

## Notes on Updated Diffusion Coefficients\*

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The need to update the diffusion coefficients stems from the theoretical understanding that the repulsive part of the Lennard-Jones (L-J) 12-6 potential function is too stiff to accurately account for diffusion coefficients at high temperatures [1]. Replacing the repulsive part of the potential by a softer, exponential function led to an increase in most of the diffusion coefficients involving H and H<sub>2</sub> [1] from those predicted by the Sandia Transport subroutine library [2]. Recent studies [3,4] showed that even the exponential function may be too restricted and suggested that the diffusion coefficients of key pairs be directly modeled without resorting to the use of tabulated L-J 12-6 collision integrals.

In this work an update for diffusion coefficients is provided for selected pairs. Within the framework of Sandia PREMIX [5] and similar codes, implementing these updates is quite easy and adequate, even if diffusion coefficients are available for only a few pairs. The current updates are based on Refs. 3, 4, and 6-9 (see Table 1). These diffusion coefficients were obtained from the potential functions directly calculated from high-level quantum chemistry calculations, and in many cases, compared to available experimental data.

To use these diffusion coefficients in flame modeling, the temperature dependence of binary diffusion coefficients at 1 atm was fitted, as in Ref. 2, by

$$\ln D_{ij} = d_0 + d_1 \ln T + d_2 (\ln T)^2 + d_3 (\ln T)^3,$$

where  $d_k$  ( $k=0,3$ ) is the polynomial coefficient, tabulated in Table 1 for selected pairs. For the mixture-averaged transport formulation, the above polynomial is sufficient for flame simulations. The multi-component transport formulation as well as the computation of thermal diffusion ratio in both transport formulations, however, requires the input of the ratios of collision integrals [2,10], i.e.,  $A_{ij}^* = \Omega_{ij}^{(2,2)} / (2\Omega_{ij}^{(1,1)})$ ,  $B_{ij}^* = (5\Omega_{ij}^{(1,2)} - \Omega_{ij}^{(1,3)}) / (3\Omega_{ij}^{(1,1)})$  and  $C_{ij}^* = \Omega_{ij}^{(1,2)} / (3\Omega_{ij}^{(1,1)})$ . These ratios are given for each pair in the following forms,

$$A_{ij}^* = a_0 + a_1 \ln T_{ij}^* + a_2 (\ln T_{ij}^*)^2 + a_3 (\ln T_{ij}^*)^3,$$

$$B_{ij}^* = b_0 + b_1 \ln T_{ij}^* + b_2 (\ln T_{ij}^*)^2 + b_3 (\ln T_{ij}^*)^3,$$

$$C_{ij}^* = c_0 + c_1 \ln T_{ij}^* + c_2 (\ln T_{ij}^*)^2 + c_3 (\ln T_{ij}^*)^3,$$

where  $a_k$ ,  $b_k$ , and  $c_k$  ( $k=0,3$ ) are the polynomial coefficients whose values are found in Table 1, and  $T_{ij}^*$  is the reduced temperature determined by the collision well depth  $\varepsilon_{ij}$  as  $T_{ij}^* = kT / \varepsilon_{ij}$ .

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\* Middha, P. and Wang, H. "First-principle calculation for the high-temperature diffusion coefficients of small pairs: the H-Ar case." *Combustion Theory and Modeling* **9**, pp. 353-363 (2005).

Table 1  
Summary of polynomial coefficients for updated binary diffusion coefficients and ratios of collision integrals

Pair	Diffusion coefficients, $D_{ij}$				Ref. <sup>a</sup>	$A_{ij}^*$			
	$d_0$	$d_1$	$d_2 \times 10^2$	$d_3 \times 10^3$		$a_0$	$a_1 \times 10$	$a_2 \times 10^2$	$a_3 \times 10^3$
H-He	-9.6699	2.1002	-7.7060	5.4611	[3]	0.93003	0.80150	-0.94733	0.63459
H-Ar	-9.0511	1.6161	-0.2878	1.3054	[4]	0.68819	1.53423	-1.76995	0.88796
H-H <sub>2</sub>	-11.7498	3.1507	-25.7472	15.8916	[3]	0.68565	1.53390	-1.36735	0.32210
H-O <sub>2</sub>	-11.0410	2.4043	-10.2797	5.3264	[6]	1.29254	-1.84989	4.27103	-2.60823
H-N <sub>2</sub>	-13.2703	3.5187	-29.6649	16.4314	[7]	1.33865	-0.85454	0.92291	0.04406
H <sub>2</sub> -He	-12.7513	3.4244	-28.4726	15.9317	[3]	0.59534	2.07809	-2.48477	1.00128
H <sub>2</sub> -N <sub>2</sub>	-10.9994	2.2026	-8.1155	4.4061	[8]	1.31648	-1.32021	2.41620	-1.20259
H <sub>2</sub> -H <sub>2</sub>	-9.9610	2.0560	-6.4977	4.1368	[9]	1.32209	-1.20749	2.20471	-1.05955

  

	$B_{ij}^*$				$C_{ij}^*$			
	$b_0$	$b_1 \times 10$	$b_2 \times 10^2$	$b_3 \times 10^3$	$c_0$	$c_1 \times 10$	$c_2 \times 10^2$	$c_3 \times 10^3$
H-He	0.87638	1.02383	-1.48030	0.98804	1.06002	-0.59928	1.02650	-0.73451
H-Ar	0.69683	1.71580	-2.43568	1.36548	0.67027	1.14334	-1.50407	0.51876
H-H <sub>2</sub>	0.67795	1.37471	-1.10587	0.16577	0.65119	0.82160	-0.43894	-0.27358
H-O <sub>2</sub>	1.99270	-2.72201	2.05951	0.16444	1.27566	-2.27862	4.44995	-2.74619
H-N <sub>2</sub>	-2.20300	15.91601	-25.33938	13.64477	1.27616	-2.25934	4.64183	-3.10151
H <sub>2</sub> -He	0.67715	1.35792	-1.14253	0.18886	0.65192	0.83651	-0.44501	-0.25987
H <sub>2</sub> -H <sub>2</sub>	3.63140	-11.39793	16.94208	-8.12678	1.29811	-1.78141	2.95671	-1.70201
H <sub>2</sub> -N <sub>2</sub>	1.94230	-4.19106	6.71192	-3.36850	1.29073	-1.93012	3.39899	-1.96836

<sup>a</sup> The fits are based on diffusion coefficients directly taken from the referenced paper, or those computed using the potential functions given in the referenced paper.

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