

Geol. 656 Isotope Geochemistry

Lecture 19

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STABLE ISOTOPE THEORY: EQUILIBRIUM FRACTIONATION

INTRODUCTION

Stable isotope geochemistry is concerned with variations of the isotopic compositions of light elements arising from chemical fractionations rather than nuclear processes. The elements most commonly studied are H, Li, B, C, N, O, Si, S and Cl. Of these, O, H, C, and S are by far the most important. These elements have several common characteristics:

- They have low atomic mass.
- The relative mass difference between the isotopes is large.
- They form bonds with a high degree of covalent character.
- The elements exist in more than one oxidation state (C, N, and S), form a wide variety of compounds (O), or are important constituents of naturally-occurring solids and fluids.
- The abundance of the rare isotope is sufficiently high (generally at least tenths of a percent) to facilitate analysis.

It was once thought that elements not meeting these criteria would not show measurable variation in isotopic composition. However, as new techniques offering greater sensitivity and higher precision have become available (particularly use of the MC-ICP-MS), geochemists have begun to explore isotopic variations of metals such as Mg, Ca, Ti, Cr, Fe, Zn, Cu, Ge, Mo, Tl, and Pb. The isotopic variations observed in these metals have generally been quite small, except in materials affected or produced by biological processes, where fractionations are a little larger, but still smaller than the former group of elements. Nevertheless, some geologically useful information has been obtained from isotopic study of these metals and exploration of their isotope geochemistry continues.

Stable isotopes can be applied to a variety of problems. One of the most common is geothermometry. This use derives from the extent of isotopic fractionation varying inversely with temperature: fractionations are large at low temperature and small at high temperature. Another application is process identification. For instance, plants that produce 'C₄' hydrocarbon chains (that is, hydrocarbon chains 4 carbons long) as their primary photosynthetic products fractionate carbon differently than to plants that produce 'C₃' chains. This fractionation is retained up the food chain. This allows us to draw some inferences about the diet of fossil mammals from the stable isotope ratios in their bones. Sometimes stable isotopes are used as 'tracers' much as radiogenic isotopes are. So, for example, we can use oxygen isotope ratios in igneous rocks to determine whether they have assimilated crustal material.

NOTATION AND DEFINITIONS

The δ Notation

Variations in stable isotope ratios are typically in the parts per thousand range and hence are generally reported as *permil variations*, δ , from some standard. Oxygen isotope fractionations are generally reported in permil deviations from SMOW (standard mean ocean water):

$$\delta^{18}\text{O} = \left[\frac{(\text{}^{18}\text{O}/\text{}^{16}\text{O})_{\text{sam}} - (\text{}^{18}\text{O}/\text{}^{16}\text{O})_{\text{SMOW}}}{(\text{}^{18}\text{O}/\text{}^{16}\text{O})_{\text{SMOW}}} \right] \times 10^3 \quad 19.1$$

The same formula is used to report other stable isotope ratios. Hydrogen isotope ratios, δD , are reported relative to SMOW, carbon isotope ratios relative to Pee Dee Belemite carbonate (PDB), nitrogen isotope ratios relative to atmospheric nitrogen, and sulfur isotope ratios relative to troilite in the Canyon Diablo iron meteorite. Cl isotopes are also reported relative to seawater; Li and B are reported relative to NBS (which has now become NIST: National Institute of Standards and Technology) standards.

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Table 19.1. Isotope Ratios of Stable Isotopes

Element	Notation	Ratio	Standard	Absolute Ratio
Hydrogen	δD	D/H ($^2H/^1H$)	SMOW	1.557×10^{-4}
Lithium	$\delta ^6Li$	$^6Li/^7Li$	NBS L-SVEC	0.08306
Boron	$\delta ^{11}B$	$^{11}B/^{10}B$	NBS 951	4.044
Carbon	$\delta ^{13}C$	$^{13}C/^{12}C$	PDB	1.122×10^{-2}
Nitrogen	$\delta ^{15}N$	$^{15}N/^{14}N$	atmosphere	3.613×10^{-3}
Oxygen	$\delta ^{18}O$	$^{18}O/^{16}O$	SMOW, PDB	2.0052×10^{-3}
	$\delta ^{17}O$	$^{17}O/^{16}O$	SMOW	3.76×10^{-4}
Chlorine	$\delta ^{37}Cl$	$^{37}Cl/^{35}Cl$	seawater	~ 0.31978
Sulfur	$\delta ^{34}S$	$^{34}S/^{32}S$	CDT	4.43×10^{-2}

Unfortunately, a dual standard has developed for reporting O isotopes. Isotope ratios of carbonates are reported relative to the PDB carbonate standard. This value is related to SMOW by:

$$\delta^{18}O_{PDB} = 1.03086\delta^{18}O_{SMOW} + 30.86 \quad 19.2$$

Table 19.1 lists the values for standards used in stable isotope analysis.

The Fractionation Factor

An important parameter in stable isotope geochemistry is the *fractionation factor*, α . It is defined as:

$$\alpha_{A-B} \equiv \frac{R_A}{R_B} \quad 19.3$$

where R_A and R_B are the isotope ratios of two phases, A and B.

The fractionation of isotopes between two phases is often also reported as $\Delta_{A-B} = \delta_A - \delta_B$. The relationship between Δ and α is:

$$\Delta \approx (\alpha - 1)10^3 \quad \text{or} \quad \Delta \approx 10^3 \ln \alpha \quad 19.4$$

We derive it as follows. Rearranging equ. 19.1, we have:

$$R_A = (\delta_A + 10^3)R_{STD}/10^3 \quad 19.5$$

where R denotes an isotope ratio. Thus α may be expressed as:

$$\alpha = \frac{(\delta_A + 10^3)R_{STD}/10^3}{(\delta_B + 10^3)R_{STD}/10^3} = \frac{(\delta_A + 10^3)}{(\delta_B + 10^3)} \quad 19.6$$

Subtracting 1 from each side and rearranging, and since δ is generally $\ll 10^3$, we obtain:

$$\alpha - 1 = \frac{(\delta_A - \delta_B)}{(\delta_B + 10^3)} \approx \frac{(\delta_A - \delta_B)}{10^3} = \Delta \times 10^{-3} \quad 19.7$$

The second equation in 19.4 results from the approximation that for $x \approx 1$, $\ln x \approx 1 - x$. As we will see, α is related to the equilibrium constant of thermodynamics by

$$\alpha_{A-B} = (K/K_\infty)^{1/n} \quad 19.8$$

where n is the number of atoms exchanged, K_∞ is the equilibrium constant at infinite temperature, and K is the equilibrium constant is written in the usual way (except that concentrations are used rather than activities because the ratios of the activity coefficients are equal to 1, i.e., there are no isotopic effects on the activity coefficient).

THEORY OF ISOTOPIC FRACTIONATIONS

Isotope fractionation can originate from both *kinetic* effects and *equilibrium* effects. The former might be intuitively expected (since for example, we can readily understand that a lighter isotope will diffuse

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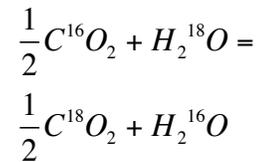
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faster than a heavier one), but the latter may be somewhat surprising. After all, we have been taught that oxygen is oxygen, and its properties are dictated by its electronic structure. In the following sections, we will see that quantum mechanics predicts that mass affects the strength of chemical bonds and the vibrational, rotational, and translational motions of atoms. These quantum mechanical effects predict the small differences in the chemical properties of isotopes quite accurately. We shall now consider the manner in which isotopic fractionations arise.

The electronic structures of all isotopes of an element are identical and since the electronic structure governs chemical properties, these properties are generally identical as well. Nevertheless, small differences in chemical behavior arise when this behavior depends on the frequencies of atomic and molecular vibrations. The energy of a molecule can be described in terms of several components: electronic, nuclear spin, translational, rotational and vibrational. The first two terms are negligible and play no role in isotopic fractionations. The last three terms are the modes of motion available to a molecule and are the cause of differences in chemical behavior among isotopes of the same element. Of the three, vibration motion plays the most important role in isotopic fractionations. Translational and rotational motion can be described by classical mechanics, but an adequate description of vibrational motions of atoms in a lattice or molecule requires the application of quantum theory. As we shall see, *temperature-dependent equilibrium isotope fractionations arise from quantum mechanical effects on vibrational motions*. These effects are, as one might expect, generally small. For example, the equilibrium constant for the reaction:

for the reaction:



is only about 1.04 at 25°C.

Figure 19.1 is a plot of the potential energy of a diatomic molecule as a function of distance between the two atoms. This plot looks broadly similar to one we might construct for two masses connected by a spring. When the distance between masses is small, the spring is compressed, and the potential energy of the system correspondingly high. At great distances between the masses, the spring is stretched and the energy of the system also high. At some intermediate distance, there is no stress on the spring, and the potential energy of the system is at a minimum (energy would be nevertheless be conserved because kinetic energy is at a maximum when potential energy is at a mini-

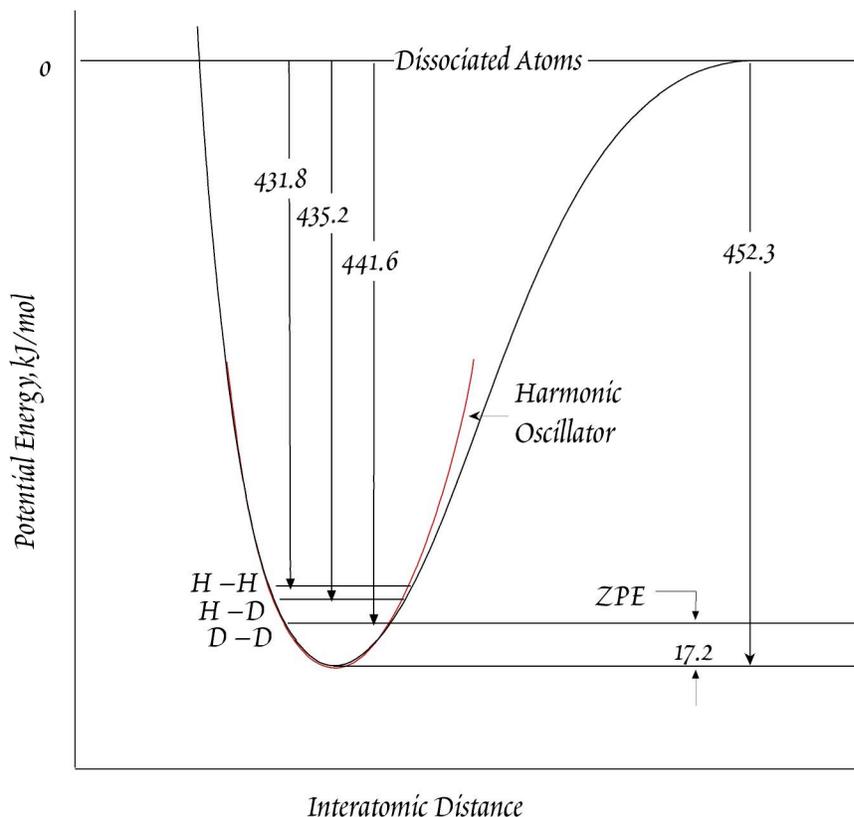


Figure 19.1. Energy-level diagram for the hydrogen atom. Fundamental vibration frequencies are 4405 cm⁻¹ for H₂, 3817 cm⁻¹ for HD, and 3119 cm⁻¹ for D₂. The zero-point energy of H₂ is greater than that for HD which is greater than that for D₂. From O'Neil (1986).

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mum). The diatomic oscillator, for example consisting of a Na and a Cl ion, works in an analogous way. At small interatomic distances, the electron clouds repel each other (the atoms are compressed); at large distances, the atoms are attracted to each other by the net charge on atoms. At intermediate distances, the potential energy is at a minimum. The energy and the distance over which the atoms vibrate are related to temperature.

In quantum theory, a diatomic oscillator cannot assume just any energy: only discrete energy levels may be occupied. The permissible energy levels, as we shall see, depend on mass. Quantum theory also tells us that even at absolute 0 the atoms will vibrate at a ground frequency ν_0 . The system will have energy of $1/2 h\nu_0$, where h is Planck's constant. This energy level is called the *Zero Point Energy (ZPE)*. Its energy depends the electronic arrangements, the nuclear charges, and the positions of the atoms in the molecule or lattice, all of which will be identical for isotopes of the same element. However, the energy also depends on the masses of the atoms involved, and thus will be different for different isotopes. *The vibrational energy level for a given quantum number will be lower for a bond involving a heavier isotope of an element, as suggested in Figure 19.1. Thus bonds involving heavier isotopes will be stronger.* If a system consists of two possible atomic sites with different bond energies and two isotopes of an element available to fill those sites, *the energy of the system is minimized when the heavy isotope occupies the site with the stronger bond.* Thus at equilibrium, the heavy isotope will tend to occupy the site with the stronger bond. This, in brief, is why equilibrium fractionations arise. Because bonds involving lighter isotopes are weaker and more readily broken, the lighter isotopes of an element participate more readily in a given chemical reaction. If the reaction fails to go to completion, which is often the case, this tendency gives rise to kinetic fractionations of isotopes. There are other causes of kinetic fractionations as well, and will consider them in due course. We will now consider in greater detail the basis for equilibrium fractionation, and see that they can be predicted from statistical mechanics.

Equilibrium Fractionations

Urey (1947) and Bigeleisen and Mayer (1947) pointed out the possibility of calculating the equilibrium constant for isotopic exchange reactions from the *partition function*, q , of statistical mechanics. In the following discussion, bear in mind that quantum theory states that only discrete energies are available to an atom or molecule.

At equilibrium, the ratio of the number of molecules having internal energy E_i to the number having the zero point energy E_0 is:

$$\frac{n_i}{n_0} = g_i e^{-E_i/kT} \quad 19.9$$

where n_0 is the number of molecules with ground-state or zero point energy, n_i is the number of molecules with energy E_i and k is Boltzmann's constant, T is the thermodynamic, or absolute, temperature, and g is a statistical weight factor used to account for possible degenerate energy levels* (g is equal to the number of states having energy E_i). The average energy (per molecule) in a system is given by the *Boltzmann distribution function*, which is just the sum of the energy of all possible states times the number of particles in that state divided by the number of particles in those states:

$$\bar{E} = \frac{\sum_i n_i E_i}{\sum_i n_i} = \frac{\sum_i g_i E_i e^{-E_i/kT}}{\sum_i g_i e^{-E_i/kT}} \quad 19.10$$

The *partition function*, q , is the denominator of this equation:

* The energy level is said to be 'degenerate' if two or more states have the same energy level E_i .

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$$q = \sum g_i e^{-E_i / kT} \quad 19.11$$

Substituting 19.11 into 19.10, we can rewrite 19.10 in terms of the partial derivatives of q :

$$E = kT^2 \frac{\partial \ln q}{\partial T} \quad 19.12$$

We will return to these equations shortly, but first let's see how all this relates to some parameters that are more familiar from thermodynamics and physical chemistry. It can also be shown (but we won't) from statistical mechanics that *entropy*[†] is related to energy and q by

$$S = \frac{U}{T} R \ln q \quad 19.13$$

Where R is the ideal gas constant and U is the internal energy of a system. We can rearrange this as:

$$U - TS = -R \ln q \quad 19.14$$

And for the entropy and energy changes of a reaction, we have:

$$\Delta U - T \Delta S = -R \ln \prod q_n^{\xi} \quad 19.15$$

where ξ in this case is the stoichiometric coefficient. In this notation, the stoichiometric coefficient is taken to have a negative sign for reactants (left side of reaction) and a positive sign for products (right side of reaction). The left hand side of this equation is simply the Gibbs Free Energy change of reaction under conditions of constant volume (as would be the case for an isotopic exchange reaction), so that

$$\Delta G = -R \ln \prod q_n^{\xi} \quad 19.16$$

The Gibbs Free Energy change is related to the equilibrium constant, K , by:

$$\Delta G = -RT \ln K \quad 19.17$$

so the equilibrium constant for an isotope exchange reaction is related to the partition function as:

$$K = \prod q_n^{\xi} \quad 19.18$$

For example, in the reaction involving exchange of ¹⁸O between H₂O and CO₂, the equilibrium constant is simply:

$$K = \frac{q_{C^{16}O_2}^{1/2} q_{H_2^{18}O}}{q_{C^{18}O_2}^{1/2} q_{H_2^{16}O}} \quad 19.19$$

The point of all this is simply that: *the usefulness of the partition function is that it can be calculated from quantum mechanics, and from it we can calculate equilibrium fractionations of isotopes.*

The partition function can be written as:

$$q_{total} = q_{tr} q_{vib} q_{rot} \quad 19.20$$

i.e., the product of the translational, rotational and vibrational partition functions. It is convenient to treat these three modes of motion separately. Let's now do so.

[†] Entropy is defined in the second law of thermodynamics, which states:

$$dS = \frac{dQ_{rev}}{T}$$

where Q_{rev} is heat gained by a system in a reversible process. Entropy can be thought of as a measure of the randomness of a system.

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Translational Partition Function

Writing a version of equation 19.11 for translational energy, q_{trans} is expressed as:

$$q_{trans} = \sum_i g_{tr,i} e^{-E_{tr,i}/kT} \quad 19.21$$

Now all that remains is to find an expression for translational energy and a way to do the summation. At temperatures above about 2 K, translational energy levels are so closely spaced that they essentially form a continuum, so we can use a classical mechanical approach to calculating the energy. The quantum translational energy of a particle in a cubical box is given by:

$$E_{trans} = \frac{n^2 h^2}{8md^2} \quad 19.22$$

where n is the quantum energy level, h is Planck's constant, d is the length of the side of the cube, and m is mass of the particle. Substituting 19.22 into 19.21 and integrating:

$$q_{trans} = \int_0^\infty e^{-n^2 h^2 / 8md^2 kT} dn = \frac{(2\pi mkT)^{1/2}}{h} d \quad 19.23$$

gives an expression for q_{trans} for each dimension. The total three-dimensional translational partition function is then:

$$q_{trans} = \frac{(2\pi mkT)^{3/2}}{h} V \quad 19.24$$

where V is volume and is equal to d^3 . (It may seem odd that the volume should enter into the calculation, but since it is the ratio of partition functions that are important in equations such as 19.19, all terms in 19.24 except mass will eventually cancel.) If translation motion were the only component of energy, the equilibrium constant for exchange of isotopes would be simply the ratio of the molecular weights raised to the $3/2$ power. If we define the translational contribution to the equilibrium constant as K_{tr} as:

$$K_{tr} = \prod q_{tr}^{\xi} \quad 19.25$$

K_{tr} reduces to the product of the molecular masses raised to the stoichiometric coefficient times three-halves:

$$K_{tr} = \prod_i M_i^{\xi_i 3/2} \quad 19.26$$

where we have replace m with M , the molecular mass. Thus the translational contribution to the partition function and fractionation factor is independent of temperature.

Rotational Partition Function

The allowed quantum *rotational* energy states are:

$$E_{rot} = \frac{j(j+1)h^2}{8\pi^2 I} \quad 19.27$$

where j is the rotational quantum number and I is the moment of inertia. For a diatomic molecule, $I = \mu d^2$, where d is the bond length, m_i is the atomic mass of atom i , and μ is reduced mass:

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad 19.28$$

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A diatomic molecule will have two rotational axes, one along the bond axis, the other perpendicular to it. Hence in a diatomic molecule, j quanta of energy may be distributed $2j+1$ ways because there are two possibilities for every value of j except $j = 0$, for which there is only one possible way. The statistical weight factor is therefore $2j + 1$. Hence:

$$q_{rot} = \sum_j (2j+1) e^{j(j+1)h^2/8\pi^2 I_i kT} \quad 19.29$$

Again the spacing between energy levels is relatively small (except for hydrogen) and 19.29 may be evaluated as an integral. For a diatomic molecule, the partition function for rotation is given by:

$$q_{rot} = \frac{8\pi^2 I kT}{\sigma h^2} \quad 19.30$$

where σ is a symmetry factor. It is 1 for a heteronuclear diatomic molecule (such as CO or $^{18}\text{O}^{16}\text{O}$), and 2 for a homonuclear diatomic molecule such as $^{16}\text{O}_2$. Equ. 19.30 also holds for linear polyatomic molecules with the symmetry factor equal to 2 if the molecule has a plane of symmetry (e.g., CO_2) and 1 if it does not. For non-linear polyatomic molecules, the partition function is given by:

$$q_{rot} = \frac{8\pi^2 (8\pi^2 ABC)^{1/2} (kT)^{3/2}}{\sigma h^3} \quad 19.31$$

where A, B, and C are the principal moments of inertia of the molecule and σ is equal to the number of equivalent ways of orienting the molecule in space (e.g., 2 for H_2O , 12 for CH_4). In calculating the rotational contribution to the partition function and equilibrium constant, all terms cancel except for moment of inertia and the symmetry factor, and the contribution of rotational motion to isotope fractionation is also independent of temperature. For diatomic molecules we may write:

$$K_{rot} = \prod_i \left(\frac{I_i}{\sigma_i} \right)^{\xi} \quad 19.32$$

In general, bond lengths are also independent of the isotope involved, so the moment of inertia term may be replaced by the reduced masses.

Vibrational Partition Function

We will simplify the calculation of the vibrational partition function by treating the diatomic molecule as a harmonic oscillator (as Fig. 19.1 suggests, this is a good approximation in most cases). In this case the quantum energy levels are given by:

$$E_{vib} = \left(n + \frac{1}{2} \right) h\nu \quad 19.33$$

where n is the vibrational quantum number and ν is vibrational frequency. Unlike rotational and vibrational energies, the spacing between vibrational energy levels is large at geologic temperatures, so the partition function cannot be integrated. Instead, it must be summed over all available energy levels. Fortunately, the sum has a simple form: for diatomic molecules the summation is simply equal to:

$$q_{vib} = \frac{e^{-h\nu/2kT}}{1 - e^{-h\nu/2kT}} \quad 19.34$$

For molecules consisting of more than two atoms, there are many vibrational motions possible. In this case, the vibrational partition function is the product of the partition functions for each mode of motion, with the individual partition functions given by 19.34. For a non-linear polyatomic molecule consisting of i atoms and the product is performed over all vibrational modes, ℓ , the partition function is given by:

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$$q_{vib} = \prod_{\ell} \frac{e^{-hv_{\ell}/2kT}}{1 - e^{-hv_{\ell}/2kT}} \quad 19.35$$

(There are $3i-5$ modes of motion for *linear* polyatomic molecules, hence the product is in 19.35 carried out to $3i-5$ for such.)

At room temperature, the exponential term in the denominator approximates to 0, and the denominator therefore approximates to 1, so the relation simplifies to:

$$q_{vib} \cong e^{-hv/2kT} \quad 19.36$$

Thus at low temperature, the vibrational contribution to the equilibrium constant approximates to:

$$K_{vib} = \prod_{\ell} e^{-\xi_{\ell} hv_{\ell}/2kT} \quad 19.37$$

which has an exponential temperature dependence.

The full expression for the equilibrium constant calculated from partition functions for diatomic molecules is then:

$$K = \prod_i (q_i^{tr} q_i^{rot} q_i^{vib})^{\xi_i} = \prod_i \left(M_i^{3/2} \left[\frac{I_i}{\sigma_i} \right] \frac{e^{-\xi_i hv_i/2kT}}{1 - e^{-\xi_i hv_i/2kT}} \right)^{\xi_i} \quad 19.38$$

By use of the Teller-Redlich spectroscopic theorem*, this equation simplifies to:

$$K = \prod_i \left(\frac{1}{\sigma_i} m_i^{3/2} \frac{e^{-U/2}}{1 - e^{-U}} \right)^{\xi_i} \quad 19.39$$

where m is the mass of the isotope exchanged and U is defined as:

$$U = \frac{hv}{kT} = \frac{hc\omega}{kT} \quad 19.40$$

and ω is the vibrational wave number and c the speed of light.

Example of fractionation factor calculated from partition functions

To illustrate the use of partition functions in calculating theoretical fractionation factors, we will do the calculation for a very simple reaction: the exchange of ^{18}O and ^{16}O between O_2 and CO :



The choice of diatomic molecules greatly simplifies the equations. Choosing even a slightly more complex model, such as CO_2 would complicate the calculation because there are more vibrational modes possible. Chacko et al. (2001) provide an example of the calculation for more complex molecules such as CO_2 .

The equilibrium constant for our reaction is:

$$K = \frac{[{}^{16}\text{O}_2][\text{C}^{18}\text{O}]}{[{}^{18}\text{O}^{16}\text{O}][\text{C}^{16}\text{O}]} \quad 19.42$$

* The Teller-Redlich Theorem relates the products of the frequencies for each symmetry type of the two isotopes to the ratios of their masses and moments of inertia:

$$\left(\frac{m_2}{m_1} \right)^{3/2} \frac{I_1}{I_2} \left(\frac{M_1}{M_2} \right)^{3/2} = \frac{U_1}{U_2}$$

where m is the isotope mass and M is the molecular mass. We need not concern ourselves with its details.

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where we are using the brackets in the unusual chemical sense to denote concentration. We can use concentrations rather than activities or fugacities because the activity coefficient of a phase is independent of its isotopic compositions. The fractionation factor, α , is defined as:

$$\alpha = \frac{(^{18}\text{O}/^{16}\text{O})_{\text{CO}}}{(^{18}\text{O}/^{16}\text{O})_{\text{O}_2}} \quad 19.43$$

We must also consider the exchange reaction: $^{18}\text{O}^{18}\text{O} + ^{16}\text{O}^{16}\text{O} = 2^{16}\text{O}^{18}\text{O}$ for which we can write a second equilibrium constant, K_2 . It turns out that when both reactions are considered, $\alpha \approx 2K$. The reason for this is as follows. The isotope ratio in molecular oxygen is related to the concentration of the 2 molecular species as:

$$\left(\frac{^{18}\text{O}}{^{16}\text{O}}\right)_{\text{O}_2} = \frac{[^{18}\text{O}^{16}\text{O}]}{[^{18}\text{O}^{16}\text{O}] + 2[^{16}\text{O}_2]} \quad 19.44$$

($^{16}\text{O}_2$ has 2 ^{16}O atoms, so it must be counted twice) whereas the ratio in CO is simply:

$$\left(\frac{^{18}\text{O}}{^{16}\text{O}}\right)_{\text{CO}} = \frac{[\text{C}^{18}\text{O}]}{[\text{C}^{16}\text{O}]} \quad 19.45$$

Letting the isotope ratio equal R , we can solve 19.44 for $[^{18}\text{O}^{16}\text{O}]$:

$$[^{18}\text{O}/^{16}\text{O}] = 2 \frac{[^{16}\text{O}_2]R_{\text{O}_2}}{1 - R_{\text{O}_2}} \quad 19.46$$

and substitute it into 19.42:
$$K = \frac{(1 - R_{\text{O}_2})[\text{C}^{18}\text{O}]}{2R_{\text{O}_2}[\text{C}^{16}\text{O}]} = 2 \frac{(1 - R_{\text{O}_2})R_{\text{CO}}}{2R_{\text{O}_2}} \quad 19.47$$

Since the isotope ratio is a small number, the term $(1 - R) \approx 1$, so that:

$$K \approx 2 \frac{R_{\text{CO}}}{2R_{\text{O}_2}} = \frac{\alpha}{2} \quad 19.48$$

We can calculate K from the partition functions as:

$$K = \frac{q_{^{16}\text{O}_2} q_{\text{C}^{18}\text{O}}}{q_{^{18}\text{O}^{16}\text{O}} q_{\text{C}^{16}\text{O}}} \quad 19.49$$

where each partition function is the product of the translational, rotational, and vibrational partition functions. However, we will proceed by calculating an equilibrium constant for each mode of motion. The total equilibrium constant will then be the product of all three partial equilibrium constants. For translational motion, we noted the ratio of partition functions reduces to the ratio of molecular masses raised to the 3/2 power. Hence:

$$K_{tr} = \frac{q_{^{16}\text{O}_2} q_{\text{C}^{18}\text{O}}}{q_{^{18}\text{O}^{16}\text{O}} q_{\text{C}^{16}\text{O}}} = \left(\frac{M_{^{16}\text{O}_2} M_{\text{C}^{18}\text{O}}}{M_{^{18}\text{O}^{16}\text{O}} M_{\text{C}^{16}\text{O}}} \right)^{3/2} = \left(\frac{32 \times 30}{34 \times 28} \right)^{3/2} = 1.0126 \quad 19.50$$

We find that CO would be 12.6‰ richer in ^{18}O if translational motions were the only modes of energy available.

In the expression for the ratio of rotational partition functions, all terms cancel except the moment of inertia and the symmetry factors. The symmetry factor is 1 for all the molecules involved except $^{16}\text{O}_2$. In this case, the terms for bond length also cancel, so the expression involves only the reduced masses. So the expression for the rotational equilibrium constant becomes:

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$$K_{rot} = \frac{q_{16O_2} q_{C^{18}O}}{q_{18O^{16}O} q_{C^{16}O}} = \left(\frac{I_{16O_2} I_{C^{18}O}}{2 I_{18O^{16}O} I_{C^{16}O}} \right) = \frac{1}{2} \left(\frac{16 \times 16}{18 \times 16} \times \frac{12 \times 18}{12 \times 16} \right) = \frac{0.9916}{2} \quad 19.51$$

(ignore the 1/2, it will cancel out later). If rotation were the only mode of motion, CO would be 8% poorer in ^{18}O .

The vibrational equilibrium constant may be expressed as:

$$K_{vib} = \frac{q_{16O_2} q_{C^{18}O}}{q_{18O^{16}O} q_{C^{16}O}} = e^{\frac{-h(\nu_{16O_2} + \nu_{C^{18}O} - \nu_{C^{16}O} - \nu_{18O^{16}O})}{2KT}} \quad 19.52$$

Since we expect the difference in vibrational frequencies to be quite small, we may make the approximation $e^x = x + 1$. Hence:

$$K_{vib} \cong 1 + \frac{h}{2KT} \left[\left\{ \nu_{C^{16}O} - \nu_{C^{18}O} \right\} - \left\{ \nu_{16O_2} - \nu_{18O^{16}O} \right\} \right] \quad 19.53$$

Let's make the simplification that the vibration frequencies are related to reduced mass as in a simple Hooke's Law harmonic oscillator:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad 19.54$$

where k is the forcing constant, and depends on the nature of the bond, and will be the same for all isotopes of an element. In this case, we may write:

$$\nu_{C^{18}O} = \nu_{C^{16}O} \sqrt{\frac{\mu_{C^{16}O}}{\mu_{C^{18}O}}} = \nu_{C^{16}O} \sqrt{\frac{6.857}{7.2}} = 0.976 \nu_{C^{16}O} \quad 19.55$$

A similar expression may be written relating the vibrational frequencies of the oxygen molecule:

$$\nu_{16O^{18}O} = 0.9718 \nu_{16O_2}$$

Substituting these expressions in the equilibrium constant expression, we have:

$$K_{vib} = 1 + \frac{h}{2kT} \left(\nu_{C^{16}O} [1 - 0.976] - \nu_{16O_2} [1 - 0.9718] \right)$$

The measured vibrational frequencies of CO and O₂ are $6.50 \times 10^{13} \text{ sec}^{-1}$ and $4.74 \times 10^{13} \text{ sec}^{-1}$. Substituting these values and values for the Planck and Boltzmann constants, we obtain:

$$K_{vib} = 1 + \frac{5.544}{T}$$

At 300 K (room temperature), this evaluates to 1.0185.

We may now write the total equilibrium constant expression as:

$$K = K_{tr} K_{rot} K_{vib} \cong \left(\frac{M_{16O_2} M_{C^{18}O}}{M_{18O^{16}O} M_{C^{16}O}} \right)^{3/2} \left(\frac{\mu_{16O_2} \mu_{C^{18}O}}{2 \mu_{18O^{16}O} \mu_{C^{16}O}} \right) \times \left\{ 1 + \frac{h}{4\pi kT} \left[\left(\sqrt{\frac{k}{\mu_{C^{16}O}}} - \sqrt{\frac{k}{\mu_{C^{18}O}}} \right) - \left(\sqrt{\frac{k}{\mu_{16O_2}}} - \sqrt{\frac{k}{\mu_{18O^{16}O}}} \right) \right] \right\} \quad 19.56$$

Evaluating this at 300 K we have:

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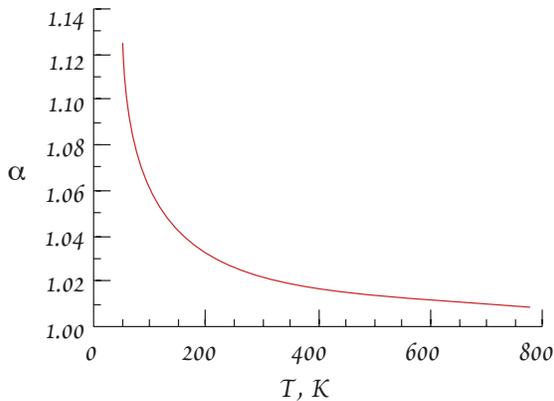


Figure 19.2. Fractionation factor, $\alpha = \frac{(^{18}\text{O}/^{16}\text{O})_{\text{CO}}}{(^{18}\text{O}/^{16}\text{O})_{\text{O}_2}}$, calculated from partition functions as a function of temperature.

$$K = 1.0126 \times \frac{0.9916}{2} \times 1.0185 = \frac{1.023}{2}$$

Since $\alpha = 2K$, the fractionation factor is 1.023 at 300 K and would decrease by about 6 per mil per 100° temperature increase (however, we must bear in mind that our approximations hold only at low temperature). This temperature dependence is illustrated in Figure 19.2. Thus CO would be 23 permil richer in the heavy isotope, ^{18}O , than O_2 . This illustrates an important rule of stable isotope fractionations:

The heavy isotope goes preferentially in the chemical compound in which the element is most strongly bound.

Translational and rotational energy modes are, of course, not available to solids. Thus isotopic fractionations between solids are entirely controlled by the vibrational partition function. In principle, fractionations between coexisting solids could be calculated as we have done above. The task is considerably complicated by the variety of vibrational modes available to a lattice. The lattice may be treated as a large polyatomic molecule having $3N-6$ vibrational modes, where N is the number of atoms in the unit cell. For large N , this approximates to $3N$. Vibrational frequency and heat capacity are closely related because thermal energy in a crystal is stored as vibrational energy of the atoms in the lattice. Einstein and Debye independently treated the problem by assuming the vibrations arise from independent harmonic oscillations. Their models can be used to predict heat capacities in solids.

The vibrational motions available to a lattice may be divided into 'internal' or 'optical' vibrations between individual radicals or atomic groupings within the lattice such as CO_3 , and Si-O . The vibrational frequencies of these groups can be calculated from the Einstein function and can be measured by optical spectroscopy. In addition, there are vibrations of the lattice as a whole, called 'acoustical' vibrations, which can also be measured, but may be calculated from the Debye function. From either calculated or observed vibrational frequencies, partition function ratios may be calculated, which in turn are directly related to the fractionation factor. Generally, the optical modes are the primary contribution to the partition function ratios. For example, for partitioning of ^{18}O between water and quartz, the contribution of the acoustical modes is less than 10%. The ability to calculate fractionation factors is particularly important at low temperatures where reaction rates are quite slow, and experimental determination of fractionation therefore difficult. Figure 19.3 shows the calculated

temperature dependencies of the fractionation of oxygen between water and quartz. From Kawabe (1978).

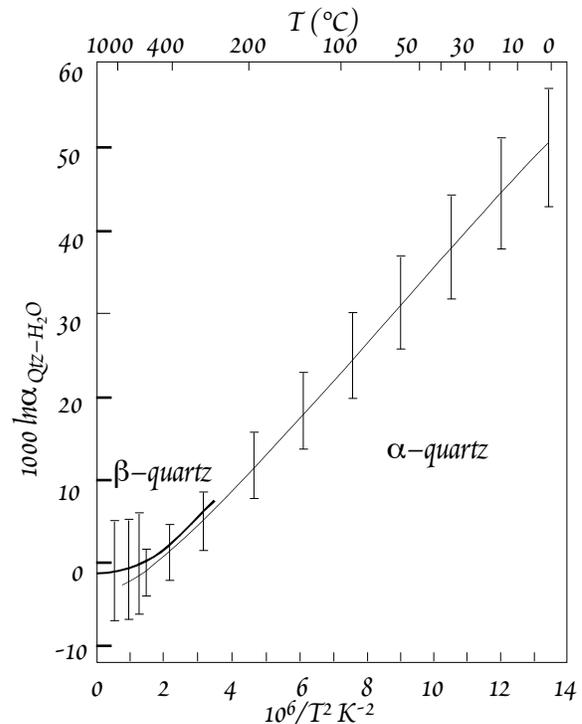


Figure 19.3. Calculated temperature dependencies of the fractionation of oxygen between water and quartz. From Kawabe (1978).

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culated fractionation factor between quartz and water as a function of temperature.

FRACTIONATION OF SEVERAL ISOTOPES

In the example in the previous section we considered only the fractionation between ^{18}O and ^{16}O , and indeed almost all research on oxygen isotope fraction focuses on just these two isotopes. However, a third isotope of oxygen, ^{17}O , exists, although it is an order of magnitude less abundant than ^{18}O (which is two orders of magnitude less abundant than ^{16}O). The reason for this focus is that, based on the theory we have just reviewed, mass fractionation should depend on mass difference. The mass difference between ^{17}O and ^{16}O is half the difference between ^{18}O and ^{16}O , hence we expect the fractionation between ^{17}O and ^{16}O to be half that between ^{18}O and ^{16}O . In the example of fractionation between CO and O_2 in the previous section, it is easy to show from equation 19.56 that through the range of temperatures we expect near the surface of the Earth (or Mars) that the ratio of fractionation factors $\Delta^{17}\text{O}/\Delta^{18}\text{O}$ should be ≈ 0.53 . In the limit of infinite temperature, $\Delta^{17}\text{O}/\Delta^{18}\text{O} \approx 0.52$. The empirically observed ratio for terrestrial fractionation (and also within classes of meteorites) is $\Delta^{17}\text{O}/\Delta^{18}\text{O} \approx 0.52$. Because the fractionation between ^{17}O and ^{16}O bears a simple relationship to that between ^{18}O and ^{16}O , the $^{17}\text{O}/^{16}\text{O}$ ratio is rarely measured. However, as we saw in Lecture 12, not all O isotope variation in solar system materials follows the expected *mass-dependent fractionation*. Furthermore, we saw that there is laboratory evidence that mass-independent fractionation can occur. Mass independent fractionation has subsequently been demonstrated to occur in nature, and indeed may provide important clues to Earth and Solar System processes and history, and we will return to this topic later.

KINETIC FRACTIONATION

Kinetic effects are normally associated with fast, incomplete, or unidirectional processes like evaporation, diffusion and dissociation reactions. As an example, recall that temperature is related to the average kinetic energy. In an ideal gas, the average kinetic energy of all molecules is the same. The kinetic energy is given by:

$$E = \frac{1}{2}mv^2 \quad 19.57$$

Consider two molecules of carbon dioxide, $^{12}\text{C}^{16}\text{O}_2$ and $^{13}\text{C}^{16}\text{O}_2$, in such a gas. If their energies are equal, the ratio of their velocities is $(45/44)^{1/2}$, or 1.011. Thus $^{12}\text{C}^{16}\text{O}_2$ can diffuse 1.1% further in a given amount of time at a given temperature than $^{13}\text{C}^{16}\text{O}_2$. This result, however, is largely limited to ideal gases, i.e., low pressures where collisions between molecules are infrequent and intermolecular forces negligible. For the case of air, where molecular collisions are important, the ratio of the diffusion coefficients of the two CO_2 species is the ratio of the square roots of the reduced masses of CO_2 and air (mean molecular weight 28.8):

$$\frac{D_{^{12}\text{CO}_2}}{D_{^{13}\text{CO}_2}} = \frac{\sqrt{\mu_{^{13}\text{CO}_2}}}{\sqrt{\mu_{^{12}\text{CO}_2}}} = \frac{17.561}{17.406} = 1.0044 \quad 19.58$$

Hence we would predict that gaseous diffusion will lead to only a 4.4‰ fractionation.

In addition, molecules containing the heavy isotope are more stable and have higher dissociation energies than those containing the light isotope. This can be readily seen in Figure 19.4. The energy required to raise the D_2 molecule to the energy where the atoms dissociate is 441.6 kJ/mole, whereas the energy required to dissociate the H_2 molecule is 431.8 kJ/mole. Therefore it is easier to break bonds such as C-H than C-D. Where reactions go to completion, this difference in bonding energy plays no role: isotopic fractionations will be governed by the considerations of equilibrium discussed in the previous lecture. *Where reactions do not achieve equilibrium the lighter isotope will be preferentially concentrated in the reaction products*, because of this effect of the bonds involving light isotopes in the reactants being

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more easily broken. Large kinetic effects are associated with biologically mediated reactions (e.g., bacterial reduction), because such reactions generally do not achieve equilibrium. Thus ^{12}C is enriched in the products of photosynthesis in plants (hydrocarbons) relative to atmospheric CO_2 , and ^{32}S is enriched in H_2S produced by bacterial reduction of sulfate.

We can express this in a more quantitative sense. The rate at which reactions occur is given by:

$$R = Ae^{-E_b/kT} \quad 19.59$$

where A is a constant called the frequency factor and E_b is the barrier energy. Referring to Figure 19.1, the barrier energy is the difference between the dissociation energy, ϵ , and the zero-point energy. The constant A is independent of isotopic composition, thus the ratio of reaction rates between the HD molecule and the H_2 molecule is:

$$\frac{R_D}{R_H} = \frac{e^{-(\epsilon-1/2h\nu_D)/kT}}{e^{-(\epsilon-1/2h\nu_H)/kT}} \quad 19.60$$

or

$$\frac{R_D}{R_H} = e^{(v_H - v_D)h/2kT} \quad 19.61$$

Substituting for the various constants, and using the wavenumbers given in the caption to Figure 19.1 (remembering that $\omega = cv$ where c is the speed of light) the ratio is calculated as 0.24; in other words we expect the H_2 molecule to react four times faster than the HD molecule, a very large difference. For heavier elements, the rate differences are smaller. For example, the same ratio calculated for $^{16}\text{O}_2$ and $^{18}\text{O}^{16}\text{O}$ shows that the ^{16}O will react about 15% faster than the $^{18}\text{O}^{16}\text{O}$ molecule.

The greater translational velocities of lighter molecules also allows them to break through a liquid surface more readily and hence evaporate more quickly than a heavy molecule of the same composition. The transition from liquid to gas in the case of water also involves breaking hydrogen bonds that form between the hydrogen of one molecule and an oxygen of another. This bond is weaker if ^{16}O is involved rather than ^{18}O , and thus is broken more easily, meaning H_2^{16}O is more readily available to transform into the gas phase than H_2^{18}O . Thus water vapor above the ocean typically has $\delta^{18}\text{O}$ around -13 per mil, whereas at equilibrium the vapor should only be about 9 per mil lighter than the liquid.

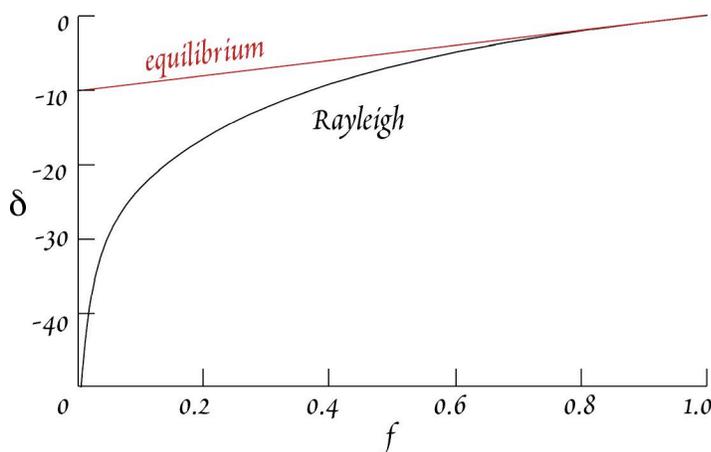


Figure 19.4. Fractionation of isotope ratios during Rayleigh and equilibrium condensation. δ is the per mil difference between the isotopic composition of original vapor and the isotopic composition as a function of f , the fraction of vapor remaining.

Let's explore this example a bit further. An interesting example of a kinetic effect is the fractionation of O isotopes between water and water vapor. This is another example of Rayleigh distillation (or condensation), as is fractional crystallization. Let A be the amount of the species containing the major isotope, H_2^{16}O , and B be the amount of the species containing the minor isotope, H_2^{18}O . The rate at which these species evaporate is proportional to the amount present:

$$dA = k_A A \quad 19.62a$$

$$\text{and } dB = k_B B \quad 19.62b$$

Since the isotopic composition affects the reaction, or evaporation, rate, $k_A \neq k_B$. We'll call this ratio of the rate constants α . Then

$$\frac{dB}{dA} = \alpha \frac{B}{A} \quad 19.63$$

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Rearranging and integrating, we have

$$\ln \frac{B}{B^\circ} = \alpha \ln \frac{A}{A^\circ} \quad \text{or} \quad \frac{B}{B^\circ} = \left(\frac{A}{A^\circ} \right)^\alpha \quad 19.64$$

where A° and B° are the amount of A and B originally present. Dividing both sides by A/A°

$$\frac{B/A}{B^\circ/A^\circ} = \left(\frac{A}{A^\circ} \right)^{\alpha-1} \quad 19.65$$

Since the amount of B makes up only a trace of the total amount of H_2O present, A is essentially equal to the total water present, and A/A° is essentially identical to f , the fraction of the original water remaining. Hence:

$$\frac{B/A}{B^\circ/A^\circ} = f^{\alpha-1} \quad 19.66$$

Subtracting 1 from both sides, we have

$$\frac{B/A - B^\circ/A^\circ}{B^\circ/A^\circ} = f^{\alpha-1} - 1 \quad 19.67$$

Comparing the left side of the equation to 26.1, we see the permil fractionation is given by:

$$\delta = 1000(f^{\alpha-1} - 1) \quad 19.68$$

Of course, the same principle applies when water condenses from vapor. Assuming a value of α of 1.01, δ will vary with f , the fraction of vapor remaining, as shown in Figure 28.1.

Even if the vapor and liquid remain in equilibrium throughout the condensation process, the isotopic composition of the remaining vapor will change continuously. The relevant equation is:

$$\delta = \left(1 - \frac{1}{(1-f)/\alpha + f} \right) \times 1000 \quad 19.69$$

The effect of equilibrium condensation is also shown in Figure 19.4.

REFERENCES AND SUGGESTIONS FOR FURTHER READING

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