₂	340.16	0.107		+1.0		
328.66		0.213	+7.6	22		C ₂ H ₅ OH+He	298.16	0.459		-7.1		
H ₂ O+CH ₄	307.66	0.257	-12.1	21	(CH ₃) ₂ CO+H ₂	296.16	0.411	-3.1	20			
	328.76	0.291	-12.1									

small molecules (NH₃, H₂O, HCl) and within a factor of approximately 2 for larger polar molecules (e. g. CHCl₃, CH₃OH, C₂H₅OH).

In the present paper this potential is applied to binary mixtures containing polar gases, specifically to polar-nonpolar mixtures since no data exist for polar-polar mixtures.

The potential, Eq. (1), may be arranged into the familiar 12-6 form

$$\langle \phi \rangle_{ij} = \epsilon^*_{ij} \left[(\gamma^*_{ij}/\gamma)^{12} - 2(\gamma^*_{ij}/\gamma)^6 \right] \quad (2)$$

in which the parameters ϵ^*_{ij} and γ^*_{ij} are functions of temperature.

$$\epsilon^*_{ij} = \epsilon^0_{ij} \left[1 + \mu_i^2 \mu_j^2 \beta / 3 \epsilon^0_{ij} \gamma^0_{ij} + (\mu_i^2 \alpha_j + \mu_j^2 \alpha_i) / 2 \epsilon^0_{ij} \gamma^{05}_{ij} \right]^2 \quad (3)$$

$$\gamma^*_{ij} = \gamma^0_{ij} (\epsilon_{ij} / \epsilon^*_{ij})^{1/2} \quad (4)$$

In this form the usual 12-6 integral tables may be used to evaluate properties once values for ϵ^0_{ij} , γ^0_{ij}

and the dipole moments and polarizabilities are assigned to the pair i, j .

Combining Rules for Potential Parameters

The unlike-pair interactions may be approximated from those for like-pairs. It is clear from Eq. (3) that ϵ^*_{ij} can not be a geometric mean of ϵ^*_{ii} and ϵ^*_{jj} . The dispersion force parameter ϵ^0_{ij} is expected to be close to geometric mean of ϵ^0_{ii} and ϵ^0_{jj} and the arithmetic mean rule is used for γ^0_{ij} .

$$\epsilon^0_{ij} = (\epsilon^0_{ii} \epsilon^0_{jj})^{1/2} \quad (5)$$

$$\gamma^0_{ij} = (\gamma^0_{ii} + \gamma^0_{jj}) / 2 \quad (6)$$

Using dipole moments and polarizabilities, ϵ^*_{ij} and γ^*_{ij} can be calculated by Eqs. (3) and (4).

When one member of the pair is nonpolar, ϵ^*_{ij} and γ^*_{ij} are no longer temperature dependent since the term in $\mu_i^2 \mu_j^2$ is then zero. Nevertheless, ϵ^*_{ij} is not a geometric mean since the dipole-induced dipole

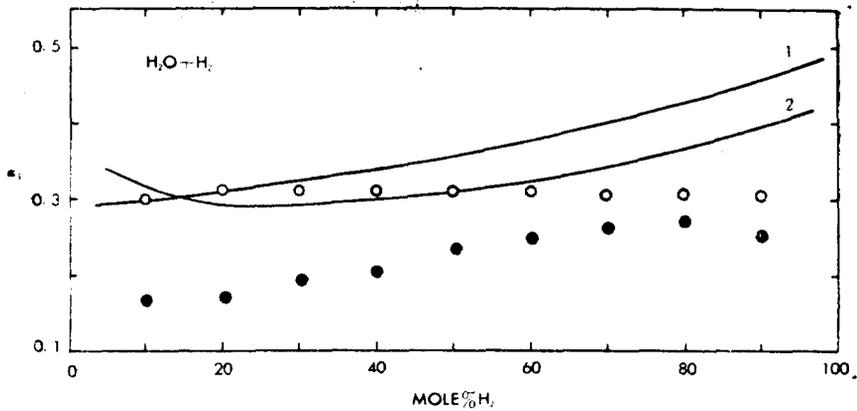


Fig. 1. Thermal diffusion factors for $\text{H}_2\text{O}-\text{H}_2$ system. Curve 1 and open circles refer to calculated and experimental values at 566°K , and curve 2 and solid circles to those at 368°K

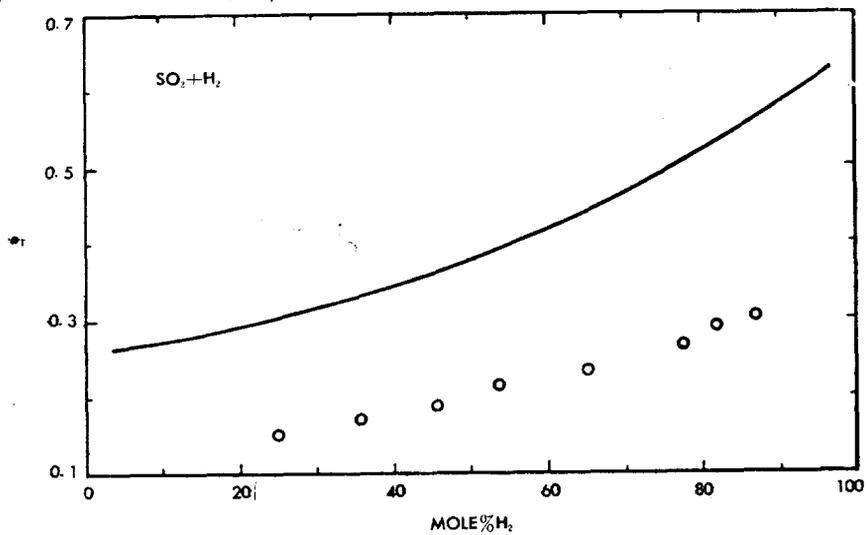


Fig. 2. Thermal diffusion factors for SO_2+H_2 system at 376°K . Curve refers to the calculated values and circles experimental values

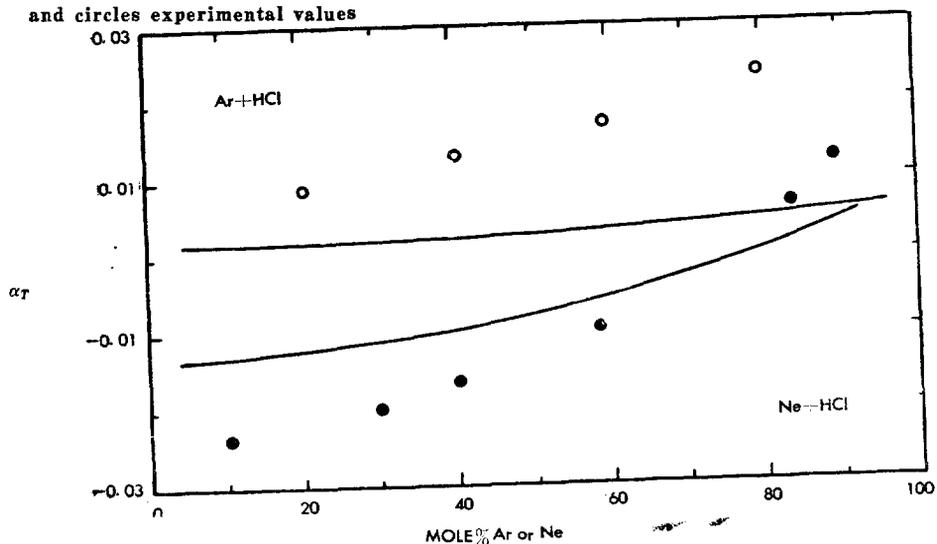


Fig. 3. Thermal diffusion factors for $\text{Ar}+\text{HCl}$ and $\text{Ne}+\text{HCl}$ system at 383°K . Curve 1 and open circles refer to the calculated and experimental values for $\text{Ar}+\text{HCl}$, respectively, curve 2 and solid circles refer to $\text{Ne}+\text{HCl}$

interaction is included in the potential.

Calculations

Making use of the combining rules in Eqs. (5) and (6) and the empirical values, previously obtained from gas viscosities, of ϵ^0 and γ^0 in like-pair interactions, the viscosity, diffusion coefficient, and thermal diffusion factor were calculated and compared with experimental properties for the binary systems in Tables II, III and Figures 1, 2, and 3. The potential parameters used in the calculation are given in Table I along with dipole moments and polarizabilities. Also the two temperatures used in the determination of the like-pair parameters for polar molecules are included. Thermal conductivity is not considered here because of its dependence on the internal energy transfer.

Viscosity

From kinetic theory the expression for the viscosity of binary mixture can be written as⁽³⁾

$$\eta_m = \frac{1-Z}{X+Y} \quad (7)$$

$$X = \frac{x_1^2}{n_1} + \frac{2x_1x_2}{n_{12}} + \frac{x_2^2}{n_2}$$

$$Y = \frac{3}{5} A^*_{12} \left\{ \frac{x_1^2}{n_1} \left(\frac{M_1}{M_2} \right) + \frac{2x_1x_2}{n_{12}} \left(\frac{M_1+M_2}{4M_1M_2} \right) \left(\frac{n_{12}^2}{n_1n_2} \right) + \frac{x_2^2}{n_2} \left(\frac{M_2}{M_1} \right) \right\}$$

$$Z = \frac{3}{5} A^*_{12} \left\{ x_1^2 \left(\frac{M_1}{M_2} \right) + 2x_1x_2 \left[\left(\frac{M_1+M_2}{4M_1M_2} \right) \left(\frac{n_{12}}{n_1} + \frac{n_{12}}{n_2} \right) - 1 \right] + x_2^2 \left(\frac{M_2}{M_1} \right) \right\}$$

where x is mole fraction of the component, M molecular weight and A^*_{12} is the ratio of collision integrals, $\Omega^{*(1,2)}$ over $\Omega^{*(2,2)}$, for the unlike interaction. n_i is viscosity of pure component i and n_{12} is the hypothetical viscosity due to the unlike pair interaction.

In Table II the calculated viscosities and the deviations from experimental data are presented. The average deviation of calculated values from experiment is about 1.3% which favorably compares with the results of Mason and Monchick.⁽⁴⁾ The agreement is within experimental error and not worse than those of the 12-6 potential⁽⁵⁾ or modified Buckingham model⁽⁵⁾⁽⁶⁾ for nonpolar spherical molecules.

Diffusion

The diffusion coefficient of binary mixtures, D_{12} ,

is calculated by⁽³⁾

$$D_{12} = \frac{0.002628(T^3/2m)^{1/2}}{P\sigma_{12}^2\Omega^{*(1,1)}} \quad (8)$$

where m is reduced molecular weight, P the pressure in atmosphere, T in $^\circ K$, and σ the separation at zero potential in \AA . The calculated values are compared with experiment in Table III. The average deviation of calculated values from experimental data is about 5.5% which again confirms that this model is as good as either the 12-6 potential or the modified Buckingham model for nonpolar molecules.

It is interesting to compare the parameters for $H_2O + O_2$ system with those obtained by others. The values by Eqs. (3) and (4) are $\sigma_{12} = 3.49 \text{\AA}$ and $\epsilon^*_{12}/k = 167.7^\circ K$ which lie between Mason and Monchick's⁽⁵⁾ ($\sigma_{12} = 3.072 \text{\AA}$, $\epsilon^*_{12}/k = 239^\circ K$.) for the Stockmayer potential and Walker and Westernberg's⁽⁷⁾ ($\sigma_{12} = 3.335 \text{\AA}$, $\epsilon_{12}/k = 80^\circ K$.) for the 12-6 potential. The systems involving H_2O as one component shows improved agreement with experiment over Mason and Monchick's results.

Thermal Diffusion Factor

The thermal diffusion factor is a complex function of temperature, concentration and molecular interaction. It is hard to predict this property theoretically. Two approximations are those of Chapman-Cowling⁽⁸⁾ and Kihara-Mason.⁽⁹⁾⁽¹⁰⁾ Kihara's first approximation was used because of its simplicity. This is known to give more accurate results than Chapman-Cowling's first approximation and differs from the second approximation by a few percent. In Kihara's first approximation, the thermal diffusion factor, α_T , is written as

$$\alpha_T = (6C^*_{12} - 5) \frac{x_1S_1 - x_2S_2}{x_1^2 Q_1 + x_2^2 Q_2 + x_1x_2 Q_{12}} \quad (9)$$

$$S_1 = \frac{M_1}{M_2} \left(\frac{2M_2}{M_1+M_2} \right)^{1/2} \left[\frac{\Omega^*_{11}(2,2)}{\Omega^*_{12}(1,1)} \right] \left[\frac{\gamma^*_{11}}{\gamma^*_{12}} \right] - \left[\frac{4M_1M_2}{(M_1+M_2)^2} \right] A^*_{12} - \frac{15M_2(M_2-M_1)}{2(M_1+M_2)^2}$$

$$Q_1 = \frac{2}{M_2(M_1+M_2)} \left(\frac{2M_2}{M_1+M_2} \right)^{1/2} \times \left[\frac{\Omega^*_{11}(2,2)}{\Omega^*_{12}(1,1)} \right] \left[\frac{\gamma^*_{11}}{\gamma^*_{12}} \right]^2 \times \left(M_1^2 + 3M_2^2 + \frac{8}{5} M_1M_2A^*_{12} \right)$$

$$Q_{12} = \frac{15(M_1-M_2)^2}{(M_1+M_2)^2} + \left[\frac{32M_1M_2}{(M_1+M_2)^2} \right] A^*_{12} + \frac{8}{5} \frac{(M_1M_2)^{1/2}}{(M_1M_2)^{1/2}} \left[\frac{\Omega^*_{11}(2,2)}{\Omega^*_{12}(1,1)} \right] \left[\frac{\Omega^*_{22}(2,2)}{\Omega^*_{12}(1,1)} \right] \left[\frac{\gamma^*_{11}\gamma^*_{22}}{\gamma^*_{12}^2} \right]^2$$

Similarly, S_2 and Q_2 are obtained from S_1 and Q_1 by an interchange of subscripts on the collision integral and the separation at potential minimum, γ^* , refer to the different binary interactions and C_{12}^* is the ratio of collision integrals, $\Omega_L^{*(1,2)}$ over $\Omega_L^{*(1,1)}$, for the unlike interaction.

The experimental data for the systems H_2O+H_2 ⁽¹¹⁾, SO_2+H_2 ⁽¹²⁾, $Ar+HCl$ ⁽¹³⁾ and $Ne+NH_3$ ⁽¹⁴⁾ are compared with calculated values in Figures 1, 2, and 3. The overall agreement is fair and compares with other calculations for polar gases. For the H_2O+H_2 system the data of Whalley seems too uncertain with the trend of the calculated values. However, the $Ne+NH_3$ system shows a good agreement and the inversion point is correctly predicted as shown in Figure 3.

Discussion

It can be said from the results that the 12-6-6 potential can be used for polar gas mixtures with success. The 12-6-6 model gives correlation at least as good as, or better than the more elaborate model of Monchick and Mason for mixtures containing polar gases. When comparing the result on viscosities of binary mixtures between these two models one should bear in mind that Monchick and Mason used the experimental data for pure components to force the calculated values to fit at both ends of the composition range. When the calculated viscosity was used for one component in $H_2+(C_2H_5)_2O$ system the deviation was the largest among all the system used in their calculation.

In the case of those systems containing NH_3 as one component, the deviation is the largest at the polar end of composition. This arises from the fact that when the parameters for NH_3 were obtained from the viscosities at two different temperatures, T_1 and T_2 , given in Table I the deviations at other temperatures were rather large. Thus, at low temperatures near those used in the fit, this trend disappears.

As the agreement is not very good for the thermal diffusion factor which is the most sensitive to the unlike interaction it is suggested that the combining rules can be refined to give better agreement between experiment and calculation. However, the agreement in the diffusion and viscosity does not warrant any further complications in the combining rules.

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