Introduction to Stable Isotopes

Notation

Fractionation

Gear
Definitions

Isotopes
Atoms of the same element (i.e., same number of protons and electrons) but different numbers of neutrons.

Stable Isotope
Do not undergo radioactive decay, but they may be radiogenic (i.e., produced by radioactive decay).

Usually the number of protons and neutrons is similar, and the less abundant isotopes are often “heavy”, i.e., they have an extra neutron or two.
## Nomenclature \(^{A}_{Z}X\)

<table>
<thead>
<tr>
<th>Name</th>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic number</td>
<td>Z</td>
<td>Number of protons in nucleus</td>
</tr>
<tr>
<td>Neutron number</td>
<td>N</td>
<td>Number of neutrons in nucleus</td>
</tr>
<tr>
<td>Mass number</td>
<td>A</td>
<td>Number of nucleons in nucleus</td>
</tr>
</tbody>
</table>

## Nuclide classification

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isotope</td>
<td>Same Z, different N and A</td>
</tr>
<tr>
<td>Isobar</td>
<td>Same A, different Z and N</td>
</tr>
<tr>
<td>Isotone</td>
<td>Same N, different A and Z</td>
</tr>
</tbody>
</table>
Figure 2.1. Partial chart of the elements. Each square represents a particular nuclide. The shaded squares are stable atoms and the unshaded squares are unstable or radioactive nuclides. Arrows at the left side of the diagram show the shifts in proton and neutron number caused by different decay mechanisms: beta decay (a), positron decay and beta capture (b), and alpha decay (c). Modified from Faure (1986).
Table 1. Vertebrate isotope systems and their applications

<table>
<thead>
<tr>
<th>Element</th>
<th>Isotope</th>
<th>Fractional abundance</th>
<th>Standard for δ value calculation</th>
<th>Isotopic range in vertebrates</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>$^1\text{H}$</td>
<td>0.999844</td>
<td>Standard Mean Ocean Water (SMOW)</td>
<td>-175 to +70‰</td>
<td>migration, habitat use, diet, trophic level, osmoregulatory physiology</td>
</tr>
<tr>
<td></td>
<td>$^2\text{H}$</td>
<td>0.000156</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td>$^{12}\text{C}$</td>
<td>0.98889</td>
<td>PeeDee Belemnite Limestone (PDB)</td>
<td>-60 to +5‰</td>
<td>diet, digestive physiology, habitat use, migration</td>
</tr>
<tr>
<td></td>
<td>$^{13}\text{C}$</td>
<td>0.01111</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrogen</td>
<td>$^{14}\text{N}$</td>
<td>0.99634</td>
<td>Air</td>
<td>-30 to +30‰</td>
<td>trophic level, diet, habitat use, migration, starvation, reproduction</td>
</tr>
<tr>
<td></td>
<td>$^{15}\text{N}$</td>
<td>0.00366</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxygen</td>
<td>$^{16}\text{O}$</td>
<td>0.99755</td>
<td>SMOW or PDB</td>
<td>0 to +35‰</td>
<td>habitat use, migration, diet, thermoregulation, osmoregulation</td>
</tr>
<tr>
<td></td>
<td>$^{17}\text{O}$</td>
<td>0.00039</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$^{18}\text{O}$</td>
<td>0.00206</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulphur</td>
<td>$^{32}\text{S}$</td>
<td>0.9493</td>
<td>Canyon Diablo Troilite</td>
<td>-15 to +20‰</td>
<td>habitat use, migration, diet</td>
</tr>
<tr>
<td></td>
<td>$^{33}\text{S}$</td>
<td>0.0076</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$^{34}\text{S}$</td>
<td>0.0429</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$^{36}\text{S}$</td>
<td>0.0002</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcium</td>
<td>$^{40}\text{Ca}$</td>
<td>0.96941</td>
<td>NIST 915a (CaF$_2$)</td>
<td>-3.1 to +1.8‰</td>
<td>trophic level, habitat use, migration</td>
</tr>
<tr>
<td></td>
<td>$^{42}\text{Ca}$</td>
<td>0.00647</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$^{43}\text{Ca}$</td>
<td>0.00135</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$^{44}\text{Ca}$</td>
<td>0.02086</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$^{46}\text{Ca}$</td>
<td>0.00004</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$^{48}\text{Ca}$</td>
<td>0.00187</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Strontium</td>
<td>$^{84}\text{Sr}$</td>
<td>0.0056</td>
<td>Bulk Earth ($\varepsilon$) or Sea Water ($\delta$)</td>
<td>0.7043-0.7583</td>
<td>habitat use, migration, diet</td>
</tr>
<tr>
<td></td>
<td>$^{86}\text{Sr}$</td>
<td>0.0986</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$^{87}\text{Sr}$</td>
<td>0.0700</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$^{88}\text{Sr}$</td>
<td>0.8258</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1. The range of values is defined by data in cited papers.
2. Study of migration is a potential application of all isotope systems.
What makes for a stable isotope system that shows large variation?

1) Low atomic mass

2) Relatively large mass differences between stable isotopes

3) Element tends to form highly covalent bonds

4) Element has more than one oxidation state or forms bonds with a variety of different elements

5) Rare isotopes aren’t in too low abundance to be measured accurately
Since natural variations in isotope ratios are small, we use δ notation

\[ \delta^H X = \left( \frac{R_{sample}}{R_{standard}} - 1 \right) \times 1000 \]

where \( R \) = heavy/light isotope ratio for element \( X \) and units are parts per thousand (or per mil, ‰)

e.g. \( \delta^{18}O \) (spoken “delta O 18)
or \( \delta^{34}S \) (spoken “delta S 34)

Don’t ever say “del”. Don’t ever say “parts per mil”. It makes you sound like a knuckle-head.
TABLE 2.1: Common mistakes in terminology and phraseology.

<table>
<thead>
<tr>
<th>Mistake</th>
<th>Recommended expressions</th>
<th>Explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Referring to the symbol δ as del δ(^{13})O, not δ(^{18})O</td>
<td>Since the time of the early Greeks, the name of this symbol has been, and remains, delta.</td>
<td>The word del describes either of two things in mathematics and science: an operator ((\nabla)) or the partial derivative ((\delta)).</td>
</tr>
<tr>
<td>δ(^{13})C composition</td>
<td>δ(^{13})C value; carbon isotope composition</td>
<td>δ(^{13})C values are numbers; a composition of numbers has no meaning.</td>
</tr>
<tr>
<td>Isotopically depleted water</td>
<td>18O (or D) depleted water</td>
<td>A given sample of water is neither depleted nor enriched in isotopes.</td>
</tr>
<tr>
<td>Heavy (light) δ(^{18})O values</td>
<td>High (low) δ(^{18})O values</td>
<td>As numbers, δ values can be high or low, positive or negative, but not heavy or light.</td>
</tr>
<tr>
<td>Isotopically negative</td>
<td>Relatively low δ values</td>
<td>Isotopic ratios are neither negative nor positive; they are lower or higher than those of the standards.</td>
</tr>
<tr>
<td>Depleted δ(^{13})C value</td>
<td>Low δ(^{13})C value (relative to another) isotopically heavy (light) carbonates</td>
<td>δ(^{13})C values are numbers; as such, they cannot be depleted or enriched.</td>
</tr>
<tr>
<td>Enriched (depleted) carbonates.</td>
<td>(relatively) 18O-rich or 13C-poor carbonates reservoir of (isotopically) light carbon</td>
<td>The words enrich and deplete are overused and much abused. These words should be reserved for describing a process that changes the content of the heavy isotope of the element in some substance.</td>
</tr>
<tr>
<td>Oxygen isotopes in chert;</td>
<td>Oxygen isotope ratio (composition) of chert; inferred from carbon isotope measurements; isotopic composition of soil water</td>
<td>Such written mistakes are a carryover from loose oral communication.</td>
</tr>
<tr>
<td>isotopes of soil water</td>
<td></td>
<td>A matter of redundancy.</td>
</tr>
<tr>
<td>The isotopic composition of the water was δ(^{18})O = (-4.3)‰.</td>
<td>The δ(^{18})O value of the water was (-4.3)‰.</td>
<td>The phrase isotopic value is ambiguous. Does it denote R? δ? which element?</td>
</tr>
<tr>
<td>The isotopic value changed.</td>
<td>The isotopic composition changed.</td>
<td>The word signature should be used to describe the isotopic composition of a significant reservoir, such as the mantle, the ocean, or a major part of the system being studied, not to describe the isotopic composition of ordinary samples.</td>
</tr>
<tr>
<td>The isotopic signature of the rock was δ(^{18})O = 5.7‰.</td>
<td>The δ(^{18})O value of the rock was 5.7‰.</td>
<td>The introduction of new symbols that save one character of space is unnecessary at best and confusing at worst.</td>
</tr>
<tr>
<td>δ(^{15}), δ(^{18}), δ(^{13}), etc.;</td>
<td>δ(^{15})N, δ(^{18})O, δ(^{13})C, etc.</td>
<td>Misleading because the reader may take the sentence to mean that the sulfur content of a rock or mineral was measured.</td>
</tr>
<tr>
<td>15δ, 18δ, 13δ, etc.;</td>
<td></td>
<td>13C content refers to how much 13C there is in a rock. A sample of coal has a lot of 13C (a high 13C content), but a low 13C/12C ratio compared with most materials.</td>
</tr>
<tr>
<td>δ−15, δ−18, δ−13, etc.;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfur was measured.</td>
<td>The sulfur isotope composition was measured.</td>
<td></td>
</tr>
<tr>
<td>The (^{13})C content of . . .</td>
<td>The (^{13})C/(^{12})C ratio of . . .</td>
<td></td>
</tr>
</tbody>
</table>


Other notation used in ecology

1) Fraction of isotope in total mixture: $^{\text{H}}F$ or $^{\text{L}}F$ defined as $\frac{H}{(H+L)}$ or $\frac{L}{(H+L)}$

2) Ratio of isotopes: usually denoted $R$, $^{\text{H}}R$ or $^{\text{H/L}}R$, defined as $\frac{H}{L}$

3) Atom %: usually $^{\text{H}}\text{AP}$ or $^{\text{L}}\text{AP}$ defined as $100\times ^{\text{H}}F$ or $100\times ^{\text{L}}F$

Over a 200‰ range, $\delta^{\text{H}}X$ varies linearly with % heavy isotope, but has easier to remember values.

Figure 2.3. There is a linear relationship between the three types of isotope notation ($\delta$, $R$, and $F$) for natural samples in the -100 to +100‰ $\delta$ range. This example shows how $R$ and $F$ are related to $\delta$ for carbon isotopes, $\delta^{13}C = [(R_{\text{SAMPLE}}/R_{\text{STANDARD}}) - 1] \times 1000$ where $R = {^{13}F}/L = {^{13}C}/^{12}C$, $^{13}F = ^{13}C$, $L = ^{12}C$, the standard is VPDB (see Table 2.1), and $R_{\text{STANDARD}} = {^{13}F}/L = 0.011056/0.988944 = 0.011180$.  

Fry 2006
Isotope Fractionation

1) Isotopes of an element have the same number and distribution of electrons, hence they undergo the same chemical (and physical) reactions.

2) Differences in mass can, however, influence the rate or extent of chemical or physical reactions, or lead to partitioning of isotopes differentially among phases.

3) Isotopic sorting during chemical, physical, or biological processes is called **Fractionation**.
Fractionation mechanisms

**Equilibrium Isotope Fractionation**
A quantum-mechanical phenomenon, driven mainly by differences in the vibrational energies of molecules and crystals containing atoms of differing masses.

**Kinetic Isotope Fractionation**
Occur in unidirectional, incomplete, or branching reactions due to differences in reaction rate of molecules or atoms containing different masses.
Fractionation terminology

Fractionation factor:

\[ \alpha_{A/B} = \frac{^4H R_A}{^4H R_B} = \frac{(1000 + \delta^4H X_A)}{(1000 + \delta^4H X_B)} \]

<table>
<thead>
<tr>
<th>Discipline</th>
<th>Term</th>
<th>Symbol</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geochemistry</td>
<td>Often equilibrium fractionations, put heavy isotope enriched substance in numerator</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Separation</td>
<td>( \Delta_{A/B} )</td>
<td>( \delta_A - \delta_B )</td>
</tr>
<tr>
<td></td>
<td>Enrichment</td>
<td>( \varepsilon_{A/B} )</td>
<td>1000(( \alpha_{A/B} -1 ))</td>
</tr>
<tr>
<td>Biology</td>
<td>Often kinetic fractionations, put light isotope enriched substance in numerator</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Discrimination</td>
<td>( \Delta_{A/B} )</td>
<td>1000(( \alpha_{A/B} -1 ))</td>
</tr>
<tr>
<td></td>
<td>Enrichment</td>
<td>( \varepsilon_{A/B} )</td>
<td>1000 ln( \alpha_{A/B} )</td>
</tr>
</tbody>
</table>

Multiple Approximations

1000 ln\( \alpha_{A/B} \) \( \approx \) \( \delta_A - \delta_B \) \( \approx \) 1000(\( \alpha_{A/B} -1 \))
Isotope Exchange Reactions

\[ A^LX + B^HX \leftrightarrow A^HX + B^LX \]

**Equilibrium Constant (K)**

\[ K = \frac{(A^HX)(B^LX)}{(A^LX)(B^HX)} \]
\[ K = \frac{(A^HX/A^LX)}{(B^HX/B^LX)} \]

\[ K^{1/n} = \alpha_{A/B} = \frac{^{H}R_A}{^{H}R_B} = \frac{1000 + \delta^{H}X_A}{1000 + \delta^{H}X_B} \]

where \(^{H}R = \) heavy/light isotope ratio in A or B
and \( n = \) number of exchange sites (1 in this case)

\[ \Delta G_{rxn} = -RT \ln K \]

where \( R \) is the gas constant and \( T \) is in kelvin

Hence, the isotopic distribution at equilibrium is a function of the free energy of the reaction (bond strength) and temperature

\[ H^{12}CO_3^- (aq) + ^{13}CO_2 (g) \leftrightarrow H^{13}CO_3^- (aq) + ^{12}CO_2 (g) \]

\[ K_{HCO_3/CO_2} = 1.0092 \ (0^\circ C) \]
\[ K_{HCO_3/CO_2} = 1.0068 \ (30^\circ C) \]
Bond energy (E) is quantized in discrete states. The minimum E state is not at the curve minimum, but at some higher point.

Possible energy states are given by the following equation:

\[ E = (n + \frac{1}{2})h\nu, \]

where \( n \) is a quantum number, \( h \) is Plank’s constant, and \( \nu \) is the vibrational frequency of the bond.

\[ \nu = (\frac{1}{2}\pi)\sqrt{(k/\mu)}, \]

where \( k \) is the force constant of the bond (invariant among isotopes), and \( \mu \) is the reduced mass.

\[ \mu = (m_1m_2)/(m_1+m_2) \]

As bond energy is a function of \( \mu \), E is lower when a heavier isotope is substituted for a lighter one.

Zero Point Energy Difference

Consider a C-O bond where we substitute \(^{18}\text{O}\) for \(^{16}\text{O}\).

\[ m_1 = 12, \quad m_2 = 16 \text{ or } 18, \]

\[ ^{16}\mu = 12*16/28 = 6.85714, \quad ^{18}\mu = 12*18/30 = 7.2000 \]

For E, most terms dropout, so \( ^{18}\nu/^{16}\nu = \sqrt{(^{16}\mu/^{18}\mu)} = 0.9759. \)

So, \( ^{18}\text{E} < ^{16}\text{E} \)
Equilibrium Isotope Fractionation

From vibrational frequency calculations, we can determine values for $\alpha (= K^{1/n})$. The derivation is time consuming, so here are some general rules.

1) Equilibrium fractionation usually decrease as $T$ increases, roughly proportional to $1/T^2$.
2) All else being equal, isotopic fractionations are largest for light elements and for isotopes with very different masses, roughly scaling as $\mu$.
3) At equilibrium, heavy isotopes will tend to concentrate in phases with the stiffest bonds. The magnitude of fractionation will be roughly proportional to the difference in bond stiffness between the equilibrated substances. Stiffness is greatest for short, strong chemical bonds, which correlates with:
   a) high oxidation state in the element
   b) high oxidation state in its bonding partner
   c) bonds for elements near the top of the periodic table
   d) highly covalent bonds
Often expressed in equations of the form:

\[ 1000 \ln \alpha = a \left( \frac{10^6}{T^2} \right) + b \left( \frac{10^3}{T} \right) + c \]

where \( T \) is in kelvin, and \( a, b, \) and \( c \) are constants.
**Equilibrium Fractionation, Closed System**

In a closed systems, fractionation between 2 phases must obey conservation of mass (i.e., the total number of atoms of each isotope in the system is fixed). In a system with 2 phases (A and B), if $f_B$ is the fraction of B then $1-f_B$ is the fraction of A.

$$\delta_{\Sigma} = \delta_A (1-f_B) + \delta_B f_B$$

$$\delta_A = \delta_{\Sigma} + f_B (\delta_A - \delta_B)$$

$$\delta_A = \delta_{\Sigma} + f_B \varepsilon_{A/B}$$

$$\delta_B = \delta_{\Sigma} -(1-f_B) \varepsilon_{A/B}$$

Equilibrium Fractionation, Closed System

$\varepsilon_{A/B} \approx 50\%$

$\alpha_{AB} = 1.05$

$\delta_{\Sigma} = 0$
Equilibrium Fractionation, Open System

Consider a system where a transformation takes place at equilibrium between phase A and B, but then phase B is immediately removed. This is the case of Rayleigh Fractionation/Distillation. I won’t present the derivation here, but the equations that describe this phenomenon are:

\[
R_A = R_{A0} f(\alpha_{A/B}-1)
\]

\[
\delta_A = ((1000 + \delta_{A0}) f(\alpha_{A/B}-1)) - 1000
\]

\[
\delta_B = ((1000 + \delta_A)/\alpha_{A/B}) - 1000
\]

where \(R_A\) is the isotopic ratio of phase A after a certain amount of distillation, \(R_{A0}\) is the initial isotopic ratio of phase A, \(f\) is the fraction of phase A remaining (\(A/A_0 = \) fraction of phase A remaining), and \(\alpha_{A/B}\) is the equilibrium fractionation factor between phase A and B.
Equilibrium Fractionation, Open System

Fig. 4. $\delta^{18}O$ in a cloud vapor and condensate plotted as a function of the fraction of remaining vapor in the cloud for a Rayleigh process. The temperature of the cloud is shown on the lower axis. The increase in fractionation with decreasing temperature is taken into account. (After Dansgaard 1964)
Equilibrium Fractionation, Open System

\[ \varepsilon_{A/B} \approx 10 \text{‰} \]

\( A = \text{pond} \)
\( B = \text{evaporate} \)
\( C = \Sigma \text{evaporate} \)

*Figure 2.3. Isotopic change under open- and closed-system Rayleigh conditions for evaporation with a fractionation factor \( \alpha = 1.01 \) for an initial liquid composition of \( \delta^{18}O = 0 \). The \( \delta^{18}O \) of the remaining water (solid line A), the instantaneous vapor being removed (solid line B), and the accumulated vapor being removed (solid line C) all increase during single-phase, open-system, evaporation under equilibrium conditions. The \( \delta^{18}O \) of water (dashed line D) and vapor (dashed line E) in a two-phase closed system also increase during evaporation, but much less than in an open system; for a closed system, the \( \delta \) values of the instantaneous and cumulative vapor are identical. Modified from Gat and Gonfiantini (1981).*
Kinetic Isotope Fractionation

Consider a unidirectional reaction where the reactant must pass over an energy barrier in the form of an activated complex to form the product. The energy required to surmount this barrier, $E_a$, is the difference in energy between the activated complex and the reactant. We know from the earlier discussion that a reactant molecule with a heavier isotope will have a lower zero point energy than a reactant with a lighter isotope. The activated complex is pretty unstable, so isotopic substitutions don’t affect its energy state. As a consequence, the heavier isotope has a higher $E_a$ than the lighter isotope and reacts slower, leading to a heavy isotope depletion in the product.
Kinetic Fractionation, Closed System

We can define a kinetic rate constant for the reaction above:

\[ k = Ae^{-\frac{E_a}{RT}} \]

where \( A \) is the amount of reactant

If \( H \) refers to the reactant with the heavy isotope, for \( R \rightarrow P \):

\[
\frac{dA}{dt} = kA \quad \text{and} \quad \frac{d^{\text{H}}A}{dt} = ^{\text{H}}k^{\text{H}}A
\]

If \( \beta \equiv \frac{^{\text{H}}k}{k} \), then

\[
\frac{d^{\text{H}}A}{A} = \beta \frac{dA}{A}
\]

Integrating this equation between \( A_0 \) and \( A \) for both isotopes, we get:

\[
\ln\left(\frac{^{\text{H}}A}{^{\text{H}}A_0}\right) = \beta \ln\left(\frac{A}{A_0}\right) \quad \text{or} \quad \frac{^{\text{H}}A}{^{\text{H}}A_0} = \left(\frac{A}{A_0}\right)^\beta
\]

If we divide by \( A/A_0 \), we get:

\[
\left(\frac{^{\text{H}}A}{^{\text{H}}A_0}\right)/\left(\frac{A}{A_0}\right) = \left(\frac{A}{A_0}\right)^{\beta-1}
\]

Recall that \( R_A \approx \frac{^{\text{H}}A}{A} \) and that \( R_{A0} = \frac{^{\text{H}}A_0}{A_0} \),

therefore \( R_A/R_{A0} = \left(\frac{A}{A_0}\right)^{\beta-1} \)

If \( f \equiv A/A_0 \), we get:

\[
R_A = R_{A0}f^{\beta-1}
\]

This is just the Rayleigh Equation again.

So, a closed system kinetic fractionation behaves just like an open system equilibrium fractionation. Not surprising, the unidirectional nature of the reaction is, in effect, removing the reactant from the product.
Kinetic Fractionation, Closed System

Isotope Effect

Fractionation

Fractionation between pooled product and unconsumed reactant is variable
\[ A = f(\text{yield, isotope effect}) \]

Fractionation between instantaneously forming product and unconsumed reactant is constant
\[ B = f(\text{isotope effect}) \]

Figure 4. Schematic representation of a closed system and the isotopic fractionations occurring within it as a reaction proceeds to completion. Curve \( P' \) represents the isotopic composition of the instantaneously-forming product, and \( P \) represents the isotopic composition of the pooled product.
Kinetic Fractionation, Open System

Consider a system with 1 input and 2 outputs (i.e., a branching system). At steady state, the amount of R entering the system equals the amounts of products leaving: \( R = P + Q \). A similar relationship holds for isotopes: \( \delta_R = \delta_P f_P + (1-f_P)\delta_Q \). Again, this should look familiar; it is identical to closed system, equilibrium behavior, with exactly the same equations:

\[
\begin{align*}
\delta_P &= \delta_R + (1-f_P)\varepsilon_{P/Q} \\
\delta_Q &= \delta_R - f_P\varepsilon_{P/Q}
\end{align*}
\]
Open Systems at Steady State
Open system approaching steady state

Figure 3. Isotopic compositions as a function of time. Time is expressed in units of \( \tau \), the time constant for the system. As noted, \( \tau = m/\varphi \), where \( m \) is the quantity of intermediate present at steady state. Values of \( \delta \) refer to reactant A (broken line), product B (upper solid line), and the carbon transmitted by reaction 2 (lower solid line).
Nier-type mass Spectrometer

**Ion Source**
Gas molecules ionized to + ions by $e^-$ impact
Accelerated towards flight tube with k.e.:

$$0.5mv^2 = e^+V$$
where $e^+$ is charge, $m$ is mass, $v$ is velocity, and $V$ is voltage

**Magnetic analyzer**
Ions travel with radius:

$$r = \frac{(1/H) \times (2mV/e^+)^{0.5}}{}$$
where $H$ is the magnetic field
higher mass > $r$

**Counting electronics**
Dual Inlet
sample and reference analyzed alternately 6 to 10 x viscous flow through capillary change-over valve
1 to 100 µmole of gas required highest precision

Continuous Flow
sample injected into He stream cleanup and separation by GC high pumping rate
1 to 100 nanomoles gas reference gas not regularly altered with samples loss of precision
EA Carbon and Nitrogen combustion - solids

Solid autosampler

O₂ Pulsed injection per sample

Quartz tube

Combustion 1050°C

Chromium oxide

Quartz chips

Silvered cobaltous Cobaltic oxide

Quartz wool

Constant flow He IN 100mL/min

Quartz wool

Reduction 850°C

Copper

Water trap Magnesium perchlorate

GC column 3m PempakQ

TCD

Diluter (Optional use)

IsoPrime IRMS

Reference Gas Injector System

Pneumatic needle valve Purge

NUPRO isolation valve

Stand-by valve

EA (HT) Oxygen/Hydrogen pyrolysis - solids

Solid autosampler

Oxygen setup

Hydrogen setup

Constant flow He IN 100mL/min

Ceramic outer tube

Glassy carbon inner tube

Glassy carbon chips

Quartz wool

Furnace 1260°C

GC column 1m 6A molecular sieve packed column

TCD

Diluter (Optional use)

IsoPrime IRMS

Open split

Reference Gas Injector System

Pneumatic needle valve Purge

NUPRO isolation valve

Stand-by valve

*90°C for Hydrogen