

Exercise 41

In contrast to the situation of Exercise 40, experiments show that the reaction $\text{H}_2 + \text{Br}_2 \longrightarrow 2\text{HBr}$ satisfies the rate law

$$\frac{d[\text{HBr}]}{dt} = k[\text{H}_2][\text{Br}_2]^{1/2}$$

and so for this reaction the differential equation becomes

$$\frac{dx}{dt} = k(a - x)(b - x)^{1/2}$$

where $x = [\text{HBr}]$ and a and b are the initial concentrations of hydrogen and bromine.

- (a) Find x as a function of t in the case where $a = b$. Use the fact that $x(0) = 0$.
- (b) If $a > b$, find t as a function of x . [*Hint:* In performing the integration, make the substitution $u = \sqrt{b - x}$.]

Solution**Part (a)**

In the case where $a = b$, the differential equation simplifies to

$$\frac{dx}{dt} = k(a - x)^{3/2}.$$

This equation is separable, so we can solve for $x(t)$ by bringing all terms with x to the left and all constants and terms with t to the right and then integrating both sides.

$$\begin{aligned} dx &= k(a - x)^{3/2} dt \\ \frac{dx}{(a - x)^{3/2}} &= k dt \\ \int \frac{dx}{(a - x)^{3/2}} &= \int k dt \end{aligned}$$

Use a u -substitution to solve the integral on the left.

$$\begin{aligned} \text{Let } u &= a - x \\ du &= -dx \end{aligned}$$

$$\begin{aligned} \int \frac{-du}{u^{3/2}} &= \int k dt \\ -\frac{1}{-\frac{1}{2}u^{1/2}} &= kt + C \\ 2\frac{1}{(a - x)^{1/2}} &= kt + C \\ \frac{2}{kt + C} &= (a - x)^{1/2} \\ \frac{4}{(kt + C)^2} &= a - x \\ x(t) &= a - \frac{4}{(kt + C)^2} \end{aligned}$$

We're told that $x(0) = 0$, so we can determine C .

$$\begin{aligned}x(0) &= a - \frac{4}{C^2} = 0 \\a &= \frac{4}{C^2} \\C^2 &= \frac{4}{a} \\C &= \pm \frac{2}{\sqrt{a}}\end{aligned}$$

We choose C to be $+\frac{2}{\sqrt{a}}$ so that the denominator doesn't equal 0 for any $t > 0$. Therefore,

$$x(t) = a - \frac{4}{\left(kt + \frac{2}{\sqrt{a}}\right)^2}, \quad a = b.$$

Part (b)

Now we assume that $a > b$, so the differential equation remains as given.

$$\frac{dx}{dt} = k(a-x)(b-x)^{1/2}$$

The equation is separable, so to solve for $x(t)$ we have to bring all terms with x to the left and all constants and terms with t to the right and then integrate both sides.

$$\begin{aligned}dx &= k(a-x)(b-x)^{1/2} dt \\ \frac{dx}{(a-x)(b-x)^{1/2}} &= k dt \\ \int \frac{dx}{(a-x)(b-x)^{1/2}} &= \int k dt\end{aligned}$$

Use the u -substitution given in the hint to solve the integral on the left.

$$\begin{aligned}\text{Let } u &= \sqrt{b-x} \quad \rightarrow \quad u^2 = b-x \quad \rightarrow \quad u^2 - b + a = a-x \\ du &= -\frac{1}{2\sqrt{b-x}} dx \quad \rightarrow \quad -2 du = \frac{1}{\sqrt{b-x}} dx\end{aligned}$$

$$\int \frac{-2 du}{u^2 + (a-b)} = \int k dt$$

Recall that

$$\int \frac{du}{u^2 + a^2} = \frac{1}{a} \tan^{-1} \frac{u}{a}.$$

So

$$\begin{aligned}\frac{-2}{\sqrt{a-b}} \tan^{-1} \frac{u}{\sqrt{a-b}} &= kt + C_1 \\ -\frac{2}{\sqrt{a-b}} \tan^{-1} \frac{\sqrt{b-x}}{\sqrt{a-b}} - C_1 &= kt \\ t(x) &= -\frac{1}{k} \left(\frac{2}{\sqrt{a-b}} \tan^{-1} \frac{\sqrt{b-x}}{\sqrt{a-b}} + C_1 \right).\end{aligned}$$

If we use the initial condition, $x(0) = 0$, as we did before, we get

$$\begin{aligned}t(0) &= -\frac{1}{k} \left(\frac{2}{\sqrt{a-b}} \tan^{-1} \frac{\sqrt{b}}{\sqrt{a-b}} + C_1 \right) = 0 \\ \frac{2}{\sqrt{a-b}} \tan^{-1} \frac{\sqrt{b}}{\sqrt{a-b}} + C_1 &= 0 \\ C_1 &= -\frac{2}{\sqrt{a-b}} \tan^{-1} \frac{\sqrt{b}}{\sqrt{a-b}}.\end{aligned}$$

Therefore,

$$\begin{aligned}t(x) &= -\frac{1}{k} \left(\frac{2}{\sqrt{a-b}} \tan^{-1} \frac{\sqrt{b-x}}{\sqrt{a-b}} - \frac{2}{\sqrt{a-b}} \tan^{-1} \frac{\sqrt{b}}{\sqrt{a-b}} \right) \\ t(x) &= -\frac{2}{k\sqrt{a-b}} \left(\tan^{-1} \frac{\sqrt{b-x}}{\sqrt{a-b}} - \tan^{-1} \frac{\sqrt{b}}{\sqrt{a-b}} \right) \\ t(x) &= \frac{2}{k\sqrt{a-b}} \left(\tan^{-1} \frac{\sqrt{b}}{\sqrt{a-b}} - \tan^{-1} \frac{\sqrt{b-x}}{\sqrt{a-b}} \right), \quad a > b.\end{aligned}$$