Supporting Information: Engineering Model for Predicting the Intra-Diffusion Coefficients of Hydrogen and Oxygen in Vapor, Liquid and Supercritical Water based on Molecular Dynamics Simulations

Ioannis N. Tsimpanogiannis*,† Samadarshi Maity,‡ Alper T. Celebi,‡ and Othonas A. Moultos*,‡

†*Chemical Process & Energy Resources Institute (CPERI), Centre for Research & Technology Hellas (CERTH), 57001, Thermi-Thessaloniki, Greece*

‡*Engineering Thermodynamics, Process & Energy Department, Faculty of Mechanical, Maritime and Materials Engineering, Delft University of Technology, Leeghwaterstraat 39, 2628CB Delft, The Netherlands*

E-mail: o.moultos@tudelft.nl,i.n.tsimpanogiannis@certh.gr

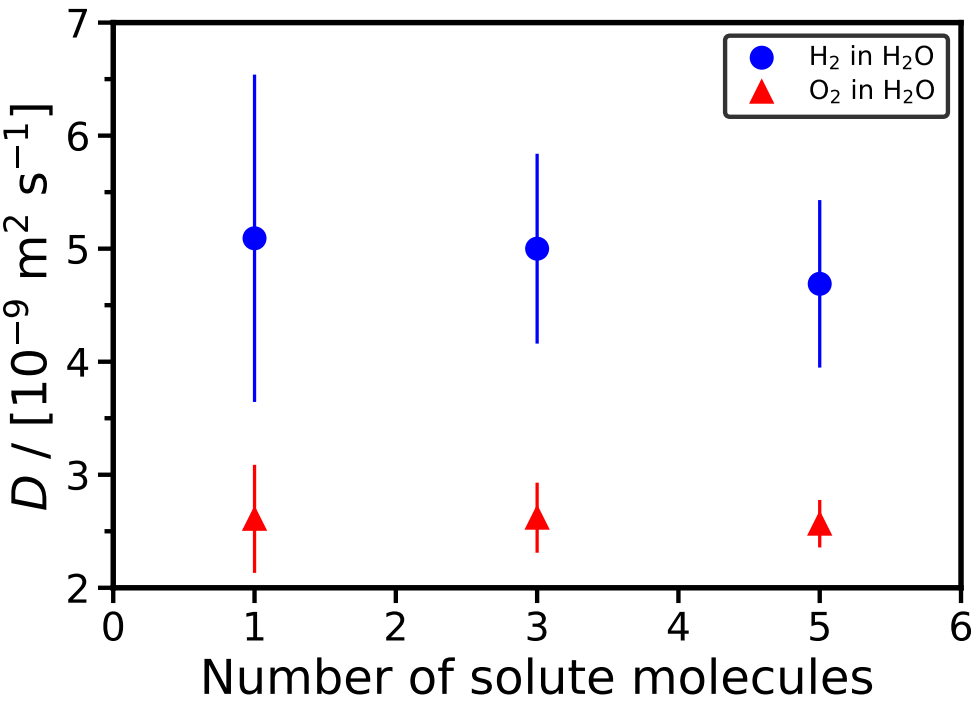
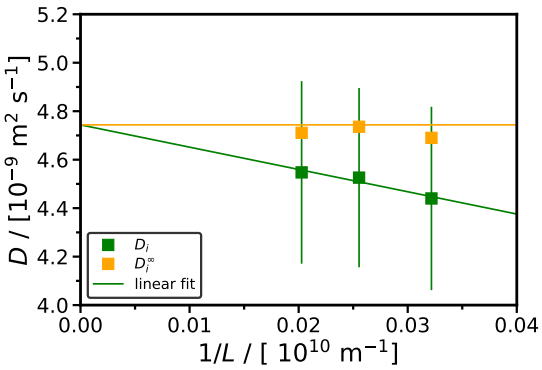


Figure S1: The effect of the number of solutes in the computation of intra-diffusivity of H_2 and O_2 in H_2O at 298.15 K and 0.1 MPa. The number of H_2O molecules used is 1,000. The Buch,[1] Bohn[2] and TIP4P/2005[3] force fields are used for H_2, O_2 and H_2O, respectively.

(a)



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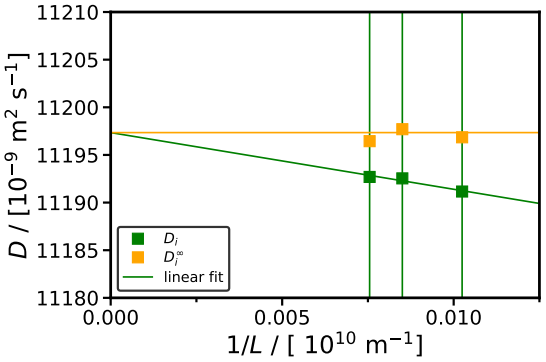

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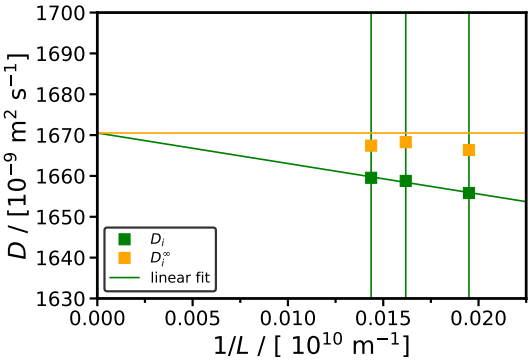
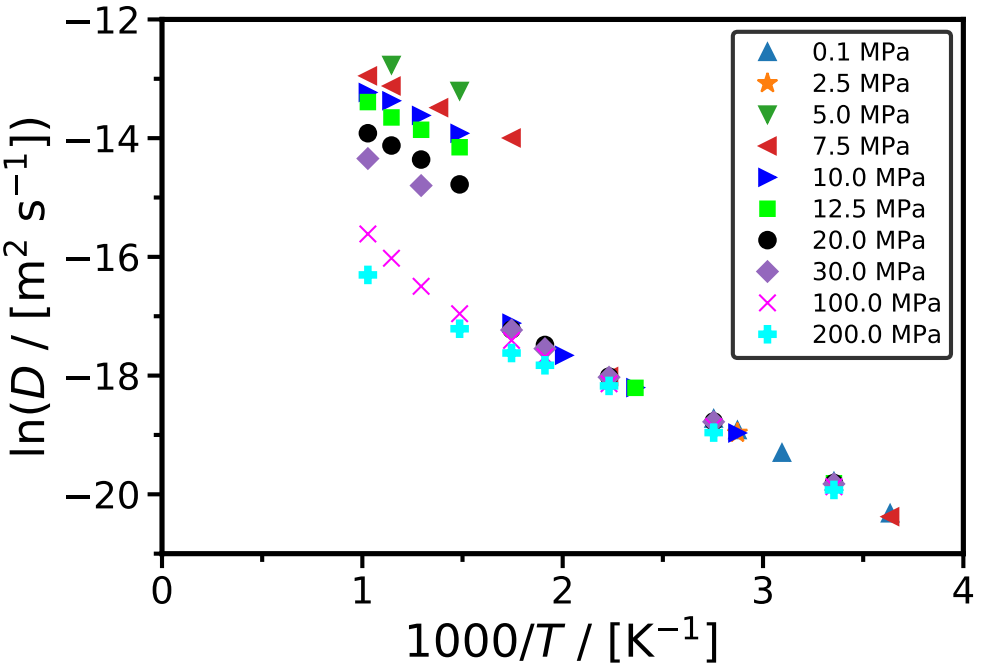


Figure S2: Finite-size dependence of the intra-diffusion coefficients of H_2 in (a) liquid in liquid H_2O (298.15 K and 0.1 MPa), (b) vapor H_2O (873.15 K and 5 MPa) and (c) supercritical H_2O (873.15 K and 30 MPa). The Bohn[2] and TIP4P/2005[3] force fields are used for H_2 and H_2O, respectively. L is the simulation box size. For the liquid phase (a), simulations using 1,000, 2,000 and 4,000 H_2O molecules were used, while for the vapor (b) and supercritical (c) phases, 400, 700 and 1,000 H_2O molecules were used. The green symbols represent the diffusivities computed in MD simulations. The orange symbols represent the corrected for system-size effects diffusivities using the Yeh-Hummer correction.[4–7] The green line is a linear fit to the MD data and the orange line is the intra-diffusivity extrapolated at infinite system size based on the linear fit to the MD data. The error bars shown in (b) and (c) are in the order of 10% which is larger than the scale of the figure (chosen to clearly show the system-size dependency of D_i).

(a)



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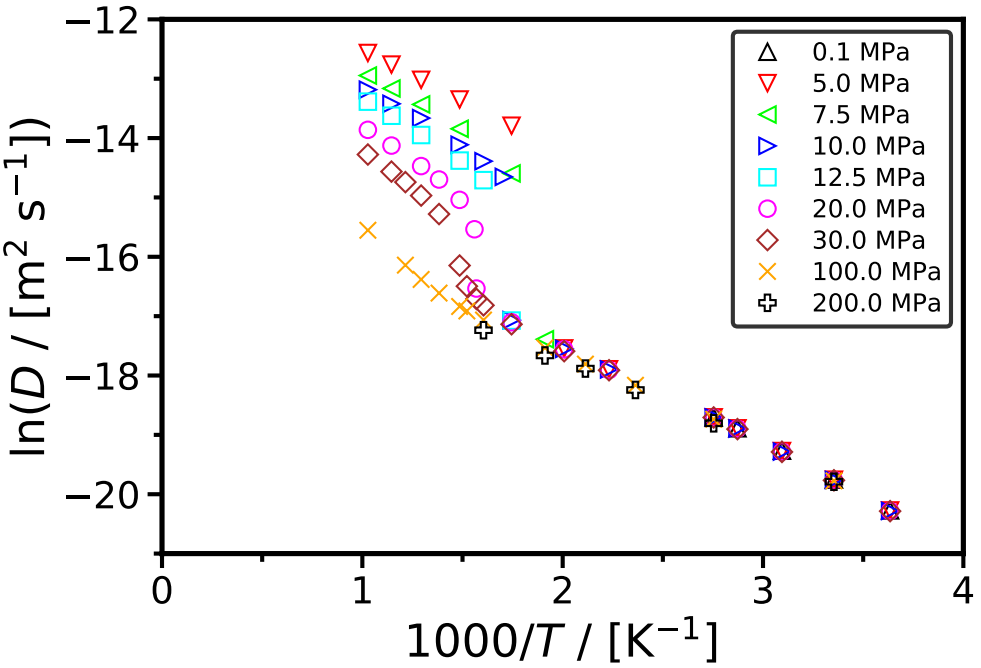
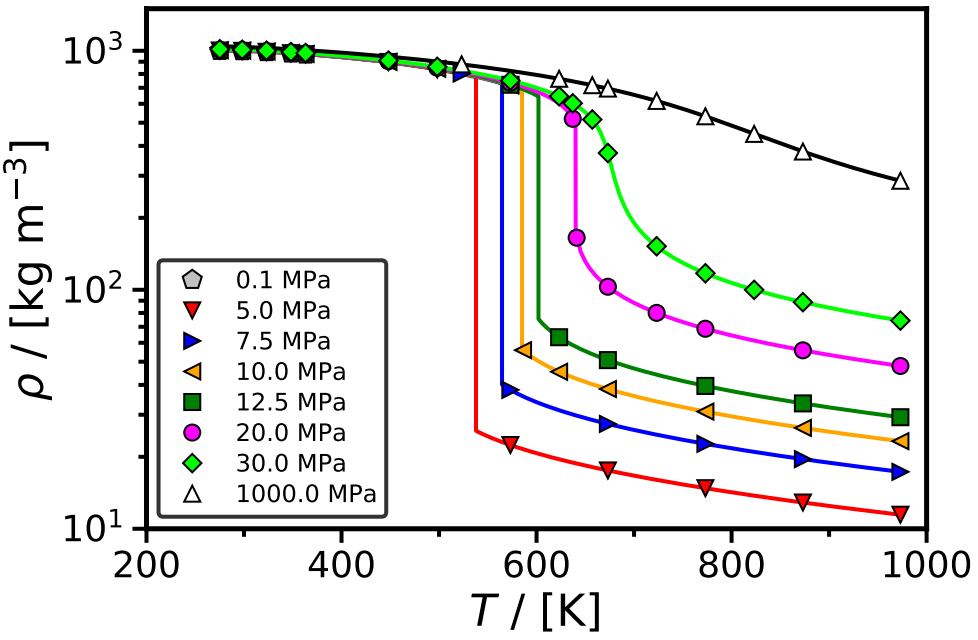


Figure S3: Arrhenius-type plots of the computed intra-diffusion coefficients of (a) O_2 in H_2O and (b) pure H_2O. The Bohn[2] and TIP4P/2005[3] force fields are used for O_2 and H_2O, respectively. The intra-diffusion coefficients are corrected for system-size effects using the Yeh-Hummer correction.[4–7] The error bars have been omitted for clarity. All raw MD data shown here along with the respective uncertainties are listed in Tables 8 (O_2 in H_2O) and 9 (pure H_2O) of the main manuscript.

(a)



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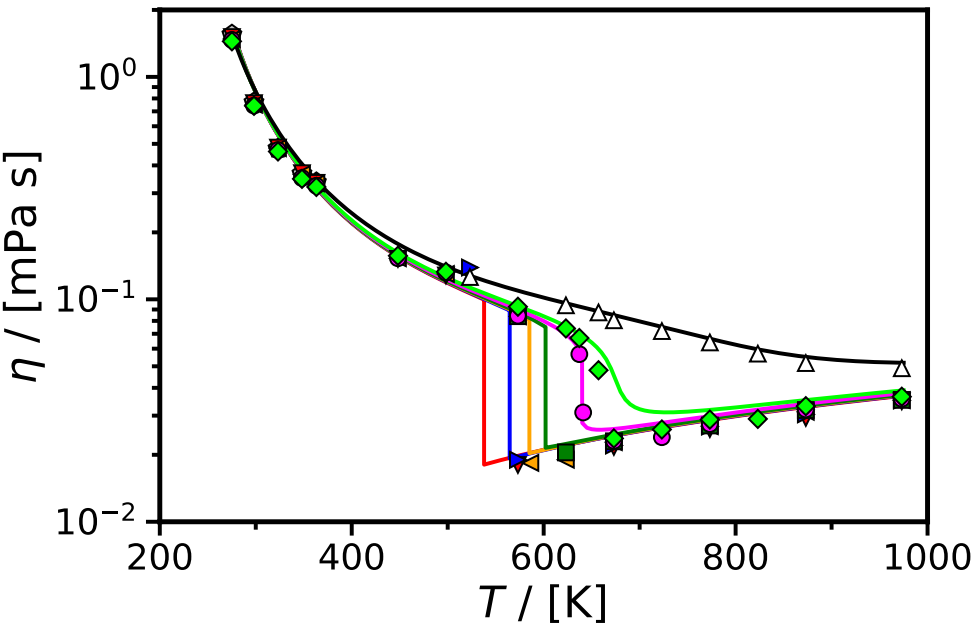

Figure S4: The (a) density and (b) shear viscosity of pure H_2O computed with the TIP4P/2005[3] force field. The lines denote data from NIST.[8] The error bars are smaller than the symbol size. The symbols denoting the different pressures are the same in (a) and (b). All MD raw data shown here along with the respective uncertainties are listed in Tables S6 (density) and S7 (shear viscosity).

Table S1: Parameters for the TIP4P/2005[3] water force field.

H-$\widehat{\text{O}}$-H (°)	104.52
$l_{\text{O-H}}$ / [Å]	0.9572
σ_{OO} / [Å]	3.1589
σ_{HH} / [Å]	0
$\epsilon_{\text{OO}}/k_{\text{B}}$ / [K]	93.2
$\epsilon_{\text{HH}}/k_{\text{B}}$ / [K]	0
q_{O} / [e]	-1.1128
q_{H} / [e]	0.5564

Table S2: Force field parameters for the hydrogen models used in this study. ϵ and σ are the Lennard-Jones parameters, q is the atomic partial charge, dummy site L is the geometric center of mass for the Marx and Silvera-Goldman models. The H-H bond length of the two-site and three-site force fields is 0.74 Å.

	Buch[1]	Hirschfelder[9]	Vrabec[10]	Cracknell[11]	Marx[12]	Silvera-Goldman[13]
$\epsilon_{\text{HH}}/k_{\text{B}}$/[K]	34.2	38	25.84	12.5		
σ_{HH} / [Å]	2.96	2.915	3.0366	2.59		
q_{H} / [e]					0.468	0.4932
q_{L} / [e]					-0.936	-0.9864
$\epsilon_{\text{LL}}/k_{\text{B}}$/[K]					36.7	34.27
σ_{LL} / [Å]					2.958	3.038

Table S3: Force field parameters for the oxygen models used in this study. ϵ and σ are the Lennard-Jones parameters, q is the atomic partial charge, dummy site L is the geometric center of mass for the Hansen and Vrabec and Watanabe models. The O-O bond length of the two-site and three-site force fields is denoted as d_{OO}.

	Bohn[2]	Miyano[14]	Coon[15]	Hansen[16]	Vrabec[17]	Watanabe[18]
$\epsilon_{\text{OO}}/k_{\text{B}}$/[K]	37.99	48.31	44.59			
σ_{OO} / [Å]	3.2104	3.03	3.09			
q_{O} / [e]				0.246	0.714	0.224
q_{L} / [e]				-0.123	-0.357	-0.112
$\epsilon_{\text{LL}}/k_{\text{B}}$/[K]				49.06	43.18	54.35
σ_{LL} / [Å]				3.013	3.106	3.05
d_{OO} / [Å]				0.605	0.485	0.605

Table S4: The density of pure H_2 computed using different force fields for various temperatures and pressures. T is in units of K, P in MPa, and ρ in Kg m^{-3}. All densities have uncertainties in the range of $0.1 - 1\%$.

Buch				
P / T	250	500	750	1000
0.1	0.098	0.049	0.033	0.025
7.5	6.966	3.577	2.411	1.811
15	13.411	6.946	4.747	3.585
30	24.460	13.190	9.202	6.839
Cracknell				
P / T	250	500	750	1000
0.1	0.093	0.050	0.034	0.026
7.5	6.833	3.635	2.437	1.771
15	13.630	7.022	4.661	3.574
30	25.689	13.277	9.295	7.040
Vrabec				
P / T	250	500	750	1000
0.1	0.097	0.049	0.033	0.025
7.5	6.828	3.631	2.412	1.817
15	13.235	6.890	4.724	3.554
30	23.480	13.036	8.941	6.859
Hirschfelder				
P / T	250	500	750	1000
0.1	0.099	0.049	0.033	0.024
7.5	7.004	3.564	2.418	1.805
15	13.513	7.023	4.758	3.617
30	25.140	13.222	9.116	6.960
Marx				
P / T	250	500	750	1000
0.1	0.096	0.048	0.031	0.024
7.5	7.075	3.576	2.397	1.769
15	13.259	6.926	4.699	3.567
30	24.293	13.257	9.045	6.953
Silvera-Goldman				
P / T	250	500	750	1000
0.1	0.095	0.048	0.032	0.023
7.5	7.070	3.605	2.406	1.838
15	13.296	6.851	4.774	3.604
30	23.697	13.296	8.912	6.881
NIST[8]				
P / T	250	500	750	1000
0.1	0.096	0.048	0.032	0.024
7.5	6.928	3.533	2.378	1.792
15	13.186	6.869	4.665	3.534
30	23.902	13.015	8.992	6.878

Table S5: The density of pure O_2 computed using different force fields for various temperatures and pressures. T is in units of K, P in MPa, and ρ in Kg m^{-3}. All densities have uncertainties in the range of $0.1 - 1\%$. The values from NIST[8] are shown for comparison.

T	P	ρ						
		Bohn	Miyano	Coon	Hansen	Vrabec	Watanabe	NIST
200	0.1	1.920	1.913	1.918	1.930	1.947	1.954	1.956
350	0.1	1.091	1.090	1.090	1.110	1.130	1.120	1.114
600	0.1	0.675	0.676	0.675	0.657	0.667	0.647	0.650
1000	0.1	0.389	0.417	0.405	0.392	0.384	0.387	0.390
200	50	823.016	803.890	816.979	814.846	827.600	844.637	839.970
350	50	467.700	468.400	463.100	468.800	468.500	477.100	476.940
600	50	274.212	276.134	277.481	267.935	277.329	276.200	276.140
1000	50	172.961	167.161	169.034	169.535	170.193	171.291	171.190

Table S6: The density of pure H_2O computed for a wide range of temperatures and pressures using the TIP4P/2005[3] force field. T is in units of K, P in MPa, and ρ in Kg m^{-3}. All densities have uncertainties in the range of $0.1 - 1\%$.

	ρ									
T / P	0.1	2.5	5.0	7.5	10	12.5	20	30	100	200
275.15	999.94		1002.4	1003.7	1004.9		1009.8	1014.6		
298.15	997.04		999.28		1001.5	1002.6	1006	1010.3	1038.4	1072.7
323.15	988.04		990.19		992.36		996.64	1000.8		
348.15	974.84	975.92	977.04		979.25		983.59	987.83		
363.15	965.31		967.57		969.84		974.3	978.64	1006.4	1040.1
423.15					922.39	923.77			965.39	1002.9
448.15	0.493		897.97	896.57	898.15		904.29	910.17	945.63	985.57
473.15									924.39	967.38
498.15	0.443		836.05		840.55		849.04	856.94		
523.15				803.05			816.35	825.92	877.46	928.49
573.15	0.384		22.405	38.121	715.58	720.92	735.17	751.24	824.2	886.53
586.15					55.887					
623.15					45.376	63.317		645.25	763.72	841.75
637.15							519.2	603		
641.15							165.14			
657.15								515.77	717.87	
673.15	0.327		17.537	27.459	38.431	50.783	102.96	373.47	694.86	794.43
723.15				24.749			80.05	152.09	616.9	
773.15	0.284		14.782	22.663	30.92	39.599	68.702	117.24	532.04	
823.15								99.921	449.07	
873.15	0.252		12.878	19.561	26.42	33.463	55.802	88.742	378.86	
973.15	0.226		11.449	17.304	23.251	29.29	47.985	74.304	285.92	502.56

Table S7: The shear viscosity of pure H_2O computed for a wide range of temperatures and pressures using the TIP4P/2005 force field. T is in units of K, P in MPa, and η in mPa s. σ_x is the uncertainty of quantity x (95% confidence interval of the standard deviation).

	η	σ_η	η	σ_η	η	σ_η	η	σ_η	η	σ_η	η	σ_η	η	σ_η	η	σ_η	η	σ_η	η	σ_η
T / P	0.1		2.5		5.0		7.5		10		12.5		20		30		100		200	
275.15	1.50	0.21			1.51	0.21	1.416	0.069	1.48	0.21			1.47	0.18	1.45	0.17				
298.15	0.78	0.16			0.76	0.15			0.75	0.12	0.763	0.083	0.76	0.10	0.761	0.098	0.792	0.072	0.877	0.049
323.15	0.50	0.13			0.48	0.13			0.478	0.093			0.47	0.09	0.462	0.088				
348.15	0.367	0.045	0.369	0.057	0.369	0.037			0.365	0.066			0.351	0.055	0.348	0.045				
363.15	0.326	0.036			0.334	0.041			0.332	0.065			0.322	0.034	0.32	0.037	0.340	0.031	0.370	0.018
423.15									0.188	0.041	0.188	0.039					0.200	0.016	0.220	0.012
448.15					0.152	0.023	0.167	0.016	0.153	0.018			0.158	0.015	0.157	0.016	0.178	0.025	0.198	0.018
473.15																	0.154	0.013	0.165	0.016
498.15					0.13	0.01			0.125	0.020			0.132	0.015	0.133	0.024				
523.15							0.139	0.036					0.111	0.016	0.109	0.017	0.127	0.010	0.143	0.014
573.15					0.0180	0.0004	0.017	0.001	0.085	0.014	0.084	0.002	0.090	0.009	0.092	0.015	0.109	0.018	0.127	0.015
586.15									0.018	0.002										
623.15									0.019	0.001	0.021	0.001			0.074	0.005	0.094	0.005	0.112	0.012
637.15													0.057	0.003	0.067	0.004				
641.15													0.031	0.003						
657.15															0.048	0.002	0.087	0.005		
673.15					0.022	0.001	0.022	0.001	0.0226	0.004	0.021	0.002	0.0241	0.0011	0.0237	0.0066	0.083	0.003	0.10	0.01
723.15							0.0222	0.0023					0.024	0.002	0.026	0.002	0.072	0.004		
773.15					0.0261	0.0011	0.027	0.001	0.0269	0.0015	0.027	0.001	0.0277	0.0027	0.0288	0.0043	0.065	0.004		
823.15															0.029	0.002	0.057	0.004		
873.15					0.0263	0.0015	0.029	0.001	0.03020	0.00095	0.031	0.001	0.0314	0.0025	0.0331	0.0051	0.053	0.002		
973.15					0.0348	0.0016	0.033	0.002	0.034	0.004	0.035	0.002	0.0345	0.0069	0.036	0.006	0.048	0.002	0.0696	0.0046

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