

Thermodynamics of Helium-4 Dimerization and Trimerization

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SUPPORTING INFORMATION

I. Derivation of $r = 1/Z$ (equation 10 of the article)

Suppose n_{id} moles of an ideal gas are placed in a container of volume V_{id} and kept at a constant temperature T and pressure P . If, however, the gas is now considered to be nonideal, association must be taken into account. After equilibrium is reached, there are n_1 moles of the original, monomeric species, n_2 moles of dimer, n_3 moles of trimer, etc. The volume now becomes V_{eq} . A stoichiometric accounting of the mixture gives

$$n_{\text{id}} = n_1 + 2n_2 + 3n_3 + \dots = \sum_i i n_i, \quad (\text{SI-1})$$

and total number of moles (of the real gas) in the container at equilibrium is

$$n_{\text{eq}} = n_1 + n_2 + n_3 + \dots = \sum_i n_i. \quad (\text{SI-2})$$

We now define r as the ratio of these mole numbers,

$$r \equiv \frac{n_{\text{id}}}{n_{\text{eq}}} = \frac{\sum_i i n_i}{\sum_i n_i}. \quad (\text{S-3})$$

Since $n_{\text{eq}} < n_{\text{id}}$ it follows that $r > 1$.

The compression factor Z is defined as the volume occupied by the (real) gas under equilibrium conditions, V_{eq} , divided by the volume the gas would occupy if it were ideal and at the same temperature and pressure. Thus,

$$Z = \frac{V_{\text{eq}}}{V_{\text{id}}}. \quad (\text{SI-4})$$

Applying Avogadro's law we have $Z = n_{\text{eq}}/n_{\text{id}}$. Since Z is also expressed as the quotient PV_m/RT (obtained from the equation of state), where V_m is the molar volume (at equilibrium), we can write

$$r_{\text{EOS}} = \frac{1}{Z} = \frac{RT}{PV_m}, \quad (\text{SI-5})$$

which corresponds to equation 10 of the article.

II. Derivation of eq 12 of the article

Equation 11 of the article reads

$$(r_{\text{EOS}} - 1) = x_D + 2x_T = K_D^o P x_M^2 + 2K_T^o P^2 x_M^3, \quad (\text{SI-6})$$

which is used to express $(2 - r_{\text{EOS}})^2$

$$(2 - r_{\text{EOS}})^2 = (1 - x_D - 2x_T)^2 = 1 - 2x_D - 4x_T + x_D^2 + 4x_T^2 + 4x_D x_T \quad (\text{SI-7})$$

Replacing x_D and x_T with

$$x_D = K_D^o P x_M^2 \text{ and } x_T = K_T^o P^2 x_M^3 \quad (\text{SI-8})$$

respectively, and using eq SI-6, it follows that

$$\frac{(r_{\text{EOS}} - 1)}{(2 - r_{\text{EOS}})^2} = \frac{K_D^o P x_M^2 + 2K_T^o P^2 x_M^3}{1 - 2K_D^o P x_M^2 - 4K_T^o P^2 x_M^3 + K_D^{o2} P^2 x_M^4 + 4K_D^o K_T^o P^3 x_M^5 + 4K_T^{o2} P^4 x_M^6} \quad (\text{SI-9})$$

At sufficiently low pressure, where $x_M \approx 1$, the denominator ≈ 1 , and thus

$$\frac{(r_{\text{EOS}} - 1)}{(2 - r_{\text{EOS}})^2} \approx K_D^o P + 2K_T^o P^2 \quad (\text{SI-10})$$

A second order regression is performed on eq SI-10 to obtain initial values of K_D^o and K_T^o for use in the multiple regression of SI-6 (eq 11 of the article) to obtain refined values and their standard uncertainties.

III. Table SI-1. Standard thermodynamic properties of the helium dimer equilibrium between 3.0 and 10.0 K. Rows A and B contain results obtained from the EOS and statistical thermodynamic calculations, respectively.

T/K	Note	K_D^o	ΔH_D^o	ΔG_D^o	ΔS_D^o
3.0	A	0.48317	-54.53	18.14	-24.22
	B	0.87313	-62.36	3.39	-21.91
3.5	A	0.34464	-65.58	31.00	-27.60
	B	0.59390	-72.75	15.17	-25.12
4.0	A	0.25615	-75.60	45.30	-30.22
	B	0.42534	-83.14	28.43	-27.89
4.5	A	0.19651	-85.84	60.88	-32.60
	B	0.31685	-9354	43.01	-30.34
5.0	A	0.15456	-96.38	77.62	-34.80
	B	0.24348	-103.93	58.73	-32.53
5.5	A	0.12403	-107.28	95.45	-36.86
	B	0.19186	-114.32	75.50	-34.51
6.0	A	0.10116	-118.59	114.29	-38.81
	B	0.15435	-124.72	93.22	-36.32
6.5	A	0.083623	-130.33	134.11	-40.68
	B	0.12636	-135.11	111.80	-37.53
7.0	A	0.069912	-142.57	154.85	-42.49
	B	0.10499	-145.50	131.19	-39.53
7.5	A	0.059008	-155.33	176.48	-44.24
	B	0.088354	-155.90	151.31	-40.96
8.0	A	0.050207	-168.67	198.99	-45.96
	B	0.075189	-166.29	172.13	-42.30
8.5	A	0.043016	-182.64	222.35	-47.65
	B	0.064615	-176.68	193.60	-43.56
9.0	A	0.037072	-197.31	246.56	-49.32
	B	0.056011	-187.08	215.68	-44.75
9.5	A	0.032112	-212.20	271.60	-50.93
	B	0.048930	-197.47	238.34	-45.87
10.0	A	0.027936	-226.67	297.48	-52.42
	B	0.043041	-207.86	261.55	-46.94

IV. Table SI-2. Standard thermodynamic properties of the helium trimer equilibrium between 3.0 and 10.0 K. Rows A and B contain results obtained from the EOS and statistical thermodynamic calculations, respectively.

T/K	Note	K_T°	ΔH_T°	ΔG_T°	ΔS_T°
3.0	A	0.4876	-111.0	17.92	-42.97
	B	0.5005	-125	17.3	-47.7
3.5	A	0.2449	-133.8	40.94	-49.93
	B	0.2312	-149	42.6	-54.8
4.0	A	0.1335	-154.6	66.96	-55.40
	B	0.1184	-170	71.0	-60.1
4.5	A	0.07760	-176.1	95.64	-60.38
	B	0.06567	-190	102	-64.9
5.0	A	0.04739	-198.3	126.77	-65.01
	B	0.03875	-211	135	-69.1
5.5	A	0.03010	-221.5	160.20	-69.41
	B	0.02405	-231	170	-73.0
6.0	A	0.01974	-246.0	195.81	-73.63
	B	0.01556	-251	208	-76.6
6.5	A	0.01329	-271.9	233.49	-77.75
	B	0.01042	-272	247	-80.0
7.0	A	0.009142	-299.5	273.25	-81.82
	B	0.007192	-293	287	-82.9
7.5	A	0.006390	-329.2	315.09	-85.91
	B	0.005092	-314	329	-85.7
8.0	A	0.004533	-361.3	358.94	-90.03
	B	0.003687	-334	373	-88.4
8.5	A	0.003248	-396.1	404.93	-94.24
	B	0.002722	-355	417	-90.9
9.0	A	0.002348	-434.6	453.02	-98.63
	B	0.002045	-376	463	-93.2
9.5	A	0.001707	-475.4	503.37	-103.03
	B	0.001560	-395	510	-95.3
10.0	A	0.001246	-516.9	556.08	-107.30
	B	0.001207	-412	559	-97.1

V. Table SI-3. Values of the low and high pressures used in the EOS calculation at temperatures 3.0 to 10.0 K along with the respective low and high mole fractions of dimer and trimer. The corresponding high and low values of the monomer mole fractions are 0.995 and 0.990, respectively.

	$x_{m,\text{high}} = 0.995$			$x_{m,\text{low}} = 0.990$		
T/K	$P_{\text{low}}/\text{bar}$	$x_{D,\text{low}}$	$x_{T,\text{low}}$	$P_{\text{high}}/\text{bar}$	$x_{D,\text{high}}$	$x_{T,\text{high}}$
3.0	0.010	0.00478	4.80×10^{-5}	0.021	0.00994	2.09×10^{-4}
3.5	0.015	0.00512	5.43×10^{-5}	0.029	0.00980	2.00×10^{-4}
4.0	0.020	0.00507	5.26×10^{-5}	0.039	0.00979	1.97×10^{-4}
4.5	0.026	0.00506	5.17×10^{-5}	0.051	0.00982	1.96×10^{-4}
5.0	0.033	0.00505	5.08×10^{-5}	0.065	0.00985	1.94×10^{-4}
5.5	0.040	0.00491	4.74×10^{-5}	0.081	0.00985	1.92×10^{-4}
6.0	0.049	0.00491	4.67×10^{-5}	0.099	0.00982	1.88×10^{-4}
6.5	0.060	0.00497	4.71×10^{-5}	0.12	0.00984	1.86×10^{-4}
7.0	0.072	0.00498	4.67×10^{-5}	0.144	0.00987	1.84×10^{-4}
7.5	0.084	0.00491	4.44×10^{-5}	0.17	0.00983	1.79×10^{-4}
8.0	0.10	0.00497	4.47×10^{-5}	0.20	0.00984	1.76×10^{-4}
8.5	0.116	0.00494	4.31×10^{-5}	0.232	0.00978	1.70×10^{-4}
9.0	0.135	0.00495	4.22×10^{-5}	0.27	0.00981	1.66×10^{-4}
9.5	0.156	0.00496	4.09×10^{-5}	0.312	0.00982	1.61×10^{-4}
10.0	0.180	0.00498	3.98×10^{-5}	0.36	0.00986	1.57×10^{-4}

VI. Table SI-4. Values of the LHS of eq 19 of the article between 3.0 and 10.0 K at the respective low and high pressures used in the statistical thermodynamics calculations.

T/K	P _{low} /bar	Value ^a	P _{high} /bar	Value ^a
3.0	0.010	0.000810	0.021	0.00170
3.5	0.015	0.000827	0.029	0.00160
4.0	0.020	0.000789	0.039	0.00154
4.5	0.026	0.000765	0.051	0.00150
5.0	0.033	0.000746	0.065	0.00147
5.5	0.040	0.000712	0.081	0.00144
6.0	0.049	0.000702	0.099	0.00142
6.5	0.06	0.000704	0.12	0.00141
7.0	0.072	0.000702	0.144	0.00140
7.5	0.084	0.000689	0.17	0.00139
8.0	0.10	0.000698	0.20	0.00140
8.5	0.116	0.000696	0.232	0.00139
9.0	0.135	0.000702	0.27	0.00140
9.5	0.156	0.000708	0.312	0.00142
10.0	0.18	0.000719	0.36	0.00144

^a Values of the LHS of eq 19 of the article.