CHEM1047 – Week 2 Lecture 1 – Limits and their applications

☐ *Section 4.4 of Steiner, "The Chemistry Maths Book", 2nd edition.*

☐ *Volume 1, Chapter 3 of Cockett and Doggett, "Maths for Chemists".*

It is usually impossible to manipulate infinitely small and infinitely large quantities directly. However, if the question is reformulated in terms of *finite quantities that may become arbitrarily big*, the mathematical treatment is simplified. This lecture introduces the necessary tools.

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:

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

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

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

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.

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 does. Computing the limit

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

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. It would appear that some zeroes are also smaller than others.

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:

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

There are also some less obvious limits:

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

...and some seriously exotic ones, like $x\sin(1/x)$ when x goes to zero:

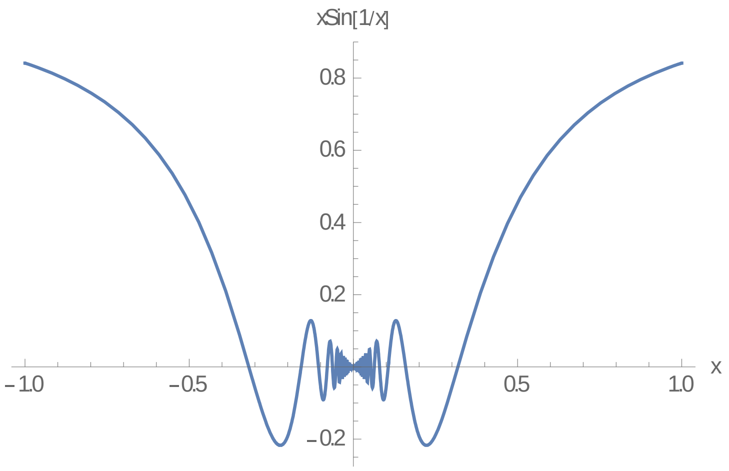

Figure 1. *The behaviour of* xsin*(1/x) around x=0. Note that, even though 1/x is not defined at zero, the function does not show any abnormal behaviour because the limit is finite.*

The formal 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 continuous function, and of function derivative, involves a limit.

The following rules may be used *when the two limits involved are finite*:

1. The limit of a sum or difference is equal to the sum or difference of limits.
2. The limit of a product or fraction is equal to the product or fraction of limits.

The calculation of less obvious limits is a creative process. Some methods are:

1. Identification of leading powers. For $x \to \infty$, x^2 is much larger than x, and the latter may be ignored in any sum. For $x \to 0$, it is the other way round. Exponential grows faster than any power, *etc.*

$$\lim_{x\to\infty} \frac{\sqrt{x^7+1}-x^2}{x+\cos(x)} = \lim_{x\to\infty} \frac{O\left(x^{7/2}\right)}{O(x)} = \infty$$

where $O\left(x^{7/2}\right)$ stands for "quantity of the order of $x^{7/2}$ for sufficiently large values of x". Similar notation exists for infinitesimally small quantities.

2. Simplification and substitution. Complicated expressions may be factored, simplified or rearranged in ways that make the limit more obvious.

$$\lim_{x\to 0}\left[\frac{1}{x}-\frac{x+1}{x^3+x}\right] = \lim_{x\to 0}\left[\frac{x^2-x}{x^3+x}\right] = \lim_{x\to 0}\left[\frac{-x}{x}\right] = -1$$

3. L'Hôpital's rule. If $\lim\left[f'(x)/g'(x)\right]$ exists, then

$$\lim \frac{f(x)}{g(x)} = \lim \frac{f'(x)}{g'(x)}$$

This rule is very powerful – consider using it whenever you have a fraction under the limit.

4. Applications: chemical equilibria

The limit of $t \to \infty$ provides a connection between chemical kinetics and chemical thermodynamics. After "an infinite time has passed", all reactions must converge to the thermal equilibrium. Even for a simple reversible reaction, the time dependence of concentrations can be quite complicated:

$$\mathrm{A} \underset{k_-}{\overset{k_+}{\rightleftarrows}} \mathrm{B}$$

$$A(t) = \frac{B_0 k_-\left(1-e^{-(k_++k_-)t}\right) + A_0\left(k_- + k_+ e^{-(k_++k_-)t}\right)}{k_- + k_+}$$

$$B(t) = \frac{A_0 k_+\left(1-e^{-(k_++k_-)t}\right) + B_0\left(k_+ + k_- e^{-(k_++k_-)t}\right)}{k_- + k_+}$$

but the infinite time limits of both expressions are simple

$$\lim_{t\to\infty} A(t) = \frac{k_-}{k_- + k_+}\left(A_0 + B_0\right) \qquad \lim_{t\to\infty} B(t) = \frac{k_+}{k_- + k_+}\left(A_0 + B_0\right)$$

and only depend on the total initial amount of substance in the system $A_0 + B_0$. Their ratio is exactly as prescribed by the equilibrium constant:

$$\lim_{t\to\infty}\frac{B(t)}{A(t)} = \frac{k_+}{k_-} = K$$

5. Applications: limit cases of reaction kinetics

Another chemical application arises in situations when some quantity (reaction rate, concentration, *etc.*) is *much smaller* or *much larger* than some other quantity. This often leads to changes in the observed behaviour. Consider the rate of nitrogen production in a reaction of hydrogen with nitric oxide

$$\mathrm{2NO} \;+\; \mathrm{2H_2} \quad\rightarrow\quad \mathrm{N_2} \;+\; \mathrm{2H_2O}$$

This is not an elementary reaction, and so the rate law is quite complicated:

$$\frac{d[\mathrm{N_2}]}{dt} = \frac{k_1 k_2 [\mathrm{H_2}][\mathrm{NO}]^2}{k_{-1} + k_2 [\mathrm{H_2}]}$$

where $k_{\pm 1,2}$ are the rates of the elementary reactions involved in the process. This reaction has two limits with respect to the concentration of hydrogen. If $k_{-1} \gg k_2[\mathrm{H_2}]$, then

$$\frac{d[\mathrm{N_2}]}{dt} = \frac{k_1 k_2}{k_{-1}}[\mathrm{H_2}][\mathrm{NO}]^2$$

and the reaction would appear to be first order with respect to hydrogen. But if $k_{-1} \ll k_2[\mathrm{H_2}]$, then

$$\frac{d[\mathrm{N_2}]}{dt} = k_1[\mathrm{NO}]^2$$

and the reaction would appear to have order zero with respect to hydrogen. When such behaviour is seen experimentally, it indicates that the reaction is not elementary, and a multi-stage process exists.

Elsewhere in physics and chemistry, the limit of $c \to \infty$ applied to relativity theory returns Newton's equations of motion, as does the limit of $\hbar \to 0$ in the case of quantum mechanics.