How much of a radioactive element is present in a decay chain at any given time? A foray into math and physics, suited to scientists and budding scientists who are comfy with basic calculus and algebra

What's the need to know or calculate the amount?

All radioactive elements decay to other elements, or daughter nuclides. In many cases, daughters themselves decay into yet other nuclides. There can be rather long decays chains, with a good example being the <u>decay chain of uranium-238</u> (²³⁸U), important in human technology as well as in the internal heat source of the Earth. At various steps in the chain, the rates of decay (conversely, the half-lives) of the nuclides vary greatly – from 163 microseconds to 4.46 billion years in the case of ²³⁸U. Any sample of a rock that contains radioactive nuclides will have a diverse distribution of amounts of the different nuclides in the chain. That distribution depends upon the processing of that rock, be it by humans or by processes that form and re-form rocks with loss or gain of various nuclides. The distribution of nuclides informs us about what has happened to that rock, for some insight into the local geology of that rock. We can also predict what nuclides will form after we process an ore and how fast. We can use this information - for planning safety measures (watch for, say, radon emissions) and for planning the use of a given radionuclide in technology (producing energy or useful medical isotopes).

Two basic ways to make the calculations

We'd like a reliable way to predict the way that the nuclide amounts rise and fall in a given batch of nuclides in a decay chain. We can readily write out a set of differential equations, one for each nuclide, each one coupling to its predecessor and to its daughter nuclide. We might do a straightforward, brute-force numerical integration of the equations together, but that's both extremely tedious and prone to errors, even catastrophic, from rounding, underflow, and overflow in mathematical operations. I'm going to present here a way to calculate, with explicit algebraic formulas, how much of each element is present, given any initial condition (any amounts of each radioactive element or radionuclide in a series of decays, or a decay chain). The algebra is rather tidy, and it sure beats numerical integration! An analytical formula lets you see directly what nuclides are building up or declining, and which ones are controlling the flow by being fast or slow in decay. You can calculate the results at any time, not needing to do the whole numerical integration every time to get to a new time.

The decay equations for individual nuclides

I assume that you, the reader, knows the basics of radioactive decay, that any nuclide decays at a constant fractional rate, so that the number of decays is proportional to the current number of nuclei. Denoting the amount of a nuclide by the symbol *A*, we have

$$\frac{number of \ decays}{unit \ time} = (rate \ constant)(current \ number \ of \ nuclei)$$

$$or$$

$$\frac{dA}{dt} = -kA$$

At a time t=1/k, the number has decayed to e⁻¹ or 37% of the original number. The half-life is then $t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$. For ²³⁸U, $t_{1/2}$ is 4.46 x10⁹ y and k is 0.693/4.4x10⁹ y, or 1.6 ten-billionths per year.

Some radioactive elements have been hanging around a long time and still have a good part of their original number of nuclei. Uranium 238 (U-238, or ²³⁸U) on Earth is a good example – its half life of 4.46 billion years is just about the age of the Earth, so about half of the amount that was present when the Earth formed is here. Other nuclides disappear fast in any circumstance. Berkelium isotopes are known to form in supernovae, but the longest-lived isotope has a half-life of 1380 years, so whatever formed in the supernova (or the neutron star merger) that seeded our Solar System with elements is long gone. Consider also the first decay product, or daughter, of ²³⁸U, which is Thorium-234, with a half-life of 24.1 days. The original atoms of that nuclide in my uranium ore sample from 2 years ago are pretty much long gone, decayed to a fraction 2 to the minus (730 days/24.1 days), or about 2⁻³⁰, which is 10⁻¹⁴.

Of course, even the short-lived daughter products get replenished by the nuclides that decay to form them. Basically, in an undisturbed sample (no chemical separations performed), the daughter nuclides quickly reach a steady state, being formed as fast as they decay. This holds on a time scale significantly longer than their own half-life.

Coupled differential equations for the nuclides in a decay chain

As noted earlier, many radionuclides sit in decay chains – a series of radioactive decays, such as A becomes B, B becomes C, C becomes D, and so on. On a separate page, I've drawn the decay chain for ²³⁸U (well, it's a net near the end, because the chain branches there, with one nuclide, bismuth-210, having two modes of decay, There is interest in using the actual proportions of different radionuclides in a chain – say, in order to figure out when and in what conditions a rock formed. For example, if thorium-230 separated out when a rock formed but uranium-234 hung around, it will be some multiple of the half-life of ²³⁴U before the "usual" steady-state amount of ^{230Th} reformed. The deficit indicates the time lapse since the chemical separation occurred.

All this said, let's proceed to solving the coupled differential equations. For the decay chain $A \rightarrow B \rightarrow C \rightarrow D$, we can write:

$$\frac{dA}{dt} = -k_A A$$
$$\frac{dB}{dt} = k_A A - k_B B \quad \text{(decay of A creates some B)}$$
$$\frac{dC}{dt} = k_B C - k_C C$$
$$\frac{dD}{dt} = k_C C - k_D D$$

We could go on, and, in fact, for the ²³⁸U decay chain, we have 16 nuclides and we might use letters up to Q.

First nuclide in a chain – a simple solution with calculus

The first equation is trivial to solve:

$$\frac{dA}{A} = -k_A t$$

Integrating both sides, and knowing that the differential, d(InA) equals dA/A, we have

$$dA/A = \ln A$$

Integrating, we get

$$\ln A \Big|_0^t = \ln A(t) / A(0) = -k_A t$$

$$\rightarrow A(t) = A(0)e^{-k_A t}$$

Solving for the amount of a daughter nuclide – an inhomogeneous differential equation, readily solved

Solving for B is a bit trickier. Without the term in A, we have the simple homogeneous equation just as for A, with the solution

$$B = B_0 e^{-k_B t}$$

Here I went to the simpler notation, $B(t) \rightarrow B$ and $B(time = 0) \rightarrow B_0$. To include the term in A, we use a readily verified form:

$$B = B_0 e^{-k_B t} + \int_0^t dt' e^{-k_B(t-t')} k_A A(t')$$

You can derive this, or just verify it by taking the derivative, recalling that the derivative of the integral with respect to its limit is just the contents under the integral sign:

$$\frac{d}{dt}\int_{0}^{t} dt' X(t') = X(t)$$

We get

$$\frac{dB}{dt} = -k_B B_0 e^{-k_B t} + k_A A(t)$$

as desired.

Now let's do the explicit integral. The inhomogeneous term, leaving out for now a factor is:

$$\int_{0}^{t} dt' e^{-k_{B}(t-t')} k_{A} A_{0} e^{-k_{A}t'} = e^{-k_{B}t} k_{A} A_{0} \int_{0}^{t} dt' e^{(k_{B}-k_{A})t'}$$
$$= e^{-k_{B}t} k_{A} A_{0} \frac{1}{k_{B}-k_{A}} e^{(k_{B}-k_{A})t'} \Big|_{0}^{t}$$
$$= e^{-k_{B}t} k_{A} A_{0} \frac{1}{k_{B}-k_{A}} \Big(e^{(k_{B}-k_{A})t} - 1 \Big)$$
$$= \frac{k_{A} A_{0}}{k_{B}-k_{A}} \Big(e^{-k_{A}t} - e^{-k_{B}t} \Big)$$

On the second line, I used the simple formula $\int dx e^{kx} = \frac{e^{kx}}{k}$.

We can verify that this gives the correct derivative, *dB/dt*:

$$\frac{dB}{dt} = -k_B B_0 e^{-k_B t} + \frac{k_A A_0}{(k_B - k_A)} \Big[k_B e^{-k_B t} - k_A e^{-k_A t} \Big]$$

This looks a bit unpromising, with the denominator k_B - k_A , but we can add and subtract identical terms:

$$\frac{dB}{dt} = -k_B B_0 e^{-k_B t} + \left[\frac{k_A A_0}{(k_B - k_A)} \right] \left[k_B e^{-k_B t} + (-k_B e^{-k_A t} + k_B e^{-k_A t}) - k_A e^{-k_A t} \right]$$

Now, in the final bracket, [], group the first two terms together, to give

$$\left\lfloor \frac{k_A A_0}{(k_B - k_A)} \right\rfloor \left[-k_B \right] \left[e^{-k_A t} - e^{-k_B t} \right]$$

That's just $-k_B$ times the inhomogeneous term in B(t) – so, with the homogeneous term, $-k_BB_0exp(-k_Bt)$. we've recovered $-k_BB(t)$. Now group the last two terms in the final bracket of the earlier equation, and you get

$$\begin{bmatrix} k_A A_0 \\ (k_B - k_A) \end{bmatrix} [k_B - k_A] e^{-k_A t}$$
$$= k_A A_0 e^{-k_A t}$$
$$= k_A A(t)$$

What the explicit equations can tell us – about nuclide amounts and about activities (decays per second)

Let's look at the formula for B(t) with just the two nuclides, for a moment. Take the case of ²³⁸U as A, with a long half-life, and ^{234Th} as B, with a very short half-life of 24.1 days. If we're looking back on the early Earth, we probably won't bother worrying about a time span of days or even years, decades,

centuries... We can then ignore the lead term in B(t), since $exp(-k_B t)$ will be essentially zero. Then we have

$$B(t) \rightarrow \frac{k_A A_0}{(k_B - k_A)} e^{-k_A t} \rightarrow \frac{k_A}{k_B} A_0 e^{-k_A t} \rightarrow \frac{k_A}{k_B} A(t)$$

At the second arrow I used the fact that k_A in the denominator is negligible compared to k_B . We see that nuclide A controls it all, and B is present at only the small fraction k_A/k_B relative to A. This makes sense. Also, one sees that the "activities" of both nuclides are equal:

$$-k_B B(t) = -k_B \frac{k_A}{k_B} A(t) = -k_A A(t)$$

That should be obvious – nuclide *B* is only replenished at the rate that *A* decays. This equality of activity holds all down the decay chain in the long term – *as long as* the first nuclide has the longest half-life and as long as we look at later nuclides at times greater than the half-lives of their predecessors. Since ²³⁸U is the longest-lived element and it starts the chain, at time somewhat greater than t equaling 1/(next shortest half-life), all the nuclides should be equally radioactive. An ore sample would be about 14 times more active than the ²³⁸U itself. Of course, some nuclides might escape, such as radon-222 if the sample melted or got a bit of anthropogenic processing, so that the equal activity condition fails after than link in the chain and the whole sample is less active.

A glimpse into an earlier time in the decay chain

Another case is when A is very little into its half-life, and even B is so (say, two relatively long-lived nuclides, but with B still shorter-lived), We have:

$$B(t) \rightarrow B_0 e^{-k_B t} + \frac{k_A}{k_B} A_0 \left(1 - e^{-k_B t}\right)$$

There is a "relaxation time," when k_B t approaches a few multiples of 1, before the ratio of A to B goes toward its steady-state value, k_A/k_B – that it, when $exp(-k_Bt)$ gets small, so that the first term starts to be negligible, and the term is parentheses heads toward 1.

Add a third nuclide in the chain and account for it

Let's add the third nuclide:

$$\frac{dC(t)}{dt} = k_B B(t) - k_C C(t)$$

We can use the same formulation of the homogeneous equation and the inhomogeneous part, to get

$$C(t) = C_0 e^{-k_C t} + k_B B_0 \int_0^t dt' e^{-k_C (t-t')} B(t')$$

Plugging in our expression for B(t'), we get for the inhomogeneous term

$$k_{B}B_{0}e^{-k_{B}t}\int_{0}^{t}dt'e^{k_{C}t'}\left[B_{0}e^{-k_{B}t'}+\frac{k_{A}A_{0}}{(k_{B}-k_{A})}(e^{-k_{A}t'}-e^{-k_{B}t'})\right]$$

Going through the same integrations, we get the final form

$$C(t) = C_0 e^{-k_C t} + \frac{k_B B_0}{(k_C - k_B)} [e^{-k_B t} - e^{-k_C t}] + \left[\frac{k_B k_A A_0}{(k_B - k_A)}\right] \left[\frac{(e^{-k_A t} - e^{-k_C t})}{(k_C - k_A)} - \frac{(e^{-k_B t} - e^{-k_C t})}{(k_C - k_B)}\right]$$

Interpreting the resulting equation for the amount of the third nuclide

The first two terms are the full analogue of the $A \rightarrow B$ case. The last term gives a hint of a generalization for a longer decay chain, which I won't pursue here.

Let's look at some cases of interest. The first one is simple: taking the example of the start of ²³⁸U decay chain, the half-lives decrease from A (which is ²³⁸U; $t_{1/2} = 4.46$ billion years) to B (^{234Th}; $t_{1/2} = 24.1$ days) to C (²³⁴Pa; $t_{1/2} = 6.7$ hours). On the time scale when k_At is modest (of order 1), we have $k_Bt >> 1$ and $k_Ct >> 1$. Thus, the terms exp(- k_Bt) and exp(- k_Ct) are effectively zero. Going term-by-term in the equation, we get

$$C(t) \rightarrow 0 + 0 + \left[\frac{k_B k_A A_0}{k_B}\right] \left[\frac{e^{-k_A t}}{k_C}\right]$$
$$= \frac{k_A A_0}{k_C} e^{-k_A t}$$
$$= \frac{k_A}{k_C} A(t)$$

This is actually obvious: nuclide A controls the flow. It fills nuclide B rapidly, which fills nuclide C rapidly.

What if the middle nuclide, B, has the fastest decay?

Another case is when the middle nuclide, *B*, is the fast one, with the shortest half life. This occurs in the ²³⁸U chain far down the line:

²¹⁴
$$Bi \longrightarrow 214$$
 $Po \longrightarrow 210$ $Pb \longrightarrow 210$ Bi
19.9 min 163 μs 29.3 y

We have $k_B >> k_A >> k_C$. Consider working on the time scale of the first nuclide, ²¹⁴Bi, our nuclide A. Let's look at the situation where $k_A t$ is of order 1, so we retain the factor $exp(-k_A t)$ explicitly. In contrast, $exp(-k_B t) \rightarrow 0$ and, since $k_C t$ is very small, $(exp(k_C t) \rightarrow 1)$. We get

$$C(t) \to C_0 + \left[\frac{k_B B_0}{-k_B}\right] [0-1] + \left[\frac{k_B k_A A_0}{k_B}\right] \left[\frac{(e^{-k_A t} - 1)}{-k_A} - \frac{(0-1)}{-k_B}\right]$$
$$= C_0 + B_0 + A_0 (1 - e^{-k_A t}) - \frac{k_A}{k_B} A_0$$

The interpretation is straightforward. The first term is the initial amount of nuclide *C*, which has not decayed significantly on this time scale. The second term is the feed-through from any initial amount of nuclide *B*, which was completely converted to nuclide *C*. The third term is the feed-through from the first nuclide, *A*, which starts out small (it's not as active as nuclide *B*) but can saturate at longer times, $k_A t >>1$. At times that $k_A t$ is small, but bigger than $k_B t$, we can expand the exponential as $1-k_A t$ plus higher order terms, getting the very good approximation of $A_0 k_A t$. That is, there's a linear growth of the amount of nuclide *C*, from the initially linear rate of decay of *A* to *B*, with the effectively immediate conversion of *B* to *C*. The final term, $-(k_A/k_B)A_{0}$, is a small deficit from "too rapid" conversion of *A* to *B*; the pool of *B* is a smaller than maximal. We might see all this behavior if a sample of uranium ore is processed to isolate the ²¹⁴Bi, which then decays.

We can also see that A and C rapidly reach the same activity (amount x decay rate), if we start with both having zero amounts, so that the decay of A starts the whole process. Basically, B is such as short-lived intermediate that it's as if A decays directly to C on any but the shortest time scales.

What if the middle nuclide, B, is the bottleneck, with the slowest decay?

A contrasting case of interest is when the intermediary nuclide *B* is the bottleneck, having the longest decay time. An example, late in the 238 U chain, is

$${}^{214}Po - \longrightarrow {}^{210}Pb - \longrightarrow {}^{210}Bi - \longrightarrow {}^{210}Po$$

$$163\mu s \qquad 29.3y \qquad 5.01d$$

Let's consider the time scale of nuclide *B*, which is ²¹⁰Bi here. We have $k_A >> k_C >> k_B$, and, thus, $exp(k_At) \rightarrow 0$, $exp(-k_Bt)$ retained explicitly, and $exp(k_Ct) \rightarrow 0$. We get

$$C(t) \to 0 + \left[\frac{k_B B_0}{k_C}\right] \left[e^{-k_B t} - 0\right] + \left[\frac{k_B k_A A_0}{-k_A}\right] \left[\frac{0 - 0}{-k_A} - \frac{(e^{-k_B t} - 0)}{k_C}\right]$$
$$= \frac{k_B}{k_C} B_0 e^{-k_B t} + \frac{k_B}{k_C} A_0 e^{-k_B t}$$

The first term shows any initial amount of nuclide *B* is decaying, while the factor k_B/k_C shows that the fraction resident in *B* is small, given the fast decay of *C*. The second term shows the rapid pass-through to *A* to *B*, which also decays. The limit of this form at long times is just zero – yes, all of the nuclides disappear, and the loss is apparent on the time scale of nuclide *B*. At any but the shortest times, we may as well consider the decay chain as starting with nuclide *B*, since all of *A* is converted to *B* quickly. If the initial amounts of *A* and *B* start at zero (nuclide *A* starts the chaine), then the activities of *B* and *C* become equal on any time scale much greater than the half-life of *C*; *C* fills to its capacity on that time scale.

The various cases – try them

With three nuclides, there are clearly six cases for the rank order of rate constants or speed of decay. With the fastest decay on the top, we may write them as

A	А	В	В	С	С
В	С	А	С	А	В
С	В	С	А	В	Α

We must examined the last case, with A the slowest to decay, the third case, with the middle nuclide fastest (and A faster than C), and the second case, with B as the bottleneck for slow decay. You might find examples of the other three cases and work out the interesting time scales.

Going to even longer chains

The algebra gets considerably more complicated. I derived the equations, specifically for the ²³⁸U chain's first four elements, using some very accurate simplifications (e.g., ignoring the change in the amount of ²³⁸U itself for times up to, say, tens of millions of years). I also set all nuclides after ²³⁸U to start with zero amount.

To see some of the numbers, I used Excel to program the equations out to 4 nuclides,

$$2^{38}U - -- \rightarrow^{234}Th - -- \rightarrow^{234}Pa - -- \rightarrow^{234}U(--- \rightarrow^{230}Th)$$

$$4.46Gy \qquad 24.1d \qquad 6.7h \qquad 245ky$$

You might find these results interesting. I included the calculation of the activities of all nuclides. Note that they reach the activity of ²³⁸U each in their own characteristic time, several multiples of their own half-lives. Note also that the equations show a bit of numerical instability for the 4th nuclide, ²³⁴U. There are better ways to group terms to avoid large relative errors from cancellation of some terms. The equations as written in the text here should be more stable, and higher precision of the arithmetic can help.

I hope that you found this interesting. I'd be happy to get comments on this website or directly to vince@lascrucesacademy.org