An Improved Kinetic Model for Highly Ionized N_2–CH_4 Shocked Flows

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The unique characteristics of Saturn's Moon Huygens make it an interesting target for exploration missions, specially after the successful Huygens probe entry in 2005. The preparation of the atmospheric entry phase of this mission evidenced that the former Nelson kinetics model of 1991 [1] needed revision, a work that was eventually carried out by Gökçen [2], who revised and updated the dataset for neutral reactions. However, the ionized reactions dataset was not revised, as justified by the fact that for the lower entry speed of the Huygens probe (about $5\mathrm{km/s}$), a velocity where the resulting ionization would be low. However, future exploration missions to Huygens might involve faster entries, with a larger degree of ionization. This means that the Gökçen model needs further updates, more specifically regarding the ionization reactions.

Such is the topic of this work. 32 reliable cross-sections from the literature have been compiled and converted into rates. A sensitivity study has been carried out for the case of the relaxation behind a shock-wave of 9 and $11\mathrm{km/s}$ respectively, and at an initial pressure of $13\mathrm{Pa}$. The sensitivity has been studied against Temperature, electon density, and CN molecule density (due to the strong radiation of the CN Violet system). This has allowed reducing this initial set of 32 rates to a final set of 18 rates. A further verification of the consistency of the neutral rates (as regarding the respectiv gas-kinetic limits) has additionally been carried out, and some neutral rates have also been replaced. A final set of 45 rates is obtained, suitable for the simulation of high-temperature, strongly ionized N_2–CH_4 Shocked Flows. The dataset is presented in Tab. 1. Updated rates are presented in red.

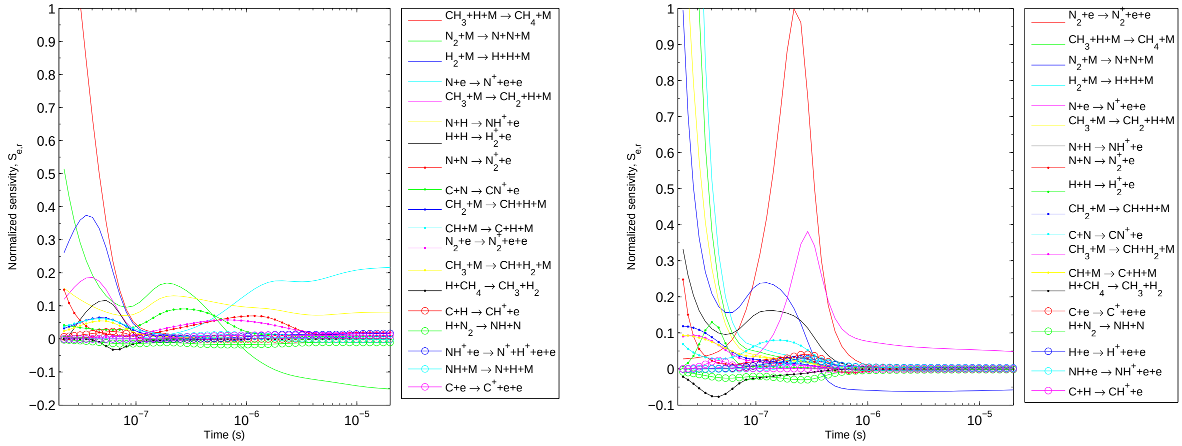

Figure 1: Sensitivity analysis for e^- concentrations, for v=$9\mathrm{km/s}$ (left) and v=$11\mathrm{km/s}$ (right).

References

[1] Nelson H. F., Park C., and Whiting E. E. 1991 *J. Thermophys. Heat Transf.* 5 157.
[2] Gökçen T. 2005 *J. Thermophys. Heat Transfer* 21 9.

Table 1: New Chemical Dataset for N_2–CH_4 flows

No.	Reaction	Rate ($\mathrm{cm}^3/\mathrm{mol/s}$)	Note.
1	$\mathrm{N_2 + Mol. \rightleftarrows N + N + Mol}$	$1.72 \times 10^{18} T^{-0.89} \exp(-111,700/T)$	a
2	$\mathrm{N_2 + Atom \rightleftarrows N + N + Atom}$	$1.21 \times 10^{19} T^{-0.89} \exp(-111,700/T)$	a
3	$\mathrm{CH_4 + M \rightleftarrows CH_3 + H + M}$	$1.06 \times 10^{22} T^{-1.46} \exp(-49,990/T)$	b,c
4	$\mathrm{CH_3 + M \rightleftarrows CH_2 + H + M}$	$2.82 \times 10^{14} \exp(-42,460/T)$	
5	$\mathrm{CH_3 + M \rightleftarrows CH + H_2 + M}$	$5.00 \times 10^{15} \exp(-42,800/T)$	
6	$\mathrm{CH_2 + M \rightleftarrows CH + H + M}$	$4.00 \times 10^{15} \exp(-41,800/T)$	
7	$\mathrm{CH_2 + M \rightleftarrows C + H_2 + M}$	$1.30 \times 10^{14} \exp(-29,700/T)$	
8	$\mathrm{CH + M \rightleftarrows C + H + M}$	$1.90 \times 10^{14} \exp(-33,700/T)$	
9	$\mathrm{C_2 + M \rightleftarrows C + C + M}$	$3.72 \times 10^{14} \exp(-69,800/T)$	
10	$\mathrm{H_2 + M \rightleftarrows H + H + M}$	$2.23 \times 10^{14} \exp(-48,350/T)$	
11	$\mathrm{CN + M \rightleftarrows C + N + M}$	$2.53 \times 10^{14} \exp(-71,000/T)$	
12	$\mathrm{NH + M \rightleftarrows N + H + M}$	$1.80 \times 10^{14} \exp(-37,600/T)$	
13	$\mathrm{HCN + M \rightleftarrows CN + H + M}$	$3.57 \times 10^{26} T^{-2.60} \exp(-62,845/T)$	
14	$\mathrm{CH_3 + N \rightleftarrows HCN + H + H}$	7.00×10^{13}	
15	$\mathrm{CH_3 + H \rightleftarrows CH_2 + H_2}$	$6.03 \times 10^{13} \exp(-7,600/T)$	
16	$\mathrm{CH_2 + N_2 \rightleftarrows HCN + NH}$	$4.82 \times 10^{12} \exp(-18,000/T)$	
17	$\mathrm{CH_2 + N \rightleftarrows HCN + H}$	5.00×10^{13}	
18	$\mathrm{CH_2 + H \rightleftarrows CH + H_2}$	$4.21 \times 10^{8} T^{-0.09} \exp(+1,560/T)$	b
19	$\mathrm{CH + N_2 \rightleftarrows HCN + N}$	$4.40 \times 10^{12} \exp(-11,060/T)$	
20	$\mathrm{CH + C \rightleftarrows C_2 + H}$	2.00×10^{14}	
21	$\mathrm{C_2 + N_2 \rightleftarrows CN + CN}$	$1.50 \times 10^{13} \exp(-21,000/T)$	
22	$\mathrm{CN + H_2 \rightleftarrows HCN + H}$	$2.95 \times 10^{05} \exp(-1,130/T)$	
23	$\mathrm{CN + C \rightleftarrows C_2 + N}$	$3.00 \times 10^{14} \exp(-18,040/T)$	
24	$\mathrm{N + H_2 \rightleftarrows NH + H}$	$1.60 \times 10^{14} \exp(-12,650/T)$	
25	$\mathrm{C + N_2 \rightleftarrows CN + N}$	$5.24 \times 10^{13} \exp(-22,600/T)$	
26	$\mathrm{C + H_2 \rightleftarrows CH + H}$	$4.00 \times 10^{14} \exp(-11,700/T)$	
27	$\mathrm{H + N_2 \rightleftarrows NH + N}$	$3.00 \times 10^{12} T^{-0.50} \exp(-71,400/T)$	
28	$\mathrm{H + H \rightleftarrows H_2^+ + e^-}$	$1.13 \times 10^{15} T^{-0.06} \exp(-129,060/T)$	a
29	$\mathrm{C + H \rightleftarrows CH^+ + e^-}$	$9.95 \times 10^{11} T^{0.52} \exp(-84,830/T)$	a
30	$\mathrm{C + N \rightleftarrows CN^+ + e^-}$	$3.80 \times 10^{12} T^{0.33} \exp(-74,810/T)$	a
31	$\mathrm{N + H \rightleftarrows NH^+ + e^-}$	$2.99 \times 10^{14} T^{-0.06} \exp(-118,760/T)$	a
32	$\mathrm{N + N \rightleftarrows N_2^+ + e^-}$	$2.13 \times 10^{10} T^{0.48} \exp(-69,190/T)$	a
33	$\mathrm{H + e^- \rightleftarrows H^+ + e^- + e^-}$	$1.36 \times 10^{15} T^{0.18} \exp(-169,000/T)$	a
34	$\mathrm{C + e^- \rightleftarrows C^+ + e^- + e^-}$	$1.24 \times 10^{15} T^{0.28} \exp(-142,700/T)$	a
35	$\mathrm{N + e^- \rightleftarrows N^+ + e^- + e^-}$	$1.67 \times 10^{13} T^{0.59} \exp(-143,220/T)$	a
36	$\mathrm{Ar + e^- \rightleftarrows Ar^+ + e^- + e^-}$	$5.52 \times 10^{13} T^{0.58} \exp(-186,210/T)$	a
37	$\mathrm{H_2 + e^- \rightleftarrows H_2^+ + e^- + e^-}$	$4.05 \times 10^{13} T^{0.52} \exp(-180,767/T)$	a
38	$\mathrm{CH + e^- \rightleftarrows CH^+ + e^- + e^-}$	$1.15 \times 10^{12} T^{0.87} \exp(-123,430/T)$	a
39	$\mathrm{NH + e^- \rightleftarrows NH^+ + e^- + e^-}$	$2.39 \times 10^{13} T^{0.59} \exp(-172,430/T)$	a
40	$\mathrm{N_2 + e^- \rightleftarrows N_2^+ + e^- + e^-}$	$5.92 \times 10^{11} T^{0.92} \exp(-178,630/T)$	a
41	$\mathrm{NH^+ + e^- \rightleftarrows N^+ + H^+ + e^- + e^-}$	$1.25 \times 10^{13} T^{0.56} \exp(-27,350/T)$	a
42	$\mathrm{N_2^+ + e^- \rightleftarrows N^+ + N + e^-}$	$7.47 \times 10^{11} T^{0.84} \exp(-80,600/T)$	a
43	$\mathrm{C^+ + N_2 \rightleftarrows N_2^+ + C}$	$1.01 \times 10^{11} T^{0.60} \exp(-53,830/T)$	a
44	$\mathrm{C^+ + N_2 \rightleftarrows CN^+ + N}$	$1.32 \times 10^{12} T^{0.33} \exp(-51,430/T)$	a
45	$\mathrm{C^+ + N_2 \rightleftarrows N^+ + CN}$	$8.93 \times 10^{13} T^{-0.14} \exp(-65,260/T)$	a

a: fit from this work.

b: detailed balancing of published reverse rate, followed by a fit to an Arrhenius form.

c: rate slightly departs from an Arrhenius form, fit is approximate.
More accurate fit for T=500–20,000K: $K_f = 1.22 \times 10^{28} T^{-2.91} \exp(-54,000/T)$
More accurate fit for T=10,000–100,000K: $K_f = 2.28 \times 10^{15} T^{-0.12} \exp(-17,960/T)$