

10 Kinetic Fractionation and Rayleigh Processes

Reading: Chapter 27 in White

Guide Questions:

- 1) If the rate of a chemical reaction involves breakage of bonds, does the rate of that reaction differ for molecules bearing light isotopes, relative to those bearing heavy isotopes? If so, why?
- 2) What is the activation energy for a reaction, and why is it different for heavy isotopes vs. light isotopes?
- 3) What is the meaning of epsilon as an indicator of isotopic fractionation?
- 4) If we measure the amount of kinetic isotopic fractionation for a given reaction, does the result always apply to the reaction, even if we change the reaction mechanism? Why or why not?
- 5) With a given reaction mechanism, does the rate of the backward reaction influence the overall isotopic fractionation?
- 6) In a rough sense, do kinetic isotope effects tend to decrease with increasing T?
- 7) Know roughly which geochemical reactions are likely to be in equilibrium, and which are probably not.
- 8) How, mathematically, does the isotopic composition of a pool of reactant vary as that reactant is progressively consumed by an isotope-fractionating process?

Kinetic Isotope Effects: Basic Theory

When a reaction is dominantly a forward reaction, and has little back-reaction, the lighter isotopes tend to react at a greater rate.

- Reaction product becomes enriched in lighter isotope relative to the reactant
- If the reactant pool is limited (e.g., closed system) the reactant becomes enriched in the heavier isotope

Example: HD vs. HH which one reacts faster?

Assume the reaction involves breaking the H-H or H-D bond.

Kinetic Theory: The rate of any chemical reaction can be described by:

$$R = ke^{-E_A/RT} \quad (1)$$

...where E_A is the activation energy and k is a constant.

- The activation energy is the energy needed to cause the reaction- e.g., to break a bond, or move an atom to a new position in a crystal lattice.
- The Boltzmann factor, $e^{-E_A/RT}$, is in there because it represents the probability that any one molecule will attain a high enough energy to get over the "activation barrier".

But E_A is usually slightly less for the lighter isotope (zero point energy is higher).

From eqn. (1), the ratio of the reaction rates:

$$\frac{R_D}{R_H} = \frac{e^{-\left(\epsilon - \frac{1}{2}h\nu_D\right)/kT}}{e^{-\left(\epsilon - \frac{1}{2}h\nu_H\right)/kT}} = e^{\left(\nu_H - \nu_D\right)\frac{h}{2kT}}$$

Where ϵ is the total dissociation energy (bottom of well to large x value) and $1/2h\nu$ represents the zero point energy (ZPE). The physics behind this equation are as follows:

- The energy needed to break the bond would be simply ϵ for both isotopes if there were no ZPE issue
- But the ZPE is an issue. It gives the ground state molecules an energy somewhat higher than the bottom of the energy well, and $ZPE_{heavy} < ZPE_{light}$.
- We thus need to subtract ZPE from ϵ to get the correct bond dissociation energy.

- The probability of a given molecule getting bumped to high enough energy to dissociate is given by our old friend the Boltzmann factor.

(Note that this is a bit simplistic: We can't always assume that after the breakage of the bonds, the energy levels of the isotopes are the same. Also, what about the fact that some molecules are in higher quantum states? But this works as a first approximation...)

Example: Evaporation tends to be a non-equilibrium (kinetic) process.

Over the oceans, equilibrium fractionation would predict delta value of -9 per mil, whereas the measured value is -13 per mil. This is because the evaporation process is not an equilibrium process, and the isotopic fractionation is greater than the equilibrium value (in this case).

Epsilon Notation

A bit more Notation: For kinetic isotope effects, there is no theoretical basis for using $1000\ln\epsilon$ as a measure of per mil isotopic fractionation. So some people have defined ϵ :

$$\epsilon = 1000(\frac{R_{\text{product}}}{R_{\text{reactant}}} - 1)$$

...and to a close approximation, $\epsilon \approx \frac{R_{\text{product}}}{R_{\text{reactant}}} - \frac{R_{\text{product}}}{R_{\text{reactant}}}$

...there is some confusion in the literature, so sometimes you may see $\epsilon \approx \frac{R_{\text{product}}}{R_{\text{reactant}}} - \frac{R_{\text{reactant}}}{R_{\text{product}}}$

Kinetic Isotope Effects- Reaction Mechanisms matter

For an equilibrium fractionation, ϵ is a thermodynamic quantity and does not depend on how the reaction happens. As long as equilibrium is attained, the fractionation is given by alpha regardless of the details of the reaction mechanisms.

For a kinetic process, this is no longer true:

- For an equilibrium process, we can calculate ϵ based on energy differences alone. Because the reaction has proceeded to equilibrium, the PATH or mechanism of the reaction doesn't matter, only the energy differences between the things in equilibrium.
- For a kinetic process, the reaction mechanism matters.
 - 1) If the reaction mechanism changes, the difference in reaction rates between heavy and light isotopes may change.
 - 2) If the amount of back-reaction changes, this can also change the size of the fractionation. Example: Evaporation in low humidity= little back-reaction, whereas at high humidity, the fractionation will approach the equilibrium value. Thus, ϵ depends on the conditions.
 - 3) As we will see with biological fractionation: In a multi-step process, fractionation may depend on the relative rates of the steps.

Example: Reaction of dissolved Se(IV) with reducing agents to form Se(0): 2 different reaction mechanisms:

1. Simple reaction with hydroxylamine- $^{80}\text{Se}/^{76}\text{Se}$ fractionation of -10‰
2. Microbial reaction, with lactate as electron donor (reducing agent): -6‰ to -8‰.

So... for a chemical reaction, if isotopic equilibrium is not achieved:

- a) A kinetic isotope effect is observed.
- b) If back reaction is minor, then the reaction will favor the lighter isotopes.
- c) The size of the effect depends on the reaction mechanism, and can even be close to zero.
- d) If back reaction is substantial, then the fractionation will be different from the "pure kinetic" case and will approach the equilibrium value as back reaction increases (equilibrium is approached).

e) If a series of steps are involved in the overall process, the overall fractionation depends on the relative rates of the steps (more on this later).

f) The kinetic fractionation will tend to decrease with increasing temperature

When is a process a kinetic process vs. an equilibrium process? Here are some guidelines:

- Solid – solid reactions (e.g., Qtz – Feldspar):
 - almost never reach equilibrium at earth surface temperatures because reaction rates are much too slow
 - *may* reach equilibrium at $>100^{\circ}\text{C}$ (esp. if fluids are present)
 - ...e.g., Qtz+ Fsp both precipitated from a common fluid
 - quickly reach equilibrium at magmatic temperatures
- Solids precipitated from aqueous solutions
 - equilibrium often approached because of intimate contact at the surface of the growing precipitate
- Precipitation of water droplets from vapor
 - equilibrium achieved- same reason
- Redox reactions-
 - Equilibrium rarely achieved at earth surface temperatures/ time scales
 - May be in equilibrium at higher T

Rayleigh fractionation- This applies to equilibrium *and* kinetic fract.

Rayleigh fractionation is the jargon we use for a case where a chemical reaction (or process like evaporation) fractionates isotopes AND the reaction products are removed from the system OR the reaction products do not back-react and are “as good as gone” from the system.

Motivation: If a process fractionates isotopes, then there are two things we can look at:

- 1) The isotope ratio of the product of the reaction/process. The product generated at any moment in time will be shifted relative to the reactant at that moment.
- 2) The isotope ratio of the reactant. This will be shifted as isotopes are preferentially consumed by the reaction.

The question is, what equation can we use to relate the progress of some reaction to the isotope data?

Example 1: During evaporation, water vapor leaves the surface of the water and is often taken away by air currents. Perhaps we can use the isotopes in the remaining water (compared to the starting value) to find the amount of evaporation. If we leave a pan of water out to evaporate, how does the delta value change as a function of the amount evaporated?

Example 2. During sulfate reduction, sulfate is consumed and lighter S isotopes are preferentially consumed. How does the $\delta^{34}\text{S}$ value depend on the amount of reduction? In other words, if we measure a certain amount of isotope shift, what must the amount of reduction be?

Our specific question:

Consider a mass of H_2O or SO_4^{2-} that is consumed by a reaction. What is the isotopic composition of the remaining H_2O or SO_4^{2-} as it is consumed by reaction?

- 1) Assume, for simplicity, that there is no addition or loss of these aside from the one reaction we consider. This is similar to saying we have a closed system.
- 2) Also assume that there is no back-reaction. This is like saying the reaction products are removed from the system we're studying.

For two isotopes, A (lighter) and B (heavier):

$$dA = k_A A, \quad dB = k_B B$$

where k 's are rate constants for the forward reaction. Assume no back reaction at all (e.g., dry wind blowing across a lake, so there's essentially no possibility that an evaporated H_2O will get back into the lake).

but $k_B/k_A = \alpha$, and

$$\frac{dB}{dA} = \alpha \frac{B}{A}$$

$$\frac{1}{B} dB = \alpha \frac{1}{A} dA \quad \dots \text{integrate}$$

$$\ln \frac{B}{B_0} = \alpha \ln \frac{A}{A_0}$$

combining: $\frac{B}{B_0} = \left(\frac{A}{A_0}\right)^\alpha$, divide both sides by $\frac{A}{A_0}$

$$\frac{B/A}{B_0/A_0} = \left(\frac{A}{A_0}\right)^{\alpha-1}$$

but $\frac{A}{A_0} = \frac{C}{C_0}$, where C is concentration (all isotopes)

$$\frac{R}{R_0} = f^{\alpha-1}, \text{ where } f \text{ is the fraction of water remaining}$$

In terms of delta notation: $\delta = (\alpha + 1000) f^{\alpha-1} - 1000$

***The equation given in White Ch 27: $\delta = 1000(f^{\alpha-1} - 1)$ applies only when $\alpha = 1$

In a closed system, the reaction product has the following composition:

$$\frac{R_{prod}}{R_0} = \frac{1}{\alpha} \frac{f^\alpha}{f} \quad \text{OR} \quad \delta_{prod} = (\alpha + 1000) \frac{1}{\alpha} \frac{f^\alpha}{f} - 1000$$