Computational Assignment

1. You are given that Na can act as a gas-phase catalysts for methane pyrolysis and initial decomposition pathways are given in Table 1. Write a code to perform micro-kinetic modeling in Matlab to plot the temporal variation of methane with time (0-2hrs). Take the following initial conditions: P_{CH4} = 0.45 atm, P_{Ar} = 0.45 atm, and P_{Na} = 0.1 atm. The total pressure was fixed at 1 atm and the initial volume of the reactor was taken as 1 litre. Also perform sensitivity analysis based on degree of rate control to find the rate-limiting steps in the whole framework.

[NB: Please contact TA's if you have doubts.]

Table 1: Initial steps of CH_4 pyrolysis catalysed by sodium vapours at 973 K. $\Delta E^{\ddagger}$ represents the activation electronic energy in kJ/mol. The forward reaction and backward reactions are denoted by subscript 'f' and 'b' respectively. We tabulate uni-molecular rate coefficients in s^{-1} and bi-molecular rate coefficients in cm^3/molecule/s. ΔE^0 is the electronic energy change, ΔH^0 is the enthalpy change, ΔS^0 is the entropy change, and ΔG^0 is the Gibbs free energy change of the reaction at standard conditions in kJ/mol. $^\bullet$ denotes radicals.

No.	Reactions (rxn)	ΔE^0	ΔH^0	$T\Delta S^0$	ΔG^0	$\Delta E_f^{\ddagger}$	k_i	$\Delta E_b^{\ddagger}$	k_{-i}
Initiation reactions									
1	$CH_4 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_3^\bullet + H^\bullet$	468	447	142	305	468	1.1×10^{-8}	-	4.1×10^{-10}
2	$Na_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} 2Na$	69	73	81	-8	69	2.2×10^{9}	-	1.5×10^{-9}
3	$Na_3 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Na_2 + Na$	28	28	52	-24	28	1.5×10^{11}	-	4.4×10^{-9}
4	$CH_4 + Na \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} NaH + CH_3^\bullet$	281	258	54	204	288	2.2×10^{-21}	6	1.9×10^{-10}
5	$CH_4 + Na \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} HNaCH_3$	266	255	27	228	278	3.2×10^{-22}	12	4.1×10^{9}
6	$CH_4 + Na_2 \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} Na_2H + CH_3^\bullet$	289	269	59	210	343	1.0×10^{-23}	54	1.9×10^{-12}
7	$CH_4 + Na_2 \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} Na_2CH_3 + H^\bullet$	388	377	82	295	381	9.4×10^{-27}	0	6.6×10^{-11}
8	$CH_4 + Na_2 \underset{k_{-8}}{\overset{k_8}{\rightleftharpoons}} HNa_2CH_3$	64	59	-60	118	272	2.3×10^{-23}	208	3.9×10^{2}
9	$CH_4 + Na_3 \underset{k_{-9}}{\overset{k_9}{\rightleftharpoons}} HNa_3CH_3$	42	41	-77	117	210	3.1×10^{-21}	168	4.7×10^{4}
Primary propagation reactions									
10	$CH_4 + H^\bullet \underset{k_{-10}}{\overset{k_{10}}{\rightleftharpoons}} CH_3^\bullet + H_2$	12	5	32	-27	62	6.9×10^{-13}	50	5.7×10^{-15}
11	$CH_4 + CH_3^\bullet \underset{k_{-11}}{\overset{k_{11}}{\rightleftharpoons}} C_2H_6 + H^\bullet$	64	68	-17	84	215	9.9×10^{-24}	150	3.8×10^{-19}
12	$HNaCH_3 \underset{k_{-12}}{\overset{k_{12}}{\rightleftharpoons}} NaCH_3 + H^\bullet$	15	8	20	-13	15	9.5×10^{9}	-	3.3×10^{-9}
13	$HNaCH_3 \underset{k_{-13}}{\overset{k_{13}}{\rightleftharpoons}} NaH + CH_3^\bullet$	15	3	27	-24	15	8.7×10^{10}	-	7.3×10^{-9}
14	$NaH \underset{k_{-14}}{\overset{k_{14}}{\rightleftharpoons}} Na + H^\bullet$	187	189	88	101	187	6.8×10^{3}	-	3.0×10^{-9}
15	$NaCH_3 \underset{k_{-15}}{\overset{k_{15}}{\rightleftharpoons}} Na + CH_3^\bullet$	139	136	95	41	139	8.4×10^{5}	-	2.3×10^{-10}
16	$Na_2H \underset{k_{-16}}{\overset{k_{16}}{\rightleftharpoons}} Na_2 + H^\bullet$	180	178	83	95	180	7.1×10^{3}	-	1.4×10^{-9}
17	$Na_2H \underset{k_{-17}}{\overset{k_{17}}{\rightleftharpoons}} Na + NaH$	62	62	76	-14	62	5.0×10^{9}	-	1.5×10^{-9}
18	$Na_2CH_3 \underset{k_{-18}}{\overset{k_{18}}{\rightleftharpoons}} Na_2 + CH_3$	80	69	60	10	80	5.8×10^{8}	-	3.1×10^{-9}
19	$Na_2CH_3 \underset{k_{-19}}{\overset{k_{19}}{\rightleftharpoons}} Na + NaCH_3$	10	7	46	-39	224	4.4×10^{-1}	-	3.7×10^{-12}
20	$Na_3H \underset{k_{-20}}{\overset{k_{20}}{\rightleftharpoons}} Na_2 + NaH$	102	93	87	7	102	1.4×10^{8}	-	5.1×10^{-10}
21	$Na_3H \underset{k_{-21}}{\overset{k_{21}}{\rightleftharpoons}} Na_3 + H^\bullet$	261	255	123	132	261	2.4×10^{1}	-	5.0×10^{-10}
22	$Na_3H \underset{k_{-22}}{\overset{k_{22}}{\rightleftharpoons}} Na_2H + Na$	109	104	91	13	109	4.7×10^{6}	-	3.9×10^{-11}
Termination reactions									
23	$H^\bullet + H^\bullet \underset{k_{-23}}{\overset{k_{23}}{\rightleftharpoons}} H_2$	-457	-442	-111	-332	-	1.9×10^{-10}	457	1.8×10^{-10}
24	$CH_3^* + CH_3^* \underset{k_{-24}}{\overset{k_{24}}{\rightleftharpoons}} C_2H_6$	-404	-378	-159	-220	-	2.8×10^{-10}	404	2.7×10^{-4}