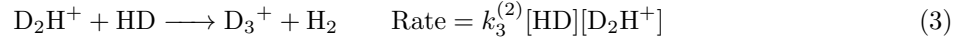
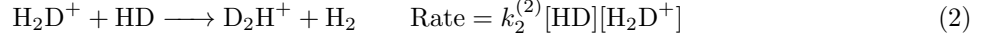
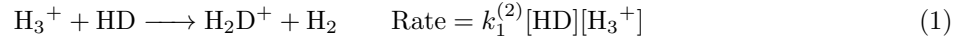


|| OVERVIEW

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:



In these equations, brackets indicate the number density (cm^{-3}), and the $k_n^{(2)}$ refer to second-order rate coefficients in units of $\text{cm}^3 \text{s}^{-1}$ so that the rate has units of $\text{cm}^{-3} \text{s}^{-1}$. 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 $[\text{HD}]$ as constant. Under these pseudo-first-order conditions, we can redefine the rate coefficients

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

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

$$\frac{d[\text{H}_3^+]}{dt} = -k_1[\text{H}_3^+] \quad (5)$$

$$\frac{d[\text{H}_2\text{D}^+]}{dt} = k_1[\text{H}_3^+] - k_2[\text{H}_2\text{D}^+] \quad (6)$$

$$\frac{d[\text{D}_2\text{H}^+]}{dt} = k_2[\text{H}_2\text{D}^+] - k_3[\text{D}_2\text{H}^+] \quad (7)$$

$$\frac{d[\text{D}_3^+]}{dt} = k_3[\text{D}_2\text{H}^+] \quad (8)$$

|| SOLVING FOR $[\text{H}_3^+]$

Solving for $[\text{H}_3^+](t)$ involved simply a normal first-order integrated rate equation. Rearranging Equation (5):

$$\begin{aligned} \frac{d[\text{H}_3^+]}{[\text{H}_3^+]} &= -k_1 dt \\ \ln[\text{H}_3^+](t) &= -k_1 t + C \\ [\text{H}_3^+](t) &= A e^{-k_1 t} \end{aligned} \quad (9)$$

At $t = 0$, $[\text{H}_3^+] = [\text{H}_3^+]_0$, so

$$\boxed{[\text{H}_3^+](t) = [\text{H}_3^+]_0 e^{-k_1 t}} \quad (10)$$

|| SOLVING FOR $[\text{H}_2\text{D}^+]$

To solve for the time evolution of $[\text{H}_2\text{D}^+]$, we substitute the result of Equation (10) into Equation (6) and rearrange:

$$\frac{d[\text{H}_2\text{D}^+]}{dt} + k_2[\text{H}_2\text{D}^+] = k_1[\text{H}_3^+]_0 e^{-k_1 t} \quad (11)$$

To make progress, we introduce a new variable μ :

$$\mu \equiv e^{k_2 t}, \quad \frac{d\mu}{dt} = k_2 e^{k_2 t} \quad (12)$$

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

$$\mu \frac{d[\text{H}_2\text{D}^+]}{dt} + [\text{H}_2\text{D}^+] \frac{d\mu}{dt} = k_1 [\text{H}_3^+]_0 e^{-(k_1 - k_2)t} \quad (13)$$

From the definition of the product rule for derivatives:

$$\frac{d}{dt} (\mu [\text{H}_2\text{D}^+]) = \mu \frac{d[\text{H}_2\text{D}^+]}{dt} + [\text{H}_2\text{D}^+] \frac{d\mu}{dt} \quad (14)$$

Substitute into Equation (13) and integrate:

$$\begin{aligned} \int \frac{d}{dt} (\mu [\text{H}_2\text{D}^+]) dt &= \int k_1 [\text{H}_3^+]_0 e^{-(k_1 - k_2)t} dt \\ \mu [\text{H}_2\text{D}^+](t) &= \frac{k_1 [\text{H}_3^+]_0}{k_2 - k_1} e^{-(k_1 - k_2)t} + C \\ [\text{H}_2\text{D}^+](t) &= \frac{k_1 [\text{H}_3^+]_0}{k_2 - k_1} e^{-k_1 t} + C e^{-k_2 t} \end{aligned} \quad (15)$$

To evaluate C , we use the boundary condition that at $t = 0$, $[\text{H}_2\text{D}^+] = 0$, and therefore

$$0 = \frac{k_1 [\text{H}_3^+]_0}{k_2 - k_1} + C, \quad C = -\frac{k_1 [\text{H}_3^+]_0}{k_2 - k_1} \quad (16)$$

Substituting, we obtain the integrated rate equation for $[\text{H}_2\text{D}^+](t)$:

$$\boxed{[\text{H}_2\text{D}^+](t) = \frac{k_1 [\text{H}_3^+]_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})} \quad (17)$$

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

$$\mu \frac{d[\text{H}_2\text{D}^+]}{dt} + [\text{H}_2\text{D}^+] \frac{d\mu}{dt} = k [\text{H}_3^+]_0 \quad (18)$$

Then

$$\begin{aligned} \int \frac{d}{dt} (\mu [\text{H}_2\text{D}^+]) dt &= \int k [\text{H}_3^+]_0 dt \\ \mu [\text{H}_2\text{D}^+](t) &= k [\text{H}_3^+]_0 kt + C \\ [\text{H}_2\text{D}^+](t) &= [\text{H}_3^+]_0 k t e^{-kt} + C e^{-kt} \end{aligned} \quad (19)$$

Again, at $t = 0$, $[\text{H}_2\text{D}^+] = 0$, so $C = 0$. The final result is therefore

$$\boxed{[\text{H}_2\text{D}^+](t) = [\text{H}_3^+]_0 k t e^{-kt}, \quad (k = k_1 = k_2)} \quad (20)$$

|| SOLVING FOR $[\text{D}_2\text{H}^+]$

The procedure is essentially the same as for $[\text{H}_2\text{D}^+]$. First, substitute Equation (17) into Equation (7) and rearrange:

$$\frac{d[\text{D}_2\text{H}^+]}{dt} + k_3[\text{D}_2\text{H}^+] = \frac{k_1 k_2 [\text{H}_3^+]_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \quad (21)$$

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

$$\mu \equiv e^{k_3 t}, \quad \frac{d\mu}{dt} = k_3 e^{k_3 t} \quad (22)$$

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

$$\begin{aligned} \mu \frac{d[\text{D}_2\text{H}^+]}{dt} + [\text{D}_2\text{H}^+] \frac{d\mu}{dt} &= \frac{k_1 k_2 [\text{H}_3^+]_0}{k_2 - k_1} (e^{-(k_1 - k_3)t} - e^{-(k_2 - k_3)t}) \\ \int \frac{d}{dt} (\mu [\text{D}_2\text{H}^+]) &= \int \frac{k_1 k_2 [\text{H}_3^+]_0}{k_2 - k_1} (e^{-(k_1 - k_3)t} - e^{-(k_2 - k_3)t}) \\ \mu [\text{D}_2\text{H}^+](t) &= \frac{k_1 k_2 [\text{H}_3^+]_0}{k_2 - k_1} \left(\frac{e^{-(k_1 - k_3)t}}{k_3 - k_1} - \frac{e^{-(k_2 - k_3)t}}{k_3 - k_2} \right) + C \\ [\text{D}_2\text{H}^+](t) &= \frac{k_1 k_2 [\text{H}_3^+]_0}{k_2 - k_1} \left(\frac{e^{-k_1 t}}{k_3 - k_1} - \frac{e^{-k_2 t}}{k_3 - k_2} \right) + C e^{-k_3 t} \end{aligned} \quad (23)$$

The boundary condition is at $t = 0$, $[\text{D}_2\text{H}^+] = 0$, so

$$C = -\frac{k_1 k_2 [\text{H}_3^+]_0}{k_2 - k_1} \left(\frac{1}{k_3 - k_1} - \frac{1}{k_3 - k_2} \right) \quad (24)$$

So the final result is

$$\boxed{[\text{D}_2\text{H}^+](t) = \frac{k_1 k_2 [\text{H}_3^+]_0}{k_2 - k_1} \left(\frac{e^{-k_1 t} - e^{-k_3 t}}{k_3 - k_1} - \frac{e^{-k_2 t} - e^{-k_3 t}}{k_3 - k_2} \right)} \quad (25)$$

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 $[\text{H}_2\text{D}^+]$. We will not do that here.

|| SOLVING FOR $[\text{D}_3^+]$

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

$$[\text{H}_3^+](t) + [\text{H}_2\text{D}^+](t) + [\text{D}_2\text{H}^+](t) + [\text{D}_3^+](t) = [\text{H}_3^+]_0 \quad (26)$$

Therefore

$$\boxed{[\text{D}_3^+](t) = [\text{H}_3^+]_0 - [\text{H}_3^+](t) - [\text{H}_2\text{D}^+](t) - [\text{D}_2\text{H}^+](t)} \quad (27)$$

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