Lecture 15
Physical Principles of Isotopic Fractionation

Isotope Fractionation

1. Non-equilibrium (unidirectional) effects
   a. Diffusion/effusion
   b. Evaporation/condensation
   c. Kinetic (bond breaking/making)
   d. Metabolic (combination of all the above)
2. Equilibrium effects
   a. Bond strength
   b. Availability of states (statistical mechanics)

1(a) Effusion *vs.* diffusion

In an ideal gas at thermal equilibrium, all molecules have the same translational kinetic energy.

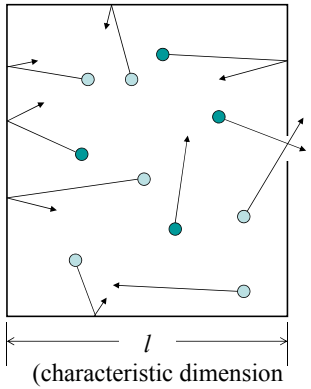
Imagine two isotopes (a and b)

$$\frac{1}{2} m_a v_a^2 = \frac{1}{2} m_b v_b^2$$

$$\frac{v_a}{v_b} = \sqrt{\frac{m_b}{m_a}}$$

The lighter isotope travels faster on average

Effusion



(characteristic dimension of container)

mean free path, $\lambda > l$

not diffusion

Rate $\propto$ collisions/cm^2

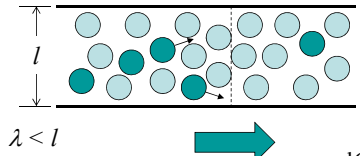
$\propto v$

$$\frac{\varphi_a}{\varphi_b} = \sqrt{\frac{m_b}{m_a}}$$

e.g., $\sqrt{\frac{^{13}C^{16}O_2}{^{12}C^{16}O_2}} = \sqrt{\frac{45}{44}} = 1.0113$

Typically low pressure (vacuum system) behavior

Diffusion



Diffusion coefficient:

$$D \propto \bar{v} \propto \left(\frac{k_B T}{m}\right)^{\frac{1}{2}}$$

$$\varphi = -D\frac{dC}{dx}$$ Fick's first law

For diffusion of gas **a** through gas **b**: $D \propto \bar{v} \propto \left(\frac{k_B T}{\mu}\right)^{\frac{1}{2}}$

where $\mu = \frac{m_a m_b}{m_a + m_b}$, **reduced mass**

Consider N_2 in O_2

Typically higher pressure behavior

Diffusion of Isotopic Species in Gases

For two isotopic species of gas **a**

a = $^{12}C^{16}O_2$, $m_a = 44.00$

a′ = $^{13}C^{16}O_2$, $m_{a'} = 44.99$

Diffusing in air → $m_b = 28.92$

$$\frac{D_a}{D_{a'}} = \frac{D_{12CO2}}{D_{13CO2}} = \left(\frac{44.00 + 28.92}{44.00 \times 28.92} \cdot \frac{44.99 \times 28.92}{44.99 + 28.92}\right)^{\frac{1}{2}}$$

$= 1.0044 \neq 1.0113$

Diffusion of Isotopic Species in Condensed Media

Expected for CO_2 in H_2O on the basis of reduced mass

$$\frac{D_{12CO2}}{D_{13CO2}} = 1.0032$$

Observed: $\frac{D_{12CO2}}{D_{13CO2}} = 1.00087$

Difference indicates that H_2O-CO_2 interactions (e. g., H-bonding) are very significant

Chemical Equilibria: Phase Change

$$H_2O_{(l)} + HDO_{(g)} \leftrightarrows HDO_{(l)} + H_2O_{(g)}$$

$$\Delta G^\circ = \Delta G_f^\circ(HDO_{(l)}) + \Delta G_f^\circ(H_2O_{(g)}) - [\Delta G_f^\circ(H_2O_{(l)}) + \Delta G_f^\circ(HDO_{(g)})]$$

$$= -57.817 + (-54.634) - [(-56.687) + (-55.719)] = -0.045 \text{ kcal/mol}$$

$$\ln K = \frac{-\Delta G^\circ}{RT} = \frac{45}{1.987 \cdot 298.16} \rightarrow K = 1.0789$$

Alternatively,

$H_2O_{(l)} \leftrightarrows H_2O_{(g)}$ $\Delta G° = 2053$ cal/mol

$HDO_{(l)} \leftrightarrows HDO_{(g)}$ $\Delta G° = 2098$ cal/mol

$$\rightarrow \frac{p^\circ_{H2O}}{p^\circ_{HDO}} = 1.0789$$

- Alpha is measure of enrichment/depletion in reaction
  - is a positive number generally very close to 1 (e.g., 0.998 or 1.013)
- e.g. addition of some carbon by chemical reaction

$$\left(\frac{\left(\frac{^{13}C}{^{12}C}\right)_X}{\left(\frac{^{13}C}{^{12}C}\right)_S}\right)_A = 1.0015 \qquad \alpha_{A-B} = 0.9970$$

$$R_B = \alpha_{A-B} R_A$$

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

$$\left(\frac{\left(\frac{^{13}C}{^{12}C}\right)_X}{\left(\frac{^{13}C}{^{12}C}\right)_S}\right)_B = \alpha_{A-B}\left(\frac{\left(\frac{^{13}C}{^{12}C}\right)_X}{\left(\frac{^{13}C}{^{12}C}\right)_S}\right)_A = 0.9985$$

- Isotope Ratio Anomaly
  - better than carrying a lot of decimals
  - fractional deviation from some standard
  - "delta" for "difference" or "deviation"
  - usually in "per mil" (parts per 1000)
  - can be negative or positive

$$\delta \equiv \left(\frac{R_X}{R_S} - 1\right) \times 1000$$

e.g.,

$$\delta^{18}O \equiv \left(\frac{\left(^{18}O/^{16}O\right)_X}{\left(^{18}O/^{16}O\right)_{SMOW}} - 1\right) \times 1000\,‰$$

$$\delta^{3}He \equiv \left(\frac{\left(^{3}He/^{4}He\right)_X}{\left(^{3}He/^{4}He\right)_{Air}} - 1\right) \times 1000$$

Always relative to reference standard

General Rules

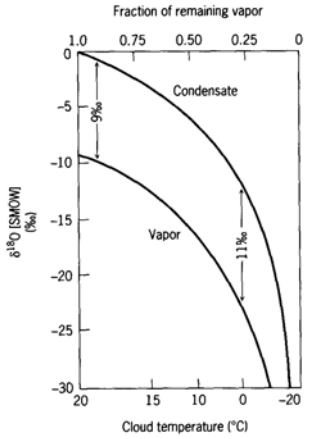
- Lighter isotopes move faster
- lighter isotopes form weaker bonds
  - effect strongly depends on binding energy
  - covalent bonds generally weaker, more strongly affected
- isotope effects generally stronger for bigger relative mass differences
  - directly proportional for same element
    - e.g. ^{16}O, ^{17}O, ^{18}O : $\delta^{18}O = 2 \times \delta^{17}O$
- isotope effects stronger at lower temperatures
  - as T >>, $\alpha \rightarrow 1$
  - for low T, $\alpha \sim 1/T^2$
  - for high T, $\alpha \sim 1/T$

Partitioning between phases

- E.g., oxygen isotope partitioning between vapor and droplets in a cloud

$$R_L = \alpha R_V$$

- $1.005 < \alpha < 1.015$ (liquid heavier)

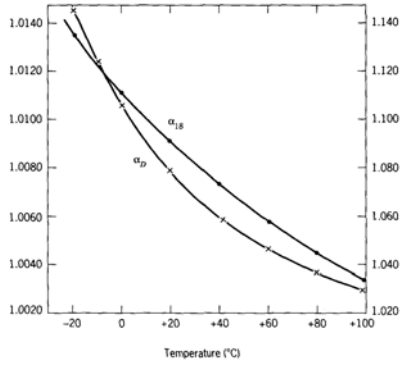


Partitioning between phases

- Vapour-droplet partitioning in a cloud $R_L = \alpha R_V$

Oxygen Isotope Fractionation ($^{18}O/^{16}O$)

Smaller scale =>

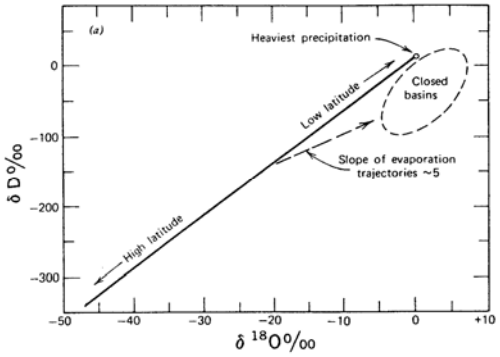


Hydrogen Isotope Fractionation ($^{2}H/^{1}H$)

BIGGER <= SCALE

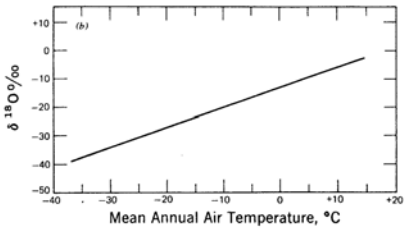
Hydrogen & oxygen isotopes tend to correlate in nature

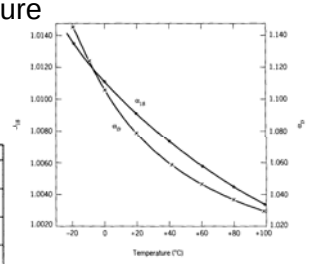
- Hydrogen effect ~ 10x Oxygen
- Why the latitude trend?



Latitude Trend in Precipitation

- Latitude trend: due to temp. effect?
  - – α depends on temperature
  - – temperature decreases poleward





$\delta^{18}O = -15.0 + 0.52\ T$

$\delta D = 10.6 + 8.2\ \delta^{18}O$

Isotope fractionation: the Rayleigh Equation

- Describes how the ratio changes with progressive removal of material, e.g. by evaporation from a water droplet:

f = fraction left

$$R_L = \alpha R_V \qquad \frac{R_V}{R_{V_0}} = f^{\alpha - 1}$$

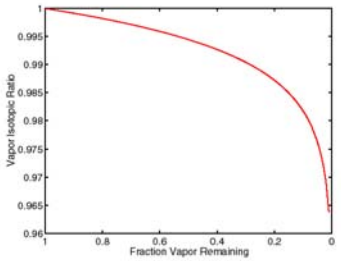
The Rayleigh Equation

$$\frac{R_V}{R_{V_0}} = f^{\alpha-1}$$

- For a vapor where droplets are forming … α = 1.008

$$R_L = \alpha R_V = \alpha R_{V_0} f^{\alpha-1}$$

f	$f^{\alpha-1}$	δ_V	$\alpha f^{\alpha-1}$	δ_L
1.000	1.00000	0.00	1.00800	8.00
0.800	0.99822	-1.78	1.00620	6.20
0.640	0.99644	-3.56	1.00441	4.41
0.512	0.99466	-5.34	1.00262	2.62
0.410	0.99288	-7.12	1.00083	0.83
0.328	0.99111	-8.89	0.99904	-0.96
0.262	0.98935	-10.65	0.99726	-2.74
0.210	0.98758	-12.42	0.99548	-4.52
0.168	0.98582	-14.18	0.99371	-6.29
0.134	0.98406	-15.94	0.99193	-8.07
0.107	0.98231	-17.69	0.99017	-9.83
0.086	0.98055	-19.45	0.98840	-11.60
0.069	0.97881	-21.19	0.98664	-13.36
0.055	0.97706	-22.94	0.98488	-15.12
0.044	0.97532	-24.68	0.98312	-16.88
0.035	0.97358	-26.42	0.98137	-18.63
0.028	0.97184	-28.16	0.97962	-20.38
0.023	0.97011	-29.89	0.97787	-22.13



For evaporation

- For the backwards reaction, then the effect is 1/α

$$R_2 = \alpha_{1\to2} R_1$$

$$R_1 = \alpha_{2\to1} R_2 = \frac{1}{\alpha_{1\to2}} R_2$$

$$\therefore \alpha_{2\to1} = \alpha_{1\to2}^{-1}$$

- e.g. for evaporation of a droplet $\frac{R_L}{R_{L_0}} = f^{\frac{1}{\alpha}-1}$
  - the remaining liquid is given by
  - the vapour is given by $\frac{R_V}{R_{L_0}} = \frac{1}{\alpha}\frac{R_L}{R_{L_0}} = \frac{1}{\alpha} f^{\frac{1}{\alpha}-1}$

Multiple Steps

- Multiple fractionations *multiply*

  e.g., for two sequential reactions

  $R_1 \Rightarrow R_2 \Rightarrow R_3$

$R_2 = \alpha_{1\text{-}2} R_1$

$R_3 = \alpha_{2\text{-}3} R_2 = \alpha_{1\text{-}2}\,\alpha_{2\text{-}3}$ $R_3 = \alpha_{1\text{-}3} R_1$

- in general then,

$$\alpha_{Total} = \alpha_1 \cdot \alpha_2 \cdot \ldots \cdot \alpha_n = \prod_i \alpha_i$$

Multiple Steps

- Since $\delta_i = (\alpha_i - 1) \times 1000$
- A convenient *approximation* is

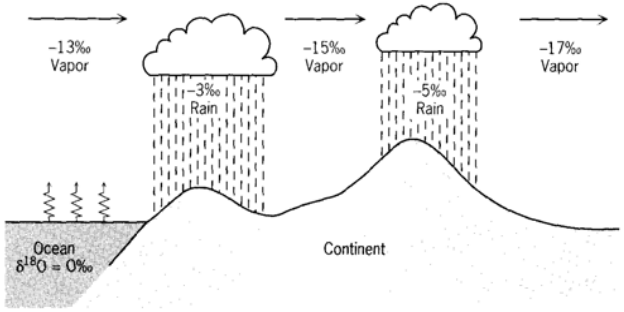
$$\delta_{Total} = \delta_1 + \delta_2 + \delta_3 + \ldots = \sum_i \delta_i$$

for small δ's only (kind of a binomial expansion approximation)

The hydrologic cycle

Successive distillations increases effect poleward

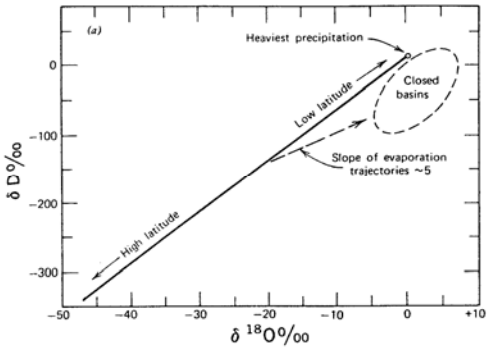
Precipitation gets lighter toward poles



Equator Pole

Hydrogen & oxygen isotopes tend to correlate in nature

- Hydrogen effect ~ 10x Oxygen
- poleward lightening
- isolated basins go off trend with severe evaporation



Fractionation factors are related to, but not necessarily equal to, equilibrium constants

For $n\ {}^{l}\mathrm{X}_m\mathrm{A} + m\ {}^{h}\mathrm{X}_n\mathrm{B} \leftrightarrows n\ {}^{h}\mathrm{X}_m\mathrm{A} + m\ {}^{l}\mathrm{X}_n\mathrm{B}$

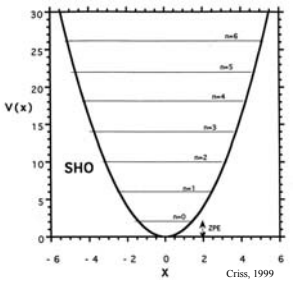
$$K = \frac{\left[{}^{h}\mathrm{X}_m A\right]^n \left[{}^{l}\mathrm{X}_n\mathrm{B}\right]^m}{\left[{}^{l}\mathrm{X}_m\mathrm{A}\right]^n \left[{}^{h}\mathrm{X}_n\mathrm{B}\right]^m}$$

$$\alpha_{\mathrm{XA/XB}} = \left(\frac{\sigma_{h\mathrm{X}m\mathrm{A}}}{\sigma_{l\mathrm{X}m\mathrm{A}}}\right)^{\frac{1}{n}} \left(\frac{\sigma_{l\mathrm{X}n\mathrm{B}}}{\sigma_{h\mathrm{X}n\mathrm{B}}}\right)^{\frac{1}{m}} K^{1/mn}$$

σ = molecular symmetry number. 1 for a heteronuclear diatomic molecule, 2 for homonuclear diatomic… 12 for methane.

See Schauble, 2004

Energy Levels for a Simple Harmonic Oscillator



Lowest level, $n = 0$, has energy = $h\nu/2$. This is the Zero-Point Energy, ZPE.

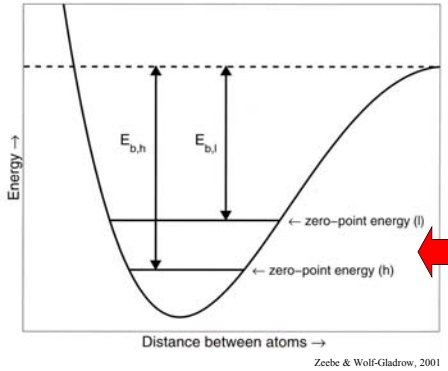
$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

k is the force constant

μ is the reduced mass

ν, and in turn the ZPE, is thus mass-dependent.

Energy Levels in Isotopically Substituted Molecules



The ZPE of the bond with the light isotope is greater than that of the bond with the heavy isotope.

In an exchange reaction, the question is which molecule has the greater ΔZPE

$C^{16}O_2 + H_2{}^{18}O \leftrightarrows C^{18}O^{16}O + H_2{}^{16}O$

$\Delta G_f^\circ(H_2O) = -56.7$ kcal/mol

?

$\Delta G_f^\circ(CO_2) = -92.3$ kcal/mol

$$\Delta ZPE \propto \nu_l \left(1 - \sqrt{\frac{\mu_l}{\mu_h}}\right)$$

Vibrational frequencies from spectroscopic data

Greater ΔZPE for CO_2 pulls equilibrium to right, favors accumulation of ^{18}O in CO_2.

Factors favoring large ΔZPE

And thus leading to concentration of the heavy isotope

Low temperatures

Stiff bonds

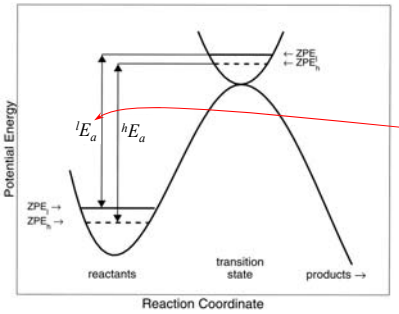
Short

Strong (multiple bonds)

Atoms with similar electronegativities

"The heavy isotope goes preferentially to the chemical compound in which the element is bound most strongly." Bigeleisen, J. (1965) Chemistry of Isotopes, *Science* **147**, 463-471.

Kinetic Isotope Effects



Bonding in transition state is weaker than in reactants.

Activation energy for light isotopic species is therefore smaller.

$$k = Ae^{\frac{-E_a}{RT}}$$

Light isotopic species react more rapidly.

Kinetic Isotope Effect Terminology

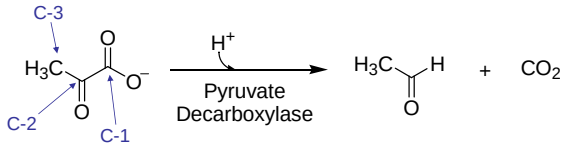
Normal = Light isotopic species reacts more rapidly

Inverse = Heavy isotopic species reacts more rapidly

Primary = Isotopic substitution at a position to which a chemical bond is made or broken influences the reaction rate

Secondary = Isotopic substitution at a remote position influences the reaction rate

Primary and Secondary Carbon Kinetic Isotope Effects



$\frac{^{12}k}{^{13}k}$	C-1	C-2	C-3
	1.007	1.015	1.001

DeNiro, M. J. & Epstein, S. (1977) Mechanism of carbon isotopic fractionation associated with lipid synthesis. *Science* **197**, 261-263.

Coexistence of Equilibrium and Kinetic Fractionations

$$CO_2 + H_2O \rightarrow H^+ + HCO_3^- \quad \frac{^{12}k}{^{13}k} = 1.013$$

$$H^+ + HCO_3^- \rightarrow CO_2 + H_2O \quad \frac{^{12}k}{^{13}k} = 1.022$$

$$^{13}\alpha_{HCO3/CO2} = 1.00897 \approx \frac{1.022}{1.013}$$

Equilibrium fractionation

Net effect of opposing KIEs. But note: *prior to equilibration,* HCO_3^- can be depleted in ^{13}C due to KIE.