Guide Questions:
1) In a general sense why do heavier isotopes of an element behave differently from lighter isotopes?
2) In the gas phase, why do lighter isotopes diffuse faster than heavier isotopes?
3) Why do water molecules bearing lighter isotopes evaporate at a slightly greater rate than those with heavier isotopes?
4) Why does calcite contain more of the heavy oxygen isotope than the water from which it is precipitated?
5) During reduction of sulfate to sulfide, why do lighter isotopes of sulfur have slightly greater reaction rates?
6) How does delta notation help us express small differences between small numbers?
7) How do we define the size of an isotopic fractionation? What variable do we use?
8) Why are lighter isotopes of an element chemically different than heavier isotopes?
   a. How are the bond enthalpies (potential energies) different? What do chemical bond energies depend on, in general?
   b. Can a given bond have any amount of energy, or is it restricted to certain energy levels? What is the relationship between the allowable energies?
   c. What is the zero point energy of chemical bond?
   d. How and why do the zero point energies differ for lighter vs. heavier isotopes?
   e. How do the bond energies of bonds involving lighter isotopes differ from those involving heavier isotopes?
9) In a chemical reaction that involves breakage of bonds, do bonds with lighter isotopes react more readily (i.e., greater reaction rate constant) or less readily than those with heavier isotopes? Why?
10) In a chemical equilibrium, do the heavier isotopes tend to go into the phase with the stronger bonds or those phase with the weaker bonds? Why?
11) How can an isotopic exchange equilibrium be quantified using the tools of thermodynamics and statistical mechanics?
   a. What is the relationship between $\Delta G^0$ for an isotopic exchange equilibrium and $\Delta S^0$?
   b. How does entropy change with increasing temperature (qualitatively) and how does this affect isotopic fractionation?
   c. How does the occupancy of energy levels above the ground state change with increasing temperature (qualitatively)?
   d. Know that partition functions provide a “shortcut” method of expressing the occupancy of energy levels and that they can be related to $\Delta G^0$ and $\Delta S^0$.
   e. Also know that partition functions can be estimated from the vibrational frequencies of bonds and other similar data.
12) What is the general form of the approximate relationship between alpha and T for T<100°C? T<100°C?
Motivation:
- Up to now, we have studied isotopic variation caused by radioactivity.
- Different isotopes of the same element are very nearly the same chemically—
  - same e⁻ config., and thus same bonding attractions.
- However, slight differences exist.
- Thus, chemical reactions may fractionate the isotopes.

**Fractionation** means to partition unevenly, i.e., light isotopes somewhat enriched in one part of the system, while heavier isotopes enriched somewhere else.
- It turns out this effect can be useful in several ways:
  1. Fractionation may be **temperature dependent** and record paleotemperatures.
  2. Different sources of an element or compound may have distinct isotope ratios, and we can thus use the isotopes as an indicator of source or mass balance.
  3. Some reactions have distinctive fractionations (e.g., very large) and their occurrence can be inferred from isotope ratios.
- **Why use isotope ratios** and not some other method?
  - Best paleotemperature indicators:
  - Isotopes are often easier to interpret as source indicators, as compared to chemical concentrations, which are more complex.
  - Isotopes are unique in their ability to record reaction pathways—chemistry holds little.

**Specific examples of what we can do:**
1. **Paleotemperature:** Faure, 1986, fig. 24.9, Calcite-water fractionation, f(T).
2. **Paleotemperature:** - Hoefs, 1987; fig. 38: Oxygen isotopes in ice core from Antarctica.
3. **Water Balance:** Brownlow fig. 2-14 = Map of Hydrogen and Oxygen isotopes in precip.
4. **Alteration of Oceanic Crust:** Brownlow, Fig. 2-23a: Rocks influenced by water.
5. **Sources of Nitrate in groundwater:** Kendall Figure: Oxygen and Nitrogen Isotopes.
6. **Mechanisms for natural gas formation:** Fig. From Whiticar, 1986, methane isotopes.

**Why does mass dependent isotopic fractionation occur?**
Slight chemical differences between isotopes:

**Example 1:** Gaseous diffusion: \( \text{H}_2 \) vs. \( \text{D}_2 \):
- Kinetic energy = \( \frac{1}{2}mv^2 \) (translational component only).
- At any given temperature: average kinetic energies equal for \( \text{H}_2 \) and \( \text{D}_2 \).
- Because \( \text{D}_2 \) is double the mass, its velocity is less by a factor of \( \sqrt{2} \).
- Thus, it diffuse more slowly.

**Example 2** Evaporation \( \text{H}_2^{16}\text{O} \) versus \( \text{H}_2^{18}\text{O} \):
- \( \text{H}_2^{16}\text{O} \) breaks free of the water surface more easily.
- Thus vapor is enriched in the lighter isotopes, depleted in the heavies.
- As evaporation proceeds, remaining water becomes enriched in heavy isotopes.

**Example 3** Precipitation of \( \text{CaCO}_3 \) from solution:
- \( \text{CO}_3^{2-} \) in solution exchanges O atoms with water—equilibrium.
- Crystal “prefers” heavier oxygen isotopes—chemical difference.
- There is a predictable partitioning of isotopes in this case.

**Example 4** Microbial reduction of \( \text{SO}_4^{2-} \):
- Sulfate reduction mediated by bacteria—desulfovibrio, e.g.
- Reaction rate slightly higher for lighter isotopes.
- Products enriched in lighter isotopes, reactants enriched in heavier isotopes.
Notation...we use delta notation (why?):

- because $^{18}\text{O}/^{16}\text{O} = 0.002002$, and typical differences are 0.1%, or even smaller:
- thus…$^{18}\text{O}/^{16}\text{O} = 0.0020004$ vs. $0.0020000$- annoying to write out all those decimal places
- We could work with percent differences (for above example, difference is 0.02%; often we can measure ratios to this level of precision or better).
- The community uses per mil differences, 10 times more sensitive than percent differences. This is delta notation:

$$\delta_{\text{sample}} = \frac{\delta_{\text{sample}} - \delta_{\text{std}}}{\delta_{\text{std}}} \times 1,000$$  ...all samples compared to international standard

People often use “big delta” for the difference between two samples:

$$\delta_{\text{sample1}} - \delta_{\text{sample2}}$$

When we develop theoretical models for isotope fractionation, we use alpha:

$$\alpha_{\text{sample1}} = \frac{R_{\text{sample1}}}{R_{\text{sample2}}}$$  this is the ratio of two isotope ratios we are comparing

Because we normally work in delta notation, we need an easy conversion between alpha and delta. For a system where phases 1 and 2 are in isotopic equilibrium:

$$\delta_{\text{sample1}} - \delta_{\text{sample2}} \approx 1000 \ln \alpha$$  (a very close approximation)  OR

$$\delta_{\text{sample1}} - \delta_{\text{sample2}} \approx 1000(\alpha - 1)$$  (a very close approximation)

**Why are different isotopes chemically different?**

- In a classical sense, bond *enthalpies* are the same: Why?
  Answer: They are determined by electronic configurations only, and all isotopes have the same number of protons and thus the same electronic config.
- BUT, effectively, bond *energies* are slightly different because of quantum effects.

Consider the potential energy “well” in the figure below. Note that the well is the same for heavy and light isotopes of an element- it is determined by electron configurations.

Because of quantum effects, the bond or molecule has certain discreet energy levels, and can’t exist with energies other than those levels.

Furthermore, even at absolute zero, there is some fundamental “vibration” energy, called the zero point energy (ZPE); the bond does not settle into the lowest energy point on the curve

Important: The zero-point energies of different isotopes are different! Higher energy levels also differ between heavy and light isotopes.
Lighter isotopes have slightly higher energies than heavier ones!

This can be proven with the tools of quantum mechanics and statistical mechanics-standard fare for a Physical Chemistry course (see brief description below).

First, note that this makes some sense from a classical point of view:
1) Given the same bond strength, the lighter isotopes vibrate faster
   Why? Think of the bond as a spring, and think about how oscillation would be different for a lead weight versus a wooden one.
2) Faster oscillation means higher energy
   Vibration frequencies determine energy levels, and differences between energy levels determine wavelengths of energy radiated or absorbed: \( E = \frac{h}{\lambda} \) where \( h \) is Plack’s constant. If we look at infrared absorption spectra, we observe that lighter isotopes give off higher frequency/shorter wavelength/higher energy photons

This means the bond for a lighter isotope is effectively weaker (i.e., they have less bonding energy and are overcome more easily) because of the quantum effects.

How are these bonding differences manifested in nature?????

1) The kinetic isotope effect: Lighter isotope bonds are more easily broken (next lecture)
   - Example: evaporation- lighter isotopes released more
   - Example: sulfate reduction by bacteria- ;lighter isotopes react faster

2) Equilibrium isotope effects (the rest of this lecture):
   - Example: Exchange of oxygen between H\(_2\)O and CO\(_2\):
     - O’s exchanged back and forth rapidly
     - Over a few hours in the lab, with shaking, and equilibrium is reached where:
       1. The heavier isotopes have partitioned preferentially into the CO\(_2\)
       2. The lighter isotopes have partitioned preferentially into the H\(_2\)O
       3. In thermodynamic terms, the system exchanged oxygen atoms between the two phases until it reached the lowest possible energy state.

Why did the CO\(_2\) end up with a greater proportion of heavier isotopes?
Consider what happens when we have a \(^{16}\)O in a \(^{16}\)CO\(_2\) molecule trade places with an \(^{16}\)O in an \(^{16}\)O in an H\(_2\)O molecule. The C-O bonds in CO\(_2\) have greater bond energies than the H-O bonds in H\(_2\)O. Now...let’s pretend for the moment that all the bonds are at their zero point energies (this would apply only to absolute zero, but the general idea applies to greater temperatures). Importantly, because CO\(_2\) has stronger bonds, the difference in zero point bond energies between \(^{16}\)O\(^2\) and \(^{18}\)O\(^{16}\)O is greater than the difference in bond energies between H\(_2\)^{18}O and H\(_2\)^{16}O. 
So, what is the lowest energy state of the system for this hypothetical case? Note that bond energies are negative, in the sense that greater bond energy means lesser energy for the system (greater stability). It turns out that the lowest energy state is when all the \( ^{18}O \) atoms go into \( CO_2 \) molecules. If this is not clear, you should play a trial and error game where you assign values to the bond strengths (just get the relative size correct, the exact values don’t matter) and see what total energy values you get for various \( ^{18}O/^{16}O \) ratios in the \( H_2O \) and \( CO_2 \).

Reality is different from this hypothetical case in two major ways:  
1) We work at temperatures above absolute zero AND  
2) We need to deal not just with the bond energies, but with entropy as well.  

Entropy (remember entropy?) is a measure of randomness, and random motions of atoms tends to work against the energy differences just discussed above. And at higher T, random motion is greater so isotopic fractionation will tend to decrease as a result.

**Theoretical predictions for isotope exchange equilibria**

The chemical equilibrium that occurs for exchange of isotopes between two phases, like in the example above, can be understood and quantitative predictions with the same tools we use for standard chemical equilibria: Thermodynamics, \( \Delta G \), and equilibrium constants (\( K_{eq} \)).

Write the relevant chemical reaction:

\[
C^{16}O_2 + H_2^{18}O = C^{18}O^{16}O + H_2^{16}O
\]

\( A_1 + B_2 = A_2 + B_1 \) where 1 refers to light isotope, 2 to heavy isotope
Then write the mass action expression:

\[ K_{eq} = \frac{[A_2][B_1]}{[A_1][B_2]} \]

and, thermodynamic analysis tells us we can relate the equilibrium constant to the free energy change:

\[ \Delta G^0 = RT \ln K_{eq} \]

But how can we get at \( \Delta G^0 \)?

The bond energy and entropy differences between isotopic species are fairly systematic, and can be estimated theoretically.

**Approach for very low T (nearing absolute zero):**

1) At very low T, essentially all of the bonds/molecules are in the ground state.
2) Estimate the zero-point (ground state) energies for the species at equilibrium.
3) Calculate \( \Delta G^0 \)
4) Calculate alpha from \( \Delta G^0 \).

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But we work at higher temp’s (e.g., 300-2000 K). More importantly, it is the change in the fractionation as temperature changes that we are most interested in—paleothermometers!!!

--- How does the picture change with increasing T, when energy levels higher than the ground state are occupied???

**Approach:**

1) Find the energies of the allowed states (energy levels).
2) As temperature increases, more and more molecules/bonds occupy the higher energy states. How do we know how many?
3) Use the tools of statistical mechanics and quantum mechanics to find out. For example: The number of molecules in a particular energy level, relative to the ground state is given by:

\[ n_i = n_0 e^{-\frac{E_i}{RT}} \]

where \( n_0 \) is the number in the ground state (this version is used when E is given in energy per mole; see White eqn. 26.9 for more complete version)

This function comes from simple models of random exchanges of energy between molecules. Let’s make a simple hypothetical model—let there be three energy levels—10, 20, and 30 kJ/mol.
- Note that $E_0$, the ground state, is not shown here.
- As this system heats up, do all of the molecules jump into a higher energy state at one moment? Of course not.
- The occupancy of higher energy levels gradually increases as $T$ increases.

4) An important tool of physical chemistry, **“partition functions”** can help us sort this out.

The partition function, $q$, is defined by: 

$$q = \sum_i e^{-E_i/kT}$$

where $i$ denotes a particular energy level. This is just a summation of the occupancies of all the levels (Note: White includes an additional factor, $g$, in case there are multiple states at the same energy).

Partition functions have the following powerful properties:

a) They express the average energy as a function of temperature and can thus be used to get equilibrium constants.

b) They have been studied well and ways have been found to relate them to things that we know about molecules:

i) Masses- which control translational energy (gases only)

ii) Moments of inertia- which control rotational energy (gases and liquids only)

iii) Vibrational frequencies- which reveal bond vibration energies

c) It turns out that, because isotopic species (e.g., C$^{16}$O vs. C$^{18}$O) are very similar in many ways, approximations can be made to simplify the partition functions to manageable equations.

5) Once we have expressions for the energy, we can then calculate $\Delta G^0$. Actually, as you will see below, we can short-cut right to equilibrium constants without getting $\Delta G^0$.

**How can this actually be done?**

**Example:** From White, 2000: CO in equilib. with O$_2$: Both gases.
\[ C^{16}O+^{18}O^{16}O = C^{18}O+^{16}O^{16}O \]

\[ K_{eq.} = \frac{\left[ C^{18}O \right]^{16}O^{16}O}{C^{16}O \left[ ^{18}O^{16}O \right]} \]

\[ K_{eq.} = \frac{q_{C^{18}O}q_{^{18}O^{16}O}}{q_{C^{16}O}q_{^{16}O^{16}O}} \]

\[ q_{tot} = q_{\text{trans}}q_{\text{rot}}q_{\text{vibr}}. \]

\[ K_{eq.} = K_{\text{trans}}K_{\text{rot}}K_{\text{vibr}}. \]

\[ K_{\text{trans}} = \frac{\left[ \frac{M_{C^{18}O}}{M_{C^{16}O}} \right]^{1/2}}{M_{C^{16}O}M_{^{18}O^{16}O}} = 1.0126 \]

\[ K_{\text{rot}} = \frac{I_{^{18}O^{16}O}}{2I_{^{16}O^{18}O}} \]

\[ I = \frac{m_1m_2}{m_1 + m_2} = 1/2 \times 0.9916 \]

\[ K_{\text{vibr}} = \frac{\hbar}{2kT} \left[ \left\{ \Omega_{^{18}O} \Omega_{C^{18}O} \right\} \cdot \left\{ \Omega_{^{16}O} \Omega_{C^{18}O} \right\} \right] = 1.0199 \]

- for T = 300 K
- q’s are partition coefficients
- M is the molecular mass
- I is the moment of rotational inertia, m’s are atomic masses
- \( \Omega \) ("nu") is vibrational frequency, h is Planck’s constant, k is Boltzmann’s constant

\[ \Omega = 2K = 2 \times 1.0126 \times 1/2 \times 0.9916 \times 1.0199 \]

\[ \Omega \approx 1000(\Omega - 1) = 19.9 \text{‰} \]

The reason for \( \Omega = 2K \) above: there are two oxygens in O₂.

But, you may ask, “Where do those expressions for \( K_{\text{trans}} \), \( K_{\text{rot}} \), and \( K_{\text{vibr}} \) come from and how can I use them?” They were worked out long ago and reflect some underlying systematics in the ways that energy exists in moving, rotating, and vibrating objects.

- The translational and rotational K’s are derived from the physics of moving and rotating bodies. All you need to do is plug in masses, etc.
- The vibrational K uses a “harmonic” (i.e., spring model) approximation to estimate bond energy levels when vibrational frequencies are known. Vibrational frequencies can be measured using Infrared spectroscopy, which is sensitive to bond vibration energies.

The Bottom Line: What you need to know…

A) Isotopic fractionation arises from the fact that vibrational energies of bonds, and translational and rotational energies of molecules, depend on the masses of the isotopes involved.

B) Vibrational energy (dominant for solids, maybe liquids too) differences caused by isotope differences can be understood to some extent by thinking about frequencies of vibrations.
C) Isotopic equilibria can be described by mass action expressions, equilibrium constants, and $\Delta G$’s just like other types of chemical reactions. The equilibrium constants are also fractionation factors.

D) A quantitative understanding of how equilibrium isotopic fractionation factors change as a function of temperature can be gained through the use of partition functions. The resulting models are approximate, and thus the calculations serve as a semi-quantitative guide to interpret experimental data.

The theory gives us some general rules of thumb, such as:

1) **The heavy isotope partitions preferentially into sites where the element is most strongly bound.** This comes from the vibrational term, where the difference in frequency (and thus difference in energy) between the isotopic species appears:

$$K_{\text{vibr}} = 1 + \frac{\hbar}{2kT} \left[ \frac{\Delta C^{13}O \Delta C^{15}O}{\Delta C^{16}O \Delta C^{18}O} \right]$$

The compound with the greater bond energy (and thus higher frequency) will generally have greater difference between isotopes. In the case above, greater $K$ means greater alpha, which means CO is enriched in heavy isotope relative to O$_2$.

2) **Isotopic fractionation generally decreases with increasing temperature.**

From the partition coefficients analysis, the following have been worked out:

$$\ln a = A/T^2 + B$$

is often used to model temperature dependence above 100°C

$$\ln a = A/T + B$$

is often used to model temperature dependence below 100°C

For example, you often get a linear plot of laboratory measurements of isotopic fractionation (in per mil) vs. $1/T$ for temperatures below 100°C.

In some cases, however, isotopic fractionations can have maxima, minima, and “crossovers” as a function of T (see Valley and Cole, Ch. 1, Fig. 4). So we cannot use these rules of thumb without experimental data or detailed calculations.

Also: Isotopic fractionation does not depend strongly on pressure, at pressures relevant in the crust.