

CHEM1047 – Week 6 Lecture 2 – Estimates and approximations

- Section 11.6 of Steiner, "The Chemistry Maths Book", 2nd edition.
- Sections 19.7-19.9 of Atkins and de Paula, "Elements of Physical Chemistry", 6th edition.

A common problem in all areas of physics and chemistry is that, while the fundamental equations governing a particular process are known, the solutions are in practice incomputable because they lead to very large datasets or require too many mathematical operations. In such cases, a common question is: "what is the simplest possible expression that would produce the answer *with acceptable accuracy*?" The problem of computing *the exact answer* is thus replaced with the problem of computing a *good enough answer* within some realistic parameter ranges. Such solutions are called *approximations*. They are not expected to produce accurate results in all situations, but may be designed to work for those parameter values that are encountered in practice.

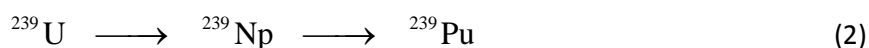
Before we start building and analysing approximations, it is useful to review some areas of chemistry where approximations are used. A typical scenario is that the exact model of some process is too complicated for a solution to be realistic. In such cases, approximate solutions are used instead. An important matter is the accuracy of the approximation – it must be carefully monitored.

1. Steady state approximation in reaction kinetics

Consider a chemical process converting a reactant A into a product B *via* an intermediate I :



A good example is production of plutonium by neutron irradiation of naturally occurring uranium. When a neutron is captured by the nucleus of ^{238}U , its mass number goes up by one unit, and the following chain of transformations takes place as neutrons decay into protons, electrons, and antineutrinos:



The equations describing the rates of change in the quantities of the three substances are:

$$\begin{cases} \frac{d[A]}{dt} = -k_1[A] \\ \frac{d[I]}{dt} = +k_1[A] - k_2[I], \\ \frac{d[B]}{dt} = +k_2[I] \end{cases} \quad [A] = a_0 \text{ when } t = 0 \quad (3)$$

The analytical solution is messy, but a computer may be asked to find and plot it:

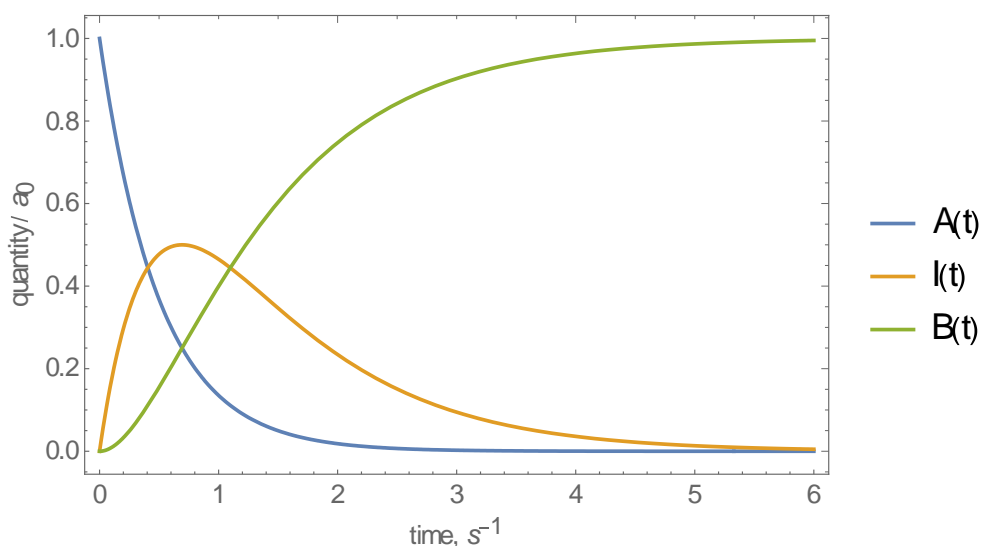


Figure 1. Solution of Equations (3) when $k_1 = 2.0 \text{ s}^{-1}$ and $k_2 = 1.0 \text{ s}^{-1}$, computed and plotted using *Mathematica*.

When the two reaction rates are comparable, nothing can be done – the problem must be solved exactly. However, in the fairly common case when the second reaction is much faster than the first, the plot looks in a way that suggests a reasonable approximation:

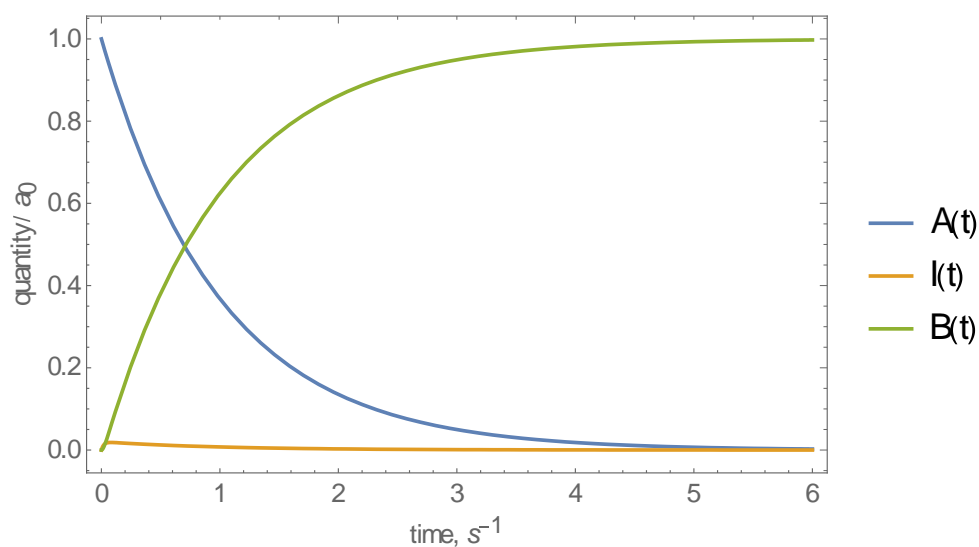


Figure 2. Solution of Equations (3) when $k_1 = 1.0 \text{ s}^{-1}$ and $k_2 = 50.0 \text{ s}^{-1}$, computed and plotted using *Mathematica*.

Note that the concentration of the intermediate is never large, and its derivative is always small because there is barely any change in that curve. To a reasonable accuracy, we may put that derivative to zero:

$$\frac{d[I]}{dt} \approx 0 \quad \Rightarrow \quad \begin{cases} \frac{d[A]}{dt} = -k_1[A] \\ 0 = +k_1[A] - k_2[I] \\ \frac{d[B]}{dt} = +k_2[I] \end{cases} \quad (4)$$

with the result that one of the three differential equations became algebraic, and the concentration of the intermediate may be eliminated from the system:

$$k_1[A] = k_2[I] \Rightarrow \begin{cases} \frac{d[A]}{dt} = -k_1[A] \\ \frac{d[B]}{dt} = +k_1[A] \end{cases} \quad (5)$$

The first equation is easy to solve:

$$\frac{d[A]}{dt} = -k_1[A], \quad [A](0) = a_0 \Rightarrow [A](t) = a_0 e^{-k_1 t} \quad (6)$$

At which point the second equation also becomes easy to solve:

$$\frac{d[B]}{dt} = +k_1 a_0 e^{-k_1 t}, \quad [B](0) = 0 \Rightarrow [B](t) = a_0 (1 - e^{-k_1 t}) \quad (7)$$

Because the approximation we have made only holds when the second reaction is much faster than the first, our final solution has a condition attached:

$$\begin{cases} [A](t) = a_0 e^{-k_1 t} \\ [B](t) = a_0 (1 - e^{-k_1 t}) \\ [I](t) = (k_1/k_2) a_0 e^{-k_1 t} \end{cases} \quad k_2 \gg k_1 \quad (8)$$

Plotting the approximation alongside the exact solution (Figure 3) convinces us that the approximation is good – the curves are almost on top of one another.

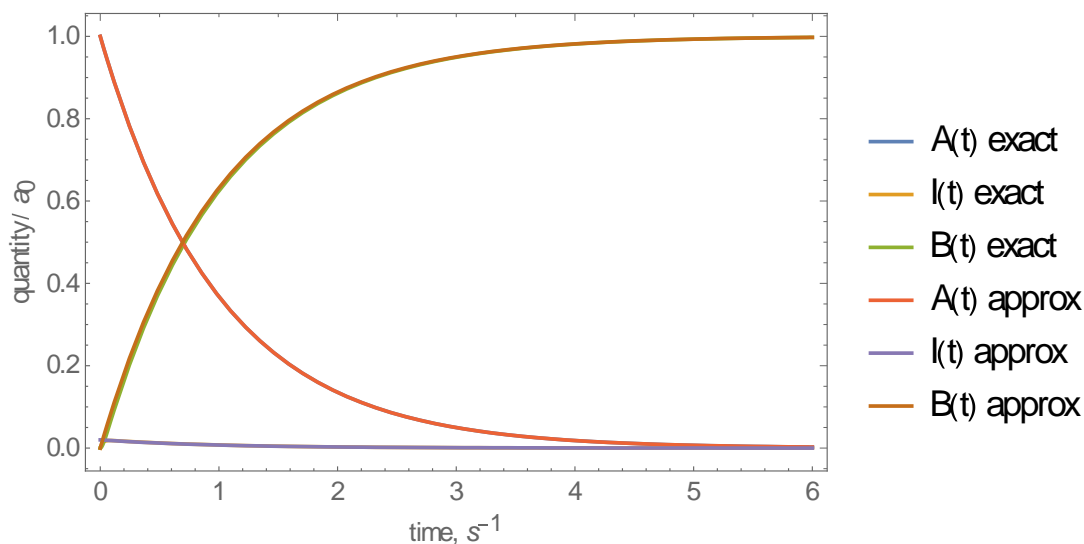


Figure 3. Exact solutions of Equations (3) when $k_1 = 1.0 \text{ s}^{-1}$ and $k_2 = 50.0 \text{ s}^{-1}$, plotted alongside the approximate solutions in Equations (8).

2. Approximate potentials in vibrational spectroscopy

The description of the stretching energy of a chemical bond as the energy of two balls on a spring is an example of a really bad approximation:

$$E(r) = \frac{1}{2}k(r - r_{\text{eq}})^2 \quad (9)$$

Here k is the force constant of the spring, and r_{eq} is the equilibrium bond length. This formula provides an excellent example of approximations going horribly wrong when used outside of their range of applicability. The fallacies of Equation (9) include:

1. Bond dissociation cannot happen – as the atoms are moved further apart, the energy goes to infinity.
2. Atoms can pass through each other – as the inter-atomic distance goes to zero, the energy does not go to infinity.
3. The force constant does not depend on the inter-atomic distance when it clearly should.

Surprisingly, there are situations when Equation (9) is usable, but they involve very small displacements from the equilibrium distance for very stiff bonds.

A better approximation to the energy of a chemical bond is called Morse potential:

$$E(r) = E_{\text{eq}} \left[1 - e^{-a(r-r_{\text{eq}})} \right]^2 \quad (10)$$

Here a is a measure of bond stiffness and E_{eq} is the equilibrium energy of the bonded pair of atoms relative to the atoms at infinite distance. This approximation fixes the infinite distance problem, but still has the collision problem, although to a lesser extent.

The collision problem is solved by the Lennard-Jones approximation, which does actually go to infinity for the zero inter-atomic distance:

$$E(r) = E_{\text{eq}} \left[\left(\frac{r_{\text{eq}}}{r} \right)^{12} - 2 \left(\frac{r_{\text{eq}}}{r} \right)^6 \right] \quad (11)$$

The exact solution for the bond stretching potential problem requires solving Schrödinger's equation repeatedly for different inter-atomic distances and plotting the energy as a function of the distance.

3. High- and low-temperature approximations in thermodynamics

The partition function (a complicated object from which all properties of a thermodynamic ensemble may be derived) for an ensemble of harmonic oscillators is:

$$Q(T) = \frac{1}{1 - e^{-\Delta E/kT}} \quad (12)$$

where ΔE is energy level spacing, k is Boltzmann's constant, and T is temperature. If this function is plotted against $kT/\Delta E$ (Figure 4), the graph suggests approximations for the cases of very low and very high temperatures.

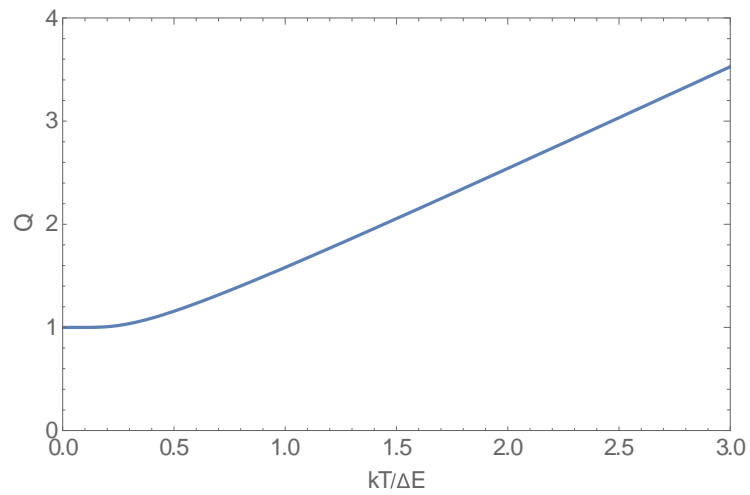


Figure 4. Equation (12), plotted in *Mathematica* as a function of $kT/\Delta E$.

At very low temperatures, Equation (12) may be approximated by a constant, and at very high temperatures – by a straight line. A systematic method for obtaining such approximations is called power series – it is the subject of the next lecture.