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NOx Formation and Control: On Thermochemistry of NNH

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Abstract : The NNH species mechanism pathway is an important consideration in current NOx combustion pollutants formation at high temperatures, and low residence time control modelling. However, no detailed Table of NNH thermochemical properties exists in the open chemicals databases. Attempt is made in this paper at developing a detailed NNH thermochemical data Table. The 7-term NASA polynomial coefficients for NNH are applied. No 9-term coefficients yet cited. The thermochemical quantities tabulations follow the format of Barin as reported in the survey by Jacobson of available source compendia of thermochemical data. Two Methods of solutions by additivity for the energies of formations, by, linking dynamically, related and consistent listings in terms of the choice of stable molecule reference elements, lead to similar results. NASA coefficients were used to precision, but round-off of final listed results is to 3-decimals.Curve-fitted equations of equilibrium constant for the two methods, with predictions accurate to within maximum deviations of ±0.50-percent,and ±0.02-percentfrom tabulated data, and averaged absolute uncertainties of 0.08-percent,and 0.01-percent in the 1000 -to-6000 K temperature range, respectively are presented.
Keywords : Thermo chemistry; NNH; Pollutant Formation; NOx Chemistry; Combustion Reactions.

Introduction:

A survey of methods for presentation of thermochemical data Tables were reported by Jacobson [1]; and the importance of the NNH radical and intermediate species to NOx chemistry in formation and reduction/removal have been reported by Dean and Bozzelli [2],and Flagan [3]. The NNH species complete thermochemical data Table within combustion reactions high temperatures range of interest is however, not available in the major thermochemical databases in the open literature such as The United States (US),Joint Army, Navy and Air force (JANAF) Tables [4]. An abridged Table in [5], based on the 7-term NASA polynomial coefficients, within the temperature range 200 -to-3000 K is available for C_P, S, and ΔH; the ΔH data was reportedly obtained by private communication from C. F. Melius. The free energy functions and equilibrium constant were not reported. In a joint collaborative report (ANL-05/210), (TAE 960) by the US Argonne National Laboratory ANL and Technion of the Israel Institute of Technology as reported by Burcat and Ruscic [6], coefficients for NNH species are listed, using the Gordon and McBride NASA polynomial coefficients [7] reporting format. Calculations for NNH thermo-chemical parameters presented in this paperare based on the ANL/Technion [6] report and cover the temperature range 200 -to-6000 K, with the standard state reference temperature taken as 298.15 K.

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The Empirical Equations Applied

The respective equations for specific heat, C_p, enthalpy, H, and entropy, $S$for the calculations are presented in eqs. (1-to-3) as programmed. The values for the gas constant, R, are as recommended by JANAF [4]. Thus,R=1.987165 cal/mol.K = 8.3143 J/mol.K, which implies, 1 cal = 4.184 J.

$$C_P^o(T,R) = (a_1 + a_2T + a_3T^2 + a_4T^3 + a_5T^4)R \quad (1)$$

$$H^O(T,R) = \left[a_1 + a_2\frac{T}{2} + a_3\frac{T^2}{3} + a_4\frac{T^3}{4} + a_5\frac{T^4}{5} + \frac{b_1}{T}\right]RT \quad (2)$$

$$S^O(T,R) = \left[a_1 \ln T + a_2T + a_3\frac{T^2}{2} + a_4\frac{T^3}{3} + a_5\frac{T^4}{4} + b_2\right]R \quad (3)$$

Table 1, lists the values of the, $a_i$and b_i coefficients abstracted from Burcat and Ruscic [6]. Burcat and Ruscic [6], adopted the Gordon and McBride [7] NASA polynomial coefficients presentation format.

2.1. Derived Thermodynamic Relations

Equations (1-to-3) are used to derive the thermodynamic parameters of interest – Gibbs free energy, the Free energy function, Sensible energy, the Energies of formation and the Equilibrium constant.Gibbs free energy, G, wereobtained by the relations (4)-method m1, and (4a)-method m2; and the free energy function by eq. (5):

$$G^o(T,R) = [H^o(298.15) + H^o(T;T = 298.15)] - [TS^o(T;T = 298.15)] \quad (4)$$

$$G^o(T,R) = \left[a_1T(1 - \ln T) - \frac{1}{2}a_2T^2 - \frac{1}{6}a_3T^3 - \frac{1}{12}a_4T^4 - \frac{1}{20}a_5T^5 + b_1 - b_2T\right]R \quad (4a)$$

$$The\ Free\ Energy\ Function = \frac{-[G^o(T,R) - H^o(298.15,R)]}{T} \quad (5)$$

The Sensible energy was calculated by the relationship of (6):

$$H^o(T) - H^o(298.15) = \int_{T=298.15}^{T} C_P^o(T,R)dT \quad (6)$$

Note thatin eq. (4), the expression (*T; T=298.15*) in the source enthalpy and entropy terms, indicates, integrating between the reference state temperature, T = *298.15K*, and the temperature, T, of interest for which the Gibbs free energy of formation is required.By considering a substance, Z, formation in the form of: $uX + vY \leftrightarrow Z$, the Heats of formation, $\Delta_f H^o(T)Z$ and Gibbs free energy of formation, $\Delta_f G^o(T)Z$, were respectivelyobtained from the relationships:

$$\Delta_f H^o(T)Z = H^o(T,R)Z - uH^o(T,R)X - vH^o(T,R)Y \quad (7)$$

$$\Delta_f G^o(T)Z = G^o(T,R)Z - uG^o(T,R)X - vG^o(T,R)Y \quad (8)$$

Where,u and v, are stoichiometric coefficients;X and Y, are the assigned reference state elements [8], for the formation of species Z, which in this instance are N_2 and H_2, for which properties were generated with NASA coefficients [7] for inter-consistency.The Equilibrium constant of formation, K_P, is presented as recommended by JANAF [4], in the form of, $\mathrm{Log}_{10}\,\mathrm{K_P}$, using the Gordon and McBride [7]type eq. (9):

$$\mathrm{Log}_{10} K_P = \frac{-\Delta_f G^o(T,R)Z}{2.3025851.RT} \quad (9)$$

Calculated NNH thermo-chemical properties values are presented in Tables 2, 2a and Tables 3, 3a based on the $G^o(T,R)$ applied, for units in cal/mol, and kcal/mol, or J/mol, and kJ/mol where required.

Table 1.Values of NNH Coefficients and Temperature Range of Application. ***Source*:Burcat & Ruscic, [6]**

Coefficients	Temperature Range of Validity	
	≤ 1000 K	≥1000 K
a_1	0.43446927e+01	0.37667545e+01
a_2	-0.48497072e-02	0.28915081e-02
a_3	0.20059459e-04	-0.10416620e-05
a_4	-0.21726464e-07	0.16842594e-09
a_5	0.79469538e-11	-0.10091896e-13
b_1	0.28791973e+05	0.28650697e+05
b_2	0.29779411e+01	0.44705068e+01
$H^o(298.15)/R$	0.30009829e+05 (not used in the program, but tallies with results obtained)	

Table 2. Thermochemical data of NNH in cal/mol and kcal/mol units with $G^o(T,R)$ obtained by eq. (4) – method m1

T (K)	C_P^o cal/mol.K	S^o cal/mol.K	H^o kcal/mol	G^o kcal/mol	$-(G^o-H^o_{298})$ cal/mol.K	$H^o - H^o_{298}$ kcal/mol	$\Delta_f H^o$ kcal/mol	$\Delta_f G^o$ kcal/mol	$\log_{10} K_P$
200	7.981	50.422	58.838	48.754	54.403	-0.796	59.853	61.226	-66.904
298.15	8.284	53.657	59.634	43.637	53.657	0.000	59.634	61.946	-45.408
300	8.292	53.708	59.650	43.537	53.657	0.015	59.631	61.961	-45.138
400	8.798	56.160	60.503	38.039	53.988	0.869	59.439	62.768	-34.295
500	9.371	58.184	61.412	32.319	54.630	1.777	59.293	63.618	-27.807
600	9.922	59.942	62.377	26.411	55.372	2.742	59.196	64.492	-23.491
700	10.403	61.509	63.394	20.337	56.139	3.759	59.136	65.380	-20.413
800	10.798	62.925	64.454	14.115	56.900	4.820	59.102	66.275	-18.105
900	11.135	64.216	65.551	7.757	57.642	5.917	59.084	67.173	-16.312
1000	11.476	65.407	66.681	1.275	58.360	7.047	59.079	68.072	-14.877
1100	11.717	66.512	67.841	-5.642	59.343	8.438	59.089	68.449	-13.600
1200	11.936	67.541	69.024	-12.396	60.025	9.621	59.104	69.267	-12.615
1300	12.135	68.504	70.228	-19.249	60.679	10.825	59.125	70.084	-11.782
1400	12.314	69.410	71.450	-26.195	61.307	12.047	59.150	70.899	-11.068
1500	12.475	70.266	72.690	-33.229	61.909	13.287	59.178	71.711	-10.448
1600	12.619	71.075	73.945	-40.347	62.488	14.542	59.209	72.522	-9.906
1700	12.748	71.844	75.213	-47.543	63.046	15.810	59.242	73.331	-9.427
1800	12.863	72.576	76.494	-54.815	63.583	17.091	59.277	74.138	-9.002
1900	12.964	73.275	77.785	-62.158	64.101	18.382	59.313	74.943	-8.620
2000	13.054	73.942	79.086	-69.569	64.602	19.683	59.349	75.746	-8.277
2100	13.133	74.581	80.396	-77.046	65.086	20.993	59.385	76.547	-7.966
2200	13.202	75.193	81.713	-84.585	65.554	22.309	59.420	77.346	-7.684
2300	13.262	75.781	83.036	-92.184	66.008	23.633	59.455	78.144	-7.425
2400	13.314	76.347	84.365	-99.841	66.448	24.961	59.489	78.941	-7.189
2500	13.359	76.891	85.698	-107.553	66.875	26.295	59.521	79.736	-6.970
2600	13.398	77.416	87.036	-115.318	67.290	27.633	59.552	80.529	-6.769
2700	13.431	77.922	88.378	-123.136	67.693	28.975	59.581	81.322	-6.583
2800	13.460	78.411	89.722	-131.003	68.085	30.319	59.608	82.113	-6.409
2900	13.484	78.884	91.069	-138.918	68.466	31.666	59.634	82.904	-6.248
3000	13.506	79.342	92.419	-146.879	68.838	33.016	59.657	83.694	-6.097
3100	13.524	79.785	93.770	-154.886	69.200	34.367	59.677	84.483	-5.956
3200	13.540	80.214	95.124	-162.936	69.553	35.721	59.696	85.271	-5.824
3300	13.554	80.631	96.478	-171.029	69.898	37.075	59.712	86.059	-5.699
3400	13.567	81.036	97.834	-179.162	70.234	38.431	59.726	86.847	-5.582

3500	13.579	81.430	99.192	-187.336	70.563	39.789	59.738	87.634	-5.472
3600	13.591	81.812	100.550	-195.548	70.884	41.147	59.747	88.420	-5.368
3700	13.602	82.185	101.910	-203.798	71.198	42.507	59.754	89.207	-5.269
3800	13.613	82.548	103.271	-212.085	71.505	43.868	59.759	89.993	-5.176
3900	13.624	82.901	104.633	-220.408	71.806	45.229	59.762	90.779	-5.087
4000	13.636	83.247	105.996	-228.765	72.100	46.592	59.763	91.565	-5.003
4100	13.648	83.583	107.360	-237.157	72.388	47.957	59.762	92.352	-4.923
4200	13.660	83.912	108.725	-245.582	72.671	49.322	59.759	93.138	-4.846
4300	13.673	84.234	110.092	-254.040	72.947	50.689	59.754	93.924	-4.774
4400	13.687	84.548	111.460	-262.529	73.219	52.057	59.748	94.711	-4.704
4500	13.700	84.856	112.829	-271.049	73.485	53.426	59.739	95.497	-4.638
4600	13.714	85.157	114.200	-279.600	73.747	54.797	59.729	96.284	-4.575
4700	13.728	85.453	115.572	-288.181	74.003	56.169	59.717	97.071	-4.514
4800	13.742	85.742	116.946	-296.791	74.255	57.542	59.704	97.858	-4.456
4900	13.756	86.025	118.320	-305.430	74.503	58.917	59.689	98.646	-4.400
5000	13.768	86.303	119.697	-314.096	74.746	60.293	59.672	99.434	-4.346
5100	13.780	86.576	121.074	-322.790	74.985	61.671	59.654	100.222	-4.295
5200	13.790	86.844	122.452	-331.512	75.220	63.049	59.633	101.011	-4.245
5300	13.797	87.106	123.832	-340.259	75.452	64.429	59.611	101.800	-4.198
5400	13.803	87.364	125.212	-349.033	75.679	65.809	59.586	102.590	-4.152
5500	13.805	87.618	126.592	-357.832	75.903	67.189	59.560	103.380	-4.108
5600	13.803	87.866	127.973	-366.657	76.123	68.570	59.531	104.170	-4.065
5700	13.797	88.111	129.353	-375.506	76.340	69.950	59.499	104.961	-4.024
5800	13.786	88.351	130.732	-384.379	76.554	71.329	59.465	105.753	-3.985
5900	13.769	88.586	132.110	-393.276	76.764	72.707	59.427	106.545	-3.947
6000	13.745	88.817	133.485	-402.196	76.972	74.082	59.386	107.338	-3.910

Table 2a.Thermochemical data of NNH in J/mol and kJ/mol units with $G^o(T,R)$ as in eq. (4) –method m1

T (K)	C_P^o J/mol.K	S^o J/mol.K	H^o kJ/mol	G^o kJ/mol	$-(G^o - H$ J/mol.K	$H^o - H^o_{298}$kJ/mol	$\Delta_f H^o$ kJ/mol	$\Delta_f G^o$ kJ/mol	$\log_{10} K_P$
200	33.391	210.967	246.180	203.987	227.621	-3.331	250.425	256.168	-66.904
298.15	34.661	224.500	249.511	182.576	224.500	0.000	249.511	259.184	-45.408
300	34.695	224.714	249.575	182.161	224.500	0.064	249.494	259.244	-45.138
400	36.810	234.973	253.146	159.157	225.885	3.635	248.691	262.620	-34.295
500	39.207	243.443	256.946	135.225	228.572	7.435	248.084	266.177	-27.807
600	41.516	250.798	260.984	110.505	231.676	11.473	247.675	269.837	-23.491
700	43.525	257.353	265.239	85.092	234.884	15.728	247.426	273.552	-20.413
800	45.181	263.277	269.677	59.055	238.069	20.166	247.284	277.294	-18.105
900	46.589	268.681	274.267	32.454	241.175	24.756	247.206	281.051	-16.312
1000	48.015	273.662	278.995	5.333	244.177	29.485	247.188	284.813	-14.877
1100	49.024	278.286	283.848	-23.608	248.289	35.305	247.227	286.393	-13.600
1200	49.941	282.592	288.797	-51.864	251.145	40.254	247.292	289.815	-12.615
1300	50.771	286.623	293.833	-80.537	253.882	45.291	247.378	293.231	-11.782
1400	51.520	290.413	298.949	-109.600	256.508	50.406	247.482	296.640	-11.068
1500	52.194	293.991	304.135	-139.032	259.028	55.592	247.601	300.041	-10.448
1600	52.798	297.379	309.385	-168.812	261.452	60.842	247.731	303.433	-9.906
1700	53.337	300.597	314.692	-198.922	263.784	66.150	247.870	306.817	-9.427
1800	53.817	303.659	320.051	-229.346	266.031	71.508	248.015	310.193	-9.002
1900	54.242	306.581	325.454	-260.069	268.200	76.911	248.164	313.561	-8.620
2000	54.617	309.373	330.897	-291.077	270.294	82.355	248.315	316.920	-8.277
2100	54.947	312.046	336.376	-322.359	272.319	87.833	248.466	320.273	-7.966
2200	55.235	314.608	341.885	-353.902	274.279	93.343	248.615	323.618	-7.684

2300	55.487	317.069	347.422	-385.697	276.177	98.879	248.760	326.956	-7.425
2400	55.705	319.436	352.982	-417.733	278.018	104.439	248.902	330.288	-7.189
2500	55.894	321.714	358.562	-450.001	279.805	110.019	249.037	333.614	-6.970
2600	56.056	323.909	364.159	-482.493	281.540	115.617	249.167	336.935	-6.769
2700	56.196	326.027	369.772	-515.200	283.226	121.229	249.288	340.251	-6.583
2800	56.315	328.073	375.398	-548.115	284.866	126.855	249.402	343.563	-6.409
2900	56.418	330.051	381.035	-581.232	286.463	132.492	249.507	346.871	-6.248
3000	56.507	331.965	386.681	-614.543	288.018	138.138	249.603	350.175	-6.097
3100	56.584	333.820	392.336	-648.043	289.533	143.793	249.690	353.476	-5.956
3200	56.651	335.617	397.998	-681.725	291.011	149.455	249.767	356.775	-5.824
3300	56.711	337.361	403.666	-715.584	292.453	155.123	249.835	360.071	-5.699
3400	56.766	339.055	409.340	-749.615	293.861	160.797	249.894	363.366	-5.582
3500	56.816	340.701	415.019	-783.813	295.235	166.476	249.942	366.659	-5.472
3600	56.864	342.303	420.703	-818.174	296.579	172.160	249.982	369.950	-5.368
3700	56.910	343.861	426.391	-852.692	297.893	177.849	250.012	373.241	-5.269
3800	56.957	345.380	432.085	-887.364	299.178	183.542	250.033	376.531	-5.176
3900	57.004	346.860	437.783	-922.186	300.435	189.240	250.045	379.821	-5.087
4000	57.052	348.303	443.486	-957.155	301.666	194.943	250.049	383.110	-5.003
4100	57.102	349.713	449.193	-992.266	302.872	200.651	250.045	386.399	-4.923
4200	57.154	351.089	454.906	-1027.516	304.054	206.363	250.032	389.689	-4.846
4300	57.208	352.435	460.624	-1062.902	305.212	212.082	250.012	392.979	-4.774
4400	57.264	353.751	466.348	-1098.422	306.348	217.805	249.984	396.269	-4.704
4500	57.322	355.038	472.077	-1134.071	307.463	223.534	249.949	399.560	-4.638
4600	57.381	356.299	477.812	-1169.848	308.556	229.270	249.907	402.852	-4.575
4700	57.439	357.534	483.553	-1205.750	309.630	235.011	249.858	406.145	-4.514
4800	57.497	358.743	489.300	-1241.774	310.684	240.757	249.802	409.440	-4.456
4900	57.553	359.930	495.053	-1277.918	311.720	246.510	249.738	412.735	-4.400
5000	57.606	361.093	500.811	-1314.179	312.738	252.268	249.668	416.032	-4.346
5100	57.654	362.234	506.574	-1350.555	313.738	258.031	249.590	419.330	-4.295
5200	57.695	363.354	512.341	-1387.045	314.722	263.799	249.505	422.630	-4.245
5300	57.728	364.453	518.112	-1423.645	315.690	269.570	249.412	425.931	-4.198
5400	57.750	365.533	523.886	-1460.354	316.642	275.344	249.310	429.235	-4.152
5500	57.759	366.592	529.662	-1497.171	317.578	281.119	249.199	432.540	-4.108
5600	57.752	367.633	535.438	-1534.092	318.500	286.895	249.078	435.848	-4.065
5700	57.727	368.655	541.212	-1571.116	319.408	292.669	248.945	439.157	-4.024
5800	57.680	369.659	546.982	-1608.242	320.302	298.440	248.801	442.470	-3.985
5900	57.608	370.644	552.747	-1645.467	321.183	304.204	248.643	445.784	-3.947
6000	57.509	371.612	558.503	-1682.790	322.050	309.960	248.470	449.102	-3.910

Table 3. Thermochemical data of NNH in cal/mol and kcal/mol units with $G^o(T,R)$ obtained by eq. (4a) – method m2

T (K)	C_P^o cal/mol.K	S^o cal/mol.K	H^o kcal/mol	G^o kcal/mol	$-(G^o - H^o_{298})/$ cal/mol.K	$H^o - H^o_{298}$ kcal/mol	$\Delta_f H^o$ kcal/mol	$\Delta_f G^o$ kcal/mol	$\log_{10} K_P$
200	7.981	50.422	58.838	48.754	54.403	-0.796	59.853	61.226	-66.904
298.15	8.284	53.657	59.634	43.637	53.657	0.000	59.634	61.946	-45.408
300	8.292	53.708	59.650	43.537	53.657	0.015	59.631	61.961	-45.138
400	8.798	56.160	60.503	38.039	53.988	0.869	59.439	62.768	-34.295
500	9.371	58.184	61.412	32.319	54.630	1.777	59.293	63.618	-27.807
600	9.922	59.942	62.377	26.411	55.372	2.742	59.196	64.492	-23.491
700	10.403	61.509	63.394	20.337	56.139	3.759	59.136	65.380	-20.412
800	10.798	62.925	64.454	14.115	56.900	4.820	59.102	66.274	-18.105
900	11.135	64.216	65.551	7.757	57.642	5.917	59.084	67.171	-16.311

1000	11.476	65.407	66.681	1.275	58.360	7.047	59.079	68.069	-14.877
1100	11.717	66.512	67.841	-5.322	59.051	8.438	59.089	68.971	-13.703
1200	11.936	67.541	69.024	-12.025	59.716	9.621	59.104	69.869	-12.725
1300	12.135	68.504	70.228	-18.828	60.356	10.825	59.125	70.765	-11.897
1400	12.314	69.410	71.450	-25.724	60.970	12.047	59.150	71.659	-11.187
1500	12.475	70.266	72.690	-32.708	61.562	13.287	59.178	72.552	-10.571
1600	12.619	71.075	73.945	-39.776	62.131	14.542	59.209	73.442	-10.032
1700	12.748	71.844	75.213	-46.922	62.680	15.810	59.242	74.331	-9.556
1800	12.863	72.576	76.494	-54.143	63.210	17.091	59.277	75.218	-9.133
1900	12.964	73.275	77.785	-61.436	63.721	18.382	59.313	76.102	-8.754
2000	13.054	73.942	79.086	-68.797	64.216	19.683	59.349	76.985	-8.413
2100	13.133	74.581	80.396	-76.224	64.694	20.993	59.385	77.866	-8.104
2200	13.202	75.193	81.713	-83.713	65.158	22.309	59.420	78.745	-7.823
2300	13.262	75.781	83.036	-91.261	65.607	23.633	59.455	79.623	-7.566
2400	13.314	76.347	84.365	-98.868	66.043	24.961	59.489	80.499	-7.330
2500	13.359	76.891	85.698	-106.530	66.466	26.295	59.521	81.374	-7.114
2600	13.398	77.416	87.036	-114.246	66.877	27.633	59.552	82.247	-6.913
2700	13.431	77.922	88.378	-122.013	67.277	28.975	59.581	83.119	-6.728
2800	13.460	78.411	89.722	-129.830	67.666	30.319	59.608	83.991	-6.556
2900	13.484	78.884	91.069	-137.695	68.044	31.666	59.634	84.861	-6.395
3000	13.506	79.342	92.419	-145.606	68.413	33.016	59.657	85.731	-6.245
3100	13.524	79.785	93.770	-153.562	68.773	34.367	59.677	86.599	-6.105
3200	13.540	80.214	95.124	-161.562	69.124	35.721	59.696	87.468	-5.974
3300	13.554	80.631	96.478	-169.605	69.466	37.075	59.712	88.335	-5.850
3400	13.567	81.036	97.834	-177.688	69.801	38.431	59.726	89.202	-5.734
3500	13.579	81.430	99.192	-185.812	70.127	39.789	59.738	90.069	-5.624
3600	13.591	81.812	100.550	-193.974	70.447	41.147	59.747	90.936	-5.521
3700	13.602	82.185	101.910	-202.174	70.759	42.507	59.754	91.802	-5.423
3800	13.613	82.548	103.271	-210.410	71.064	43.868	59.759	92.668	-5.330
3900	13.624	82.901	104.633	-218.683	71.363	45.229	59.762	93.534	-5.241
4000	13.636	83.247	105.996	-226.990	71.656	46.592	59.763	94.400	-5.158
4100	13.648	83.583	107.360	-235.332	71.943	47.957	59.762	95.266	-5.078
4200	13.660	83.912	108.725	-243.707	72.224	49.322	59.759	96.132	-5.002
4300	13.673	84.234	110.092	-252.114	72.500	50.689	59.754	96.998	-4.930
4400	13.687	84.548	111.460	-260.553	72.770	52.057	59.748	97.864	-4.861
4500	13.700	84.856	112.829	-269.024	73.035	53.426	59.739	98.730	-4.795
4600	13.714	85.157	114.200	-277.524	73.295	54.797	59.729	99.597	-4.732
4700	13.728	85.453	115.572	-286.055	73.551	56.169	59.717	100.464	-4.672
4800	13.742	85.742	116.946	-294.615	73.802	57.542	59.704	101.331	-4.614
4900	13.756	86.025	118.320	-303.203	74.048	58.917	59.689	102.198	-4.558
5000	13.768	86.303	119.697	-311.820	74.291	60.293	59.672	103.066	-4.505
5100	13.780	86.576	121.074	-320.464	74.529	61.671	59.654	103.934	-4.454
5200	13.790	86.844	122.452	-329.135	74.763	63.049	59.633	104.802	-4.405
5300	13.797	87.106	123.832	-337.832	74.994	64.429	59.611	105.671	-4.357
5400	13.803	87.364	125.212	-346.556	75.220	65.809	59.586	106.540	-4.312
5500	13.805	87.618	126.592	-355.305	75.444	67.189	59.560	107.410	-4.268
5600	13.803	87.866	127.973	-364.079	75.663	68.570	59.531	108.280	-4.226
5700	13.797	88.111	129.353	-372.878	75.879	69.950	59.499	109.151	-4.185
5800	13.786	88.351	130.732	-381.701	76.092	71.329	59.465	110.023	-4.146
5900	13.769	88.586	132.110	-390.548	76.302	72.707	59.427	110.895	-4.108
6000	13.745	88.817	133.485	-399.418	76.509	74.082	59.386	111.767	-4.071

Table 3a. Thermochemical data of NNH in J/mol and kJ/mol units with $G^o(T,R)$ as in eq. (4a) – method m2

T (K)	C_P^O J/mol.K	S^o J/mol.K	H^o kJ/mol	G^o kJ/mol	$-(G^o - H^o_{298})/T$ J/mol.K	$H^o - H^o_{298}$ kJ/mol	$\Delta_f H^o$ kJ/mol	$\Delta_f G^o$ kJ/mol	$\log_{10} K_P$
200	33.391	210.967	246.180	203.987	227.621	-3.331	250.425	256.168	-66.904
298.15	34.661	224.500	249.511	182.576	224.500	0.000	249.511	259.184	-45.408
300	34.695	224.714	249.575	182.161	224.500	0.064	249.494	259.244	-45.138
400	36.810	234.973	253.146	159.157	225.885	3.635	248.691	262.620	-34.295
500	39.207	243.443	256.946	135.225	228.572	7.435	248.084	266.176	-27.807
600	41.516	250.798	260.984	110.505	231.676	11.473	247.675	269.835	-23.491
700	43.525	257.353	265.239	85.092	234.884	15.728	247.426	273.549	-20.412
800	45.181	263.277	269.677	59.055	238.069	20.166	247.284	277.290	-18.105
900	46.589	268.681	274.267	32.454	241.175	24.756	247.206	281.044	-16.311
1000	48.015	273.662	278.995	5.333	244.177	29.485	247.188	284.803	-14.877
1100	49.024	278.286	283.848	-22.267	247.071	35.305	247.227	288.574	-13.703
1200	49.941	282.592	288.797	-50.313	249.853	40.254	247.292	292.330	-12.725
1300	50.771	286.623	293.833	-78.776	252.529	45.291	247.378	296.080	-11.897
1400	51.520	290.413	298.949	-107.630	255.101	50.406	247.482	299.823	-11.187
1500	52.194	293.991	304.135	-136.852	257.575	55.592	247.601	303.557	-10.571
1600	52.798	297.379	309.385	-166.422	259.958	60.842	247.731	307.283	-10.032
1700	53.337	300.597	314.692	-196.322	262.255	66.150	247.870	311.001	-9.556
1800	53.817	303.659	320.051	-226.536	264.470	71.508	248.015	314.711	-9.133
1900	54.242	306.581	325.454	-257.049	266.611	76.911	248.164	318.412	-8.754
2000	54.617	309.373	330.897	-287.848	268.679	82.355	248.315	322.105	-8.413
2100	54.947	312.046	336.376	-318.920	270.681	87.833	248.466	325.791	-8.104
2200	55.235	314.608	341.885	-350.253	272.620	93.343	248.615	329.470	-7.823
2300	55.487	317.069	347.422	-381.838	274.499	98.879	248.760	333.142	-7.566
2400	55.705	319.436	352.982	-413.664	276.323	104.439	248.902	336.807	-7.330
2500	55.894	321.714	358.562	-445.722	278.093	110.019	249.037	340.467	-7.114
2600	56.056	323.909	364.159	-478.004	279.813	115.617	249.167	344.122	-6.913
2700	56.196	326.027	369.772	-510.502	281.486	121.229	249.288	347.772	-6.728
2800	56.315	328.073	375.398	-543.207	283.114	126.855	249.402	351.417	-6.556
2900	56.418	330.051	381.035	-576.114	284.698	132.492	249.507	355.059	-6.395
3000	56.507	331.965	386.681	-609.215	286.242	138.138	249.603	358.697	-6.245
3100	56.584	333.820	392.336	-642.505	287.747	143.793	249.690	362.332	-6.105
3200	56.651	335.617	397.998	-675.977	289.215	149.455	249.767	365.964	-5.974
3300	56.711	337.361	403.666	-709.627	290.648	155.123	249.835	369.594	-5.850
3400	56.766	339.055	409.340	-743.448	292.047	160.797	249.894	373.222	-5.734
3500	56.816	340.701	415.019	-777.436	293.413	166.476	249.942	376.849	-5.624
3600	56.864	342.303	420.703	-811.587	294.749	172.160	249.982	380.474	-5.521
3700	56.910	343.861	426.391	-845.895	296.056	177.849	250.012	384.099	-5.423
3800	56.957	345.380	432.085	-880.358	297.334	183.542	250.033	387.722	-5.330
3900	57.004	346.860	437.783	-914.970	298.585	189.240	250.045	391.346	-5.241
4000	57.052	348.303	443.486	-949.728	299.810	194.943	250.049	394.969	-5.158
4100	57.102	349.713	449.193	-984.629	301.010	200.651	250.045	398.592	-5.078
4200	57.154	351.089	454.906	-1019.670	302.186	206.363	250.032	402.215	-5.002
4300	57.208	352.435	460.624	-1054.846	303.339	212.082	250.012	405.838	-4.930
4400	57.264	353.751	466.348	-1090.156	304.470	217.805	249.984	409.463	-4.861
4500	57.322	355.038	472.077	-1125.595	305.579	223.534	249.949	413.088	-4.795
4600	57.381	356.299	477.812	-1161.163	306.668	229.270	249.907	416.713	-4.732
4700	57.439	357.534	483.553	-1196.854	307.737	235.011	249.858	420.340	-4.672
4800	57.497	358.743	489.300	-1232.668	308.787	240.757	249.802	423.968	-4.614
4900	57.553	359.930	495.053	-1268.602	309.819	246.510	249.738	427.597	-4.558
5000	57.606	361.093	500.811	-1304.654	310.833	252.268	249.668	431.227	-4.505
5100	57.654	362.234	506.574	-1340.820	311.830	258.031	249.590	434.859	-4.454
5200	57.695	363.354	512.341	-1377.100	312.810	263.799	249.505	438.493	-4.405
5300	57.728	364.453	518.112	-1413.490	313.774	269.570	249.412	442.128	-4.357
5400	57.750	365.533	523.886	-1449.990	314.722	275.344	249.310	445.765	-4.312
5500	57.759	366.592	529.662	-1486.596	315.656	281.119	249.199	449.404	-4.268
5600	57.752	367.633	535.438	-1523.308	316.575	286.895	249.078	453.046	-4.226
5700	57.727	368.655	541.212	-1560.122	317.479	292.669	248.945	456.689	-4.185
5800	57.680	369.659	546.982	-1597.038	318.370	298.440	248.801	460.335	-4.146
5900	57.608	370.644	552.747	-1634.053	319.248	304.204	248.643	463.983	-4.108
6000	57.509	371.612	558.503	-1671.166	320.113	309.960	248.470	467.635	-4.071

2.2. *Curve Fit Equations for the Equilibrium Constant*

Within the high temperature range of interest in combustion reactions, 1000-to-6000K, a curve fit for the equilibrium constant, K_P,in units of $(atm^{-1/2})$with a pinned temperature at 3000 K, results in the following:

For Tables (2) and (2a) in the range 1000 -to- 3000 K – eq. (10):

$$K_{P(2-2a)1} = 4.1172.T^{-0.6248} exp^{-\left(31355/_{T}\right)} \quad (10)$$

For Tables (2) and (2a) in the range 3000 -to- 6000 K, - eq. (10a):

$$K_{P(2-2a)2} = 0.0279.T^{-0.04127} exp^{-\left(30386/_{T}\right)} \quad (10a)$$

For Tables (3) and (3a) in the range 1000 -to- 3000 K – eq. (11):

$$K_{P(3-3a)1} = 3.0033 \times 10^{-3}.T^{0.1599} exp^{-\left(29551/_{T}\right)} \quad (11)$$

For Tables (3) and (3a) in the range 3000 -to- 6000 K, - eq. (11a):

$$K_{P(3-3a)2} = 0.01637.T^{-0.02712} exp^{-\left(30148/_{T}\right)} \quad (11a)$$

3. Accuracy and Uncertainties

Since the Enthalpies and Gibbs Energies of Formation changes of reactions allow for the prediction of other thermodynamic properties [1, 6], randomly selected data from the abridged table of GRI_**Mech** [5] provided by C. F. Melius is taken as the precise standard (PS). Table 4 shows errors in calculated (Calc) tabular results in this paper,in comparison with the accepted as precise standard results of C. F. Melius.For illustration, in Tables 5 and 6,are the fractional errors, *FE*,(as percentages) in equilibrium constant calculated with eqs. (10), (10a) and (11), (11a) for selected temperatures, in comparison with data in Tables 2, 2a and 3, 3a respectively.

Table 4. Fractional Uncertainty of Thermochemical data of NNH by $\Delta_f H^o_{Calc}$ Evaluation

Temperature (K)	$\Delta_f H^o_{PS}$ (kcal/mol)	$\Delta_f H^o_{Calc}$ (kcal/mol)	$\%FE_{r-\Delta fHo}$
200	59.85	59.85	0
298.15	59.64	59.63	0.0168
500	59.29	59.29	0
1000	59.08	59.08	0
1200	59.10	59.10	0
1500	59.17	59.18	-0.0169
2000	59.35	59.35	0
2200	59.42	59.42	0
2500	59.52	59.52	0
3000	59.65	59.66	-0.0168
Average Absolute Percentage Error			0.0051

Note: $\%FE_{r-\Delta fHo} = 100(\Delta_f H^o_{PS} - \Delta_f H^o_{Calc})/\Delta_f H^o_{PS}$

The uncertainty in the results reported by [6] in Table 4, is ±5.43 % max @ 298.15 K.

Table 5. Fractional Uncertainty (Percentage Error) Estimation, in Calculated Equilibrium Constant, K_P,

Temperature (K)	***Log K_P in Table 2 or2a***	***Log K_P Calculated***	***$\%FE_{r\text{-}LogKp}$***
1000	-14.877	-14.877	0.000
1500	-10.448	-10.448	0.000
2000	-8.277	-8.257	0.242
2500	-6.970	-6.955	0.215
3000	-6.097	-6.097	0.000
3500	-5.472	-5.471	0.018
4000	-5.003	-5.002	0.020
4500	-4.638	-4.638	0.000
5000	-4.346	-4.346	0.000
5500	-4.108	-4.108	0.000
6000	-3.910	-3.910	0.000
Average Absolute Percentage Error			0.045

Note: The averaged absolute uncertainty for Table 2 and 2a, is 0.078 percent for the complete range (1000 -to-6000 K).

Table 6. Fractional Uncertainty (Percentage Error) Estimation, in Calculated Equilibrium Constant, K_P, with Curve-Fit Eqs. (11) and (11a) for selected temperatures, in Comparison with Data in Table 3 and 3a

Temperature(K)	***Log K_P in Table 3 or 3a***	***Log K_P Calculated***	***$\%FE_{r\text{-}LogKp}$***
1000	-14.877	-14.877	0.000
1500	-10.571	-10.570	0.009
2000	-8.413	-8.411	0.024
2500	-7.114	-7.113	0.014
3000	-6.245	-6.244	0.016
3500	-5.624	-5.623	0.018
4000	-5.158	-5.157	0.019
4500	-4.795	-4.795	0.000
5000	-4.505	-4.505	0.000
5500	-4.268	-4.268	0.000
6000	-4.071	-4.071	0.000
Average Absolute Percentage Error			0.009

Note: The averaged absolute uncertainty in Table 6, compares with the 0.01 percent for the complete range (1000 -to-6000 K).

4. Conclusions

Due to the increased concentrations of atoms in extreme high temperature flame fronts, the importance of NNH reaction pathways have been reported [2], and, the accurate model predictions of the likely high NOx concentrations is thus of concern. In high temperature (*≥2200 K*) NOx formation, and low temperature(*≤1900 K*) reduction, the NNH species has been observed [9, 3, 2], when the breaking and stability of nitrogen-nitrogen bond are considered respectively. This contribution of the NNH thermo-chemical properties dataTable is to add to the existing literature of Nitrogen and NOx chemistry, as more stringent legislative demands for greener environments for NOx removalare put in place, and better technological searches in real-time Data Driven Control-Oriented (DDCO) sensors with ease of least-squares calibration and bias correction [10], for low temperature NOx control and removal through N_2 formation arebeing made, with such concerns for species concentration changes during the stages of the combustion process or simply, combustion aging concerns. Observe thatresults in the two methods of solution are comparable, for example, below the Tables' pinned temperature of 1000 K (i.e. the range 200-to-1000 K), same values for the equilibrium constantsof formation are obtained, but, with deviations of about ± 4 percent maximum, in the range, 1000-to-6000 K, with greater deviations at higher temperatures depending on the accepted frame. Other listed thermo-chemical properties values deviations are below ± 1 percent. Validation of results, and, for the method of solution was, by comparison with the published output in the abridged Table of GRI_MECH 3.0[5] earlier referred to.Since, the full NASA coefficients as displayed in Table 1 were programmed in Microsoft EXCEL™ to the degree of precision as is, it is taken that any uncertainties in the results presentation will be overcome in line with the observations of Burcat and Ruscic [6], that the accuracy of the NASA polynomials coefficients is much better than any modelling generated errors, which as indicated by the low error (uncertainty) results in computed average absolute percentage error in Tables 4, 5 and 6, is evidence of the smoothness in the curve fitting, by the selected paired data points.

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