Appendix 3, Rises and runs, slopes and sums: tools from calculus

Sometimes we will want to explore how a quantity changes as a condition is varied. Calculus was invented to do just this. We certainly do not need the full machinery of calculus, just a few of its key ideas and tools, described here. There are two different regimes, according to whether we are interested in a small change in conditions (in which case we use slopes) or a large change in conditions (in which case we use sums).

> *If you are not yet familiar with calculus, the ideas and tools presented here are all that you need (and a bit more!) to appreciate their application in general chemistry. They may even make your future study of calculus easier.*

> *If you are already familiar with calculus, then the material here probably will be quite familiar, with one possible exception. The discussion of the natural logarithm emphasizes its definition in terms of the sum of small changes in a quantity divided by the value of the quantity at each point in its change. If you are like me, on first exposure you may not have appreciated that the natural logarithm arises as this special kind of sum, and so that it cannot be "derived" from something more fundamental. Indeed, it is for this reason that it comes up "naturally" in chemistry and so is quite accessible to us.*

Slopes

If we are interested in the effect, df, on a property, f, of a small change, dx, in conditions, we can evaluate this as the product of the rate at which f changes when x is changed times the small change in x,

$$df = \text{change in } f \text{ due to small change } dx = \frac{df}{dx}\, dx\,.$$

The rate of change, df/dx, is the *slope* of the plot of f versus x. It is called the *derivative*. If we have an expression for the dependence of f on x, then it is easy to get an expression for the slope without having to make a plot of f versus x. The process is called *differentiation*.

The key idea of differentiation is that slopes—rise over run—are computed in the limit that the run is tiny. Here is what this statement means in general terms. If x changes from x_1 to x_2, then the slope of the variation is defined in the usual way

$$\frac{\Delta f}{\Delta x} = \frac{f(x_2) - f(x_1)}{x_2 - x_1}\,.$$

To specify that the run, $x_2 - x_1$, is tiny, we write

$$x_2 = x_1 + dx\,,$$

and so

$$x_2 - x_1 = dx\,,$$

with the understanding that dx is tiny. Using this last relation in the expression for the slope, we get

$$\frac{d f}{d x} = \lim_{d x \to 0} \frac{f(x + d x) - f(x)}{d x} ,$$

where we have replace the specific value $x_1$by the general value x. This is as the fundamental definition of slope for tiny runs. To see just what the definition means and how powerful it is, let's apply it to the several kinds of variations, $f(x)$, that arise in chemistry.

■ Linear variation, $f(x) = a\,x$

The simplest example is a linear variations, $a\,x$. If we plot this we will get a straight line extending from the origin with slope a. Here is what we get using the definition of slope.

$$\begin{aligned}\frac{d f}{d x} \\ &= \frac{f(x + d x) - f(x)}{d x} \\ &= \frac{a(x + d x) - a\,x}{d x} \\ &= \frac{a\,x + a\,d x - a\,x}{d x} \\ &= a\,.\end{aligned}$$

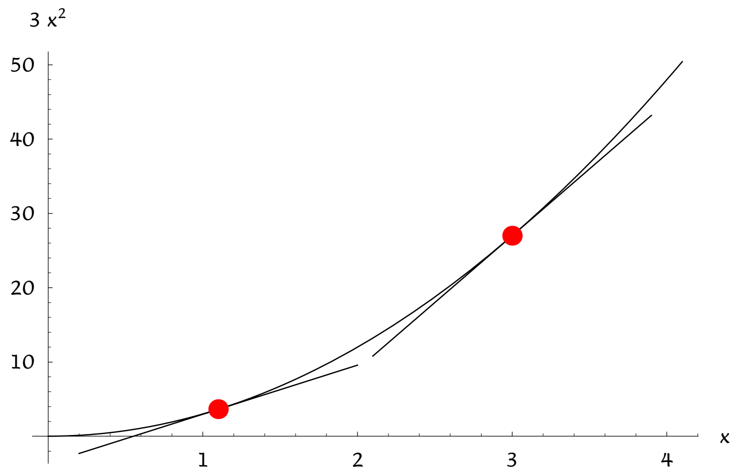
Just as we expect, the slope evaluates to a.

■ Quadratic variation, $f(x) = a\,x^2$

Here is what we get for a quadratic variation, $a\,x^2$.

$$\begin{aligned}\frac{d f}{d x} \\ &= \frac{f(x + d x) - f(x)}{d x} \\ &= \frac{a(x + d x)^2 - a\,x^2}{d x} \\ &= \frac{a\,x^2 + 2\,a\,x\,d x + a(d x)^2 - a\,x^2}{d x} \\ &= 2\,a\,x + a\,d x \\ &= 2\,a\,x\,.\end{aligned}$$

In the last step, we use the fact that we are interested in values $d x$ that are tiny ("infinitesimally small") and so that, in the numerator of the second to last line, the term $a\,d x$ is negligible compared to $2\,a\,x$. Here is a plot of $f = 3\,x^2$ and the slope, $d f / d x = 6\,x$ at several points.



Function $3x^2$ and its slope, $6x$, at $x = 1.1$ and $x = 3$. The straight lines are the slope of the function when it has the values indicated by the dots.

I find it almost magical that we can evaluate an analytical expression for the slope of the function—the line tangent to the plot of the function—at any point.

■ General variation, $f(x) = a\,x^n$

We can show in the same way that for positive integers n, the slope $f(x) = a\,x^n$ is

$$\frac{d f}{d x} = n\,a\,x^{n-1}.$$

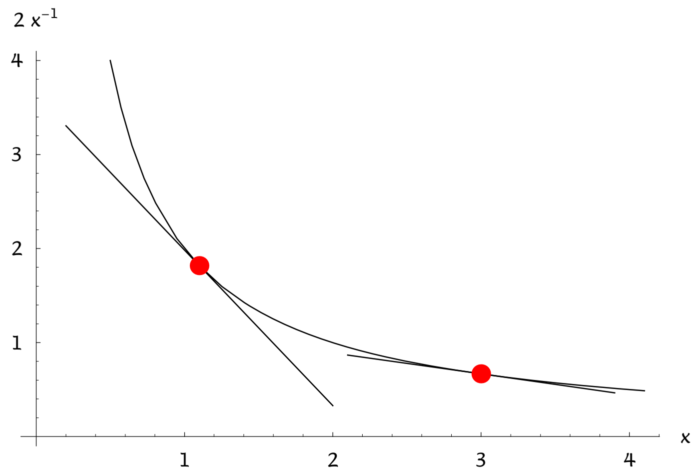
See if you can do this.

■ Inverse linear variation, $f(x) = a\,x^{-1}$

Here is the slope when a property is inversely proportional to a quantity x.

$$\begin{aligned}\frac{d f}{d x} &= \frac{f(x + d x) - f(x)}{d x} \\ &= \left(\frac{a}{x + d x} - \frac{a}{x}\right) \Big/ d x \\ &= \left(\frac{a\,x}{(x + d x)\,x} - \frac{a(x + d x)}{x(x + d x)}\right) \Big/ d x \\ &= \left(\frac{a\,x - a\,x - a\,d x}{x^2 - x\,d x}\right) \Big/ d x \\ &= \left(\frac{-a}{x^2 - x\,d x}\right) \\ &= -\frac{a}{x^2}\,.\end{aligned}$$

In the last step, we use the fact that we are interested in values dx that are tiny ("infinitesimally small") and so that, in the denominator of the second to last line, the term $x\,d x$ is negligible compared to x^2. Here is a plot of $f = 2\,x^{-1}$ and the slope, $d f / d x = -2\,x^{-2}$ at several points.



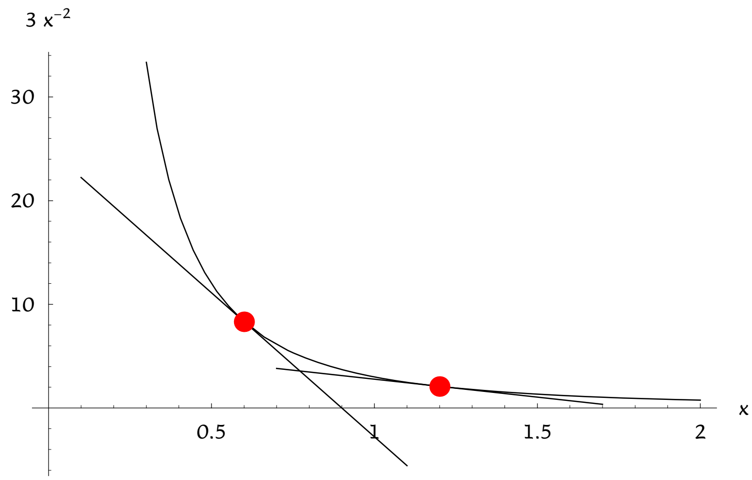
Function $2x^{-1}$ and its slope, $-2x^{-2}$, at $x = 1.1$ and $x = 3$. The straight lines are the slope of the function when it has the values indicated by the dots.

■ Inverse quadratic variation, $f(x) = a\,x^{-2}$

Here is the slope when a property is inversely proportional to the square of a quantity x.

$$\begin{aligned}\frac{df}{dx} &= \frac{f(x + dx) - f(x)}{dx} \\ &= \left(\frac{a}{(x + dx)^2} - \frac{a}{x^2}\right)\Big/ dx \\ &= \left(\frac{a\,x^2}{(x + dx)^2\,x^2} - \frac{a(x + dx)^2}{x^2 (x + dx)^2}\right)\Big/ dx \\ &= \left(\frac{a\,x^2 - a\,x^2 - 2\,a\,x\,dx - a\,dx^2}{x^4 + 2\,x^3\,dx + x^2\,dx^2}\right)\Big/ dx \\ &= \frac{-2\,a\,x - a\,dx}{x^4 + 2\,x^3\,dx + x^2\,dx^2} \\ &= -\frac{2\,a}{x^3}\,.\end{aligned}$$

In the last step, we use the fact that we are interested in values dx that are tiny ("infinitesimally small") and so that, in the second to last line, in the numerator the term $a\,dx$ is negligible compared to $2\,a\,x$, and in the denominator the terms $2\,x^3\,dx + x^2\,dx^2$ are negligible compared to x^4. Here is a plot of $f = 3\,x^{-2}$ and the slope, $df/dx = -6\,x^{-3}$ at several points.



Function $3x^{-2}$ and its slope, $-6x^{-3}$, at $x = 0.6$ and $x = 1.2$. The straight lines are the slope of the function when it has the values indicated by the dots.

■ General variation, $f(x) = a\,x^{-n}$

We can show in the same way that for positive integers n, the slope of $f(x) = a\,x^{-n}$ is

$$\frac{df}{dx} = -n\,a\,x^{-(n+1)}.$$

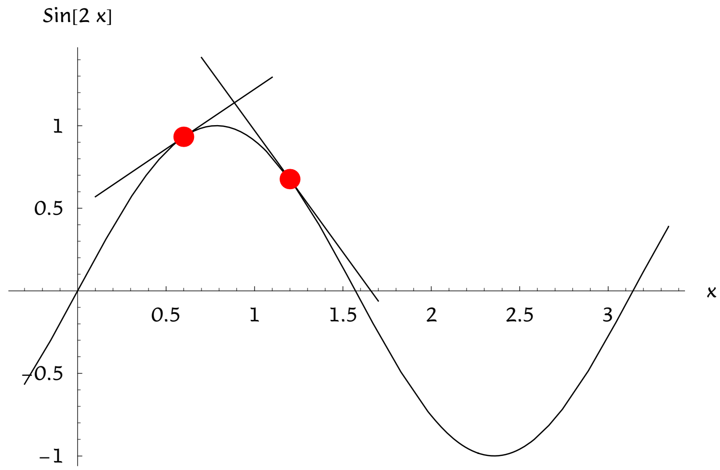
See if you can do this.

■ Trigonometric variation, $f(x) = \sin(a\,x)$

Here is the slope when a property is proportional to the $\sin(a\,x)$.

$$\begin{aligned}\frac{df}{dx} \\ &= \frac{f(x + dx) - f(x)}{dx} \\ &= \frac{\sin(a\,x + a\,dx) - \sin(a\,x)}{dx} \\ &= \frac{\sin(a\,x)\cos(a\,dx) + \cos(a\,x)\sin(a\,\mathrm{dx}) - \sin(a\,x)}{dx} \\ &= \frac{\sin(a\,x) + \cos(a\,x)\,a\,dx - \sin(a\,x)}{dx} \\ &= a\cos(a\,x)\end{aligned}$$

Here we use the trigonometric identity $\sin(a + b) = \sin(a)\cos(b) + \cos(a)\sin(b)$, and the fact that for x tiny, $\sin(x) = x$ and $\cos(x) = 1$. Here is a plot of $f = \sin(2\,x)$ and the slope, $df/dx = 2\cos(2\,x)$ at several points.



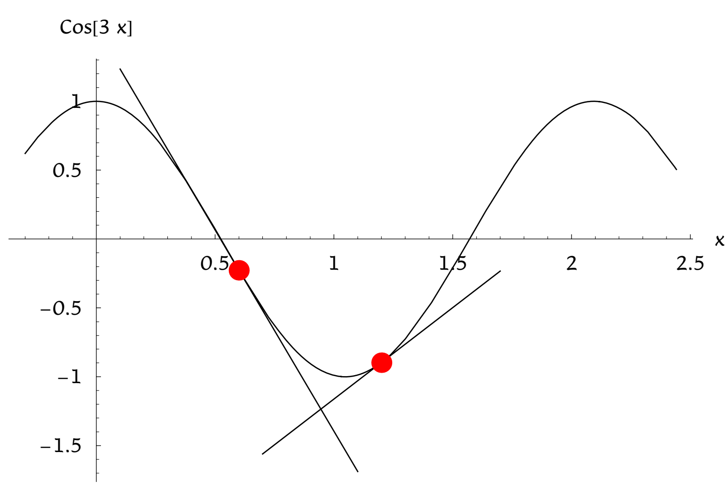
Function $\sin(2\,x)$ and its slope, $2\cos(2\,x)$, at $x = 0.6$ and $x = 1.2$. The straight lines are the slope of the function when it has the values indicated by the dots.

■ Trigonometric variation, $f(x) = \cos(a\,x)$

Here is the slope when a property is proportional to the $\cos(a\,x)$.

$$\begin{aligned}\frac{df}{dx} &= \frac{f(x + dx) - f(x)}{dx} \\ &= \frac{\cos(a\,x + a\,dx) - \cos(a\,x)}{dx} \\ &= \frac{\cos(a\,x)\cos(a\,dx) - \sin(a\,x)\sin(a\,\mathrm{dx}) - \cos(a\,x)}{dx} \\ &= \frac{\cos(a\,x) - \sin(a\,x)\,a\,dx - \cos(a\,x)}{dx} \\ &= -a\sin(a\,x)\end{aligned}$$

Here we use the trigonometric identity $\cos(a + b) = \cos(a)\cos(b) - \sin(a)\sin(b)$, and the fact that for x tiny, $\sin(x) = x$ and $\cos(x) = 1$. Here is a plot of $f = \cos(3\,x)$ and the slope, $df/dx = -\sin(3\,x)$ at several points.



Function $\cos(3\,x)$ and its slope, $-3\cos(3\,x)$, at $x = 0.6$ and $x = 1.2$. The straight lines are the slope of the function when it has the values indicated by the dots.

Sums

Assume that a quantity represented by a function f depends on a variable x. We are often interested to know the effect of a large change, Δx, on the value of f. Let's introduce the notation Δf for the effect of a large change in x on $f(x)$. A way to determine Δf is to sum up all of the small changes, $d f$, that occur as x is changes throughout the large range Δx. This summing up is represented by the symbol $\int$ (for ***S***um) as follows.

$$\Delta f = \text{change in } f \text{ due to large change } \Delta x = \int_{f(x)}^{f(x+\Delta x)} d f = f(x+\Delta x) - f(x)$$

The *key idea* is that the way to use this relation is to interpret the small changes, $d f$, being summed to be the product of a slope, $d f / d x$, and a small change in conditions, $d x$,

$$d f = \frac{d f}{d x} d x,$$

and then to work backwards to see which function $f(x)$ has $d f / d x$ as its slope. You may want to read the last sentence again. It really is the key to determining the cumulative effect of successive small changes.

Here is an example. In some chemical reactions a reactant, A, disappears at a rate proportional to the square of its concentration, [A]. We can express this as

$$\frac{d[\mathrm{A}]}{d t} = -k\,[\mathrm{A}]^2,$$

where the minus sign takes care of the fact that the concentration *decreases* with time. Tis expression says that the small change in concentration, $d[\mathrm{A}]$, that occurs during the passage of the small amount of time, $d t$, is proportional to the square of the concentration *at the time of the change*. Since [A] thereby changes as time passes, so to does the rate. We can rearrange this expression to

$$-\frac{d[\mathrm{A}]}{[\mathrm{A}]^2} = k\, d t.$$

In this form we can see how to sum the change in concentration that takes place over a large change in time, say from $t = 0$ to t. The sum on the right hand side is just k times the total elapsed time, $k(t - 0) = k\,t$. To evaluate the sum on the left hand side, we interpret it as

$$d f = \frac{d f}{d x} d x \to d f = \frac{d f}{d[\mathrm{A}]} d[\mathrm{A}] = -\frac{1}{[\mathrm{A}]^2} d[\mathrm{A}],$$

That is, we interpret $-1/[\mathrm{A}]^2$ as the slope $d f / d[\mathrm{A}]$ of an (as yet unknown) function of the concentration. That is, this interpretation means that what we need to know is which function of [A] has as derivative $-1/[\mathrm{A}]^2$.

From our analysis of derivatives, we know the answer: $-1/[\mathrm{A}]^2$ is the derivative of $1/[\mathrm{A}]$. This means that $f = 1/[\mathrm{A}]$, and so the sum on the left hand side is

$$\Delta f = f(x+\Delta \mathrm{x}) - f(x) \to \frac{1}{[\mathrm{A}] \text{ at } t} - \frac{1}{[\mathrm{A}] \text{ at } t = 0} = \frac{1}{[\mathrm{A}]_t} - \frac{1}{[\mathrm{A}]_0}.$$

In this way we get an explicit expression for the cumulative change in $-1/[A]^2$ as concentration changes continuously from $[A]_0$ to $[A]_t$. In this example the result is the expression

$$k\,t = \frac{1}{[A]_t} - \frac{1}{[A]_0}$$

relating the concentration of A at any time t to its initial concentration.

This example illustrates the general procedure for doing sums. It is less systematic than getting expressions for slopes, that is, than evaluating derivatives. The key idea is always the same, to look at what is being summed in terms of a slope and then to figure out which function has that as its slope.

A remarkable special case: $f(x) = \ln(x)$

How should we handle the sum

$$\int_{f(x)}^{f(x+\Delta x)} d f = \int_{x}^{x+\Delta x} \frac{1}{x}\, d x \text{ ?}$$

That is, what function has as its derivative

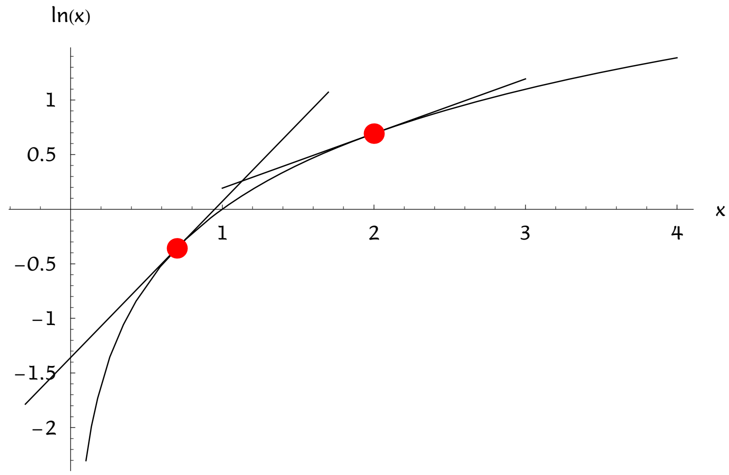
$$\frac{d f}{d x} = \frac{1}{x} \text{ ?}$$

Neither $f(x) = x^n$ nor $f(x) = x^{-n}$, for positive integer n will do. This is a real puzzle. In fact, there is *no* analytic explicit functional form that has as its derivative $1/x$. What do we do? What we do is to *define the answer in terms of the sum*. The sum is known as the *natural logarithm,*

$$\ln(x) \equiv \int_1^x \frac{1}{x}\, d x\,.$$

with the understanding that $x > 0$. Such a definition is known as an *integral representation* of a function.

Here is a plot that shows that the sum is indeed $\ln(x)$.



Function log(*x*) and its slope, $1/x$, at $x = 0.7$ and $x = 2$. The straight lines are the slope of the function when it has the values indicated by the dots.

The plot was constructed using the values of log(*x*) for the curve and the values $1/x$ for the slope. In this way we confirm graphically that the natural logarithm is a function defined in terms of a sum—what is called an *integral representation*.

But how do we compute such a sum? The answer is to compute it by breaking the sum up into pieces. If the pieces are large, our answer for the sum will not be very accurate. As we make the size of each piece smaller, by adding more pieces, the answer gets better quite quickly. We will see just how to do this during the discussion of work done by an expanding gas, but for now, let's realize that every time we press the log(*x*) button on our calculators, the calculator evaluates the sum for us to get the numerical values.

■ Logarithmic properties of $\int_1^x (1/x)\,dx$

The place to begin is to recall the just what a logarithm is. The *logarithm*, *y*, of a *number*, *x*, to a *base*, *b*, is the power to which the base must be raised to equal the number,

$$x = b^y$$

Expressed differently,

$$\log_b(x) = y$$

In numerical calculations, we usually work with logarithms in the base $b = 10$, and often abbreviate $\log_{10}(x)$ simply as $\log(x)$, that is, without writing the value of the base.

Base of the natural logarithm: e

The first question that you may have about the natural logarithm is what is the base? We can determine this by noting that, from the definition of the logarithm, the logarithm to base *b* of the base *b* is always 1,

$$\log_b(b) = 1\,,$$

since $b = b^1$. This means we can determine the numerical value of the base of the natural logarithm by finding the value of *x* for which the sum

$$\int_1^x \frac{1}{x}\, dx$$

is one. This number is called e and has the value $e = 2.71828$.

$$1 = \int_1^e \frac{1}{x}\, dx$$

Numerical calculations with natural logarithms are conveniently done by expressing them in terms of base 10 logarithms. Here is how to do this. Any number can be written as

$$x = 10^{\log(x)},$$

in terms of its base 10 logarithm. Taking the natural 1ogarithm of both sides, we get

$$\ln(x) = \ln[10^{\log(x)}] = \log(x)\ln(10)$$

Since ln(10) = 2.30259, this expression means that

$$\ln(x) = 2.30259 \log(x)$$

This is a very useful formula in numerical calculations with logarithms, and is worth memorizing.

Logarithmic properties of the natural logarithm

From the definition of a logarithm, two key properties follow:

$$\log_c(a\,b) = \log_c(a) + \log_c(b)\,,$$

since $c^{\log_c a}\, c^{\log_c b} = c^{\log_c a + \log_c b}$, and

$$\log_c(1/a) = -\log_c(a),$$

since $1/a = a^{-1}$. (These properties are true for any base, and so an unspecified base c is used in these relations.) From these properties, we can get the other properties of logarithms. For example, we can show that

$$\log_c(a/b) = \log_c(a) + \log_c(1/b) = \log_c(a) - \log_c(b)$$

by using the two key properties, and we can show that

$$\log_c(a^b) = b\log_c(a)$$

by interpreting a^b as the product of a times itself b times, and then repeatedly using the relation for the logarithm of a product.

$$\log_c(a^b) = \log_c(a\,a\,\ldots\,a) = \log_c(a) + \log_c(a) + \ldots + \log_c(a) = b\log_c(a)$$

These key properties are what we need to confirm that

$$\int_1^x \frac{1}{x}\, dx$$

is in fact a logarithm. That is, what we need to do is to show that the sum satisfies the two key properties of logarithms. The details given below are not at all essential to using our results, but should you want to follow along, they do show how powerful the basic ideas of "slopes and sums, rises and runs" that we have developed here are.

Natural logarithm of a product

Using the integral representation, the logarithm of a product is

$$\ln(a\,b) \equiv \int_1^{a\,b} \frac{1}{x}\, dx\,.$$

We can break the sum up into the piece from 1 to *a*, and the piece from *a* to *a b*.

$$\ln(a\,b) \equiv \int_1^{a} \frac{1}{x}\, dx + \int_a^{a\,b} \frac{1}{x}\, dx$$

The first piece is $\ln(a)$, by our definition of the natural logarithm. This means what we have to do is to show that the second piece is $\ln(b)$. We can do this by changing the scale from x to $y = x/a$. This change means a small change in dx is equivalent to $a\,dy$, that $x = a$ corresponds to $y = 1$, and that $x = a\,b$ corresponds to $y = b$. With these values, we can write the second piece as

$$\int_a^{a\,b} \frac{1}{x}\, dx = \int_1^{b} \frac{1}{a\,y}\, a\, dy = \int_1^{b} \frac{1}{y}\, dy$$

The last sum is, by our definition, $\ln(b)$ and so we have shown that

$$\ln(a\,b) = \ln(a) + \ln(b)$$

Natural logarithm of a reciprocal

Now let's consider the logarithm of an inverse,

$$\ln(1/a) \equiv \int_1^{1/a} \frac{1}{x}\, dx\,.$$

The key step in working with this expression is to realize that if we carry out a sum in the opposite direction, the value of the sum changes sign. To see this, note that

$$\int_{f(x+\Delta x)}^{f(x)} df = f(x) - f(x+\Delta x) = -[f(x+\Delta x) - f(x)] = -\int_{f(x)}^{f(x+\Delta x)} df$$

This means we can write

$$\int_1^{1/a} \frac{1}{x}\, dx = -\int_{1/a}^{1} \frac{1}{x}\, dx.$$

To rewrite the right hand side so the sum starts at 1 we can change the scale from x to $y = a\,x$. This change means a small change in dx is equivalent to dy/a, that $x = 1/a$ corresponds to $y = 1$, and that $x = 1$ corresponds to $y = a$. With these values, we can write

$$\int_{1/a}^{1} \frac{1}{x}\, dx = \int_1^a \frac{1}{y/a}\, dy/a = \int_1^a \frac{1}{y}\, dy.$$

The last sum is, by our definition, $\ln(a)$ and so we have shown that

$$\ln(1/a) = \int_1^{1/a} \frac{1}{x}\, dx = -\int_{1/a}^{1} \frac{1}{x}\, dx = -\log(a).$$

■ Postscript

I must confess that I did not appreciate at all just what the natural logarithm function was when I first learned calculus. I was not able to see the forest for the trees! It was not until I began teaching and so wanted to explain just where the natural logarithm comes from that I came to understand what we have seen here. I find the natural logarithm function quite remarkable. I hope these notes will be helpful in making easier your journey to understanding this amazing function.

Summary

Here is a summary of the results we have developed for slopes of different functions.

$f(x)$	df/dx
$a\,x$	a
$a\,x^2$	$2\,a\,x$
$a\,x^n$, integer $n > 0$	$n\,a\,x^{n-1}$
$a\ln(x)$	$a\,x^{-1}$, $x > 0$
$a\,x^{-2}$	$-2\,a\,x^{-3}$
$a\,x^{-n}$, integer $n > 1$	$-n\,a\,x^{-(n+1)}$
$\sin(a\,x)$	$a\cos(a\,x)$
$\cos(a\,x)$	$-a\sin(a\,x)$

In these expressions, a is a constant. We have also introduced the notation that $\log(x) = \log_{10}(x)$ and $\ln(x) = \log_e(x)$, and derived the equivalence $\ln(x) = 2.30259\log(x)$.