

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 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:

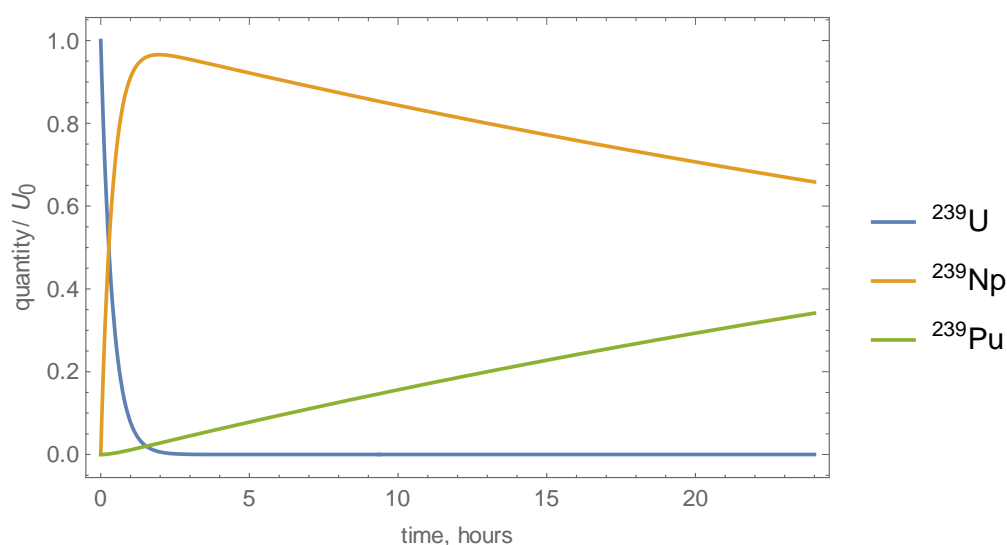
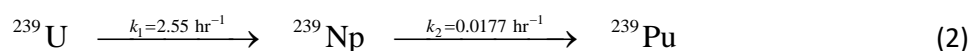
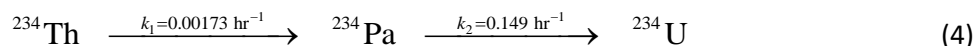


Figure 1. Solution of the kinetic equations describing the reaction in Equation (2), computed and plotted using *Mathematica*.

The half-life of ^{239}Pu is 24,110 years; on the time scale of hours its decay may be ignored. The equations describing the rates of change in the quantities of the three isotopes therefore are:

$$\begin{cases} \frac{d[\text{U}]}{dt} = -k_1[\text{U}] \\ \frac{d[\text{Np}]}{dt} = +k_1[\text{U}] - k_2[\text{Np}], & [\text{U}] = U_0 \text{ when } t = 0 \\ \frac{d[\text{Pu}]}{dt} = +k_2[\text{Np}] \end{cases} \quad (3)$$

When the two reaction rates are comparable, the problem must be solved exactly. However, in the common case when the second reaction is much faster than the first, for example:



where again the decay of ^{234}U is too slow to matter on the time scale of days. The plot looks in a way that suggests a reasonable approximation (Figure 2).

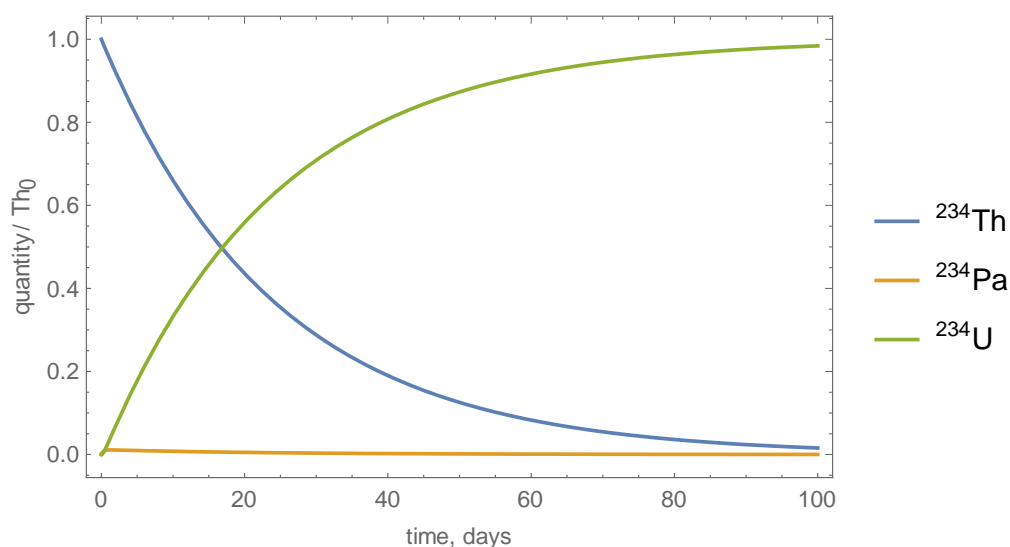


Figure 2. Solution of the kinetic equations describing the reaction in Equation (4), computed and plotted using *Mathematica*.

The quantity of the intermediate ^{234}Pa 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:

$$\frac{d[\text{Pa}]}{dt} \approx 0 \quad \Rightarrow \quad \begin{cases} \frac{d[\text{Th}]}{dt} = -k_1[\text{Th}] \\ 0 = +k_1[\text{Th}] - k_2[\text{Pa}] \\ \frac{d[\text{U}]}{dt} = +k_2[\text{Pa}] \end{cases} \quad (5)$$

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

$$k_1[\text{Th}] = k_2[\text{Pa}] \Rightarrow \begin{cases} \frac{d[\text{Th}]}{dt} = -k_1[\text{Th}] \\ \frac{d[\text{U}]}{dt} = +k_1[\text{Th}] \end{cases} \quad (6)$$

The first equation is easy to solve:

$$\frac{d[\text{Th}]}{dt} = -k_1[\text{Th}], \quad [\text{Th}](0) = [\text{Th}]_0 \Rightarrow [\text{Th}](t) = [\text{Th}]_0 e^{-k_1 t} \quad (7)$$

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

$$\frac{d[\text{U}]}{dt} = +k_1[\text{Th}]_0 e^{-k_1 t}, \quad [\text{U}](0) = 0 \Rightarrow [\text{U}](t) = [\text{Th}]_0 (1 - e^{-k_1 t}) \quad (8)$$

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:

$$\begin{cases} [\text{Th}](t) = [\text{Th}]_0 e^{-k_1 t} \\ [\text{U}](t) = [\text{Th}]_0 (1 - e^{-k_1 t}) \\ [\text{Pa}](t) = (k_1/k_2)[\text{Th}]_0 e^{-k_1 t} \end{cases} \quad k_2 \gg k_1 \quad (9)$$

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

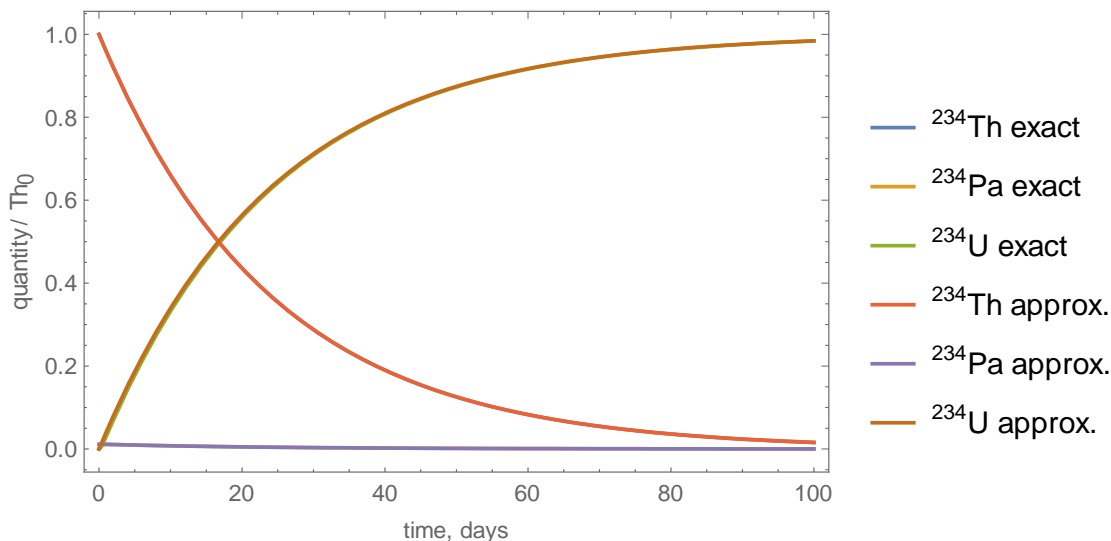


Figure 3. Solution of the kinetic equations describing the reaction in Equation (4), plotted alongside the steady state approximation solutions given by Equations (9).

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 (often used in molecular dynamics simulations) is an example of a really bad approximation:

$$E(r) = \frac{1}{2} k (r - r_{\text{eq}})^2 \quad (10)$$

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 (10) 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 (10) 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:

$$E(r) = E_{\text{eq}} \left[1 - e^{-a(r-r_{\text{eq}})} \right]^2 - E_{\text{eq}} \quad (11)$$

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.

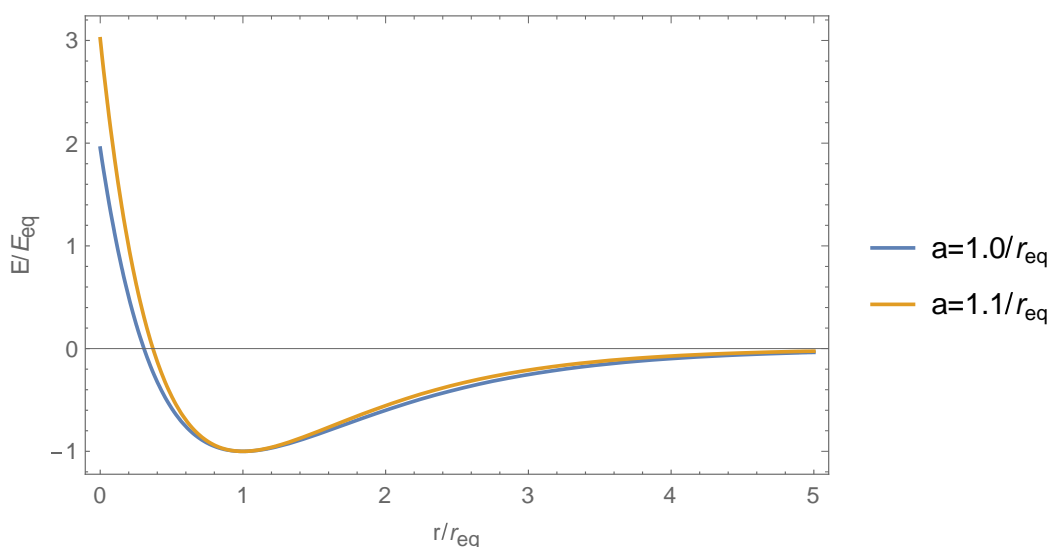


Figure 4. Morse potential, plotted in dimensionless units.

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

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

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.

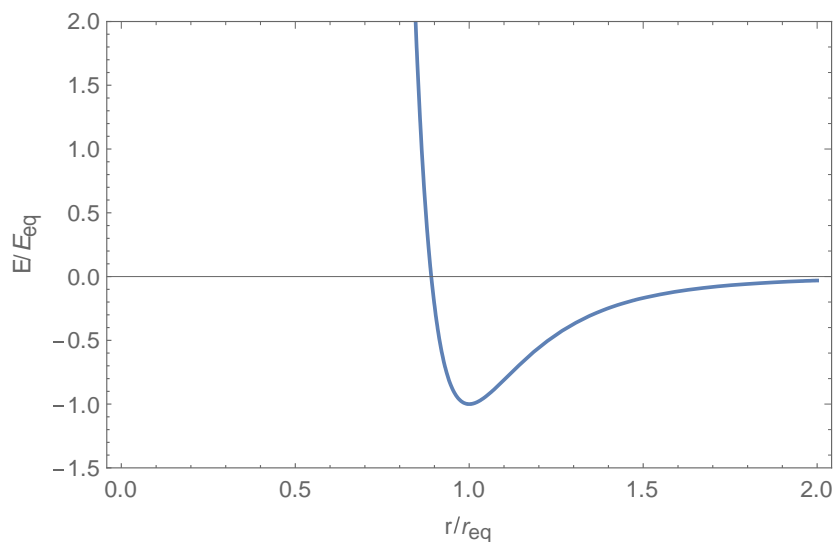


Figure 5. Lennard-Jones potential, plotted in dimensionless units.

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 quantum harmonic oscillators is:

$$Q(T) = \frac{1}{1 - e^{-\Delta E/kT}} \quad (13)$$

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.

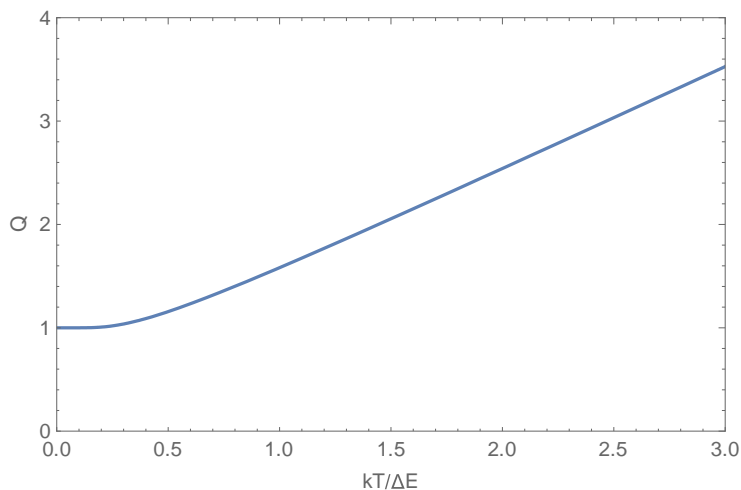


Figure 6. Equation (13), plotted in *Mathematica* as a function of $kT/\Delta E$.

At very low temperatures, Equation (13) 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.