CHEM1033 - Week 3 Lecture - Derivatives and differentiation I

Sections 7.2, 4.1-4.5 of Steiner, "The Chemistry Maths Book", 2nd edition.
Chapter 17 of Monk and Munro, "Maths for Chemistry", 2nd edition.

1. Sequences and their limits

A *sequence* is an ordered set of terms $\{a_1, a_2, a_3, \ldots\}$ with a rule that specifies each term. Sequences can be specified *explicitly* using the number of each term, for example:

$$\begin{aligned} a_n = n^2 \quad &\Rightarrow \quad a_1 = 1,\ a_2 = 4,\ a_3 = 9, \ldots \\ a_n = 1/n \quad &\Rightarrow \quad a_1 = 1,\ a_2 = 1/2,\ a_3 = 1/3, \ldots \end{aligned} \tag{1}$$

or *recursively*, where the next element of the sequence is a function of the previous elements, *e.g.*:

$$\begin{aligned} a_{n+1} = (n+1)a_n, \quad a_1 = 1 \quad &\Rightarrow \quad a_2 = 2,\ a_3 = 6,\ a_4 = 24, \ldots \\ f_n = f_{n-1} + f_{n-2}, \quad f_1 = 1, \quad f_2 = 1 \quad &\Rightarrow \quad f_3 = 2,\ f_4 = 3,\ f_5 = 5, \ldots \end{aligned} \tag{2}$$

The *limit of a sequence* is the number (if it exists) that sequence elements approach closer and closer as the index n becomes bigger and bigger, for example:

$$\lim_{n\to\infty}\left[\frac{1}{n}\right] = 0, \quad \lim_{n\to\infty}\left[\frac{2n+5}{n+1}\right] = 2, \quad \lim_{n\to\infty}\left[2^n\right] = \infty, \quad \lim_{n\to\infty}\left[\frac{\ln(2n+1)}{\sqrt{n}}\right] = 0 \tag{3}$$

An example from chemistry is the sequence of energy levels in the hydrogen atom:

$$E_n = -\frac{\mu c^2 \alpha^2}{2n^2}, \quad \lim_{n\to\infty}\left[E_n\right] = 0 \tag{4}$$

where μ is the reduced mass of the electron-nuclear system, c is the speed of light and α is the fine structure constant. The limit of this sequence is zero because the free electron is used as a zero energy reference point in atomic theory – energies of bound electrons are negative (your chemistry tutors will explain all of that in due course).

2. Infinitely large and infinitely small quantities

There are many types of infinities in mathematics, some of them much bigger than others. It is not possible to manipulate infinitely large or infinitely small quantities directly. Limits of sequences are commonly used instead. Consider the example used above of the limit of a fraction:

$$\lim_{n\to\infty}\left[\frac{2n+5}{n+1}\right] = 2 \tag{5}$$

Both the numerator and the denominator become infinitely large when n goes to infinity. Yet their ratio remains finite and approaches 2, which is the limit of this sequence. Infinitely large and small quantities are therefore commonly defined in mathematics as limits of sequences. Sequence expressions are easy to handle and the limit can be taken as the last step in the calculation.

As an example, consider the following question: *which sequence goes to zero faster with increasing* n,

$$a_n = \frac{1}{3n+5} \quad \text{or} \quad b_n = \frac{1}{(3n-5)(3n+5)}?$$

It is clear that limits of both sequences individually are zero. However, we can pitch them against each other by calculating the limit of a fraction:

$$\lim_{n\to\infty}\left[\frac{a_n}{b_n}\right] \tag{6}$$

If this limit is zero, then a_n goes to zero faster, and if it is infinite, then b_n wins. Computing the limit

$$\lim_{n\to\infty}\left[\frac{a_n}{b_n}\right]=\lim_{n\to\infty}\left[\frac{\frac{1}{3n+5}}{\frac{1}{(3n-5)(3n+5)}}\right]=\lim_{n\to\infty}\left[\frac{(3n-5)(3n+5)}{3n+5}\right]=\lim_{n\to\infty}[3n-5]=\infty \tag{7}$$

results in the conclusion that the infinitely small quantity b_n is smaller than the infinitely small quantity a_n when n becomes infinitely large.

3. Functions and their limits

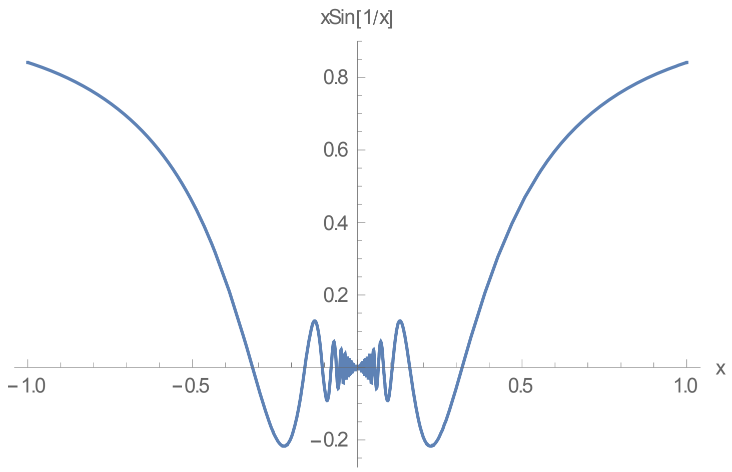
The *limit of a function* may be defined in a similar way to the limit of a sequence: it is the value (if it exists) that the function approaches when its argument approaches some specified value, for example:

$$\lim_{x\to 3}\left[x^2\right]=9,\qquad \lim_{x\to\infty}\left[\frac{1}{\sqrt{x}}\right]=0,\qquad \lim_{x\to 0}\left[x^4+6\right]=6,\qquad \lim_{x\to\pi}\left[\cos(2x)\right]=1 \tag{8}$$

There are also some less obvious limits:

$$\lim_{x\to 0}\frac{\sin x}{x}=1,\qquad \lim_{x\to\infty}\sqrt[x]{x}=1,\qquad \lim_{x\to 0}\sqrt[x]{x+1}=e \tag{9}$$

...and some seriously exotic ones:



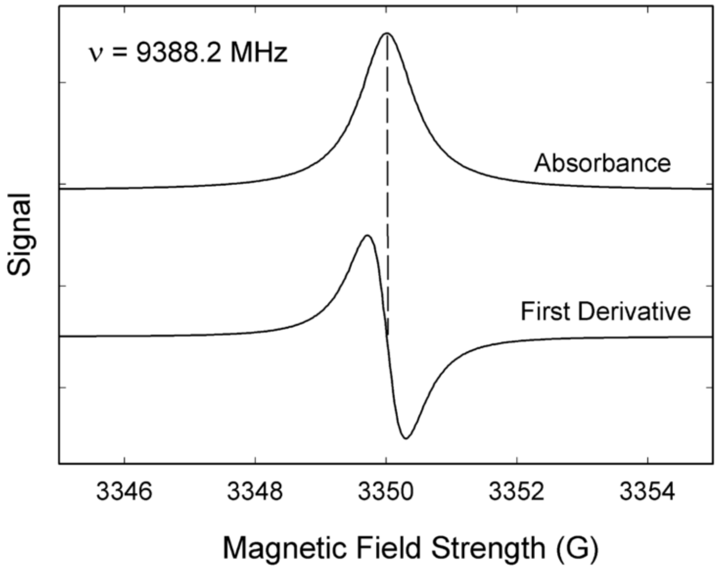
The theory of limits is a subject in its own right – we do not have sufficient time in this course to dwell on it in any detail. Limits are only introduced here because the definition of a *derivative* involves a limit.

4. Formal definition of a derivative

The *derivative* $f'(x)$ of a function $f(x)$ is defined as the following limit:

$$f'(x)=\lim_{\Delta x\to 0}\frac{f(x+\Delta x)-f(x)}{\Delta x} \tag{10}$$

The process of computing derivatives is called *differentiation*. From the physical point of view, derivative may be interpreted as the rate of change of the function: for example the derivative of a particle altitude with respect to time is that particle's vertical velocity, and the derivative of ground height with respect to distance is the slope of that ground. An example from chemical sciences is given below.



It shows, schematically, a radio wave absorbance spectrum of an organic radical as a function of the applied magnetic field. The absorbance signal is a simple bell-shaped function and its derivative indicates the rate of change in the value of that function: when the function is increasing, the derivative is positive and when it's decreasing, the derivative is negative.

The definition given in Equation (10) also allows us to derive some properties of the differentiation operation. Firstly, the derivative of a sum is a sum of derivatives:

$$\begin{aligned}\left[f(x)+g(x)\right]' &= \lim_{\Delta x\to 0}\frac{\left[f(x+\Delta x)+g(x+\Delta x)\right]-\left[f(x)+g(x)\right]}{\Delta x} = \\ &= \lim_{\Delta x\to 0}\frac{f(x+\Delta x)-f(x)}{\Delta x}+\lim_{\Delta x\to 0}\frac{g(x+\Delta x)-g(x)}{\Delta x} = f'(x)+g'(x)\end{aligned} \tag{11}$$

Secondly, constant multipliers can be taken out of the differentiation operation:

$$\left[\alpha f(x)\right]' = \lim_{\Delta x\to 0}\frac{\alpha f(x+\Delta x)-\alpha f(x)}{\Delta x} = \alpha\lim_{\Delta x\to 0}\frac{\alpha f(x+\Delta x)-\alpha f(x)}{\Delta x} = \alpha\left[f(x)\right]' \tag{12}$$

Further properties will make an appearance in the next lecture.

5. Differentiation using limits

In many cases derivatives may be computed directly from the definition given in Equation (10):

$$f(x)=2x-6 \qquad f'(x)=\lim_{\Delta x\to 0}\frac{\left[2(x+\Delta x)-6\right]-\left[2x-6\right]}{\Delta x}=\lim_{\Delta x\to 0}\frac{2\Delta x}{\Delta x}=2$$

In this case the derivative is a constant, this is because the slope of $y=2x-6$ is the same everywhere – it is a straight line. Derivatives of more complicated functions do depend on the argument:

$$f(t)=5t^2-2t+8 \qquad f'(t)=\lim_{\Delta t\to 0}\frac{\left[5(t+\Delta t)^2-2(t+\Delta t)+8\right]-\left[5t^2-2t+8\right]}{\Delta t}=[\ldots]=10t-2$$

Although the limit definition in Equation (10) is formally sufficient to calculate the derivative (if it exists) of any function, the intermediate expressions can become quite bulky even for relatively simple functions, for example:

$$f(x) = 2 - \sqrt{x+1} \qquad f'(x) = \lim_{\Delta x \to 0} \frac{\left[2 - \sqrt{x + \Delta x + 1}\right] - \left[2 - \sqrt{x+1}\right]}{\Delta x} =$$

$$= \lim_{\Delta x \to 0} \frac{\sqrt{x+1} - \sqrt{x + \Delta x + 1}}{\Delta x} = \lim_{\Delta x \to 0} \left[\frac{\sqrt{x+1} - \sqrt{x + \Delta x + 1}}{\Delta x} \frac{\sqrt{x+1} + \sqrt{x + \Delta x + 1}}{\sqrt{x+1} + \sqrt{x + \Delta x + 1}} \right] =$$

$$= \lim_{\Delta x \to 0} \left[\frac{x + 1 - x - \Delta x - 1}{\Delta x \left(\sqrt{x+1} + \sqrt{x + \Delta x + 1} \right)} \right] = \lim_{\Delta x \to 0} \left[- \frac{\Delta x}{\Delta x \left(\sqrt{x+1} + \sqrt{x + \Delta x + 1} \right)} \right] =$$

$$= \lim_{\Delta x \to 0} \left[- \frac{1}{\sqrt{x+1} + \sqrt{x + \Delta x + 1}} \right] = - \frac{1}{2\sqrt{x+1}}$$

It is therefore essential to acquire and maintain your algebraic transformation and manipulation skills in good order. The only way of doing that is to practice.

Week 4 workshop exercises

Monk and Munro, 2nd edition: self-test 17.2;

Steiner, 2nd edition: Section 7.9 (1, 4, 7, 11, 13); Section 4.13 (3, 7-9, 11-13, 18-20).

Extra difficulty exercises for the brave

Steiner, 2nd edition: Section 7.9 (8-10, 14-16); Section 4.13 (14-17, 21, 22).