QUT SCHOOL OF CHEMISTRY AND PHYSICS
PVB303 NUCLEAR AND PARTICLE PHYSICS

PRACTICAL 2: SECULAR EQUILIBRIUM SEMESTER 2, 2020

Aims:
To investigate the phenomenon of secular equilibrium and to model radioactive decay processes in a physically realistic way.

Due to COVID-19 restrictions, this prac will be computer-based. You will use a first-principles model of the underlying physical process (as opposed to a mathematical solution) to simulate experimental datasets that would ordinarily be measured in the lab. You will then fit the datasets and determine the apparent decay rate constants.

Theory:

1. Secular equilibrium

Secular equilibrium results when:
(1) a parent isotope decays to a radioactive daughter isotope, and
(2) the half-life time T_D of the daughter is significantly shorter than that of the parent, T_P (e.g. $T_P > 10000\ T_D$).

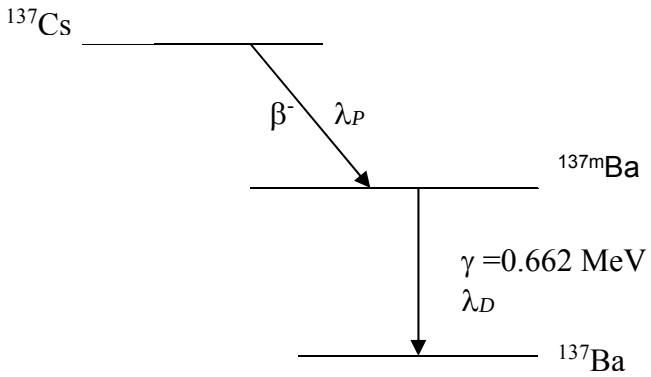
In this situation the production of the daughter isotope is slow, while the decay of the newly produced daughter is fast. As a result, a steady-state (secular-equilibrium) concentration of the daughter isotope is quickly established.

The decay

$$^{137}\mathrm{Cs} \xrightarrow{\lambda_P} {}^{137m}\mathrm{Ba} \xrightarrow{\lambda_D} {}^{137}\mathrm{Ba}$$

provides an example of a system where secular equilibrium occurs. The half-life times of ^{137}Cs and ^{137m}Ba are T_P ~ 30y and T_D ~ 153s, respectively. As a result, the production of ^{137m}Ba is very slow, but the decay of the newly produced ^{137m}Ba is fast; and the concentration of ^{137m}Ba in a ^{137}Cs sample quickly reaches a steady-state value.

The energy level scheme representing this decay is



where the decay rate constants λ are related to the respective half-life times T as $\lambda = (\ln 2)/T$. The instantaneous rates of decay or production of the three nuclides follow first-order kinetics:

$$\frac{d[^{137}\mathrm{Cs}]}{dt} = -\lambda_P[^{137}\mathrm{Cs}]$$
$$\frac{d[^{137m}\mathrm{Ba}]}{dt} = \lambda_P[^{137}\mathrm{Cs}] - \lambda_D[^{137m}\mathrm{Ba}] \qquad \text{..... (1)}$$
$$\frac{d[^{137}\mathrm{Ba}]}{dt} = \lambda_D[^{137m}\mathrm{Ba}]$$

where [...] denotes the concentration (or the absolute amount) of the respective nuclide.

(1) At long times ($t >> T_D$), a time-independent steady-state concentration of ^{137m}Ba is established, where the rate of its production equals the rate of decay:

$$\frac{d[^{137m}\mathrm{Ba}]}{dt} = \lambda_P[^{137}\mathrm{Cs}] - \lambda_D[^{137m}\mathrm{Ba}] = 0 \qquad \text{..... (2)}$$

From Eq. (2), the steady-state concentration of ^{137m}Ba can be found:

$$[^{137m}\mathrm{Ba}]_{\mathrm{sec}} = \frac{\lambda_P}{\lambda_D}[^{137}\mathrm{Cs}] \qquad \text{..... (3)}$$

This is the condition of secular equilibrium between the two radioactive species. Experimentally, this corresponds to a ^{137}Cs/^{137}Ba sample that was prepared sufficiently long ago to allow the steady state to be established. In this regime, the activity of ^{137m}Ba will be ideally constant when measured over a period of time that is significantly shorter than T_P.

(2) The other possible experimental scenario is a fresh sample of the parent isotope ^{137}Cs, where the concentration of the daughter isotope (^{137m}Ba) is initially zero. In this situation the concentration of ^{137m}Ba is time-dependent and builds up from the initial value to the steady-state value. Provided that $\lambda_D >> \lambda_P$ and the concentration of ^{137}Cs changes very slowly, the kinetics of this build-up is described by the equation

$$[^{137m}\mathrm{Ba}](t) = \frac{\lambda_P}{\lambda_D}[^{137}\mathrm{Cs}](1 - e^{-\lambda_D t}) \qquad \text{..... (4)}$$

At $t >> T_D$, [^{137m}Ba] approaches the secular equilibrium value given by Eq. (3).

(3) If the ^{137}Cs sample initially contains some ^{137m}Ba (but less than the secular-equilibrium amount), then Eq. (4) needs to be modified to take that into account. In this situation the kinetics of the build-up of [^{137m}Ba] is described by the equation

$$[^{137m}\mathrm{Ba}](t) = [^{137m}\mathrm{Ba}]_0\, e^{-\lambda_D t} + \frac{\lambda_P}{\lambda_D}[^{137}\mathrm{Cs}](1-e^{-\lambda_D t}) \qquad \text{..... (5)}$$

where $[^{137m}\mathrm{Ba}]_0$ is the initial concentration of the daughter isotope. According to Eq. (5), at $t = 0$ $[^{137m}\mathrm{Ba}] = [^{137m}\mathrm{Ba}]_0$, while at $t >> T_D$ $[^{137m}\mathrm{Ba}]$ approaches the secular equilibrium value. The two assumptions from scenario (2) are also implicit in Eq. (5), i.e. $\lambda_D >> \lambda_P$ and that the concentration of ^{137}Cs changes very slowly.

(4) If ^{137m}Ba is isolated from the parent isotope, then the rate of its fresh production becomes zero and it only undergoes decay. In this situation its kinetics is described by a decaying exponent:

$$[^{137m}\mathrm{Ba}](t) = [^{137m}\mathrm{Ba}]_0\, e^{-\lambda_D t} \qquad \text{..... (6)}$$

where $[^{137m}\mathrm{Ba}]_0$ is the initial concentration of the daughter isotope.

2. Modeling of radioactive decay

Mathematically, radioactive decay is a probabilistic process: the decay of a given individual nucleus is driven by probabilistic variables rather than a deterministic mathematical function. In addition to this, the detection process itself is not 100% efficient: there is a certain probability (usually significantly less than 1) that a given act of decay would be successfully detected. Furthermore, the detector can make a false-positive reading whereby a detection is made when no decay had actually occurred; this is most typically due to hardware noise. A physically realistic modeling of the measurement process needs to consider all of these factors. A Matlab code implementing the simulation procedure is given in the Appendix.

Suppose that a single nucleus of a radioactive species has the probability p_1 to decay and the probability $q_1 = 1 - p_1$ to survive over a time step Δt. For an elementary first-order process with the rate constant λ, $p_1 = 1 - \exp(-\lambda\, \Delta t)$. Then, in an ensemble of N such nuclei, the probability of exactly Y nuclei decaying during Δt is given by a binomial distribution:

$$P_1(Y) = p_1^Y (1-p_1)^{(N-Y)} \frac{N!}{Y!\,(N-Y)!} \qquad \text{... (7)}$$

Here $0 \le Y \le N$, i.e. in principle any number of nuclei between 0 and N could decay within a single time step. However, for a large N and small p_1, the probaility of Y being close to N is vanishingly small, and on average $\langle Y \rangle = p_1 N$ nuclei will decay each time step Δt. In most time steps the number of decays will not be exactly $\langle Y \rangle$ but would deviate from the average number according to the binomial distribution P_1.

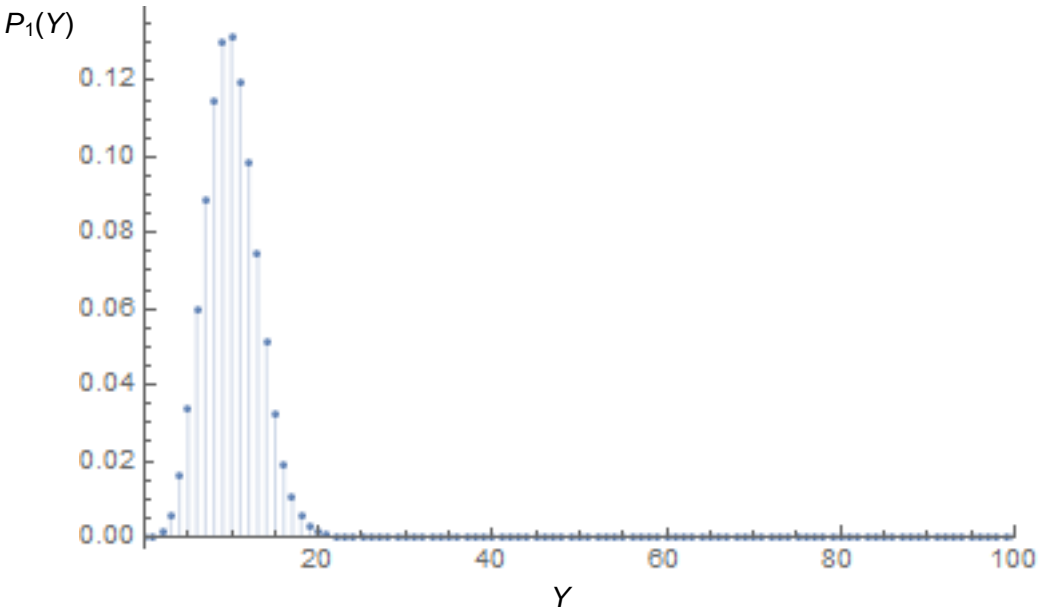
For computational efficiency, the Matlab code in the Appendix approximates the binomial distributions of ^{137}Cs and ^{137m}Ba decay numbers by the respective Gaussian distributions when N is large:

```
decays1 = double(ncs)*p1 + normrnd(0, sqrt(double(ncs)*p1*(1-p1)))
decays2 = double(nba)*p2 + normrnd(0, sqrt(double(nba)*p2*(1-p2)))
```

(The binomial-variate function binornd(j,z) is very slow when j is large, but a Gaussian variate provides a very good approximation of the binomial distribution in this limit.)

When N is small, a true binomial distribution is used:

```
decays2 = binornd(double(nba),p2)
```



Probability distribution P_1 for N = 100 and p_1 = 0.1. The extreme values Y = 0 and Y > 25 are highly improbable. On average 100×0.1 = 10 nuclei would decay in each time step in this scenario. However, the number of decays will be exactly 10 only in ~13% of the time steps; 95% of the time the number of decays in a single time step will be a binomially distributed random number between 5 and 16.

Once a decay has occurred, it may or may not be picked up by the detector. The detectors you are using in the pracs have detection efficiency f ~ 2% - i.e., on average they detect only 2% of the decaying nuclei. The distribution of true-positive detections is also a binomial distribution: If Y decays are known to have occurred, then the number of true-positive detected events could be anywhere between 0 and Y, with the average value being fY. In the Matlab code in the Appendix, this is represented by the line

```
detector = binornd(round(decays2),eff)
```

Besides true positives, the detector inevitably generates some false-positive readings. The distribution of the number of false positives can be complicated because there may be multiple physical mechanisms by which a false-positive reading could arise. Here, for the sake of simplicity we will assume this distribution also to be binomial and empirically fine-tune its shape to match the experimental observations. In the Matlab code in the Appendix, the number of false positives is represented by the term

```
binornd(round(dt*noise),0.7)
```

Objectives:

(1) First, you will investigate the decay of ^{137m}Ba isolated from its parent isotope. Simulate the kinetics of the decay and determine (by least-squares fitting) the value of λ_D as if you were analysing the results of an experimental measurement.

(2) You will then simulate the transient buildup of ^{137m}Ba to the secular-equilibrium value and again determine λ_D by least-squares fitting.

(3) Compare the two "measured" values of λ_D and discuss the results.

Experimental notes:

1) A NaI [Tl] γ-ray detector used to measure the activity of a ^{137}Cs source is in fact measuring the decay of ^{137m}Ba since ^{137}Cs emits beta particles which are not detected by the NaI detector.

2) The count rate (C) is proportional to activity of ^{137m}Ba. Hence Eq. (4) may be written as

$$C_D(t) = C_{D\,\mathrm{sec}}(1 - e^{-\lambda_D t}) \qquad \text{.....(8)}$$

3) Cs^+ and Ba^{2+} can be separated due to the differences in their chemical properties: one is a monovalent ion, while the other is divalent. The separation can be achieved by eluting the sample through an ion-exchange resin located within the Cs/Ba generator: Ba^{2+} is eluted, while Cs^+ is retained by the resin. The Cs/Ba generator used in this practical can therefore be used to provide a "fresh" sample of ^{137}Cs. However, the separation is not 100% efficient and in practice there will always be some ^{137m}Ba present in the ^{137}Cs sample at t = 0.

Procedure: Simulation and Analysis

You will need MatLab for the simulations. MatLab is available for free to QUT students and can be installed on your personal (non-QUT) computer. Download it from QUT IT Help and install it on your computer. Alternatively, you can use an already-installed copy of MatLab at one of the SEF computer labs.

1. Set the initial amounts of both ^{137}Cs and ^{137m}Ba to zero: n0cs = uint64(0) and n0ba = uint32(0). Run the MatLab simulation. This will generate the detector noise, i.e. readings that contain only false positives. Save this in Excel-readable CSV files.

2. Set the initial amounts of both ^{137}Cs and ^{137m}Ba to the values corresponding to the sample in a steady-state equilibrium: n0cs = uint64(5e14) and n0ba = uint32(5e14*lambda_p/lambda_d). Run the MatLab simulation. Save the results in CSV files.

3. Emulate the decay of ^{137m}Ba in the eluate, i.e. the decay of the daughter ^{137m}Ba nuclide separated from the parent ^{137}Cs: Set n0cs = uint64(0) and n0ba = uint32(5e14*lambda_p/lambda_d), and run the MatLab simulation. Save the resulting decay curve in CSV files.

4. Emulate the buildup of ^{137m}Ba in a fresh ^{137}Cs sample initially containing a small amount of ^{137m}Ba: Set n0cs = uint64(5e14) and n0ba = uint32(1e7), and run the MatLab simulation. Save the resulting buildup curve in CSV files.

5. Plot the results of Step 3 on ln-linear graph paper (or as a ln-linear plot in MatLab) and determine the half-life time and the decay rate constant of ^{137m}Ba.

6. To plot the results of Step 4, you need to take into account the initial non-zero amount of ^{137m}Ba in the fresh sample of ^{137}Cs:

$$C_D(t) = C_{D\text{sec}}(1 - e^{-\lambda_D t}) + xC_{D\text{sec}}e^{-\lambda_D t} \quad \text{..... (9)}$$

Eq. (9) is equivalent to Eq. (5). C_{Dsec} is the secular-equilibrium concentration of ^{137m}Ba given by Eq. (3), and x is the fraction of the daughter nuclide present at t = 0: $x = C_D(0)/C_{Dsec}$. Estimate the appropriate values of C_{Dsec} and x based on the parameter values used in your simulations.

Once an estimate of x is obtained, Eq. (9) can be linearised as

$$\ln\left[\frac{C_D(t) - C_{D\text{sec}}}{C_{D\text{sec}}} \times \frac{1}{x-1}\right] = -\lambda_D t \quad \text{..... (10)}$$

Plot your data from Step 4 on ln-linear graph paper (or as a ln-linear plot in MatLab) according to Eq. (10). [Caution: Do NOT use the code-generated file Detector_Log.csv for this purpose.] Determine the decay rate constant of ^{137m}Ba. Compare it with the value measured in Step 5.

Your report must include the following:

1. A brief background.
2. A description of the simulation performed and the data analysis.
3. The plots of the four simulated timecourses: noise, steady-state, the decay curve and the buildup curve of ^{137m}Ba. Each dataset should be shown both in the original coordinates (counts vs time) and in the Log-linear coordinates, ln(counts) vs time.
4. Least-squares fitting of the decay and the build-up, including a clear description of the model and the fitting parameters used, and the corresponding apparent decay rate constants.
5. A discussion of the curves obtained, uncertainties of the measurements and sources of error and the degree of agreement of the two measured values of λ_D.
6. Discuss whether the secular equilibrium model is applicable to the Cs/Ba system.
7. Compare the levels of noise in the noise-only timecourse and the steady-state timecourse (Steps 1 and 2, respectively). Are the two noise levels equal or not? What is the explanation?
8. Your least-squares fitted values of λ_D will most likely differ from each other as well as from the input value of λ_D (variable lambda_d in the MatLab code). Why is this?
9. Eq. (6) being a monoexponential function suggests that the decay of ^{137m}Ba (Step 3) should be a simple straight line in ln-linear coordinates. However, the ln-linear plot in Step 5 is curved upwards at long times. Why is this? Is this consistent with the experimental decay dataset on BB? What are the implications for the sensitivity of the experimental measurement?
10. In the ln-linear plot from Step 5, the scatter of data points increases as the time increases. Why is this?

APPENDIX: MatLab simulation code

The following code simulates, in a physically realistic way, the two-step decay sequence ^{137}Cs → ^{137m}Ba → ^{137}Ba as well as the detection process for the ^{137m}Ba decays. (See the manual section "Modeling of radioactive decay" for the description of the simulation procedure.)

The initial amounts of ^{137}Ca and ^{137}mBa are the values of the variables n0cs and n0ba, respectively.

The output (the decay curve) is saved in the arrays:
time (list of time steps)
detector (the number of ^{137m}Ba decays in a given time step)
logdet (ln of the number of decays)

Set the variables n0cs and n0ba to the appropriate values in order to simulate the four measurements described under the Procedure.

```
dt = 1;              % Time step = 1 s; you can change this if required
nt = 2000;           % Keep simulation time dt*nt = 2000 s

tp = 30.17*525948.766*60;   % T1/2 for 137Cs (in s)
lambda_p = log(2)/tp;       % Decay rate constant for 137Cs (s^-1)
td = 2.552*60;              % T1/2 for 137mBa (in s)
lambda_d = log(2)/td;       % Decay rate constant for 137mBa (s^-1)
n0cs = uint64(5e14);        % Initial number of 137Cs nuclei
ncs = n0cs                  % Current number of 137Cs nuclei
p1 = 1 - exp(-lambda_p*dt); % Probability of decay of a given 137Cs nucleus per time step

n0ba = uint32(5e14*lambda_p/lambda_d)       % Initial number of 137mBa nuclei
nba = n0ba;                 % Current number of 137mBa nuclei
p2 = 1 - exp(-lambda_d*dt); % Probability of decay of a given 137mBa nucleus per time step
eff = 0.02;                 % Detector efficiency (2%)
pnoise = 0.8;               % Empirical noise parameters
noise = 10/pnoise;

times = [dt:dt:nt*dt];      % Array with the time axis values
detector = 0*times;         % Array with detector reads for each time step
logdet = detector;          % Log (ln) of the detector reads

for ii = 1:nt
   % The number of 137Cs decays in the current time step.
   % Matlab's binomial RN generator can't handle very large integers,
   % so we approximate a binomial variate by using Gaussian noise.
   % Since the number of decays must be non-negative,
   % any negative values are replaced with 0.
   decays1 = double(ncs)*p1 + normrnd(0, sqrt(double(ncs)*p1*(1-p1)));
   decays1 = max(decays1, 0);
   % Each 137Cs decay decreases the number of 137Cs nuclei
   % and increases the number of 137mBa nuclei:
   ncs = ncs - decays1
   nba = nba + decays1;

   % The number of 137mBa decays in the current time step.
```

```
    % For 137mBa decay we use a true binomial variate when nba is small,
    % otherwise use a Gaussian approximation (which is much faster):
    if (nba < 10000)
       decays2 = binornd(double(nba),p2);
    else
       decays2 = double(nba)*p2 + normrnd(0, sqrt(double(nba)*p2*(1-p2)));
       decays2 = max(decays2, 0);
    end  % End of If
    % Each 137mBa decay decreases the number of 137mBa nuclei:
    nba = nba - decays2
    ii   % Lazy progress indicator

    % Detector reads include true positives and false positives:
    detector(ii) = binornd(round(decays2),eff) + binornd(round(dt*noise),0.7);
    logdet(ii) = log(detector(ii));
end   % End of For

% Save the results: Change the directory and file names as appropriate
csvwrite("C:\KM\Classes\PVB303\Pracs\Times.csv", transpose(times));
csvwrite("C:\KM\Classes\PVB303\Pracs\Detector.csv", transpose(detector));
csvwrite("C:\KM\Classes\PVB303\Pracs\Detector_Log.csv", transpose(logdet));
```