

CHE – 631A

COMPUTATIONAL ASSIGNMENT

CRE

Given,

Na acts as a gas-phase catalysts for methane pyrolysis.

$P_{CH_4} = 0.45 \text{ atm}$, $P_{Ar} = 0.45 \text{ atm}$, and $P_{Na} = 0.1 \text{ atm}$

Total pressure = 1 atm and the initial volume of the reactor = 1 litre

Time span(0-2hrs)

First, we input the values of reaction coefficients of both forward and backward reactions of all 24 reactions.

Then, input the values of initial conditions given.

Then calculate the initial concentration / moles of those using ideal gas equation relation.

Conc. = $n/v = P/RT$

On calculating, we get Conc of $CH_4 = 0.0056364 \text{ mol/m}^3$

And Conc of Na = $0.0012525 \text{ mol/m}^3$

Since, the pressure is kept constant (isobaric condition) in this batch reactor (considered), volume of the reactor changes continuously. This is accounted by considering the relation:

$$n_0 \cdot v_0 = n_i \cdot v_i \quad (\text{initial and final conditions})$$

Then, write the rate of formation for each of the 16 species (including intermediates that are formed), we form the set of differential equations.

$r_1 = d[CH_4]/dt$	$n_1 = [CH_4]$
$r_2 = d[CH_3^*]/dt$	$n_2 = [CH_3^*]$
$r_3 = d[H^*]/dt$	$n_3 = [H^*]$
$r_4 = d[Na_2]/dt$	$n_4 = [Na_2]$
$r_5 = d[Na]/dt$	$n_5 = [Na]$
$r_6 = d[Na_3]/dt$	$n_6 = [Na_3]$
$r_7 = d[NaH]/dt$	$n_7 = [NaH]$
$r_8 = d[HNaCH_3]/dt$	$n_8 = [HNaCH_3]$
$r_9 = d[Na_2H]/dt$	$n_9 = [Na_2H]$

$$\begin{array}{ll}
r_{10} = d[\text{Na}_2\text{CH}_3]/dt & n_{10} = [\text{Na}_2\text{CH}_3] \\
r_{11} = d[\text{HNa}_2\text{CH}_3]/dt & n_{11} = [\text{HNa}_2\text{CH}_3] \\
r_{12} = d[\text{HNa}_3\text{CH}_3]/dt & n_{12} = [\text{HNa}_3\text{CH}_3] \\
r_{13} = d[\text{H}_2]/dt & n_{13} = [\text{H}_2] \\
r_{14} = d[\text{C}_2\text{H}_6]/dt & n_{14} = [\text{C}_2\text{H}_6] \\
r_{15} = d[\text{NaCH}_3]/dt & n_{15} = [\text{NaCH}_3] \\
r_{16} = d[\text{Na}_3\text{H}]/dt & n_{16} = [\text{Na}_3\text{H}]
\end{array}$$

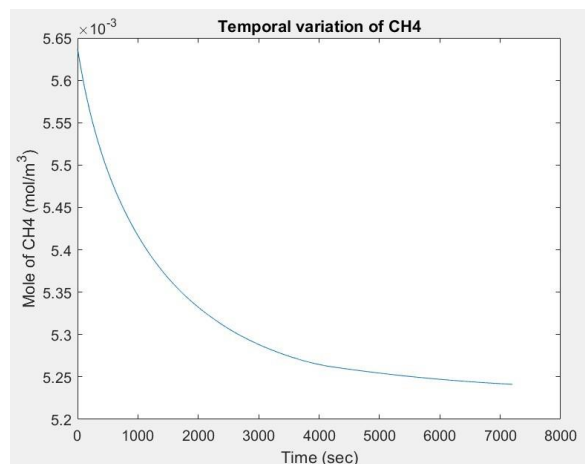
Then, solve all these ODEs using in-built ODE solver ODE15s.

$$[t,y]=\text{ode15s}(@\text{rates},t,z);$$

where rates is the function, t is the time span (2hrs), and z is the initial conditions calculated.

We plot the temporal variation of methane dissociation by gas-phase sodium clusters at 973 K. (i.e.,) CH₄ concentration (in mol/m³) with time (in sec).

The results of the code is shown below:



Then

To identify the reaction steps which are rate-controlling, we perform sensitivity analysis based on the degree of rate control (DRC).

$$\begin{aligned}
X_i &= (k_i / r) \left(\partial r / \partial k_i \right) \text{ at const } K_{eq}, k_j \neq i \\
&= \left(\partial \ln r / \partial \ln k_i \right) \text{ at const } K_{eq}, k_j \neq i
\end{aligned}$$

By, changing the K_f value by multiplying it with 1.05, and calculating its corresponding k_b value, and then checking how this affects the reaction rate by using these new(modified) reaction coefficients, we calculate DRC.

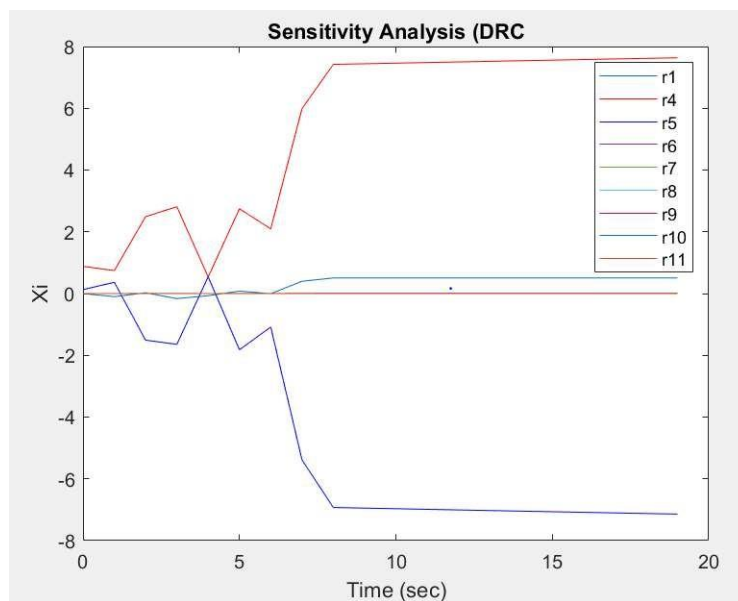
The codes used for modification are :

$$K_{eq} = k_f / k_b;$$

$$k_{fn} = 1.05 * k_f;$$

$$k_{bn} = k_{fn} / K_{eq};$$

Plotting the Ξ_i values for the reactions gives us the result submitted below :



We notice that reactions 4, 5 and 10 are sensitive.

Submitted by
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