‖ Overview

In Hugo et al. 2009, the deuteration of H_3 was investigated in an ion trap at 13.5 K. The key reactions and their rates are:

$$H_3{}^+ + HD \longrightarrow H_2D^+ + H_2 \qquad \text{Rate} = k_1^{(2)}[HD][H_3{}^+] \tag{1}$$
$$H_2D^+ + HD \longrightarrow D_2H^+ + H_2 \qquad \text{Rate} = k_2^{(2)}[HD][H_2D^+] \tag{2}$$
$$D_2H^+ + HD \longrightarrow D_3{}^+ + H_2 \qquad \text{Rate} = k_3^{(2)}[HD][D_2H^+] \tag{3}$$

In these equations, brackets indicate the number density (cm^{-3}), and the $k_n^{(2)}$ refer to second-order rate coefficients in units of $cm^3\ s^{-1}$ so that the rate has units of $cm^{-3}\ s^{-1}$. At the low temperature, the reverse reactions are negligible. Furthermore, under the experimental conditions, HD is present in excess, and it is reasonable to treat [HD] as constant. Under these pseudo-first-order conditions, we can redefine the rate coefficients

$$k_n \equiv k_n^{(2)}[HD] \tag{4}$$

Using the rates above, we obtain a set of coupled differential equations describing the time evolution of the number densities.

$$\frac{d[H_3{}^+]}{dt} = -k_1[H_3{}^+] \tag{5}$$
$$\frac{d[H_2D^+]}{dt} = k_1[H_3{}^+] - k_2[H_2D^+] \tag{6}$$
$$\frac{d[D_2H^+]}{dt} = k_2[H_2D^+] - k_3[D_2H^+] \tag{7}$$
$$\frac{d[D_3{}^+]}{dt} = k_3[D_2H^+] \tag{8}$$

‖ Solving for $[H_3{}^+]$

Solving for $[H_3{}^+](t)$ involved simply a normal first-order integrated rate equation. Rearranging Equation (5):

$$\frac{d[H_3{}^+]}{[H_3{}^+]} = -k_1\ dt$$
$$\ln[H_3{}^+](t) = -k_1 t + C$$
$$[H_3{}^+](t) = Ae^{-k_1 t} \tag{9}$$

At $t = 0$, $[H_3{}^+] = [H_3{}^+]_0$, so

$$\boxed{[H_3{}^+](t) = [H_3{}^+]_0 e^{-k_1 t}} \tag{10}$$

‖ Solving for $[H_2D^+]$

To solve for the time evolution of $[H_2D^+]$, we substitute the result of Equation (10) into Equation (6) and rearrange:

$$\frac{d[H_2D^+]}{dt} + k_2[H_2D^+] = k_1[H_3{}^+]_0 e^{-k_1 t} \tag{11}$$

To make progress, we introduce a new variable μ:

$$\mu \equiv e^{k_2 t}, \quad \frac{\mathrm{d}\mu}{\mathrm{d}t} = k_2 e^{k_2 t} \tag{12}$$

Now we multiply both sides of Equation (11) by μ to get

$$\mu\frac{\mathrm{d}[\mathrm{H_2D^+}]}{\mathrm{d}t} + [\mathrm{H_2D^+}]\frac{\mathrm{d}\mu}{\mathrm{d}t} = k_1[\mathrm{H_3}^+]_0 e^{-(k_1-k_2)t} \tag{13}$$

From the definition of the product rule for derivatives:

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\mu[\mathrm{H_2D^+}]\right) = \mu\frac{\mathrm{d}[\mathrm{H_2D^+}]}{\mathrm{d}t} + [\mathrm{H_2D^+}]\frac{\mathrm{d}\mu}{\mathrm{d}t} \tag{14}$$

Substitute into Equation (13) and integrate:

$$\begin{aligned}
\int \frac{\mathrm{d}}{\mathrm{d}t}\left(\mu[\mathrm{H_2D^+}]\right)\,\mathrm{d}t &= \int k_1[\mathrm{H_3}^+]_0 e^{-(k_1-k_2)t}\,\mathrm{d}t \\
\mu[\mathrm{H_2D^+}](t) &= \frac{k_1[\mathrm{H_3}^+]_0}{k_2-k_1} e^{-(k_1-k_2)t} + C \\
[\mathrm{H_2D^+}](t) &= \frac{k_1[\mathrm{H_3}^+]_0}{k_2-k_1} e^{-k_1 t} + Ce^{-k_2 t}
\end{aligned} \tag{15}$$

To evaluate C, we use the boundary condition that at $t = 0$, $[\mathrm{H_2D^+}] = 0$, and therefore

$$0 = \frac{k_1[\mathrm{H_3}^+]_0}{k_2-k_1} + C, \quad C = -\frac{k_1[\mathrm{H_3}^+]_0}{k_2-k_1} \tag{16}$$

Substituting, we obtain the integrated rate equation for $[\mathrm{H_2D^+}](t)$:

$$\boxed{[\mathrm{H_2D^+}](t) = \frac{k_1[\mathrm{H_3}^+]_0}{k_2-k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right)} \tag{17}$$

However, note that if $k_1 = k_2 \equiv k$, the denominator goes to 0. Looking back, Equation (13) becomes instead

$$\mu\frac{\mathrm{d}[\mathrm{H_2D^+}]}{\mathrm{d}t} + [\mathrm{H_2D^+}]\frac{\mathrm{d}\mu}{\mathrm{d}t} = k[\mathrm{H_3}^+]_0 \tag{18}$$

Then

$$\begin{aligned}
\int \frac{\mathrm{d}}{\mathrm{d}t}\left(\mu[\mathrm{H_2D^+}]\right)\,\mathrm{d}t &= \int k[\mathrm{H_3}^+]_0\,\mathrm{d}t \\
\mu[\mathrm{H_2D^+}](t) &= k[\mathrm{H_3}^+]_0 kt + C \\
[\mathrm{H_2D^+}](t) &= [\mathrm{H_3}^+]_0 kte^{-kt} + Ce^{-kt}
\end{aligned} \tag{19}$$

Again, at $t = 0$, $[\mathrm{H_2D^+}] = 0$, so $C = 0$. The final result is therefore

$$\boxed{[\mathrm{H_2D^+}](t) = [\mathrm{H_3}^+]_0 kte^{-kt}, \quad (k = k_1 = k_2)} \tag{20}$$

‖ Solving for $[D_2H^+]$

The procedure is essentially the same as for $[H_2D^+]$. First, substitute Equation (17) into Equation (7) and rearrange:

$$\frac{d[D_2H^+]}{dt} + k_3[D_2H^+] = \frac{k_1k_2[H_3{}^+]_0}{k_2-k_1}\left(e^{-k_1t} - e^{-k_2t}\right) \tag{21}$$

As before, we introduce the variable μ and its derivative:

$$\mu \equiv e^{k_3t}, \quad \frac{d\mu}{dt} = k_3e^{k_3t} \tag{22}$$

Multiplying both sides of Equation (21) by μ, we obtain (just like before):

$$\begin{aligned}
\mu\frac{d[D_2H^+]}{dt} + [D_2H^+]\frac{d\mu}{dt} &= \frac{k_1k_2[H_3{}^+]_0}{k_2-k_1}\left(e^{-(k_1-k_3)t} - e^{-(k_2-k_3)t}\right) \\
\int \frac{d}{dt}\left(\mu[D_2H^+]\right) &= \int \frac{k_1k_2[H_3{}^+]_0}{k_2-k_1}\left(e^{-(k_1-k_3)t} - e^{-(k_2-k_3)t}\right) \\
\mu[D_2H^+](t) &= \frac{k_1k_2[H_3{}^+]_0}{k_2-k_1}\left(\frac{e^{-(k_1-k_3)t}}{k_3-k_1} - \frac{e^{-(k_2-k_3)t}}{k_3-k_2}\right) + C \\
[D_2H^+](t) &= \frac{k_1k_2[H_3{}^+]_0}{k_2-k_1}\left(\frac{e^{-k_1t}}{k_3-k_1} - \frac{e^{-k_2t}}{k_3-k_2}\right) + Ce^{-k_2t}
\end{aligned} \tag{23}$$

The boundary condition is at $t = 0$, $[D_2H^+] = 0$, so

$$C = -\frac{k_1k_2[H_3{}^+]_0}{k_2-k_1}\left(\frac{1}{k_3-k_1} - \frac{1}{k_3-k_2}\right) \tag{24}$$

So the final result is

$$\boxed{[D_2H^+](t) = \frac{k_1k_2[H_3{}^+]_0}{k_2-k_1}\left(\frac{e^{-k_1t} - e^{-k_3t}}{k_3-k_1} - \frac{e^{-k_2t} - e^{-k_3t}}{k_3-k_2}\right)} \tag{25}$$

Note that if $k_1 = k_2$ or $k_1 = k_3$ or $k_2 = k_3$, we would have to rederive an alternative form of this equation like we did for $[H_2D^+]$. We will not do that here.

‖ Solving for $[D_3{}^+]$

This one is very easy. Using conservation of mass, we know that

$$[H_3{}^+](t) + [H_2D^+](t) + [D_2H^+](t) + [D_3{}^+](t) = [H_3{}^+]_0 \tag{26}$$

Therefore

$$\boxed{[D_3{}^+](t) = [H_3{}^+]_0 - [H_3{}^+](t) - [H_2D^+](t) - [D_2H^+](t)} \tag{27}$$

where we can insert Equations (10), (17), and (25).