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Microkinetic modelling of methane pyrolysis using $ZnCl_2$ catalyst

In the given problem statement, we were provided with 22 possible intermediate reaction steps for a given reaction having 15 different chemical species and using them we had to find the suitable rate law for the decomposition of methane.

Calculations:

Finding the initial boundary conditions for the problem:

It was given the partial pressure of CH_4 = 0.45 atm

Now, Concentration in mol/m^3 is given as C = $\frac{P}{R \times T}$, where P is in Pascals,

R is 8.314 J/mol K and T is given to be 1273K.

Now after putting the value we obtain C_{CH_4} = 4.30mol/m^3

Similarly, the partial pressure of $ZnCl_2$ = 0.1 atm , C_{ZnCl_2} = 0.957 mol/m^3

So, for the rest of the 13 chemical species, the initial concentration will be zero.

Approach:

We can write the rate of formation of each of the chemical species in terms of the reactions rates. Now this will give us a differential equation and for 15 chemical species, we shall obtain 15 different ordinary differential equations. Now by solving these ordinary differential equations we can get the concentration vs time plots for each of these chemical species. We would need initial conditions to solve these equations, but those are already known to us, as the initial concentrations. Now these ordinary differential equations are stiff differential equations, meaning to get an accurate solution of this equation we need a very small step size. In Matlab, there are predefined functions like ode15s or ode 23s, that can solve such differential equations, hence we use those to find the solutions. Here we have integrated in time interval from 0 to 2 seconds. We then plot the concentration vs time data and analyse it for all the species.

Matlab Code:

The code contains two scripts in matlab , in one script named ‘equations_1.m’ contains the function equations_1 which takes two parameters time and concentration. This function is called from the other script to get the results of the ode for each chemical species. The concentration of each species is defined as the variable C here. Now the rate constants for the forward and backward reactions are given for each reaction, but the unit of the rate constant is cm^3/molecule/sec. We have to multiply the bimolecular reactions with this Avogadro number. We have written all the rate constants separately as the forward and backward reactions.

$$CH_4 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_3^* + H^*$$

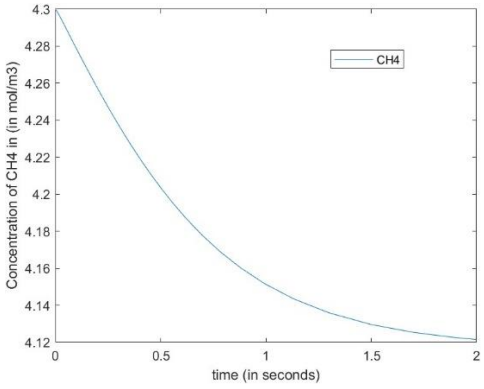
For the given reaction , we can write the rate of reaction as $K_1[CH_4]$ - $K_{-1}[CH_3*][H^*]$ (eq1)

As K_1 and - K_{-1} are known, hence r1 = $K_1[CH_4]$ - $K_{-1}[CH_3*][H*]$ has only the species concentrations as unknown. Thus we can write the rates r2, r3, r4 till r22 for all the 22 reactions like this. Now using these rates , we can write the rate of formation for each of the chemical species.

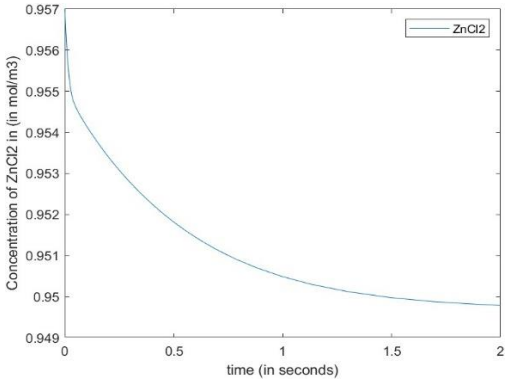
$\frac{d[CH_4]}{dt}$ = -r1-r3-r4-r5-r6-r7-r8-r9-r10 (eq2)

Where r1 , r3 , r4 , r5 , r6 , r7 , r8 , r9 and r10 are respective rates of the equations which can be expanded like in the form (eq1). Now (eq2) is an ode , and just like (eq2) we can construct such ode's for all the 15 species. Now the matlab function 'equations_1' returns the values of the concentrations of each of these species in the form of vectors when called . The advantage of having them in individual vectors is that the concentrations of each of the chemical species will be stored in each of these column vectors and hence they can be easily plotted. We then solve these ode's using the ode23s in the time interval 0 to 2 seconds. The resuts are plotted as such.

For CH_4 we get



For ZnCl_2 we get



For all the other species: