## A.2 Exponentials and logarithms

The exponential function arises in the mathematical description of all sorts of physical processes, from chemical kinetics to quantum mechanics. In this section we will review the properties of this function and the related natural logarithm, and give an example of how the exponential arises in chemical kinetics.

The form of the exponential which is of most interest to us is

$$\mathrm{e}^{-Ax} \quad \text{which is often written} \quad \exp(-Ax)$$

where A is a constant. Figure A.1 shows a plot of this function for three different values of A.
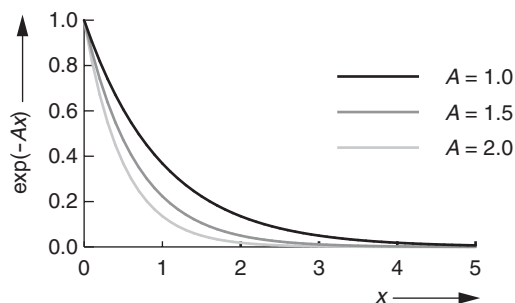
Fig. A.1 Plots of the exponential function for three different values of the constant A; note that as A increases, the rate of decay of the function increases.

You can see from this plot why the exponential function is often called an 'exponential decay'. When $x = 0$ the function is 1 (for all values of A), and then as x increases the function decays away towards zero; the larger the constant A, the faster the decay rate. For negative x, $\exp(-Ax)$ is positive and goes on increasing as x becomes more and more negative; this behaviour is not usually encountered in physical systems, so we have not plotted it.

The *natural logarithm*, denoted ln, is closely related to the exponential:

$$\text{if} \ \ C = \mathrm{e}^D \ \ \text{then} \ \ \ln C = D.$$

It follows from this definition of the logarithm that

$$\mathrm{e}^{\ln C} = C.$$

Any number raised to the power of zero is 1, thus $\mathrm{e}^0 = 1$ and so it follows that $\ln 1 = 0$.

A negative exponent is equivalent to the reciprocal:

$$\mathrm{e}^{-L} \equiv \frac{1}{\mathrm{e}^L}.$$

When two exponentials are multiplied, their exponents add:

$$\mathrm{e}^L \times \mathrm{e}^M \equiv \mathrm{e}^{L+M}.$$

This leads to the following result for the addition of logarithms:

$$\ln L + \ln M \equiv \ln (LM),$$

i.e. the addition of the logarithms of two numbers gives the logarithm of their product. Subtraction of the logarithms gives the logarithm of the ratio:

$$\ln L - \ln M \equiv \ln \frac{L}{M}.$$

From this we find the following relationship

$$\ln \frac{1}{A} \equiv \ln 1 - \ln A$$
$$\equiv -\ln A,$$

where we have used $\ln 1 = 0$.

The half life

The exponential function $\exp(-Ax)$ has an interesting property which is that starting from *any* value of x, the *increase* in x needed to make the function fall to *half* its initial value is *only* a function of A. This is easy to prove in the following way.

If the initial value of x is x_0, then the value of the function at this point is $\exp(-Ax_0)$. Let the value of x at which the function has fallen to half its initial value be $(x_0 + \delta)$; δ can be found in the following way:

$$\tfrac{1}{2} \text{ value at } x_0 = \text{value at } (x_0 + \delta)$$
$$\tfrac{1}{2} \times e^{-Ax_0} = e^{-A(x_0+\delta)}$$
$$\tfrac{1}{2} \times e^{-Ax_0} = e^{-Ax_0}\, e^{-A\delta}$$
$$\tfrac{1}{2} = e^{-A\delta}$$
$$\text{or} \ \ \ln \tfrac{1}{2} = -A\delta.$$

To go to the last line we have taken logarithms of both sides. Rearranging this last equation enables us to find an expression for δ, the increase in x:

$$\delta = \frac{\ln \tfrac{1}{2}}{-A}$$
$$= \frac{\ln 2}{A}.$$

We have now proved what was stated earlier, which is that the value of δ is *independent* of the choice of x_0 and only depends on the constant A; this is illustrated in Fig. A.2. If the variable x is time, then δ is called the *half life* because it is the time needed for the exponential to fall to half its initial value.

First-order reactions

In this section we will show how the exponential function arises in the mathematical description of the rates of chemical reactions. Suppose we have a reaction in which the rate is proportional to the concentration of a reactant A:

$$\text{rate} = k_1[\text{A}]$$
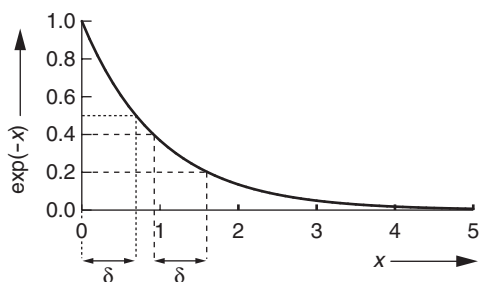
Fig. A.2 A property of the exponential function is that the increase in x needed for the function to fall to half its initial value is independent of the initial value. The plot shows that the interval, δ, needed for the function to fall from 1.0 to 0.5 is the same as that needed for the function to fall from 0.4 to 0.2. As shown in the text, this interval turns out to be (ln 2 / A); in this case A = 1 so δ = 0.69.

where [A] is the concentration of A at time t and k_1 is the rate constant. As was described on p. 136, such a rate law is said to be *first order* as the concentration of the reactant is raised to the power of 1; k_1 is therefore described as a first order rate constant.

Using calculus the rate can be written as a differential:

$$\frac{d[A]}{dt} = -k_1[A]. \tag{A.1}$$

We need the minus sign as A is a reactant whose concentration decreases as the reaction proceeds, i.e. d[A]/dt is negative.

Equation A.1 is a *differential equation* whose variables, [A] and t, can be separated; we will put the terms in [A] on the left-hand side, and those in t on the right-hand side:

$$\frac{d[A]}{dt} = -k_1[A]$$

$$\text{hence} \quad \frac{1}{[A]}\,d[A] = -k_1 dt.$$

Now the left-hand side can be integrated with respect to [A] and the right-hand side with respect to t:

$$\int \frac{1}{[A]}\,d[A] = \int -k_1 dt$$
$$\ln[A] = -k_1 t + \text{const.} \tag{A.2}$$

The constant of integration can be found by supposing that at $t = 0$ the concentration of A is $[A]_0$; substituting these values into Eq. A.2 we find

$$\ln[A]_0 = \text{const.}$$

Substituting this value for the constant into Eq. A.2 we obtain the following expression which tells us how the concentration varies with time:

$$\ln[A] = -k_1 t + \ln[A]_0. \tag{A.3}$$

This equation is of the form $y = mx + c$, and so if we plot $\ln[A]$ against t we will obtain a straight line with slope $-k_1$. Such a plot is therefore a method for determining the value of the first-order rate constant, k_1.

Equation Eq. A.3 can be rewritten in the following steps:

$$\ln[A] = -k_1 t + \ln[A]_0$$
$$\ln[A] - \ln[A]_0 = -k_1 t$$
$$\ln \frac{[A]}{[A]_0} = -k_1 t$$
$$\frac{[A]}{[A]_0} = \exp(-k_1 t)$$
$$[A] = [A]_0 \exp(-k_1 t)$$

where on the last line but one we have taken the natural logarithm of both sides.

What the last line shows is that for a first-order reaction the concentration of reactant A decays exponentially with time, with the rate of the decay being set by the value of the rate constant, k_1. So, Fig. A.1 on p. A–2 could be a plot of concentration against time for different values of the rate constant.

The half life for the reaction, i.e. the time for the concentration to fall to half its initial value, is given by $\ln 2 / k_1$. So the larger the rate constant, the shorter the half life, as we would expect.