Supporting Information for the manuscript

Analytical description of the H/D exchange kinetic of macromolecule.

AUTHOR NAMES

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Isotopic exchange, Kinetic, ESI, Proteins, FT ICR, Orbitrap.

ABSTRACT

We present the accurate analytical solution obtained for the system of rate equations describing the isotope exchange process for molecule containing arbitrary number of equivalent labile atoms. The exact solution was obtained using Methematica 7.0 software and this solution has the form of the time-dependent Gaussian distribution. For the case when forward exchange considerable overlaps the back exchange it is possible to estimate the activation energy of the reaction by obtaining a temperature dependence of the reaction degree. Using previously developed approach

for performing H/D exchange directly in the ESI source, we have estimated the activation energies for several ions and they were found to be in a range 0.04eV - 0.3eV. Since the value of the activation energy depends on the type of the functional group, the developed approach can have potential analytical applications for determining of types of functional groups in complex mixtures, such as petroleum, humic substances, bio-oil etc.

SUPPORTING INFORMATION

The analytical solution of the system of rate equations:

$$\begin{aligned}
&\frac{dM_0}{dt} = -k_D M_0 + k_H \frac{1}{N} M_1 \\
&\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\
&\frac{dM_i}{dt} = \left(-k_D \frac{N-i}{N} - k_H \frac{i}{N}\right) M_i + k_H \frac{i+1}{N} M_{i+1} + k_D \frac{N-(i-1)}{N} M_{i-1}, \\
&\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\
&\frac{dM_N}{dt} = k_D \frac{1}{N} M_{N-1} - k_H M_N
\end{aligned} \tag{1}$$

with the initial conditions:

$$M_0\big|_{t=0} = M_0^0; \quad M_i\big|_{t=0} = 0, 0 < i \le N. \tag{2}$$

was performed using software Mathematica 7.0. The full code including guessing and proving the solution is presented below.

In[112]:=
```
(*
Consider the kinetics of the exchange as a function of the occupancy of the surface
*)
(* Provide values of constants, number of labile atoms and maximum time*)
Kd = 1
Kh = 0
Ndeuteriums = 30
InitialNumber = 0
Tmax = 80

(*Fill matrix*)
SystemMatrix = Table[0, {i, Ndeuteriums + 1}, {j, Ndeuteriums + 1}]

SystemMatrix[[1, 1]] = -Kd;
SystemMatrix[[1, 2]] = Kh * 1 / Ndeuteriums;

For [i = 1, i < Ndeuteriums, i++,

 SystemMatrix[[i + 1, i]] = Kd * (Ndeuteriums - (i - 1)) / Ndeuteriums;
 SystemMatrix[[i + 1, i + 1]] =
  -Kd * (Ndeuteriums - i) / Ndeuteriums - Kh * (i) / Ndeuteriums;
 SystemMatrix[[i + 1, i + 2]] = Kh * (i + 1) / Ndeuteriums;
]


SystemMatrix[[Ndeuteriums + 1, Ndeuteriums]] = Kd * (1) / Ndeuteriums;
SystemMatrix[[Ndeuteriums + 1, Ndeuteriums + 1]] = -Kh;

(*Check matrix*)
MatrixForm[SystemMatrix]

(*
Define equilibrium concentrations.To do this,
equate the derivatives to zero and model one of the
 equations on the condition of a constant amount of concentrati.
*)
SystemMatrix2 =
 ReplacePart[SystemMatrix, Ndeuteriums + 1 → Table[1, {i, Ndeuteriums + 1}]]
MassConservationCondition = Table[0, {i, Ndeuteriums + 1}];
MassConservationCondition[[Ndeuteriums + 1]] = 1
EquilibriumConcentrations = LinearSolve[SystemMatrix2, MassConservationCondition]

Print["The equilibrium distribution of the concentrations:"]
ListPlot[Table[{i, EquilibriumConcentrations[[i]]}, {i, Ndeuteriums + 1}],
 Filling -> Axis, PlotRange → Full]
```

```
(* Initial conditions*)

InitialConditions = Table[Mi[0] == 0, {i, 0, Ndeuteriums}];
InitialConditions[[InitialNumber + 1]] = (MInitialNumber[0] == 1)

(* Define the vector of concentrations*)
ConcentrationVector = Table[Mi[x], {i, 0, Ndeuteriums}];

(* Computed the right part of the system
describing the dynamics of concentrations.Left side-
 the vector of first derivatives*)
RightHand = SystemMatrix.ConcentrationVector

Equations = Table[Mi'[x] == RightHand[[i + 1]], {i, 0, Ndeuteriums}]
Eq = Join[Equations, InitialConditions]

(*
Looking for a numerical solution
*)
Solution = NDSolve[Eq, Table[Mi, {i, 0, Ndeuteriums}], {x, Tmax}]


Print[ "The dependence of the intensity of isotope peaks from time"]
Plot[Evaluate[Table[Mi[x], {i, 0, Ndeuteriums}] /. Solution],
 {x, 0, Tmax}, PlotRange → Full]

(*Calculate shape of the isotopic distribution for Tmax*)
IsotopeDistribution = Evaluate[Table[Mi[Tmax], {i, 0, Ndeuteriums}] /. Solution][[1]];

Print[ "The shape of the isotopic distribution for Tmax"]
ListPlot[Table[{i, IsotopeDistribution[[i]]}, {i, Ndeuteriums + 1}],
 Filling -> Axis, PlotRange → Full]
(*The calculated shape of the isotopic distribution for an arbitrary t<Tmax*)
Manipulate[
 ListPlot[Table[{i, Evaluate[Table[Mi[t], {i, 0, Ndeuteriums}] /. Solution][[1]][[i]]},
   {i, Ndeuteriums + 1}], Filling -> Axis, PlotRange → Full], {t, 0, Tmax}]
```

Out[112]= 1

Out[113]= 0

Out[114]= 30

Out[115]= 0

Out[116]= 80

```
Out[117]= {{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0},
  {0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0},
  {0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0},
  {0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0},
  {0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0},
  {0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0},
  {0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0},
  {0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0},
  {0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0},
  {0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0},
  {0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0},
  {0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0},
  {0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0},
  {0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0},
  {0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0},
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  {0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0},
  {0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0},
  {0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0},
  {0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0},
  {0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0},
  {0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0},
  {0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0},
  {0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0},
  {0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0},
  {0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0},
  {0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0},
  {0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0},
  {0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0},
  {0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0},
  {0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0}}
```

Out[123]//MatrixForm=

$$
\begin{pmatrix}
-1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
1 & -\frac{29}{30} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & \frac{29}{30} & -\frac{14}{15} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & \frac{14}{15} & -\frac{9}{10} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & \frac{9}{10} & -\frac{13}{15} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{13}{15} & -\frac{5}{6} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & \frac{5}{6} & -\frac{4}{5} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & \frac{4}{5} & -\frac{23}{30} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{23}{30} & -\frac{11}{15} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{11}{15} & -\frac{7}{10} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{7}{10} & -\frac{2}{3} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{2}{3} & -\frac{19}{30} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{19}{30} & -\frac{3}{5} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{3}{5} & -\frac{17}{30} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{17}{30} & -\frac{8}{15} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{8}{15} & -\frac{1}{2} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{2} & -\frac{7}{15} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{7}{15} & -\frac{13}{30} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{13}{30} & -\frac{2}{5} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{2}{5} & -\frac{11}{30} & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{11}{30} & -\frac{1}{3} \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{3} \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0
\end{pmatrix}
$$

Out[124]=

$$\{\{-1, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0\},$$

$$\{1, -\frac{29}{30}, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0\},$$

$$\{0, \frac{29}{30}, -\frac{14}{15}, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0,$$

$$0, 0, 0, 0, 0, 0, 0, 0, 0\}, \{0, 0, \frac{14}{15}, -\frac{9}{10}, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0,$$

$$0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0\}, \{0, 0, 0, \frac{9}{10}, -\frac{13}{15}, 0,$$

$$0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0\},$$

$$\{0, 0, 0, 0, \frac{13}{15}, -\frac{5}{6}, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0\},$$

$$\{0, 0, 0, 0, 0, \frac{5}{6}, -\frac{4}{5}, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0\},$$

$$\{0, 0, 0, 0, 0, 0, \frac{4}{5}, -\frac{23}{30}, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0\},$$

$$\{0, 0, 0, 0, 0, 0, 0, \frac{23}{30}, -\frac{11}{15}, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0,$$

$$0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0\}, \{0, 0, 0, 0, 0, 0, 0, 0, \frac{11}{15},$$

$$-\frac{7}{10}, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0\},$$

$$\{0, 0, 0, 0, 0, 0, 0, 0, 0, \frac{7}{10}, -\frac{2}{3}, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0\},$$

$$\{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, \frac{2}{3}, -\frac{19}{30}, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0\},$$

$$\{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, \frac{19}{30}, -\frac{3}{5}, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0\},$$

$$\{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, \frac{3}{5}, -\frac{17}{30}, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0\},$$

$$\{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, \frac{17}{30},$$

$$-\frac{8}{15}, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0\},$$

$$\{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, \frac{8}{15}, -\frac{1}{2}, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0\},$$

$$\{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, \frac{1}{2}, -\frac{7}{15}, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0\},$$

$$\{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, \frac{7}{15}, -\frac{13}{30}, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0\},$$

$$\{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, \frac{13}{30}, -\frac{2}{5}, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0\},$$

$$\{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, \frac{2}{5}, -\frac{11}{30}, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0\},$$

$$\{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, \frac{11}{30}, -\frac{1}{3}, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0\},$$

$$\{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, \frac{1}{3}, -\frac{3}{10}, 0, 0, 0, 0, 0, 0, 0, 0, 0\},$$

$$\{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, \frac{3}{10}, -\frac{4}{15}, 0, 0, 0, 0, 0, 0, 0, 0\},$$

$$\{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, \frac{4}{15}, -\frac{7}{30}, 0, 0, 0, 0, 0, 0, 0\},$$

$$\{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, \frac{7}{30}, -\frac{1}{5}, 0, 0, 0, 0, 0, 0\},$$

$$\{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, \frac{1}{5}, -\frac{1}{6}, 0, 0, 0, 0, 0\},$$

$$\{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, \frac{1}{6}, -\frac{2}{15}, 0, 0, 0, 0\},$$

$$\{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, \frac{2}{15}, -\frac{1}{10}, 0, 0, 0\},$$

$$\{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, \frac{1}{10}, -\frac{1}{15}, 0, 0\},$$

$$\{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, \frac{1}{15}, -\frac{1}{30}, 0\},$$

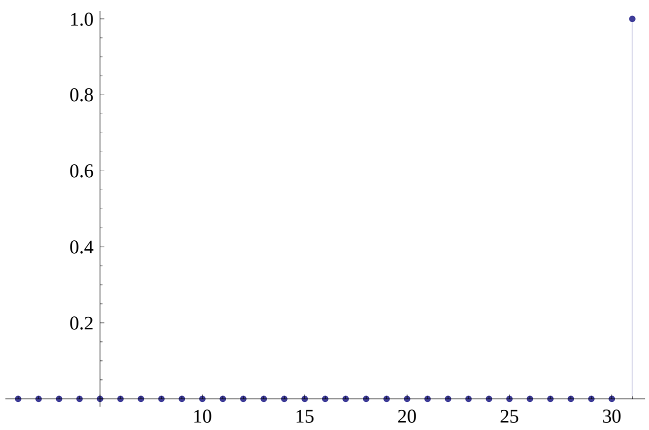
$$\{1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1\}\}$$

Out[125]= 1

Out[126]= $\{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 1\}$

The equilibrium distribution of the concentrations:

Out[128]=



Out[130]= $M_0[0] == 1$

Out[132]= $\left\{-M_0[x],\ M_0[x]-\frac{29 M_1[x]}{30},\ \frac{29 M_1[x]}{30}-\frac{14 M_2[x]}{15},\ \frac{14 M_2[x]}{15}-\frac{9 M_3[x]}{10},\ \frac{9 M_3[x]}{10}-\frac{13 M_4[x]}{15},\ \frac{13 M_4[x]}{15}-\frac{5 M_5[x]}{6},\ \frac{5 M_5[x]}{6}-\frac{4 M_6[x]}{5},\ \frac{4 M_6[x]}{5}-\frac{23 M_7[x]}{30},\ \frac{23 M_7[x]}{30}-\frac{11 M_8[x]}{15},\ \frac{11 M_8[x]}{15}-\frac{7 M_9[x]}{10},\ \frac{7 M_9[x]}{10}-\frac{2 M_{10}[x]}{3},\ \frac{2 M_{10}[x]}{3}-\frac{19 M_{11}[x]}{30},\ \frac{19 M_{11}[x]}{30}-\frac{3 M_{12}[x]}{5},\ \frac{3 M_{12}[x]}{5}-\frac{17 M_{13}[x]}{30},\ \frac{17 M_{13}[x]}{30}-\frac{8 M_{14}[x]}{15},\ \frac{8 M_{14}[x]}{15}-\frac{M_{15}[x]}{2},\ \frac{M_{15}[x]}{2}-\frac{7 M_{16}[x]}{15},\ \frac{7 M_{16}[x]}{15}-\frac{13 M_{17}[x]}{30},\ \frac{13 M_{17}[x]}{30}-\frac{2 M_{18}[x]}{5},\ \frac{2 M_{18}[x]}{5}-\frac{11 M_{19}[x]}{30},\ \frac{11 M_{19}[x]}{30}-\frac{M_{20}[x]}{3},\ \frac{M_{20}[x]}{3}-\frac{3 M_{21}[x]}{10},\ \frac{3 M_{21}[x]}{10}-\frac{4 M_{22}[x]}{15},\ \frac{4 M_{22}[x]}{15}-\frac{7 M_{23}[x]}{30},\ \frac{7 M_{23}[x]}{30}-\frac{M_{24}[x]}{5},\ \frac{M_{24}[x]}{5}-\frac{M_{25}[x]}{6},\ \frac{M_{25}[x]}{6}-\frac{2 M_{26}[x]}{15},\ \frac{2 M_{26}[x]}{15}-\frac{M_{27}[x]}{10},\ \frac{M_{27}[x]}{10}-\frac{M_{28}[x]}{15},\ \frac{M_{28}[x]}{15}-\frac{M_{29}[x]}{30},\ \frac{M_{29}[x]}{30}\right\}$

Out[133]= $\left\{(M_0)'[x]==-M_0[x],\ (M_1)'[x]==M_0[x]-\frac{29 M_1[x]}{30},\ (M_2)'[x]==\frac{29 M_1[x]}{30}-\frac{14 M_2[x]}{15},\ (M_3)'[x]==\frac{14 M_2[x]}{15}-\frac{9 M_3[x]}{10},\ (M_4)'[x]==\frac{9 M_3[x]}{10}-\frac{13 M_4[x]}{15},\ (M_5)'[x]==\frac{13 M_4[x]}{15}-\frac{5 M_5[x]}{6},\ (M_6)'[x]==\frac{5 M_5[x]}{6}-\frac{4 M_6[x]}{5},\ (M_7)'[x]==\frac{4 M_6[x]}{5}-\frac{23 M_7[x]}{30},\ (M_8)'[x]==\frac{23 M_7[x]}{30}-\frac{11 M_8[x]}{15},\ (M_9)'[x]==\frac{11 M_8[x]}{15}-\frac{7 M_9[x]}{10},\ (M_{10})'[x]==\frac{7 M_9[x]}{10}-\frac{2 M_{10}[x]}{3},\ (M_{11})'[x]==\frac{2 M_{10}[x]}{3}-\frac{19 M_{11}[x]}{30},\ (M_{12})'[x]==\frac{19 M_{11}[x]}{30}-\frac{3 M_{12}[x]}{5},\ (M_{13})'[x]==\frac{3 M_{12}[x]}{5}-\frac{17 M_{13}[x]}{30},\ (M_{14})'[x]==\frac{17 M_{13}[x]}{30}-\frac{8 M_{14}[x]}{15},\ (M_{15})'[x]==\frac{8 M_{14}[x]}{15}-\frac{M_{15}[x]}{2},\ (M_{16})'[x]==\frac{M_{15}[x]}{2}-\frac{7 M_{16}[x]}{15},\ (M_{17})'[x]==\frac{7 M_{16}[x]}{15}-\frac{13 M_{17}[x]}{30},\ (M_{18})'[x]==\frac{13 M_{17}[x]}{30}-\frac{2 M_{18}[x]}{5},\ (M_{19})'[x]==\frac{2 M_{18}[x]}{5}-\frac{11 M_{19}[x]}{30},\ (M_{20})'[x]==\frac{11 M_{19}[x]}{30}-\frac{M_{20}[x]}{3},\ (M_{21})'[x]==\frac{M_{20}[x]}{3}-\frac{3 M_{21}[x]}{10},\ (M_{22})'[x]==\frac{3 M_{21}[x]}{10}-\frac{4 M_{22}[x]}{15},\ (M_{23})'[x]==\frac{4 M_{22}[x]}{15}-\frac{7 M_{23}[x]}{30},\ (M_{24})'[x]==\frac{7 M_{23}[x]}{30}-\frac{M_{24}[x]}{5},\ (M_{25})'[x]==\frac{M_{24}[x]}{5}-\frac{M_{25}[x]}{6},\ (M_{26})'[x]==\frac{M_{25}[x]}{6}-\frac{2 M_{26}[x]}{15},\ (M_{27})'[x]==\frac{2 M_{26}[x]}{15}-\frac{M_{27}[x]}{10},\ (M_{28})'[x]==\frac{M_{27}[x]}{10}-\frac{M_{28}[x]}{15},\ (M_{29})'[x]==\frac{M_{28}[x]}{15}-\frac{M_{29}[x]}{30},\ (M_{30})'[x]==\frac{M_{29}[x]}{30}\right\}$

Out[134]=

$$\Big\{(M_0)'[x] == -M_0[x],\ (M_1)'[x] == M_0[x] - \frac{29\, M_1[x]}{30},\ (M_2)'[x] == \frac{29\, M_1[x]}{30} - \frac{14\, M_2[x]}{15},$$

$$(M_3)'[x] == \frac{14\, M_2[x]}{15} - \frac{9\, M_3[x]}{10},\ (M_4)'[x] == \frac{9\, M_3[x]}{10} - \frac{13\, M_4[x]}{15},\ (M_5)'[x] == \frac{13\, M_4[x]}{15} - \frac{5\, M_5[x]}{6},$$

$$(M_6)'[x] == \frac{5\, M_5[x]}{6} - \frac{4\, M_6[x]}{5},\ (M_7)'[x] == \frac{4\, M_6[x]}{5} - \frac{23\, M_7[x]}{30},\ (M_8)'[x] == \frac{23\, M_7[x]}{30} - \frac{11\, M_8[x]}{15},$$

$$(M_9)'[x] == \frac{11\, M_8[x]}{15} - \frac{7\, M_9[x]}{10},\ (M_{10})'[x] == \frac{7\, M_9[x]}{10} - \frac{2\, M_{10}[x]}{3},\ (M_{11})'[x] == \frac{2\, M_{10}[x]}{3} - \frac{19\, M_{11}[x]}{30},$$

$$(M_{12})'[x] == \frac{19\, M_{11}[x]}{30} - \frac{3\, M_{12}[x]}{5},\ (M_{13})'[x] == \frac{3\, M_{12}[x]}{5} - \frac{17\, M_{13}[x]}{30},$$

$$(M_{14})'[x] == \frac{17\, M_{13}[x]}{30} - \frac{8\, M_{14}[x]}{15},\ (M_{15})'[x] == \frac{8\, M_{14}[x]}{15} - \frac{M_{15}[x]}{2},\ (M_{16})'[x] == \frac{M_{15}[x]}{2} - \frac{7\, M_{16}[x]}{15},$$

$$(M_{17})'[x] == \frac{7\, M_{16}[x]}{15} - \frac{13\, M_{17}[x]}{30},\ (M_{18})'[x] == \frac{13\, M_{17}[x]}{30} - \frac{2\, M_{18}[x]}{5},$$

$$(M_{19})'[x] == \frac{2\, M_{18}[x]}{5} - \frac{11\, M_{19}[x]}{30},\ (M_{20})'[x] == \frac{11\, M_{19}[x]}{30} - \frac{M_{20}[x]}{3},\ (M_{21})'[x] == \frac{M_{20}[x]}{3} - \frac{3\, M_{21}[x]}{10},$$

$$(M_{22})'[x] == \frac{3\, M_{21}[x]}{10} - \frac{4\, M_{22}[x]}{15},\ (M_{23})'[x] == \frac{4\, M_{22}[x]}{15} - \frac{7\, M_{23}[x]}{30},\ (M_{24})'[x] == \frac{7\, M_{23}[x]}{30} - \frac{M_{24}[x]}{5},$$

$$(M_{25})'[x] == \frac{M_{24}[x]}{5} - \frac{M_{25}[x]}{6},\ (M_{26})'[x] == \frac{M_{25}[x]}{6} - \frac{2\, M_{26}[x]}{15},\ (M_{27})'[x] == \frac{2\, M_{26}[x]}{15} - \frac{M_{27}[x]}{10},$$

$$(M_{28})'[x] == \frac{M_{27}[x]}{10} - \frac{M_{28}[x]}{15},\ (M_{29})'[x] == \frac{M_{28}[x]}{15} - \frac{M_{29}[x]}{30},\ (M_{30})'[x] == \frac{M_{29}[x]}{30},\ M_0[0] == 1,$$

$$M_1[0] == 0,\ M_2[0] == 0,\ M_3[0] == 0,\ M_4[0] == 0,\ M_5[0] == 0,\ M_6[0] == 0,\ M_7[0] == 0,\ M_8[0] == 0,$$

$$M_9[0] == 0,\ M_{10}[0] == 0,\ M_{11}[0] == 0,\ M_{12}[0] == 0,\ M_{13}[0] == 0,\ M_{14}[0] == 0,\ M_{15}[0] == 0,\ M_{16}[0] == 0,$$

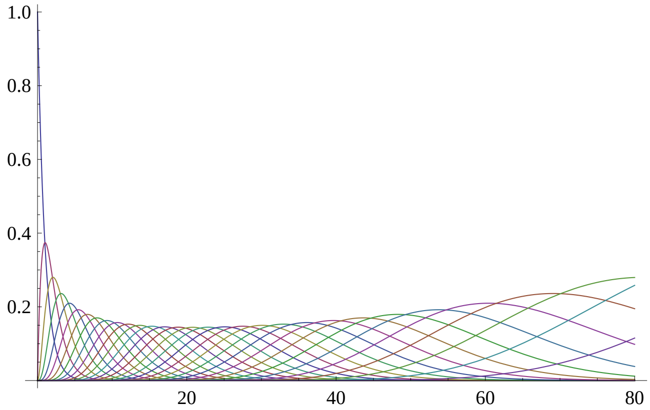
$$M_{17}[0] == 0,\ M_{18}[0] == 0,\ M_{19}[0] == 0,\ M_{20}[0] == 0,\ M_{21}[0] == 0,\ M_{22}[0] == 0,\ M_{23}[0] == 0,$$

$$M_{24}[0] == 0,\ M_{25}[0] == 0,\ M_{26}[0] == 0,\ M_{27}[0] == 0,\ M_{28}[0] == 0,\ M_{29}[0] == 0,\ M_{30}[0] == 0\Big\}$$

Out[135]=
```
{{M0 → InterpolatingFunction[{{0., 80.}}, <>],
  M1 → InterpolatingFunction[{{0., 80.}}, <>],
  M2 → InterpolatingFunction[{{0., 80.}}, <>],
  M3 → InterpolatingFunction[{{0., 80.}}, <>],
  M4 → InterpolatingFunction[{{0., 80.}}, <>],
  M5 → InterpolatingFunction[{{0., 80.}}, <>],
  M6 → InterpolatingFunction[{{0., 80.}}, <>],
  M7 → InterpolatingFunction[{{0., 80.}}, <>],
  M8 → InterpolatingFunction[{{0., 80.}}, <>],
  M9 → InterpolatingFunction[{{0., 80.}}, <>],
  M10 → InterpolatingFunction[{{0., 80.}}, <>],
  M11 → InterpolatingFunction[{{0., 80.}}, <>],
  M12 → InterpolatingFunction[{{0., 80.}}, <>],
  M13 → InterpolatingFunction[{{0., 80.}}, <>],
  M14 → InterpolatingFunction[{{0., 80.}}, <>],
  M15 → InterpolatingFunction[{{0., 80.}}, <>],
  M16 → InterpolatingFunction[{{0., 80.}}, <>],
  M17 → InterpolatingFunction[{{0., 80.}}, <>],
  M18 → InterpolatingFunction[{{0., 80.}}, <>],
  M19 → InterpolatingFunction[{{0., 80.}}, <>],
  M20 → InterpolatingFunction[{{0., 80.}}, <>],
  M21 → InterpolatingFunction[{{0., 80.}}, <>],
  M22 → InterpolatingFunction[{{0., 80.}}, <>],
  M23 → InterpolatingFunction[{{0., 80.}}, <>],
  M24 → InterpolatingFunction[{{0., 80.}}, <>],
  M25 → InterpolatingFunction[{{0., 80.}}, <>],
  M26 → InterpolatingFunction[{{0., 80.}}, <>],
  M27 → InterpolatingFunction[{{0., 80.}}, <>],
  M28 → InterpolatingFunction[{{0., 80.}}, <>],
  M29 → InterpolatingFunction[{{0., 80.}}, <>],
  M30 → InterpolatingFunction[{{0., 80.}}, <>]}}
```

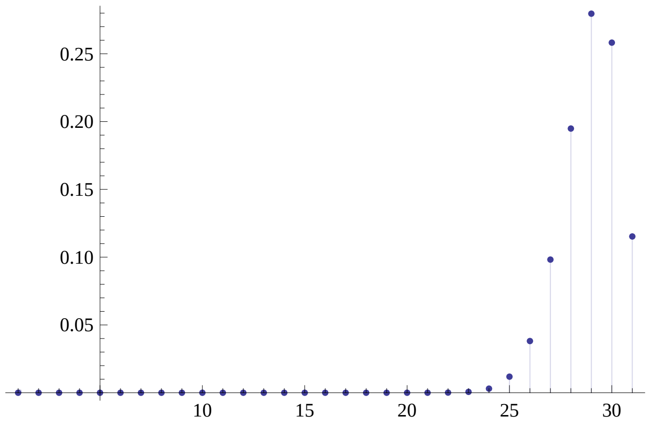
The dependence of the intensity of isotope peaks from time

Out[137]=

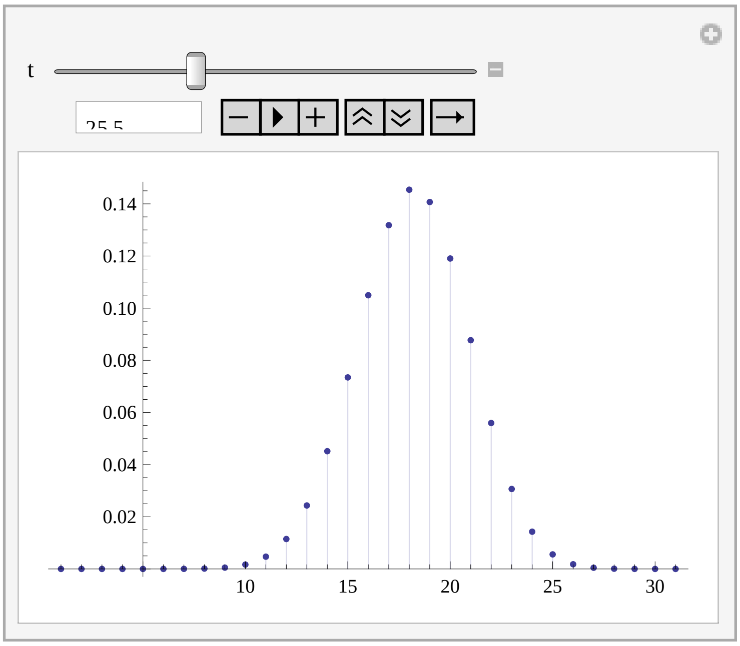


The shape of the isotopic distribution for Tmax

Out[140]=



Out[141]=



In[61]:=

```
(*
Looking for an analytical solution
*)

Kd = Kdd
Kh = Khh
Ndeuteriums = 5
InitialNumber = 0
Tmax = 50
(*Fill matrix*)
```

```
SystemMatrix = Table[0, {i, Ndeuteriums + 1}, {j, Ndeuteriums + 1}]

SystemMatrix[[1, 1]] = -Kd;
SystemMatrix[[1, 2]] = Kh * 1 / Ndeuteriums;

For [i = 1, i < Ndeuteriums, i++,

 SystemMatrix[[i + 1, i]] = Kd * (Ndeuteriums - (i - 1)) / Ndeuteriums;
 SystemMatrix[[i + 1, i + 1]] =
  -Kd * (Ndeuteriums - i) / Ndeuteriums - Kh * (i) / Ndeuteriums;
 SystemMatrix[[i + 1, i + 2]] = Kh * (i + 1) / Ndeuteriums;
]


SystemMatrix[[Ndeuteriums + 1, Ndeuteriums]] = Kd * (1) / Ndeuteriums;
SystemMatrix[[Ndeuteriums + 1, Ndeuteriums + 1]] = -Kh;

(*Check matrix*)
MatrixForm[SystemMatrix]

(* Initial conditions*)

InitialConditions = Table[Mi[0] == 0, {i, 0, Ndeuteriums}];
InitialConditions[[InitialNumber + 1]] = (MInitialNumber[0] == 1)

(* Define the vector of concentrations *)
ConcentrationVector = Table[Mi[x], {i, 0, Ndeuteriums}];

(* Compute the right part of the system
describing the dynamics of concentrations.Left side-
 the vector of first derivatives *)
RightHand = SystemMatrix.ConcentrationVector

Equations = Table[Mi'[x] == RightHand[[i + 1]], {i, 0, Ndeuteriums}]
Eq = Join[Equations, InitialConditions]

SolutionA = DSolve[Eq, Table[Mi, {i, 0, Ndeuteriums}], x]
Print["These are analytical solution:"]
AnaliticalSolution = Evaluate[Table[Mi[x], {i, 0, Ndeuteriums}] /. SolutionA]
SolutionDerivative = D[AnaliticalSolution, x]

MatrixForm[SystemMatrix.AnaliticalSolution[[1]]]
MatrixForm[SolutionDerivative[[1]]]
SystemMatrix.AnaliticalSolution[[1]] - SolutionDerivative[[1]]

Print["Check that the analytic solution indeed satisfies system::"]
Simplify[SystemMatrix.AnaliticalSolution[[1]] - SolutionDerivative[[1]]] 0
```

```
Out[61]= Kdd

Out[62]= Khh

Out[63]= 5

Out[64]= 0

Out[65]= 50

Out[66]= {{0, 0, 0, 0, 0, 0}, {0, 0, 0, 0, 0, 0}, {0, 0, 0, 0, 0, 0},
          {0, 0, 0, 0, 0, 0}, {0, 0, 0, 0, 0, 0}, {0, 0, 0, 0, 0, 0}}
```

Out[72]//MatrixForm=

$$\begin{pmatrix} -\text{Kdd} & \frac{\text{Khh}}{5} & 0 & 0 & 0 & 0 \\ \text{Kdd} & -\frac{4\,\text{Kdd}}{5}-\frac{\text{Khh}}{5} & \frac{2\,\text{Khh}}{5} & 0 & 0 & 0 \\ 0 & \frac{4\,\text{Kdd}}{5} & -\frac{3\,\text{Kdd}}{5}-\frac{2\,\text{Khh}}{5} & \frac{3\,\text{Khh}}{5} & 0 & 0 \\ 0 & 0 & \frac{3\,\text{Kdd}}{5} & -\frac{2\,\text{Kdd}}{5}-\frac{3\,\text{Khh}}{5} & \frac{4\,\text{Khh}}{5} & 0 \\ 0 & 0 & 0 & \frac{2\,\text{Kdd}}{5} & -\frac{\text{Kdd}}{5}-\frac{4\,\text{Khh}}{5} & \text{Khh} \\ 0 & 0 & 0 & 0 & \frac{\text{Kdd}}{5} & -\text{Khh} \end{pmatrix}$$

Out[74]= $M_0[0] == 1$

Out[76]= $$\left\{-\text{Kdd}\,M_0[x]+\frac{1}{5}\text{Khh}\,M_1[x],\ \text{Kdd}\,M_0[x]+\left(-\frac{4\,\text{Kdd}}{5}-\frac{\text{Khh}}{5}\right)M_1[x]+\frac{2}{5}\text{Khh}\,M_2[x],\right.$$
$$\frac{4}{5}\text{Kdd}\,M_1[x]+\left(-\frac{3\,\text{Kdd}}{5}-\frac{2\,\text{Khh}}{5}\right)M_2[x]+\frac{3}{5}\text{Khh}\,M_3[x],$$
$$\frac{3}{5}\text{Kdd}\,M_2[x]+\left(-\frac{2\,\text{Kdd}}{5}-\frac{3\,\text{Khh}}{5}\right)M_3[x]+\frac{4}{5}\text{Khh}\,M_4[x],$$
$$\left.\frac{2}{5}\text{Kdd}\,M_3[x]+\left(-\frac{\text{Kdd}}{5}-\frac{4\,\text{Khh}}{5}\right)M_4[x]+\text{Khh}\,M_5[x],\ \frac{1}{5}\text{Kdd}\,M_4[x]-\text{Khh}\,M_5[x]\right\}$$

Out[77]= $$\left\{(M_0)'[x]==-\text{Kdd}\,M_0[x]+\frac{1}{5}\text{Khh}\,M_1[x],\ (M_1)'[x]==\text{Kdd}\,M_0[x]+\left(-\frac{4\,\text{Kdd}}{5}-\frac{\text{Khh}}{5}\right)M_1[x]+\frac{2}{5}\text{Khh}\,M_2[x],\right.$$
$$(M_2)'[x]==\frac{4}{5}\text{Kdd}\,M_1[x]+\left(-\frac{3\,\text{Kdd}}{5}-\frac{2\,\text{Khh}}{5}\right)M_2[x]+\frac{3}{5}\text{Khh}\,M_3[x],$$
$$(M_3)'[x]==\frac{3}{5}\text{Kdd}\,M_2[x]+\left(-\frac{2\,\text{Kdd}}{5}-\frac{3\,\text{Khh}}{5}\right)M_3[x]+\frac{4}{5}\text{Khh}\,M_4[x],$$
$$\left.(M_4)'[x]==\frac{2}{5}\text{Kdd}\,M_3[x]+\left(-\frac{\text{Kdd}}{5}-\frac{4\,\text{Khh}}{5}\right)M_4[x]+\text{Khh}\,M_5[x],\ (M_5)'[x]==\frac{1}{5}\text{Kdd}\,M_4[x]-\text{Khh}\,M_5[x]\right\}$$

Out[78]= $$\left\{(M_0)'[x]==-\text{Kdd}\,M_0[x]+\frac{1}{5}\text{Khh}\,M_1[x],\ (M_1)'[x]==\text{Kdd}\,M_0[x]+\left(-\frac{4\,\text{Kdd}}{5}-\frac{\text{Khh}}{5}\right)M_1[x]+\frac{2}{5}\text{Khh}\,M_2[x],\right.$$
$$(M_2)'[x]==\frac{4}{5}\text{Kdd}\,M_1[x]+\left(-\frac{3\,\text{Kdd}}{5}-\frac{2\,\text{Khh}}{5}\right)M_2[x]+\frac{3}{5}\text{Khh}\,M_3[x],$$
$$(M_3)'[x]==\frac{3}{5}\text{Kdd}\,M_2[x]+\left(-\frac{2\,\text{Kdd}}{5}-\frac{3\,\text{Khh}}{5}\right)M_3[x]+\frac{4}{5}\text{Khh}\,M_4[x],$$
$$(M_4)'[x]==\frac{2}{5}\text{Kdd}\,M_3[x]+\left(-\frac{\text{Kdd}}{5}-\frac{4\,\text{Khh}}{5}\right)M_4[x]+\text{Khh}\,M_5[x],\ (M_5)'[x]==\frac{1}{5}\text{Kdd}\,M_4[x]-\text{Khh}\,M_5[x],$$
$$\left.M_0[0]==1,\ M_1[0]==0,\ M_2[0]==0,\ M_3[0]==0,\ M_4[0]==0,\ M_5[0]==0\right\}$$

Out[79]=
$$\left\{\left\{M_0 \to \text{Function}\left[\{x\}, \frac{\left(e^{\frac{1}{5}(-Kdd-Khh)\,x}\,Kdd+Khh\right)^5}{(Kdd+Khh)^5}\right],\right.\right.$$
$$M_1 \to \text{Function}\left[\{x\}, -\frac{5\left(-1+e^{\frac{1}{5}(-Kdd-Khh)\,x}\right)Kdd\left(e^{\frac{1}{5}(-Kdd-Khh)\,x}\,Kdd+Khh\right)^4}{(Kdd+Khh)^5}\right],$$
$$M_2 \to \text{Function}\left[\{x\}, \frac{10\left(-1+e^{\frac{1}{5}(-Kdd-Khh)\,x}\right)^2 Kdd^2\left(e^{\frac{1}{5}(-Kdd-Khh)\,x}\,Kdd+Khh\right)^3}{(Kdd+Khh)^5}\right],$$
$$M_3 \to \text{Function}\left[\{x\}, -\frac{10\left(-1+e^{\frac{1}{5}(-Kdd-Khh)\,x}\right)^3 Kdd^3\left(e^{\frac{1}{5}(-Kdd-Khh)\,x}\,Kdd+Khh\right)^2}{(Kdd+Khh)^5}\right],$$
$$M_4 \to \text{Function}\left[\{x\}, \frac{5\left(-1+e^{\frac{1}{5}(-Kdd-Khh)\,x}\right)^4 Kdd^4\left(e^{\frac{1}{5}(-Kdd-Khh)\,x}\,Kdd+Khh\right)}{(Kdd+Khh)^5}\right],$$
$$\left.\left.M_5 \to \text{Function}\left[\{x\}, -\frac{\left(-1+e^{\frac{1}{5}(-Kdd-Khh)\,x}\right)^5 Kdd^5}{(Kdd+Khh)^5}\right]\right\}\right\}$$

```
These are analytical solution:
```

Out[81]=
$$\left\{\left\{\frac{\left(e^{\frac{1}{5}(-Kdd-Khh)\,x}\,Kdd+Khh\right)^5}{(Kdd+Khh)^5}, -\frac{5\left(-1+e^{\frac{1}{5}(-Kdd-Khh)\,x}\right)Kdd\left(e^{\frac{1}{5}(-Kdd-Khh)\,x}\,Kdd+Khh\right)^4}{(Kdd+Khh)^5},\right.\right.$$
$$\frac{10\left(-1+e^{\frac{1}{5}(-Kdd-Khh)\,x}\right)^2 Kdd^2\left(e^{\frac{1}{5}(-Kdd-Khh)\,x}\,Kdd+Khh\right)^3}{(Kdd+Khh)^5},$$
$$-\frac{10\left(-1+e^{\frac{1}{5}(-Kdd-Khh)\,x}\right)^3 Kdd^3\left(e^{\frac{1}{5}(-Kdd-Khh)\,x}\,Kdd+Khh\right)^2}{(Kdd+Khh)^5},$$
$$\left.\left.\frac{5\left(-1+e^{\frac{1}{5}(-Kdd-Khh)\,x}\right)^4 Kdd^4\left(e^{\frac{1}{5}(-Kdd-Khh)\,x}\,Kdd+Khh\right)}{(Kdd+Khh)^5}, -\frac{\left(-1+e^{\frac{1}{5}(-Kdd-Khh)\,x}\right)^5 Kdd^5}{(Kdd+Khh)^5}\right\}\right\}$$

Out[82]=

$$\Bigg\{\Bigg\{\frac{e^{\frac{1}{5}(-Kdd-Khh)x}\,Kdd\,(-Kdd-Khh)\left(e^{\frac{1}{5}(-Kdd-Khh)x}\,Kdd+Khh\right)^4}{(Kdd+Khh)^5},$$

$$-\frac{4\,e^{\frac{1}{5}(-Kdd-Khh)x}\left(-1+e^{\frac{1}{5}(-Kdd-Khh)x}\right)Kdd^2\,(-Kdd-Khh)\left(e^{\frac{1}{5}(-Kdd-Khh)x}\,Kdd+Khh\right)^3}{(Kdd+Khh)^5}-\frac{e^{\frac{1}{5}(-Kdd-Khh)x}\,Kdd\,(-Kdd-Khh)\left(e^{\frac{1}{5}(-Kdd-Khh)x}\,Kdd+Khh\right)^4}{(Kdd+Khh)^5},$$

$$\frac{6\,e^{\frac{1}{5}(-Kdd-Khh)x}\left(-1+e^{\frac{1}{5}(-Kdd-Khh)x}\right)^2Kdd^3\,(-Kdd-Khh)\left(e^{\frac{1}{5}(-Kdd-Khh)x}\,Kdd+Khh\right)^2}{(Kdd+Khh)^5}+\frac{4\,e^{\frac{1}{5}(-Kdd-Khh)x}\left(-1+e^{\frac{1}{5}(-Kdd-Khh)x}\right)Kdd^2\,(-Kdd-Khh)\left(e^{\frac{1}{5}(-Kdd-Khh)x}\,Kdd+Khh\right)^3}{(Kdd+Khh)^5},$$

$$-\frac{4\,e^{\frac{1}{5}(-Kdd-Khh)x}\left(-1+e^{\frac{1}{5}(-Kdd-Khh)x}\right)^3Kdd^4\,(-Kdd-Khh)\left(e^{\frac{1}{5}(-Kdd-Khh)x}\,Kdd+Khh\right)}{(Kdd+Khh)^5}-\frac{6\,e^{\frac{1}{5}(-Kdd-Khh)x}\left(-1+e^{\frac{1}{5}(-Kdd-Khh)x}\right)^2Kdd^3\,(-Kdd-Khh)\left(e^{\frac{1}{5}(-Kdd-Khh)x}\,Kdd+Khh\right)^2}{(Kdd+Khh)^5},$$

$$\frac{e^{\frac{1}{5}(-Kdd-Khh)x}\left(-1+e^{\frac{1}{5}(-Kdd-Khh)x}\right)^4Kdd^5\,(-Kdd-Khh)}{(Kdd+Khh)^5}+\frac{4\,e^{\frac{1}{5}(-Kdd-Khh)x}\left(-1+e^{\frac{1}{5}(-Kdd-Khh)x}\right)^3Kdd^4\,(-Kdd-Khh)\left(e^{\frac{1}{5}(-Kdd-Khh)x}\,Kdd+Khh\right)}{(Kdd+Khh)^5},$$

$$-\frac{e^{\frac{1}{5}(-Kdd-Khh)x}\left(-1+e^{\frac{1}{5}(-Kdd-Khh)x}\right)^4Kdd^5\,(-Kdd-Khh)}{(Kdd+Khh)^5}\Bigg\}\Bigg\}$$

Out[83]//MatrixForm=

$$-\frac{\left(-1+e^{\frac{1}{5}(-Kdd-Khh)x}\right)Kdd\,Khh\left(e^{\frac{1}{5}(-Kdd-Khh)x}\,Kdd+Khh\right)^4}{(Kdd+Khh)^5}-\frac{Kdd\left(e^{\frac{1}{5}(-Kdd-Khh)x}\,Kdd+Khh\right)^5}{(Kdd+Khh)^5}$$

$$\frac{4\left(-1+e^{\frac{1}{5}(-Kdd-Khh)x}\right)^2Kdd^2\,Khh\left(e^{\frac{1}{5}(-Kdd-Khh)x}\,Kdd+Khh\right)^3}{(Kdd+Khh)^5}-\frac{5\left(-1+e^{\frac{1}{5}(-Kdd-Khh)x}\right)Kdd\left(-\frac{4\,Kdd}{5}-\frac{Khh}{5}\right)\left(e^{\frac{1}{5}(-Kdd-Khh)x}\,Kdd+Khh\right)^4}{(Kdd+Khh)^5}+\frac{Kdd\,(\ldots}{}$$

$$-\frac{6\left(-1+e^{\frac{1}{5}(-Kdd-Khh)x}\right)^3Kdd^3\,Khh\left(e^{\frac{1}{5}(-Kdd-Khh)x}\,Kdd+Khh\right)^2}{(Kdd+Khh)^5}+\frac{10\left(-1+e^{\frac{1}{5}(-Kdd-Khh)x}\right)^2Kdd^2\left(-\frac{3\,Kdd}{5}-\frac{2\,Khh}{5}\right)\left(e^{\frac{1}{5}(-Kdd-Khh)x}\,Kdd+Khh\right)^3}{(Kdd+Khh)^5}-\frac{4\left(-1+e^{\frac{1}{5}(-Kdd\ldots}\right.}{}$$

$$\frac{4\left(-1+e^{\frac{1}{5}(-Kdd-Khh)x}\right)^4Kdd^4\,Khh\left(e^{\frac{1}{5}(-Kdd-Khh)x}\,Kdd+Khh\right)}{(Kdd+Khh)^5}-\frac{10\left(-1+e^{\frac{1}{5}(-Kdd-Khh)x}\right)^3Kdd^3\left(-\frac{2\,Kdd}{5}-\frac{3\,Khh}{5}\right)\left(e^{\frac{1}{5}(-Kdd-Khh)x}\,Kdd+Khh\right)^2}{(Kdd+Khh)^5}+\frac{6\left(-1+e^{\frac{1}{5}(-Kdd-K\ldots}\right.}{}$$

$$-\frac{\left(-1+e^{\frac{1}{5}(-Kdd-Khh)x}\right)^5Kdd^5\,Khh}{(Kdd+Khh)^5}+\frac{5\left(-1+e^{\frac{1}{5}(-Kdd-Khh)x}\right)^4Kdd^4\left(-\frac{Kdd}{5}-\frac{4\,Khh}{5}\right)\left(e^{\frac{1}{5}(-Kdd-Khh)x}\,Kdd+Khh\right)}{(Kdd+Khh)^5}-\frac{4\left(-1+e^{\frac{1}{5}(-Kdd-Khh)x}\right)^3Kdd^4\,(e\ldots}{(Kdd+Khh\ldots}$$

$$\frac{\left(-1+e^{\frac{1}{5}(-Kdd-Khh)x}\right)^5Kdd^5\,Khh}{(Kdd+Khh)^5}+\frac{\left(-1+e^{\frac{1}{5}(-Kdd-Khh)x}\right)^4Kdd^5\left(e^{\frac{1}{5}(-Kdd-Khh)x}\,Kdd+Khh\right)}{(Kdd+Khh)^5}$$

Out[84]//MatrixForm=

$$\left(\begin{array}{c}
\frac{e^{\frac{1}{5}(-Kdd-Khh)x}\,Kdd\,(-Kdd-Khh)\left(e^{\frac{1}{5}(-Kdd-Khh)x}\,Kdd+Khh\right)^4}{(Kdd+Khh)^5}\\
-\frac{4\,e^{\frac{1}{5}(-Kdd-Khh)x}\left(-1+e^{\frac{1}{5}(-Kdd-Khh)x}\right)Kdd^2\,(-Kdd-Khh)\left(e^{\frac{1}{5}(-Kdd-Khh)x}\,Kdd+Khh\right)^3}{(Kdd+Khh)^5}-\frac{e^{\frac{1}{5}(-Kdd-Khh)x}\,Kdd\,(-Kdd-Khh)\left(e^{\frac{1}{5}(-Kdd-Khh)x}\,Kdd+Khh \cdots\right.}{(Kdd+Khh)^5}\\
\frac{6\,e^{\frac{1}{5}(-Kdd-Khh)x}\left(-1+e^{\frac{1}{5}(-Kdd-Khh)x}\right)^2Kdd^3\,(-Kdd-Khh)\left(e^{\frac{1}{5}(-Kdd-Khh)x}\,Kdd+Khh\right)^2}{(Kdd+Khh)^5}+\frac{4\,e^{\frac{1}{5}(-Kdd-Khh)x}\left(-1+e^{\frac{1}{5}(-Kdd-Khh)x}\right)Kdd^2\,(-Kdd-Khh)\left(e^{\frac{1}{5}(-Kdd-Khh)} \cdots\right.}{(Kdd+Khh)^5}\\
-\frac{4\,e^{\frac{1}{5}(-Kdd-Khh)x}\left(-1+e^{\frac{1}{5}(-Kdd-Khh)x}\right)^3Kdd^4\,(-Kdd-Khh)\left(e^{\frac{1}{5}(-Kdd-Khh)x}\,Kdd+Khh\right)}{(Kdd+Khh)^5}-\frac{6\,e^{\frac{1}{5}(-Kdd-Khh)x}\left(-1+e^{\frac{1}{5}(-Kdd-Khh)x}\right)^2Kdd^3\,(-Kdd-Khh)\left(e^{\frac{1}{5}(-Kdd-Khh)} \cdots\right.}{(Kdd+Khh)^5}\\
\frac{e^{\frac{1}{5}(-Kdd-Khh)x}\left(-1+e^{\frac{1}{5}(-Kdd-Khh)x}\right)^4Kdd^5\,(-Kdd-Khh)}{(Kdd+Khh)^5}+\frac{4\,e^{\frac{1}{5}(-Kdd-Khh)x}\left(-1+e^{\frac{1}{5}(-Kdd-Khh)x}\right)^3Kdd^4\,(-Kdd-Khh)\left(e^{\frac{1}{5}(-Kdd-Khh)x}\,Kdd+Khh\right)}{(Kdd+Khh)^5}\\
-\frac{e^{\frac{1}{5}(-Kdd-Khh)x}\left(-1+e^{\frac{1}{5}(-Kdd-Khh)x}\right)^4Kdd^5\,(-Kdd-Khh)}{(Kdd+Khh)^5}
\end{array}\right.$$

Out[85]=

$$\Bigg\{-\frac{e^{\frac{1}{5}(-Kdd-Khh)x}\,Kdd\,(-Kdd-Khh)\left(e^{\frac{1}{5}(-Kdd-Khh)x}\,Kdd+Khh\right)^4}{(Kdd+Khh)^5}-$$

$$\frac{\left(-1+e^{\frac{1}{5}(-Kdd-Khh)x}\right)Kdd\,Khh\left(e^{\frac{1}{5}(-Kdd-Khh)x}\,Kdd+Khh\right)^4}{(Kdd+Khh)^5}-\frac{Kdd\left(e^{\frac{1}{5}(-Kdd-Khh)x}\,Kdd+Khh\right)^5}{(Kdd+Khh)^5},$$

$$\frac{4\,e^{\frac{1}{5}(-Kdd-Khh)x}\left(-1+e^{\frac{1}{5}(-Kdd-Khh)x}\right)Kdd^2\,(-Kdd-Khh)\left(e^{\frac{1}{5}(-Kdd-Khh)x}\,Kdd+Khh\right)^3}{(Kdd+Khh)^5}+$$

$$\frac{4\left(-1+e^{\frac{1}{5}(-Kdd-Khh)x}\right)^2Kdd^2\,Khh\left(e^{\frac{1}{5}(-Kdd-Khh)x}\,Kdd+Khh\right)^3}{(Kdd+Khh)^5}+$$

$$\frac{e^{\frac{1}{5}(-Kdd-Khh)x}\,Kdd\,(-Kdd-Khh)\left(e^{\frac{1}{5}(-Kdd-Khh)x}\,Kdd+Khh\right)^4}{(Kdd+Khh)^5}-$$

$$\frac{5\left(-1+e^{\frac{1}{5}(-Kdd-Khh)x}\right)Kdd\left(-\frac{4\,Kdd}{5}-\frac{Khh}{5}\right)\left(e^{\frac{1}{5}(-Kdd-Khh)x}\,Kdd+Khh\right)^4}{(Kdd+Khh)^5}+\frac{Kdd\left(e^{\frac{1}{5}(-Kdd-Khh)x}\,Kdd+Khh\right)^5}{(Kdd+Khh)^5},$$

$$-\frac{6\,e^{\frac{1}{5}(-Kdd-Khh)x}\left(-1+e^{\frac{1}{5}(-Kdd-Khh)x}\right)^2Kdd^3\,(-Kdd-Khh)\left(e^{\frac{1}{5}(-Kdd-Khh)x}\,Kdd+Khh\right)^2}{(Kdd+Khh)^5}-$$

$$\frac{6\left(-1+e^{\frac{1}{5}(-Kdd-Khh)x}\right)^{3}Kdd^{3}\,Khh\left(e^{\frac{1}{5}(-Kdd-Khh)x}Kdd+Khh\right)^{2}}{(Kdd+Khh)^{5}}-$$

$$\frac{4\,e^{\frac{1}{5}(-Kdd-Khh)x}\left(-1+e^{\frac{1}{5}(-Kdd-Khh)x}\right)Kdd^{2}\,(-Kdd-Khh)\left(e^{\frac{1}{5}(-Kdd-Khh)x}Kdd+Khh\right)^{3}}{(Kdd+Khh)^{5}}+$$

$$\frac{10\left(-1+e^{\frac{1}{5}(-Kdd-Khh)x}\right)^{2}Kdd^{2}\left(-\frac{3\,Kdd}{5}-\frac{2\,Khh}{5}\right)\left(e^{\frac{1}{5}(-Kdd-Khh)x}Kdd+Khh\right)^{3}}{(Kdd+Khh)^{5}}-$$

$$\frac{4\left(-1+e^{\frac{1}{5}(-Kdd-Khh)x}\right)Kdd^{2}\left(e^{\frac{1}{5}(-Kdd-Khh)x}Kdd+Khh\right)^{4}}{(Kdd+Khh)^{5}},$$

$$\frac{4\,e^{\frac{1}{5}(-Kdd-Khh)x}\left(-1+e^{\frac{1}{5}(-Kdd-Khh)x}\right)^{3}Kdd^{4}\,(-Kdd-Khh)\left(e^{\frac{1}{5}(-Kdd-Khh)x}Kdd+Khh\right)}{(Kdd+Khh)^{5}}+$$

$$\frac{4\left(-1+e^{\frac{1}{5}(-Kdd-Khh)x}\right)^{4}Kdd^{4}\,Khh\left(e^{\frac{1}{5}(-Kdd-Khh)x}Kdd+Khh\right)}{(Kdd+Khh)^{5}}+$$

$$\frac{6\,e^{\frac{1}{5}(-Kdd-Khh)x}\left(-1+e^{\frac{1}{5}(-Kdd-Khh)x}\right)^{2}Kdd^{3}\,(-Kdd-Khh)\left(e^{\frac{1}{5}(-Kdd-Khh)x}Kdd+Khh\right)^{2}}{(Kdd+Khh)^{5}}-$$

$$\frac{10\left(-1+e^{\frac{1}{5}(-Kdd-Khh)x}\right)^{3}Kdd^{3}\left(-\frac{2\,Kdd}{5}-\frac{3\,Khh}{5}\right)\left(e^{\frac{1}{5}(-Kdd-Khh)x}Kdd+Khh\right)^{2}}{(Kdd+Khh)^{5}}+$$

$$\frac{6\left(-1+e^{\frac{1}{5}(-Kdd-Khh)x}\right)^{2}Kdd^{3}\left(e^{\frac{1}{5}(-Kdd-Khh)x}Kdd+Khh\right)^{3}}{(Kdd+Khh)^{5}},$$

$$-\frac{e^{\frac{1}{5}(-Kdd-Khh)x}\left(-1+e^{\frac{1}{5}(-Kdd-Khh)x}\right)^{4}Kdd^{5}\,(-Kdd-Khh)}{(Kdd+Khh)^{5}}-\frac{\left(-1+e^{\frac{1}{5}(-Kdd-Khh)x}\right)^{5}Kdd^{5}\,Khh}{(Kdd+Khh)^{5}}-$$

$$\frac{4\,e^{\frac{1}{5}(-Kdd-Khh)x}\left(-1+e^{\frac{1}{5}(-Kdd-Khh)x}\right)^{3}Kdd^{4}\,(-Kdd-Khh)\left(e^{\frac{1}{5}(-Kdd-Khh)x}Kdd+Khh\right)}{(Kdd+Khh)^{5}}+$$

$$\frac{5\left(-1+e^{\frac{1}{5}(-Kdd-Khh)x}\right)^{4}Kdd^{4}\left(-\frac{Kdd}{5}-\frac{4\,Khh}{5}\right)\left(e^{\frac{1}{5}(-Kdd-Khh)x}Kdd+Khh\right)}{(Kdd+Khh)^{5}}-$$

$$\frac{4\left(-1+e^{\frac{1}{5}(-Kdd-Khh)\,x}\right)^3 Kdd^4 \left(e^{\frac{1}{5}(-Kdd-Khh)\,x} Kdd+Khh\right)^2}{(Kdd+Khh)^5},$$

$$\frac{e^{\frac{1}{5}(-Kdd-Khh)\,x}\left(-1+e^{\frac{1}{5}(-Kdd-Khh)\,x}\right)^4 Kdd^5\,(-Kdd-Khh)}{(Kdd+Khh)^5}+\frac{\left(-1+e^{\frac{1}{5}(-Kdd-Khh)\,x}\right)^5 Kdd^5\,Khh}{(Kdd+Khh)^5}+$$

$$\left.\frac{\left(-1+e^{\frac{1}{5}(-Kdd-Khh)\,x}\right)^4 Kdd^5\left(e^{\frac{1}{5}(-Kdd-Khh)\,x} Kdd+Khh\right)}{(Kdd+Khh)^5}\right\}$$

Check that the analytic solution indeed satisfies system::

Out[87]= {0, 0, 0, 0, 0, 0}

In[88]:=
```
(*
kd=2
   kh=3
    Nd=13
     ind=9
*)
(*
Try to guess the solution..
*)
Print["This is the solution, which we are trying to guess:"]
MAnalitical = Function[{kd, kh, Nd, ind, t} ,  (-1)^ind (Nd ! / (ind ! * (Nd - ind) !)) *
   (-1 + Exp[(-kd - kh) * t / Nd])^ind kd^ind (Exp[(-kd - kh) * t / Nd] kd + kh)^(Nd-ind) / (kd + kh)^Nd]

Print["Compare the guessed solution with analytically calculated earlier:"]
AnaliticalSolution
ProposedSolution =
 Table[MAnalitical[Kdd, Khh, Ndeuteriums, ind, x], {ind, 0, Ndeuteriums}]
Print["If it turned out the zeros,
   the solution guidanoe match found analytically informed:"]
Simplify[AnaliticalSolution[[1]] - ProposedSolution]


s1 = Function[{kd, kh, Nd, ind, t}, D[MAnalitical[kd, kh, Nd, ind, t], t]]
s2 = Function[{kd, kh, Nd, ind, t},
  MAnalitical[kd, kh, Nd, ind, t] * (-kd * (Nd - ind) / Nd - kh * ind / Nd)]
s3 = Function[{kd, kh, Nd, ind, t},
  MAnalitical[kd, kh, Nd, ind - 1, t] * (kd * (Nd - ind + 1) / Nd)]
s4 = Function[{kd, kh, Nd, ind, t}, MAnalitical[kd, kh, Nd, ind + 1, t] * (kh * (ind + 1) / Nd)]

Res = Function[{kd, kh, Nd, ind, t}, s1[kd, kh, Nd, ind, t] -
   s2[kd, kh, Nd, ind, t] - s3[kd, kh, Nd, ind, t] - s4[kd, kh, Nd, ind, t]]

Print["Calculate the difference of the derivative and of three terms:"]
Simplify[Res[Khh, Kdd, Nd, ind, t]]
```

This is the solution, which we are trying to guess:

Out[89]= $\text{Function}\left[\{kd, kh, Nd, ind, t\}, \dfrac{(-1)^{ind}\, Nd!\, \left(-1+\text{Exp}\left[\frac{(-kd-kh)\,t}{Nd}\right]\right)^{ind} kd^{ind} \left(\text{Exp}\left[\frac{(-kd-kh)\,t}{Nd}\right] kd + kh\right)^{Nd-ind}}{(ind!\,(Nd-ind)!)\,(kd+kh)^{Nd}}\right]$

Compare the guessed solution with analytically calculated earlier:

Out[91]= $$\left\{\left\{\frac{\left(e^{\frac{1}{5}(-Kdd-Khh)\,x} Kdd + Khh\right)^5}{(Kdd+Khh)^5}, -\frac{5\left(-1+e^{\frac{1}{5}(-Kdd-Khh)\,x}\right) Kdd \left(e^{\frac{1}{5}(-Kdd-Khh)\,x} Kdd + Khh\right)^4}{(Kdd+Khh)^5}, \frac{10\left(-1+e^{\frac{1}{5}(-Kdd-Khh)\,x}\right)^2 Kdd^2 \left(e^{\frac{1}{5}(-Kdd-Khh)\,x} Kdd + Khh\right)^3}{(Kdd+Khh)^5}, -\frac{10\left(-1+e^{\frac{1}{5}(-Kdd-Khh)\,x}\right)^3 Kdd^3 \left(e^{\frac{1}{5}(-Kdd-Khh)\,x} Kdd + Khh\right)^2}{(Kdd+Khh)^5}, \frac{5\left(-1+e^{\frac{1}{5}(-Kdd-Khh)\,x}\right)^4 Kdd^4 \left(e^{\frac{1}{5}(-Kdd-Khh)\,x} Kdd + Khh\right)}{(Kdd+Khh)^5}, -\frac{\left(-1+e^{\frac{1}{5}(-Kdd-Khh)\,x}\right)^5 Kdd^5}{(Kdd+Khh)^5}\right\}\right\}$$

Out[92]= $$\left\{\frac{\left(e^{\frac{1}{5}(-Kdd-Khh)\,x} Kdd + Khh\right)^5}{(Kdd+Khh)^5}, -\frac{5\left(-1+e^{\frac{1}{5}(-Kdd-Khh)\,x}\right) Kdd \left(e^{\frac{1}{5}(-Kdd-Khh)\,x} Kdd + Khh\right)^4}{(Kdd+Khh)^5}, \frac{10\left(-1+e^{\frac{1}{5}(-Kdd-Khh)\,x}\right)^2 Kdd^2 \left(e^{\frac{1}{5}(-Kdd-Khh)\,x} Kdd + Khh\right)^3}{(Kdd+Khh)^5}, -\frac{10\left(-1+e^{\frac{1}{5}(-Kdd-Khh)\,x}\right)^3 Kdd^3 \left(e^{\frac{1}{5}(-Kdd-Khh)\,x} Kdd + Khh\right)^2}{(Kdd+Khh)^5}, \frac{5\left(-1+e^{\frac{1}{5}(-Kdd-Khh)\,x}\right)^4 Kdd^4 \left(e^{\frac{1}{5}(-Kdd-Khh)\,x} Kdd + Khh\right)}{(Kdd+Khh)^5}, -\frac{\left(-1+e^{\frac{1}{5}(-Kdd-Khh)\,x}\right)^5 Kdd^5}{(Kdd+Khh)^5}\right\}$$

If it turned out the zeros, the solution guidanoe match found analytically informed:

Out[94]= $\{0, 0, 0, 0, 0, 0\}$

Out[95]= $\text{Function}[\{kd, kh, Nd, ind, t\}, \partial_t \text{MAnalitical}[kd, kh, Nd, ind, t]]$

Out[96]= $\text{Function}\left[\{kd, kh, Nd, ind, t\}, \text{MAnalitical}[kd, kh, Nd, ind, t]\left(-\frac{kd\,(Nd-ind)}{Nd} - \frac{kh\,ind}{Nd}\right)\right]$

Out[97]= $\text{Function}\left[\{kd, kh, Nd, ind, t\}, \dfrac{\text{MAnalitical}[kd, kh, Nd, ind-1, t]\,(kd\,(Nd-ind+1))}{Nd}\right]$

Out[98]= $\text{Function}\left[\{kd, kh, Nd, ind, t\}, \dfrac{\text{MAnalitical}[kd, kh, Nd, ind+1, t]\,(kh\,(ind+1))}{Nd}\right]$

Out[99]= $\text{Function}[\{kd, kh, Nd, ind, t\}, s1[kd, kh, Nd, ind, t] - s2[kd, kh, Nd, ind, t] - s3[kd, kh, Nd, ind, t] - s4[kd, kh, Nd, ind, t]]$

Calculate the difference of the derivative and of three terms:

Out[101]=

$$\frac{1}{Nd}(-1)^{ind}\left(-1+e^{-\frac{(Kdd+Khh)\,t}{Nd}}\right)^{ind} Khh^{ind}\,(Kdd+Khh)^{-Nd}$$

$$\left(Kdd+e^{-\frac{(Kdd+Khh)\,t}{Nd}}\,Khh\right)^{-ind+Nd} Nd!\left(-\frac{\left(-1+e^{\frac{(Kdd+Khh)\,t}{Nd}}\right)(1+ind)\,Kdd\,Khh}{\left(e^{\frac{(Kdd+Khh)\,t}{Nd}}\,Kdd+Khh\right)(1+ind)!\,(-1-ind+Nd)!}+\right.$$

$$\frac{ind\,(Kdd+Khh)}{\left(-1+e^{\frac{(Kdd+Khh)\,t}{Nd}}\right)ind!\,(-ind+Nd)!}+\frac{Khh\,(Kdd+Khh)\,(ind-Nd)}{\left(e^{\frac{(Kdd+Khh)\,t}{Nd}}\,Kdd+Khh\right)ind!\,(-ind+Nd)!}+$$

$$\left.\frac{ind\,Kdd-ind\,Khh+Khh\,Nd}{ind!\,(-ind+Nd)!}-\frac{\left(e^{\frac{(Kdd+Khh)\,t}{Nd}}\,Kdd+Khh\right)(1-ind+Nd)}{\left(-1+e^{\frac{(Kdd+Khh)\,t}{Nd}}\right)(-1+ind)!\,(1-ind+Nd)!}\right)$$

In[102]:=

```
(*
Select the part which should be equal to zero
*)
ZeroPart = Function[{Khh, Kdd, Nd, ind, t},
```

$$\left(-\frac{\left(-1+e^{\frac{(Kdd+Khh)\,t}{Nd}}\right)(1+ind)\,Kdd\,Khh}{\left(e^{\frac{(Kdd+Khh)\,t}{Nd}}\,Kdd+Khh\right)(1+ind)!\,(-1-ind+Nd)!}+\frac{ind\,(Kdd+Khh)}{\left(-1+e^{\frac{(Kdd+Khh)\,t}{Nd}}\right)ind!\,(-ind+Nd)!}+\right.$$

$$\frac{Khh\,(Kdd+Khh)\,(ind-Nd)}{\left(e^{\frac{(Kdd+Khh)\,t}{Nd}}\,Kdd+Khh\right)ind!\,(-ind+Nd)!}+\frac{ind\,Kdd-ind\,Khh+Khh\,Nd}{ind!\,(-ind+Nd)!}-$$

$$\left.\frac{\left(e^{\frac{(Kdd+Khh)\,t}{Nd}}\,Kdd+Khh\right)(1-ind+Nd)}{\left(-1+e^{\frac{(Kdd+Khh)\,t}{Nd}}\right)(-1+ind)!\,(1-ind+Nd)!}\right)]$$

```
Simplify[ZeroPart[Khh, Kdd, Nd, ind, t]]
```

```
ZeroPart2 = Function[{Khh, Kdd, Nd, ind, t}, ZeroPart[Khh, Kdd, Nd, ind, t] *
```

$$(1-ind+Nd)!*\left(e^{\frac{(Kdd+Khh)\,t}{Nd}}\,Kdd+Khh\right)(1+ind)!*\left(-1+e^{\frac{(Kdd+Khh)\,t}{Nd}}\right)]$$

```
Simplify[ZeroPart2[Khh, Kdd, 8, 5, t]]

(*
Rewrite the part that should be zero:
*)
```

```
ZeroPart3 = Function[{Khh, Kdd, Nd, ind, t},
  (-((-1 + E^(((Kdd + Khh) t)/Nd)) (1 + ind) Kdd Khh (1 - ind + Nd)! * (E^(((Kdd + Khh) t)/Nd) Kdd + Khh) (1 + ind)! *
        (-1 + E^(((Kdd + Khh) t)/Nd))) / ((E^(((Kdd + Khh) t)/Nd) Kdd + Khh) (1 + ind)! (-1 - ind + Nd)!) +
    (ind (Kdd + Khh) (1 - ind + Nd)! * (E^(((Kdd + Khh) t)/Nd) Kdd + Khh) (1 + ind)! * (-1 + E^(((Kdd + Khh) t)/Nd))) /
     ((-1 + E^(((Kdd + Khh) t)/Nd)) ind! (-ind + Nd)!) +
    (Khh (Kdd + Khh) (ind - Nd) (1 - ind + Nd)! * (E^(((Kdd + Khh) t)/Nd) Kdd + Khh) (1 + ind)! * (-1 + E^(((Kdd + Khh) t)/Nd))) /
     ((E^(((Kdd + Khh) t)/Nd) Kdd + Khh) ind! (-ind + Nd)!) +
    ((ind Kdd - ind Khh + Khh Nd) (1 - ind + Nd)! * (E^(((Kdd + Khh) t)/Nd) Kdd + Khh) (1 + ind)! * (-1 + E^(((Kdd + Khh) t)/Nd))) /
     (ind! (-ind + Nd)!) -
    ((E^(((Kdd + Khh) t)/Nd) Kdd + Khh) (1 - ind + Nd) (1 - ind + Nd)! * (E^(((Kdd + Khh) t)/Nd) Kdd + Khh)
        (1 + ind)! * (-1 + E^(((Kdd + Khh) t)/Nd))) / ((-1 + E^(((Kdd + Khh) t)/Nd)) (-1 + ind)! (1 - ind + Nd)!))]

Simplify[ZeroPart3[Khh, Kdd, 8, 5, t]]

ZeroPart4 = Function[{Khh, Kdd, Nd, ind, t},
  (-((-1 + E^(((Kdd + Khh) t)/Nd)) (1 + ind) Kdd Khh (1 - ind + Nd) (Nd - ind) * (-1 + E^(((Kdd + Khh) t)/Nd)))/1 +
    (ind (Kdd + Khh) (1 - ind + Nd) * (E^(((Kdd + Khh) t)/Nd) Kdd + Khh) (1 + ind))/1 +
    (Khh (Kdd + Khh) (ind - Nd) (1 - ind + Nd) * (1 + ind) * (-1 + E^(((Kdd + Khh) t)/Nd)))/1 +
```

$$\frac{(\text{ind Kdd} - \text{ind Khh} + \text{Khh Nd})\ (1 - \text{ind} + \text{Nd}) * \left(e^{\frac{(\text{Kdd}+\text{Khh})\ t}{\text{Nd}}}\ \text{Kdd} + \text{Khh}\right)\ (1 + \text{ind}) * \left(-1 + e^{\frac{(\text{Kdd}+\text{Khh})\ t}{\text{Nd}}}\right)}{1} - \frac{\left(e^{\frac{(\text{Kdd}+\text{Khh})\ t}{\text{Nd}}}\ \text{Kdd} + \text{Khh}\right)\ (1 - \text{ind} + \text{Nd}) * \left(e^{\frac{(\text{Kdd}+\text{Khh})\ t}{\text{Nd}}}\ \text{Kdd} + \text{Khh}\right)\ (1 + \text{ind})\ \text{ind}}{1}\Bigg)\Bigg]$$

Simplify[ZeroPart4[Khh, Kdd, 8, 5, t]]

Out[102]= $$\text{Function}\Bigg[\{\text{Khh}, \text{Kdd}, \text{Nd}, \text{ind}, t\}, -\frac{\left(-1 + e^{\frac{(\text{Kdd}+\text{Khh})\ t}{\text{Nd}}}\right)\ (1 + \text{ind})\ \text{Kdd Khh}}{\left(e^{\frac{(\text{Kdd}+\text{Khh})\ t}{\text{Nd}}}\ \text{Kdd} + \text{Khh}\right)\ (1 + \text{ind})!\ (-1 - \text{ind} + \text{Nd})!} + \frac{\text{ind}\ (\text{Kdd} + \text{Khh})}{\left(-1 + e^{\frac{(\text{Kdd}+\text{Khh})\ t}{\text{Nd}}}\right)\ \text{ind}!\ (-\text{ind} + \text{Nd})!} + \frac{\text{Khh}\ (\text{Kdd} + \text{Khh})\ (\text{ind} - \text{Nd})}{\left(e^{\frac{(\text{Kdd}+\text{Khh})\ t}{\text{Nd}}}\ \text{Kdd} + \text{Khh}\right)\ \text{ind}!\ (-\text{ind} + \text{Nd})!} + \frac{\text{ind Kdd} - \text{ind Khh} + \text{Khh Nd}}{\text{ind}!\ (-\text{ind} + \text{Nd})!} - \frac{\left(e^{\frac{(\text{Kdd}+\text{Khh})\ t}{\text{Nd}}}\ \text{Kdd} + \text{Khh}\right)\ (1 - \text{ind} + \text{Nd})}{\left(-1 + e^{\frac{(\text{Kdd}+\text{Khh})\ t}{\text{Nd}}}\right)\ (-1 + \text{ind})!\ (1 - \text{ind} + \text{Nd})!}\Bigg]$$

Out[103]= $$-\frac{\left(-1 + e^{\frac{(\text{Kdd}+\text{Khh})\ t}{\text{Nd}}}\right)\ (1 + \text{ind})\ \text{Kdd Khh}}{\left(e^{\frac{(\text{Kdd}+\text{Khh})\ t}{\text{Nd}}}\ \text{Kdd} + \text{Khh}\right)\ (1 + \text{ind})!\ (-1 - \text{ind} + \text{Nd})!} + \frac{\text{ind}\ (\text{Kdd} + \text{Khh})}{\left(-1 + e^{\frac{(\text{Kdd}+\text{Khh})\ t}{\text{Nd}}}\right)\ \text{ind}!\ (-\text{ind} + \text{Nd})!} + \frac{\text{Khh}\ (\text{Kdd} + \text{Khh})\ (\text{ind} - \text{Nd})}{\left(e^{\frac{(\text{Kdd}+\text{Khh})\ t}{\text{Nd}}}\ \text{Kdd} + \text{Khh}\right)\ \text{ind}!\ (-\text{ind} + \text{Nd})!} + \frac{\text{ind Kdd} - \text{ind Khh} + \text{Khh Nd}}{\text{ind}!\ (-\text{ind} + \text{Nd})!} - \frac{\left(e^{\frac{(\text{Kdd}+\text{Khh})\ t}{\text{Nd}}}\ \text{Kdd} + \text{Khh}\right)\ (1 - \text{ind} + \text{Nd})}{\left(-1 + e^{\frac{(\text{Kdd}+\text{Khh})\ t}{\text{Nd}}}\right)\ (-1 + \text{ind})!\ (1 - \text{ind} + \text{Nd})!}$$

Out[104]= $$\text{Function}\Big[\{\text{Khh}, \text{Kdd}, \text{Nd}, \text{ind}, t\}, \text{ZeroPart}[\text{Khh}, \text{Kdd}, \text{Nd}, \text{ind}, t]\ (1 - \text{ind} + \text{Nd})!\ \left(e^{\frac{(\text{Kdd}+\text{Khh})\ t}{\text{Nd}}}\ \text{Kdd} + \text{Khh}\right)\ (1 + \text{ind})!\ \left(-1 + e^{\frac{(\text{Kdd}+\text{Khh})\ t}{\text{Nd}}}\right)\Big]$$

Out[105]= 0

Out[106]= Function[{Khh, Kdd, Nd, ind, t},

$$-\frac{\left(-1+e^{\frac{(Kdd+Khh)\,t}{Nd}}\right)(1+ind)\,Kdd\,Khh\,(1-ind+Nd)!\left(e^{\frac{(Kdd+Khh)\,t}{Nd}}\,Kdd+Khh\right)(1+ind)!\left(-1+e^{\frac{(Kdd+Khh)\,t}{Nd}}\right)}{\left(e^{\frac{(Kdd+Khh)\,t}{Nd}}\,Kdd+Khh\right)(1+ind)!\,(-1-ind+Nd)!}+$$

$$\frac{ind\,(Kdd+Khh)\,(1-ind+Nd)!\left(e^{\frac{(Kdd+Khh)\,t}{Nd}}\,Kdd+Khh\right)(1+ind)!\left(-1+e^{\frac{(Kdd+Khh)\,t}{Nd}}\right)}{\left(-1+e^{\frac{(Kdd+Khh)\,t}{Nd}}\right)ind!\,(-ind+Nd)!}+$$

$$\frac{Khh\,(Kdd+Khh)\,(ind-Nd)\,(1-ind+Nd)!\left(e^{\frac{(Kdd+Khh)\,t}{Nd}}\,Kdd+Khh\right)(1+ind)!\left(-1+e^{\frac{(Kdd+Khh)\,t}{Nd}}\right)}{\left(e^{\frac{(Kdd+Khh)\,t}{Nd}}\,Kdd+Khh\right)ind!\,(-ind+Nd)!}+$$

$$\frac{(ind\,Kdd-ind\,Khh+Khh\,Nd)\,(1-ind+Nd)!\left(e^{\frac{(Kdd+Khh)\,t}{Nd}}\,Kdd+Khh\right)(1+ind)!\left(-1+e^{\frac{(Kdd+Khh)\,t}{Nd}}\right)}{ind!\,(-ind+Nd)!}-$$

$$\frac{\left(e^{\frac{(Kdd+Khh)\,t}{Nd}}\,Kdd+Khh\right)(1-ind+Nd)\,(1-ind+Nd)!\left(e^{\frac{(Kdd+Khh)\,t}{Nd}}\,Kdd+Khh\right)(1+ind)!\left(-1+e^{\frac{(Kdd+Khh)\,t}{Nd}}\right)}{\left(-1+e^{\frac{(Kdd+Khh)\,t}{Nd}}\right)(-1+ind)!\,(1-ind+Nd)!}\Bigg]$$

Out[107]= 0

Out[108]= Function[{Khh, Kdd, Nd, ind, t},

$$-\left(\left(-1+e^{\frac{(Kdd+Khh)\,t}{Nd}}\right)(1+ind)\,Kdd\,Khh\,(1-ind+Nd)\,(Nd-ind)\left(-1+e^{\frac{(Kdd+Khh)\,t}{Nd}}\right)\right)+$$

$$ind\,(Kdd+Khh)\,(1-ind+Nd)\left(e^{\frac{(Kdd+Khh)\,t}{Nd}}\,Kdd+Khh\right)(1+ind)+$$

$$Khh\,(Kdd+Khh)\,(ind-Nd)\,(1-ind+Nd)\,(1+ind)\left(-1+e^{\frac{(Kdd+Khh)\,t}{Nd}}\right)+$$

$$(ind\,Kdd-ind\,Khh+Khh\,Nd)\,(1-ind+Nd)\left(e^{\frac{(Kdd+Khh)\,t}{Nd}}\,Kdd+Khh\right)(1+ind)\left(-1+e^{\frac{(Kdd+Khh)\,t}{Nd}}\right)-$$

$$\left(e^{\frac{(Kdd+Khh)\,t}{Nd}}\,Kdd+Khh\right)(1-ind+Nd)\left(e^{\frac{(Kdd+Khh)\,t}{Nd}}\,Kdd+Khh\right)(1+ind)\,ind\Big]$$

Out[109]= 0

In[110]:=
```
(*
This is the most simplified part that needs to vanish
*)
ZeroPart4 = Function[{Khh, Kdd, Nd, ind, t},
  (-((-1 + E^((Kdd+Khh) t/Nd)) (1 + ind) Kdd Khh (1 - ind + Nd) (Nd - ind) * (-1 + E^((Kdd+Khh) t/Nd)))/1 +
   ind (Kdd + Khh) (1 - ind + Nd) * (E^((Kdd+Khh) t/Nd) Kdd + Khh) (1 + ind)/1 +
   Khh (Kdd + Khh) (ind - Nd) (1 - ind + Nd) * (1 + ind) * (-1 + E^((Kdd+Khh) t/Nd))/1 +
   (ind Kdd - ind Khh + Khh Nd) (1 - ind + Nd) * (E^((Kdd+Khh) t/Nd) Kdd + Khh) (1 + ind) * (-1 + E^((Kdd+Khh) t/Nd))/1 -
   (E^((Kdd+Khh) t/Nd) Kdd + Khh) (1 - ind + Nd) * (E^((Kdd+Khh) t/Nd) Kdd + Khh) (1 + ind) ind/1)]
Simplify[ZeroPart4[Khh, Kdd, Nd, ind, t]]
```

Out[110]=
```
Function[{Khh, Kdd, Nd, ind, t},
 -((-1 + E^((Kdd+Khh) t/Nd)) (1 + ind) Kdd Khh (1 - ind + Nd) (Nd - ind) (-1 + E^((Kdd+Khh) t/Nd))) +
 ind (Kdd + Khh) (1 - ind + Nd) (E^((Kdd+Khh) t/Nd) Kdd + Khh) (1 + ind) +
 Khh (Kdd + Khh) (ind - Nd) (1 - ind + Nd) (1 + ind) (-1 + E^((Kdd+Khh) t/Nd)) +
 (ind Kdd - ind Khh + Khh Nd) (1 - ind + Nd) (E^((Kdd+Khh) t/Nd) Kdd + Khh) (1 + ind) (-1 + E^((Kdd+Khh) t/Nd)) -
 (E^((Kdd+Khh) t/Nd) Kdd + Khh) (1 - ind + Nd) (E^((Kdd+Khh) t/Nd) Kdd + Khh) (1 + ind) ind]
```

Out[111]= 0