

### Consider the decay series $N_1 \rightarrow N_2 \rightarrow N_3$

Remember:

- 1)  $-dN_1/dt = \lambda_1 N_1$

Now we consider  $N_2$ , that is produced by decay of  $N_1$  and itself decays to  $N_3$ :

- 2)  $dN_2/dt = \lambda_1 N_1 - \lambda_2 N_2$

Remember:

- 3)  $N_1 = N_{1,0} e^{-\lambda_1 t}$

Substitute 3) into 2):

- 4)  $dN_2/dt = \lambda_1 N_{1,0} e^{-\lambda_1 t} - \lambda_2 N_2$

Rearrange:

- 5)  $dN_2/dt + \lambda_2 N_2 - \lambda_1 N_{1,0} e^{-\lambda_1 t} = 0$

Solving this first order differential equation for  $N_2$  yields:

- 6)  $N_2 = \lambda_1 / (\lambda_2 - \lambda_1) N_{1,0} (e^{-\lambda_1 t} - e^{-\lambda_2 t}) + N_{2,0} e^{-\lambda_2 t}$

The solution, as well as equivalent solutions for three nuclides and the general case, are known as Bateman (1910) equations/solutions.

The first term in equation 6) is the number of  $N_2$  atoms decayed from  $N_1$  not yet decayed to  $N_3$

The second term in equation 6) is number of  $N_2$  atoms that remain from the initial  $N_{2,0}$

### The classic Bateman paper on the famous "Bateman equations"

Bateman H., Proc. Cambridge Phil. Soc., Vol. 15, 1910, 423-427

*Mr. Bateman, Solution of a system of differential equations, etc. 423*

*The solution of a system of differential equations occurring in the theory of radio-active transformations. By H. BATEMAN, M.A., Trinity College.*

[Read 21 February 1910.]

1. It has been shown by Prof. Rutherford\* that the amounts of the primary substance and the different products in a given quantity of radio-active matter vary according to the system of differential equations,

$$\left. \begin{aligned} \frac{dP}{dt} &= -\lambda_1 P \\ \frac{dQ}{dt} &= \lambda_1 P - \lambda_2 Q \\ \frac{dR}{dt} &= \lambda_2 Q - \lambda_3 R \\ \frac{dT}{dt} &= \lambda_3 R - \lambda_4 T \\ &\dots \dots \dots \end{aligned} \right\} \dots \dots \dots (1)$$

where  $P, Q, R, S, T, \dots$  denote the number of atoms of the primary substance and successive products which are present at time  $t$ .

Prof. Rutherford has worked out the various cases in which there are only two products in addition to the primary substance, and it looks at first sight as if the results may be extended to any number of products without much labour.

Unfortunately the straightforward method is unsymmetrical and laborious, and as the results of the calculations are needed in some of the researches which are being carried on in radio-activity the author has thought it worth while to publish a simple and symmetrical method of obtaining the required formulae.

Let us introduce a set of auxiliary quantities  $p(x), q(x), r(x), \dots$  depending on a variable  $x$  and connected with the quantities  $P(t), Q(t), R(t), \dots$  by the equations,

$$p(x) = \int_0^x e^{-\lambda_1 t} P(t) dt, \quad q(x) = \int_0^x e^{-\lambda_2 t} Q(t) dt, \dots (2)$$

It is easily seen that

$$\int_0^x e^{-\lambda_1 t} \frac{dP}{dt} dt = -P(0) + x \int_0^x e^{-\lambda_1 t} P(t) dt \dots \dots (3)$$

\* Radio-activity, 2nd edition, p. 321.

**continue...**

If there are no atoms of the original daughter  $N_{2,0}$ , then 6) simplifies to:

7) 
$$N_2 = \lambda_1 / (\lambda_2 - \lambda_1) N_{1,0} (e^{-\lambda_1 t} - e^{-\lambda_2 t})$$

Example:  $^{238}\text{U} \rightarrow ^{234}\text{U} \rightarrow ^{230}\text{Th} \rightarrow \dots \rightarrow ^{206}\text{Pb}$

8) 
$$(^{230}\text{Th})_x = (^{230}\text{Th})_x + (^{230}\text{Th})_s \quad x = \text{excess, not supported, } s = \text{supported from } ^{238}\text{U}$$

Let's first consider the excess activity only, at some time, t:

9) 
$$(^{230}\text{Th})_x = (^{230}\text{Th})_{x,0} e^{-\lambda_{230} t}$$

Normalize by a "stable" isotope. Relative to the short-lived daughters,  $^{232}\text{Th}$  is "stable"

10) 
$$(^{230}\text{Th}/^{232}\text{Th})_x = (^{230}\text{Th}/^{232}\text{Th})_{x,0} e^{-\lambda_{230} t}$$

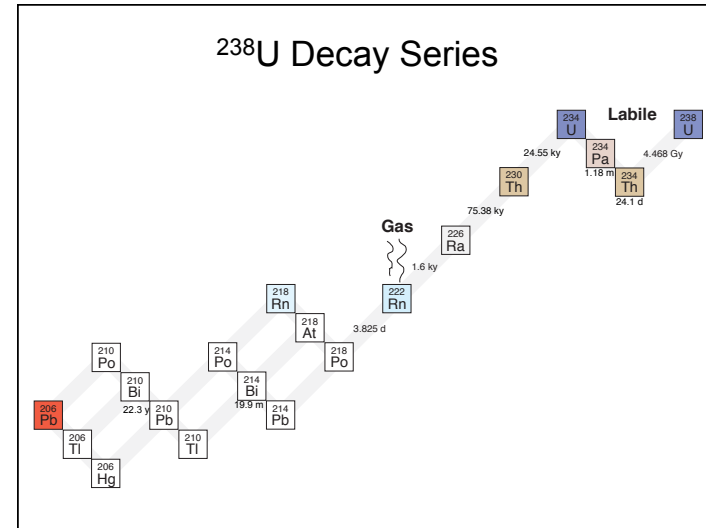
Now let's consider the  $^{238}\text{U}$ -supported ( $^{230}\text{Th}$ ) – see equation 7)

11) 
$$(^{230}\text{Th})_s = \lambda_{234} / (\lambda_{230} - \lambda_{234}) ^{234}\text{U}_0 (e^{-\lambda_{234} t} - e^{-\lambda_{230} t})$$

At secular equilibrium ( $^{234}\text{U} = ^{238}\text{U}$ ) then  $^{234}\text{U} \lambda_{234} = ^{238}\text{U}$

Also  $\lambda_{230} - \lambda_{234} \approx \lambda_{230}$  as  $\lambda_{234}$  is small:  $e^{-\lambda_{234} t} \approx 1$

**Application!**



### Application in determining chronologies of sediments

Basic decay equation:  $N = N_0 e^{-\lambda t}$  assuming no U-supported activity  
 Replace time (t) with depth in sediment column (d) divided by sedimentation rate (sr)  
 $t = d / sr$   
 Decay equation:  $N = N_0 e^{-\lambda d / sr}$   
 $\ln N = \ln N_0 - \lambda d / sr$   $t = d / sr$

In a diagram of  $\ln N$  (y axis) and  $d$  (x axis) the slope (m) is

$$m = -\lambda / sr$$

and

$$sr = -\lambda / m$$

This method is also known as the ionium ( $^{230}\text{Th}$ ) method of dating.

Faure, 1986, p. 367

### Complications...

a) Constant sedimentation rate

b) Change in sedimentation rate

c) Mixing at the top

d)  $^{238}\text{U}$ -supported  $^{230}\text{Th}$  dominates

*continue...*

11)  $^{230}\text{Th}_s = \lambda_{234}/(\lambda_{230} - \lambda_{234}) \cdot ^{234}\text{U}_0 (e^{-\lambda_{234}t} - e^{-\lambda_{230}t})$   
 $\lambda_{230} \cdot ^{230}\text{Th}_s = \lambda_{234} \cdot ^{234}\text{U}_0 (1 - e^{-\lambda_{230}t})$

12)  $(^{230}\text{Th})_s = ^{238}\text{U}_0 (1 - e^{-\lambda_{230}t})$

From equation 9)  $(^{230}\text{Th})_s = (^{230}\text{Th})_{s,0} e^{-\lambda_{230}t}$

$(^{230}\text{Th}) = (^{230}\text{Th})_{s,0} + (^{230}\text{Th})_s$

Total  $^{230}\text{Th}$  activity = initial excess  $^{230}\text{Th}$  activity +  $^{238}\text{U}$ -supported activity

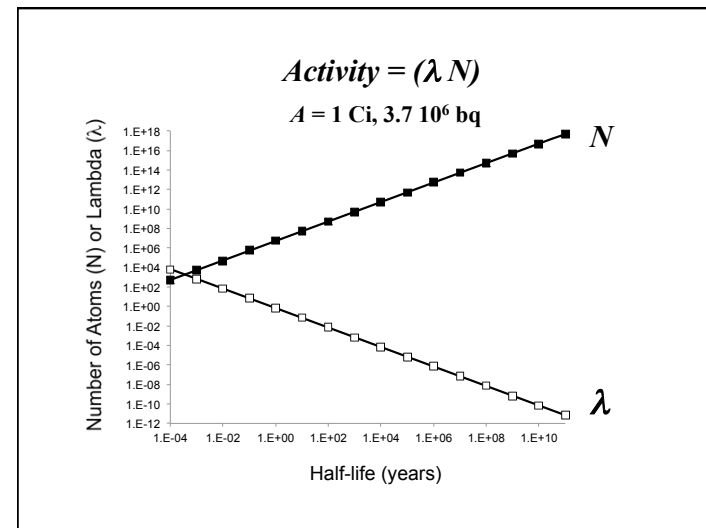
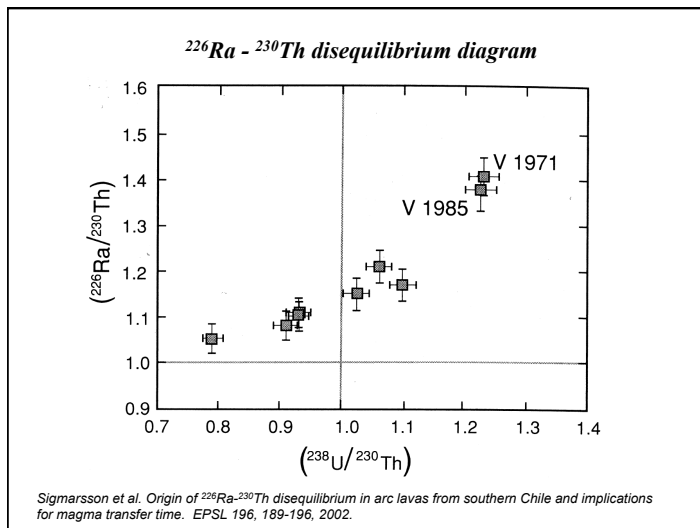
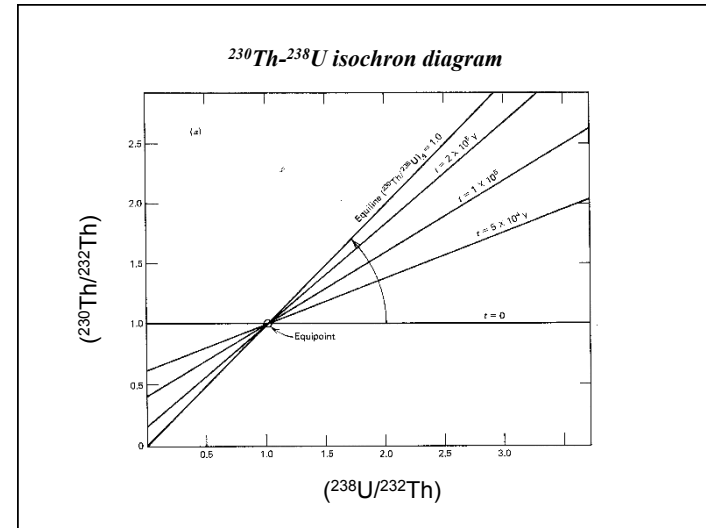
13)  $(^{230}\text{Th}) = (^{230}\text{Th})_{s,0} e^{-\lambda_{230}t} + ^{238}\text{U} (1 - e^{-\lambda_{230}t})$

Normalize to  $^{232}\text{Th}$

14)  $(^{230}\text{Th}/^{232}\text{Th}) = (^{230}\text{Th}/^{232}\text{Th})_{s,0} e^{-\lambda_{230}t} + (^{238}\text{U}/^{232}\text{Th}) (1 - e^{-\lambda_{230}t})$

If  $(^{230}\text{Th}/^{232}\text{Th})$  is plotted against  $(^{238}\text{U}/^{232}\text{Th})$ , equation 14) is a linear equation, the so-called

**$^{230}\text{Th}$ - $^{238}\text{U}$  isochron diagram**



### Measurement Uncertainties

All measurements are afflicted with uncertainties. For large number of events, binomial distributions asymptotically approach Gaussian (or normal) distributions. The spread in events (here numerical values of isotope ratios, count rates or ion currents) is equal to  $\sqrt{N}$ . According to Gaussian statistics about 2/3 of the results lie within the range  $N \pm \sqrt{N}$  (one standard deviation), about 95% lie within the range  $N \pm 2\sqrt{N}$  (two standard deviations), and ~99% lie within the range  $N \pm 3\sqrt{N}$ . The fractional uncertainty is thus  $\sqrt{N}/N$ , or  $1/\sqrt{N}$ . If you measure twice as long ( $N^*$ ) you get twice as many events

$$N^* = 2N$$

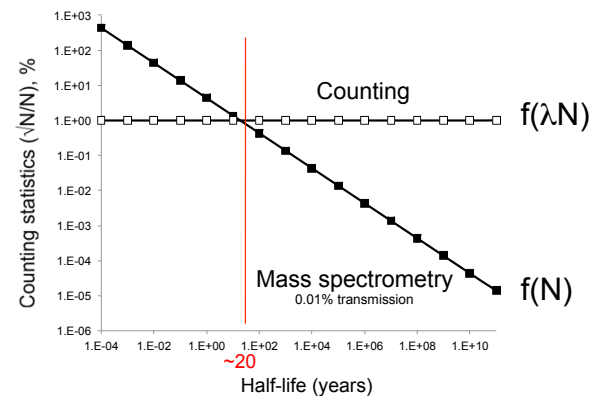
the fractional uncertainty is  $\sqrt{(2N)}/2N = 1/\sqrt{2N}$

$$\text{i.e.} \quad = \sqrt{1/2} * 1/\sqrt{N}$$

reducing the fractional uncertainty only by ~30%. The fractional uncertainty improves only as the square root of time (or ion current, or count rate). If you attempt to improve the uncertainty by a factor of two, you need to measure four times as long, or measure a four-times stronger ion current.

In order to evaluate if uncertainties associated with small ion beam intensities significantly affect the measured ratios it is often helpful to assume that all uncertainties are associated with uncertainties in the smallest ion current (least abundant isotope). By assuming an arbitrary uncertainty in the measurement of this ion current you can plot an error trend on plots of isotope ratio versus another isotope ratio (same isotope in the denominator, i.e.  $m_2 = m_d$ , if  $m_1$  and  $m_2$  are isotopes in the numerator). This trend is often distinct from an instrumental fractionation trend and helps to assess what process dominates the uncertainty of your analysis.

### Measurement Uncertainty



### The Reporting of Data & Uncertainties

70

Chapter 4 Introduction to Statistics and Statistical Mechanics

$$\text{mean concentration} = \bar{C} = \sum_{i=1}^N \frac{C_i}{N}$$

$$\text{r.m.s. deviation from average} = \sigma = \left\{ \sum_{i=1}^N \frac{(C_i - \bar{C})^2}{N} \right\}^{1/2} \quad (4.21)$$

For this particular data set,  $\bar{C}$  turns out to be 99.944 mM, but one glance at Figure 4.2 shows that not all of those digits are significant.  $\sigma$  turns out to be 0.66 mM, so we would calculate that the concentration of a typical bottle is  $99.944 \pm (1.96 \cdot 0.66)$  mM =  $99.944 \pm 1.29$  mM. In practice, we would not report so many digits: the usual convention is that the last reported digit should be uncertain by an amount between 3 and 30 units. So we would write  $99.9 \pm 1.3$  mM (the last digit, in the tenth-millimolar position, is uncertain by 13 units) in writing confidence limits for the distribution. This implies that 95% of the time a bottle selected at random would have a concentration between 98.6 and 101.2 mM.

We can also generalize result (3) at the beginning of Section 4.3 to say that the average of  $N$  measurements is expected to be in error by an amount which is proportional to  $1/\sqrt{N}$ . This is the principle behind **signal averaging**. The average of 1000 trials is expected to be  $\sqrt{1000}$  times more accurate than the result of a single trial. So we would report  $99.974 \pm (1.96 \cdot 0.66)/\sqrt{1000}$  mM =  $99.94 \pm 0.04$  mM (again to the correct number of significant digits) in writing confidence limits for the mean.

From: Warren S. Warren, 2000, *The Physical Basis of Chemistry*, 2nd ed, Harcourt Acad. Press.

Subject: Re: usual convention  
From: "Warren S. Warren" <warren.warren@duke.edu>  
Date: Thu, 06 Oct 2005 14:27:59 -0400  
To: behrenbrink@whoi.edu

Sorry about the delay in responding- it occurred because I have moved from Princeton, and my books just got unpacked!

The best source I can give you is the latest (seventh) edition of Garland, Nibler and Shoemaker, *Experiments in Physical Chemistry* (McGraw-Hill, New York, 2003). Shoemaker was the lead author on the early editions, and this is a standard reference textbook. You will find this convention on page 30, in the slightly different but equivalent form:

"Numerical values are considered to be uncertain in the last digit by plus or minus 3 or more, and perhaps slightly uncertain in the next-to-last digit. Ordinarily the next-to-last digit should not be uncertain by more than plus or minus 2."

After your inquiry, I found that most textbooks are much more vague about assigning specific rules, perhaps because statisticians do not like significant digits (for obvious reasons). The "3 to 30" rule is the one I remembered when I began experimental science.

At 05:50 PM 9/14/2005, you wrote:

Dear Prof. Warren:

Your splendid book on the physical basis of chemistry contains a statement (page 70, lines 4-6 below equation 4.21) that is very sensible and that I would like to trace to its source. My local experts here at WHOI had not seen this convention expressed in this form and could not help me locating its origin. Would you be kind enough to point me to the source of this "usual convention"?

With kind regards and thanks,  
Bernhard P-E.

Warren S. Warren, Professor of Chemistry and Radiology, Duke University  
Director, Center for Molecular and Biomolecular Imaging  
Gross Chemical Building, 135 Science Drive, Box 90346, Durham, NC 27708  
phone (919)660-1604; fax (919)287-2454