

# 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.

Geologically useful information has generally not been extracted (with some exceptions) from elements not meeting these criteria. For example,  $^{48}\text{Ca}/^{40}\text{Ca}$  has a large relative mass difference, but it tends to form ionic bonds; little fractionation has been observed. Mg is a light element, but in addition to its bonds being dominantly ionic, it is generally surrounded by the same atomic environment (octahedral O). Perhaps the biggest exception to these rules is the observation of isotope fractionation of heavy elements in inclusions of the Allende meteorite.

Stable isotopes can be applied to a variety of problems. One of the most common is geothermometry. Another 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. The extent of isotopic fractionation varies inversely with temperature: fractionations are large at low temperature and small at high temperature.

## NOTATION AND DEFINITIONS

### The $\delta$ Notation

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

$$\delta^{18}\text{O} = \left[ \frac{(^{18}\text{O}/^{16}\text{O})_{\text{sam}} - (^{18}\text{O}/^{16}\text{O})_{\text{SMOW}}}{(^{18}\text{O}/^{16}\text{O})_{\text{SMOW}}} \right] \times 10^3 \quad 25.1$$

The same formula is used to report other stable isotope ratios. Hydrogen isotope ratios,  $\delta\text{D}$ , are reported relative to SMOW, carbon isotope ratios relative to PDB, the Pee Dee Belemnite carbonate, 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. Unfortunately, a dual standard has developed for reporting O isotopes. People working mainly with carbonates (paleotemperatures) simply report  $\delta^{18}\text{O}$  relative to the PDB carbonate standard. This value is related to SMOW by:

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**Table 25.1. Isotope Ratios of Stable Isotopes**

Element	Notation	Ratio	Standard	Absolute Ratio
Hydrogen	$\delta D$	D/H ( $^2H/{}^1H$ )	SMOW	$1.557 \times 10^{-4}$
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	$1.122 \times 10^{-2}$
Nitrogen	$\delta ^{15}N$	${}^{15}N/{}^{14}N$	atmosphere	$3.613 \times 10^{-3}$
Oxygen	$\delta ^{18}O$	${}^{18}O/{}^{16}O$	SMOW, PDB	$2.0052 \times 10^{-3}$
	$\delta ^{17}O$	${}^{17}O/{}^{16}O$	SMOW	$3.76 \times 10^{-4}$
Chlorine	$\delta ^{37}Cl$	${}^{37}Cl/{}^{35}Cl$	seawater	$\sim 0.31978$
Sulfur	$\delta ^{34}S$	${}^{34}S/{}^{32}S$	CDT	$4.43 \times 10^{-2}$

$$\delta ^{18}O_{PDB} = 1.03086 \delta ^{18}O_{SMOW} + 30.86 \quad 25.2$$

Table 25.1 lists the values for standards used in stable isotope analysis.

### The Fractionation Factor

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

$$\alpha_{A-B} = \frac{R_A}{R_B} \quad 25.3$$

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  $\Delta$  and  $\alpha$  is:

$$\Delta \approx (\alpha - 1)10^3 \quad \text{or} \quad \Delta \approx 10^3 \ln \alpha \quad 25.4$$

We derive it as follows. Rearranging equ. 25.1, we have:

$$R_A = (\delta_A + 10^3)R_{STD}/10^3 \quad 25.5$$

where R denotes an isotope ratio. Thus  $\alpha$  may be expressed as:

$$\alpha = \frac{(\delta_A + 10^3)R_{STD}/10^3}{(\delta_B + 10^3)R_{STD}/10^3} = \frac{(\delta_A + 10^3)}{(\delta_B + 10^3)} \quad 25.6$$

Subtracting 1 from each side and rearranging, we obtain:

$$\alpha - 1 = \frac{(\delta_A - \delta_B)}{(\delta_B + 10^3)} \approx \frac{(\delta_A - \delta_B)}{10^3} = \Delta \times 10^{-3} \quad 25.7$$

since  $\delta$  is generally  $\ll 10^3$ . The second equation in 25.4 results from the approximation that for  $x \approx 1$ ,  $\ln x \approx 1 - x$ .

As we will see,  $\alpha$  is related to the equilibrium constant of thermodynamics by

$$\alpha_{A-B} = (K/K_\infty)^{1/n} \quad 25.8$$

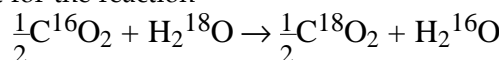
where  $n$  is the number of atoms exchanged,  $K_\infty$  is the equilibrium constant at infinite temperature, and  $K$  is the equilibrium constant is written in the usual way (except that concentrations are used rather than activities because the ratios of the activity coefficients are equal to 1, 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, a lighter isotope will diffuse faster than a heavier one), but the latter will undoubtedly seem 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 in vibrational motions*. These effects are, as one might expect, generally small. For example, the equilibrium constant for the reaction



is only about 1.04 at 25°C.

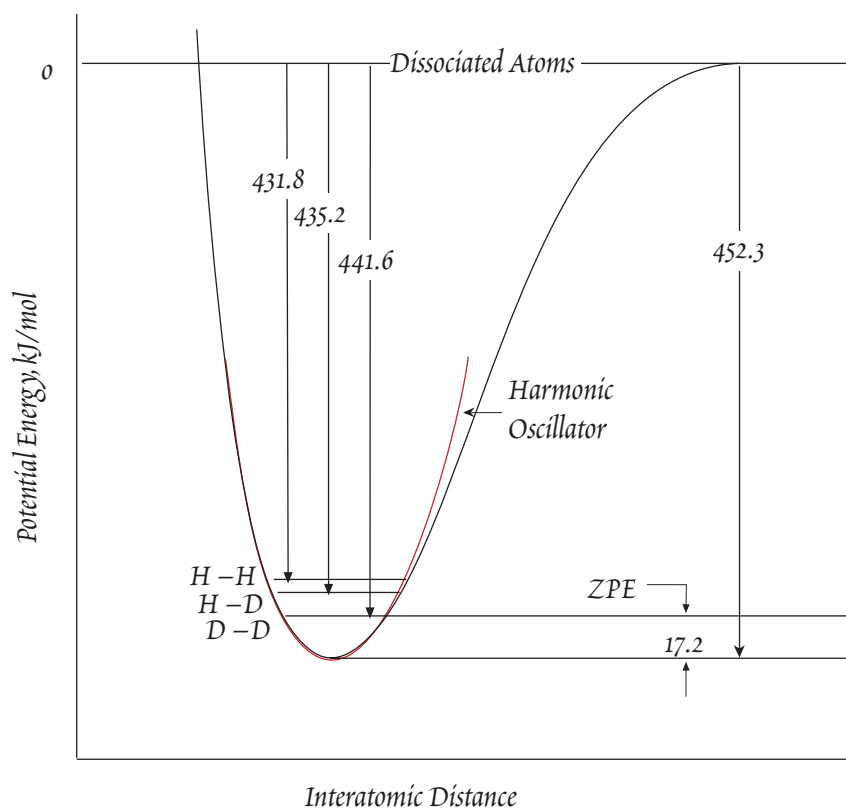


Figure 25.1. Energy-level diagram for the hydrogen atom. Fundamental vibration frequencies are  $4405\text{ cm}^{-1}$  for  $\text{H}_2$ ,  $3817\text{ cm}^{-1}$  for HD, and  $3119\text{ cm}^{-1}$  for  $\text{D}_2$ . The zero-point energy of  $\text{H}_2$  is greater than that for HD which is greater than that for  $\text{D}_2$ . From O'Neil (1986).

Figure 25.1 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 paddle ball: a child's toy consisting of a rubber ball connected to a wooden paddle by a rubber band. When the distance between the center point of the ball and paddle is very small, the ball is compressed, and the potential energy of the system correspondingly high. At great distances between the ball and paddle, the rubber band is stretched and the energy of the system also high. At some intermediate distance, there is no stress on either the ball or the rubber band, and the potential energy of the system is at a minimum (for a perfectly elastic ball and rubber band in a friction-free environment, energy would be nevertheless be conserved because kinetic energy is at a

maximum when potential energy is at a minimum). The diatomic oscillator, for example consisting of an 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  $\nu_0$ . The system will thus have an energy of  $\frac{1}{2}h\nu_0$ , where  $h$  is Planck's constant. This energy level is called the *Zero Point Energy (ZPE)*. It energy depends the electron 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, but since energy also depends inversely on the masses of the atoms involved, thus it will be different for different for isotopes. *The vibrational energy level for a given quantum number will be lower for a bond involving the a heavier isotope of an element, as suggested in Figure 25.1. 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 the next lecture. We will no 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 molecules having internal energy  $E_i$  to those having the zero point energy  $E_0$  is:

$$\frac{n_i}{n_0} = g_i e^{-E_i/kT} \quad 25.9$$

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 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:

$$\frac{\sum_i n_i E_i}{\sum_i n_i} = \frac{\sum_i g_i E_i e^{-E_i/kT}}{\sum_i g_i e^{-E_i/kT}} \quad 25.10$$

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

$$q = \sum_i g_i e^{-E_i/kT} \quad 25.11$$

Substituting 25.11 into 25.10, we can rewrite 25.10 in terms of the partial derivatives of  $q$ :

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

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$$E = kT^2 \frac{\partial \ln q}{\partial T} \quad 25.12$$

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*<sup>†</sup> is related to energy and q by

$$S = \frac{U}{T} + R \ln q \quad 25.13$$

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

$$U - TS = -R \ln q \quad 25.14$$

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

$$\Delta U - T\Delta S = -R \ln \prod q_N^\xi \quad 25.15$$

where  $\xi$  in this case is the stoichiometric coefficient. 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

$$\Delta G = -RT \ln \prod q_N^\xi \quad 25.16$$

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

$$\Delta G = -RT \ln K \quad 25.17$$

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

$$K = \prod q_N^\xi \quad 25.18$$

For example, in the reaction involving exchange of <sup>18</sup>O between H<sub>2</sub>O and CO<sub>2</sub>, the equilibrium constant is simply:

$$K = \frac{q_{C^{16}O} q_{H_2^{18}O}}{q_{C^{18}O} q_{H_2^{16}O}} \quad 25.19$$

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:

$$q_{\text{total}} = q_{\text{tr}} q_{\text{vib}} q_{\text{rot}} \quad 25.20$$

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.

For the translational motion,  $q_{\text{trans}}$  is expressed as:

$$q_{\text{trans}} = \sum_i g_{\text{tr},i} e^{-E_{\text{tr},i}/kT} \quad 25.21$$

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:

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<sup>†</sup> Entropy is defined in the second law of thermodynamics, which states:

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

where  $Q_{\text{rev}}$  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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$$E_{\text{trans}} = \frac{n^2 h^2}{8md^2} \quad 25.22$$

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. Substituting 25.22 into 25.21 and integrating:

$$q_{\text{trans}} = \int_0^\infty e^{\left(\frac{-n^2 h^2}{8md^2 kT}\right)} dn = \frac{(2\pi mkT)^{1/2}}{h} d \quad 25.23$$

gives an expression for  $q_{\text{trans}}$  for each dimension. The total translational partition function is then:

$$q_{\text{trans}} = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V \quad 25.24$$

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 25.19, all terms in 25.24 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  $K_{\text{tr}}$  as:

$$K_{\text{tr}} = \prod q_{\text{tr}}^\xi \quad 25.25$$

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

$$K_{\text{tr}} = \prod m_t^{3\xi/2} \quad 25.26$$

Thus the translational contribution to the partition function and fractionation factor is independent of temperature.

The allowed quantum *rotational* energy states are:

$$E_{\text{rot}} = \frac{j(j+1)h^2}{8\pi^2 I} \quad 25.27$$

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, and  $\mu$  is reduced mass:

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad 25.28$$

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 there for  $2j + 1$ . Hence:

$$q_{\text{rot}} = \sum (2j+1) \exp\left(\frac{j(j+1)h^2}{8\pi^2 I kT}\right) \quad 25.29$$

Again the spacing between energy levels is relatively small (except for hydrogen) and 25.29 may be evaluated as an integral. For a diatomic molecule, the partition function for rotation is given by:

$$q_{\text{rot}} = \frac{8\pi^2 I kT}{\sigma h^2} \quad 25.30$$

where  $\sigma$  is a symmetry factor equal to the number of equivalent ways of orienting the molecule in space. It is 1 for a heteronuclear diatomic molecule (such as CO or  $^{18}\text{O}^{16}\text{O}$ ), and 2 for a homonuclear molecule such as  $^{16}\text{O}_2$ . Equ. 25.30 also holds for linear polyatomic molecules and is 2 if the molecule

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has a plane of symmetry (e.g., CO<sub>2</sub>) and 1 if it does not. For non-linear polyatomic molecules, the partition function is given by:

$$q_{\text{rot}} = \frac{8\pi^2(8\pi^2 ABC)^{1/2} (kT)^{3/2}}{\sigma h^3} \quad 25.31$$

where A, B, and C are the principal moments of inertia of the molecule. 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:

$$K_{\text{rot}} = \prod_i \left( \frac{I_i}{\sigma_i} \right)^{\xi_i} \quad 25.32$$

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

We will simplify the calculation of the vibrational partition function by treating the diatomic molecule as a harmonic oscillator (as Fig. 25.1 suggests, this is a good approximation in most cases). In this case the quantum energy levels are given by:

$$E_{\text{vib}} = \left( n + \frac{1}{2} \right) h\nu \quad 25.33$$

where  $n$  is the vibrational quantum number and  $\nu$  is vibrational frequency (notice that this reduces to the zero point energy discussed above when  $n = 0$ ). 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. For diatomic molecules the summation is simply equal to:

$$q_{\text{vib}} = \frac{\exp(-h\nu/2kT)}{1 - \exp(-h\nu/2kT)} \quad 25.34$$

For a non-linear polyatomic molecule consisting of  $m$  atoms and the product is performed over all vibrational modes,  $\ell$  (there are only  $3m-5$  modes of motion for a linear polyatomic molecule, hence the product is carried out only to  $3m-5$ ):

$$q_{\text{vib}} = \prod_{\ell=1}^{3m-6} \frac{\exp(-h\nu_{\ell}/2kT)}{1 - \exp(-h\nu_{\ell}/2kT)} \quad 25.35$$

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

$$q_{\text{vib}} \cong \exp(-h\nu/2kT) \quad 25.36$$

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

$$K_{\text{vib}} = \prod_{\ell} e^{\xi_{\ell} h\nu_{\ell}/2kT} \quad 25.37$$

which has an exponential temperature dependence.

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

$$K = \prod_i \left( q_i^{\text{tr}} q_i^{\text{rot}} q_i^{\text{vib}} \right)^{\xi_i} = \prod_i \left( M_i^{3/2} \left[ \frac{I_i}{\sigma_i} \right] \left[ \frac{e^{\xi_i h\nu_i/2kT}}{1 - e^{\xi_i h\nu_i/2kT}} \right] \right)^{\xi_i} \quad 25.38$$

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

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\* The Teller-Redlich Theorem relates to products of the frequencies for each symmetry type of the two

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$$K = \prod_i \left( \frac{1}{\sigma_i} m_i^{3/2} U \frac{e^{-U/2}}{1 - e^{-U}} \right)^{\xi_i} \quad 25.39$$

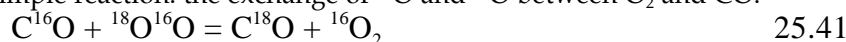
where  $m$  is the mass of the isotope exchanged and  $U$  is defined as:

$$U = \frac{h\nu}{kT} = \frac{hc\omega}{kT} \quad 25.40$$

and  $\omega$  is the vibrational wave number.

### 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  $^{18}\text{O}$  and  $^{16}\text{O}$  between  $\text{O}_2$  and  $\text{CO}$ :



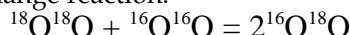
The choice of diatomic molecules greatly simplifies the equations. The equilibrium constant is:

$$K = \frac{[{}^{16}\text{O}_2][\text{C}^{18}\text{O}]}{[{}^{18}\text{O}^{16}\text{O}][\text{C}^{16}\text{O}]} \quad 25.42$$

Note 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,  $\alpha$ , is defined as:

$$\alpha = \frac{({}^{18}\text{O}/{}^{16}\text{O})_{\text{CO}}}{({}^{18}\text{O}/{}^{16}\text{O})_{\text{O}_2}} \quad 25.43$$

We must also consider the exchange reaction:



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:

$$\left( \frac{{}^{18}\text{O}}{{}^{16}\text{O}} \right)_{\text{O}_2} = \frac{[{}^{18}\text{O}^{16}\text{O}]}{[{}^{18}\text{O}^{16}\text{O}] + 2[{}^{16}\text{O}_2]} \quad 25.44$$

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

$$\left( \frac{{}^{18}\text{O}}{{}^{16}\text{O}} \right)_{\text{CO}} = \frac{[\text{C}^{18}\text{O}]}{[\text{C}^{16}\text{O}]} \quad 25.45$$

Letting the isotope ratio equal  $R$ , then we can solve 25.44 for  $[{}^{18}\text{O}^{16}\text{O}]$ :

$$[{}^{18}\text{O}^{16}\text{O}] = 2 \frac{[{}^{16}\text{O}_2] R_{\text{O}_2}}{1 - R_{\text{O}_2}} \quad 25.46$$

isotopes to the ratios of their masses and moments of inertia:

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

We need not concern ourselves with its details.



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and substitute it into 25.42: 
$$K = \frac{[1 - R_{O_2}][C^{18}O]}{2R_{O_2}[C^{16}O]} = \frac{[1 - R_{O_2}]R_{CO}}{2R_{O_2}} \quad 25.47$$

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

$$K \equiv \frac{R_{CO}}{2R_{O_2}} = \frac{\alpha}{2} \quad 25.48$$

We can calculate K from the partition functions as:

$$K = \frac{q^{16}O_2 q^{18}O}{q^{18}O^{16}O q^{16}O} \quad 25.49$$

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:

$$K_{tr} = \frac{q^{16}O_2 q^{18}O}{q^{18}O^{16}O q^{16}O} = \left( \frac{M^{16}O_2 M^{18}O}{M^{18}O^{16}O M^{16}O} \right)^{3/2} = \left( \frac{32 \times 30}{34 \times 28} \right)^{3/2} = 1.0126 \quad 25.50$$

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  $^{16}O_2$ . 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:

$$K_{rot} = \frac{q^{16}O_2 q^{18}O}{q^{18}O^{16}O q^{16}O} = \left( \frac{I^{16}O_2 I^{18}O}{2I^{18}O^{16}O I^{16}O} \right) = \frac{1}{2} \left( \frac{\frac{16 \times 16}{16 + 16} \frac{12 \times 18}{12 + 18}}{\frac{18 \times 16}{18 + 16} \frac{12 \times 16}{12 + 16}} \right) = \frac{1}{2} 0.9916 \quad 25.51$$

(ignore the 1/2, it will cancel out later). If rotational were the only mode of motion,  $^{18}O$  would be 8 per mil more abundant in  $O_2$ .

The vibrational equilibrium constant may be expressed as:

$$K_{vib} = \frac{q^{16}O_2 q^{18}O}{q^{18}O^{16}O q^{16}O} = \exp \left( \frac{-h(v_{C^{16}O} + v_{O^{18}O} - v_{C^{18}O, vib} - v_{O^{16}O_2})}{2kT} \right) \quad 25.52$$

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

$$K_{vib} \approx 1 + \frac{h}{2kT} \left[ \{v_{C^{16}O} - v_{C^{18}O}\} - \{v_{O_2} - v_{O^{16}O}\} \right] \quad 25.53$$

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

$$v = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad 25.54$$

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

$$\nu_{C^{18}O} = \nu_{C^{16}O} \sqrt{\frac{\mu_{C^{18}O}}{\mu_{C^{16}O}}} = \nu_{C^{16}O} \sqrt{\frac{20}{21}} = 0.976 \nu_{C^{16}O} \quad 25.55$$

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

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

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

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

The measured vibrational frequencies of CO and O<sub>2</sub> 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:

$$K_{\text{vib}} = 1 + \frac{5.976}{T}$$

At 300 K (room temperature), this evaluates to 1.0199.

We may now evaluate the total exchange equilibrium constant at 300 K as:

$$K = K_{\text{tr}} K_{\text{rot}} K_{\text{vib}} = 1.0126 \times \frac{1}{2} 0.9916 \times 1.0199 = \frac{1}{2} 1.024$$

Since  $\alpha = 2K$ , the fractionation factor is 1.024 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 25.2. Thus CO would be 24 permil richer in the heavy isotope, <sup>18</sup>O, than O<sub>2</sub>. 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, which for large  $N$  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<sub>3</sub>, 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,

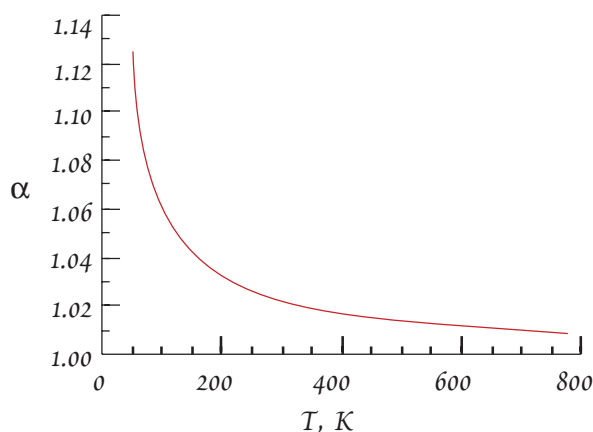


Figure 25.2. Fractionation factor,  $\alpha = (^{18}\text{O}/^{16}\text{O})_{\text{CO}} / (^{18}\text{O}/^{16}\text{O})_{\text{O}_2}$ , calculated from partition functions as a function of temperature.

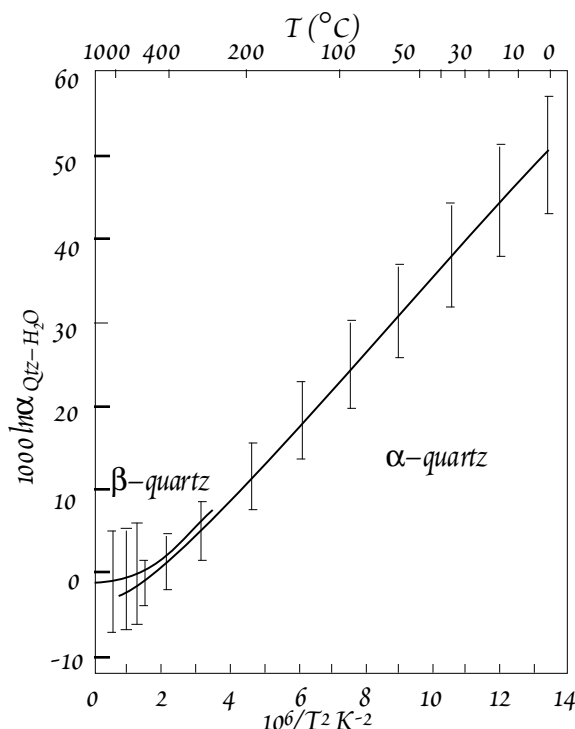


Figure 25.3. Calculated temperature dependencies of the fractionation of oxygen between water and quartz. From Kawabe (1978).

O'Neil, J. R., Theoretical and experimental aspects of isotopic fractionation, in *Stable Isotopes in High Temperature Geologic Processes, Reviews in Mineralogy Volume 16*, J. W. Valley, et al., eds., Mineralogical Society of America, Washington, pp. 1-40, 1986.

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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  $^{18}\text{O}$  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 25.3 shows the calculated fractionation factor between quartz and water as a function of temperature.

### REFERENCES AND SUGGESTIONS FOR FURTHER READING

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