Equilibrium stable isotope fractionation

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Notation for fractionation factors:

\[ \alpha_{XA-XB} = \frac{R_{XA}}{R_{XB}} \]

\[ \delta_{XA} - \delta_{XB} \approx 1000 \cdot (\alpha_{XA-XB} - 1) \approx 1000 \cdot \ln(\alpha_{XA-XB}) \]

For equilibrium isotopic fractionation, \( \alpha \) is related to the equilibrium constant of a one-atom exchange reaction:

\[ \text{light} \ X_A + \text{heavy} \ X_B \leftrightarrow \text{heavy} \ X_A + \text{light} \ X_B \]

\[ K_{eq} = \frac{[\text{heavy} \ X_A][\text{light} \ X_B]}{[\text{light} \ X_A][\text{heavy} \ X_B]} = R_{XA} \frac{1}{R_{XB}} = \alpha_{XA-XB} \]

This relationship is slightly more complicated if A or B has more than one atom of X!
Theory of equilibrium isotopic fractionation

Vibrations are quantized,  
\[ E(\text{vib}) = h\nu(n+1/2) \quad n=0,1,2,3\ldots \]

1/2\(h\nu\) is called the Zero-Point Energy (ZPE)

Rotation and Translation:

Both types of motion are also quantized, but there is no zero-point energy, and the quanta are much smaller than for vibrations. Rotational and translational quanta are much smaller than thermal energy at room temperature.
Rotational and translational quanta are so small relative to relevant thermal energies that classical mechanics gives a reasonably accurate description of non-vibrational motion.

\[ \nu_{35\text{ClO}} = 853.72 \text{ cm}^{-1} \quad (25.59 \times 10^{12} \text{ Hz}) \]

\[ \nu_{37\text{ClO}} = 846.45 \text{ cm}^{-1} \quad (25.38 \times 10^{12} \text{ Hz}) \]

\[ E(\text{vib}) = \frac{1}{2} \cdot h \nu \approx 5106 \text{ J/mol} \]

\[ E(\text{vib}) = \frac{1}{2} \cdot h \nu \approx 5063 \text{ J/mol} \]

At Equilibrium, for Cl-isotope exchange between monoatomic Cl and ClO:

\[ ^{37}\text{Cl} + ^{35}\text{ClO} \leftrightarrow ^{35}\text{Cl} + ^{37}\text{ClO} \]

\[ \Delta G_0 = \Delta E_{(\text{vib})_{\text{products}}} - \Delta E_{(\text{vib})_{\text{reactants}}} \]

\[ E_{(\text{vib})_{\text{products}}} = 5063 \text{ J/mol (}^{37}\text{ClO)} \]

\[ E_{(\text{vib})_{\text{reactants}}} = 5106 \text{ J/mol (}^{35}\text{ClO)} \]

\[ \Delta E(\text{vib}) = -43 \text{ J/mol, driving the reaction to the right and concentrating } ^{37}\text{Cl} \text{ in ClO!} \]
\[ \Delta G_0 = -kT \ln(K_{eq}) = -kT \ln(\alpha_{ClO-Cl}) \]
\[ \alpha_{ClO-Cl} = \exp(-\Delta G_0 / kT) \]

So, considering only vibrations, and if all molecules are in the ground vibrational state,

\[ \alpha_{ClO-Cl} = \exp(-\Delta G_0 / kT) = \exp(-\Delta E_{vib} / kT) \]
\[ \approx \exp(-\{1/2 \cdot h \nu_{37ClO} - 1/2 \cdot h \nu_{35ClO}\}/kT) \]
\[ = \exp\left(\frac{h}{2kT} \{ \nu_{35ClO} - \nu_{37ClO}\}\right) = 1.017 \text{ at } 298 \text{ K} \]

In reality, some molecules will be vibrationally excited:

\[ \alpha_{ClO-Cl} = \exp(-\Delta G_0 / kT) = \exp(-\Delta E_{vib} / kT) \]
\[ E_{vib} = -kT \ln(Q_{vib}) \]
\[ Q_{vib} = \sum_{n=0}^{\infty} \exp(-E_n/kT) \]
\[ Q_{vib} = \sum_{n=0}^{\infty} \exp(-h \nu(n+1)/2kT) \]
\[ = \sum_{n=0}^{\infty} \exp(-h \nu/2kT) \exp(-h \nu n/kT) \]
\[ = \exp(-h \nu/2kT) \sum_{n=0}^{\infty} \exp(-h \nu kT)^n \]
\[ \sum_{n=0}^{\infty} y^n = 1/(1-y) \]
\[ = \exp(-h \nu/2kT) \cdot 1/(1-\exp(-h \nu kT)) \]
\[ \text{ZPE} \quad \text{Excited states} \]
So by including excited vibrational states,

\[ \alpha_{\text{ClO}-\text{Cl}} = \frac{\exp(-h\nu_{37\text{ClO}}/2kT)/\{1-\exp(-h\nu_{37\text{ClO}}/kT)\}}{\exp(-h\nu_{35\text{ClO}}/2kT)/\{1-\exp(-h\nu_{35\text{ClO}}/kT)\}} \]

The final step is to include a simplified accounting for rotational and translational energies,

\[ \alpha_{\text{ClO}-\text{Cl}} = \frac{\nu_{37\text{ClO}} \exp(-h\nu_{37\text{ClO}}/2kT)/\{1-\exp(-h\nu_{37\text{ClO}}/kT)\}}{\nu_{35\text{ClO}} \exp(-h\nu_{35\text{ClO}}/2kT)/\{1-\exp(-h\nu_{35\text{ClO}}/kT)\}} \]

Rotation and translation

The effect of isotopic substitution on rotational and translational energies can be expressed in terms of vibrational frequencies!

\[ \alpha_{\text{ClO}-\text{Cl}} = 1.0096 \text{ at } 298 \text{ K} \]

(\text{the difference is due mainly to excited rotation & translation})
It is necessary to know vibrational frequencies of all relevant isotopic forms of a molecule or mineral (i.e. Na$^{35}\text{Cl}$ and Na$^{37}\text{Cl}$).

Generally, vibrational frequencies have not been measured or are incomplete for rare isotopic forms.

Predicting equilibrium isotope fractionations requires us to predict unknown vibrational frequencies.

Qualitative rules governing equilibrium isotope fractionation:

1. Fractionations are largest at low $T$ -- scaling roughly as $1/T^2$
   - Theory can be particularly useful for extending the temperature-range of experiments

2. Fractionations are largest for low mass elements -- scaling roughly as $(m_{\text{heavy}} - m_{\text{light}})/m^2$
Qualitative rules governing equilibrium isotope fractionation:

3. **Heavy isotopes prefer** **stiff** chemical bonds. **Typically this means** **short, strong** bonds, **correlating with**

a. **Oxidation state**: high charge → **stiff** bonds
   
   \( \text{C}^{4+} \leftrightarrow \text{C}^{4-}, \text{S}^{6+} \leftrightarrow \text{S}^{2-}, \text{Fe}^{3+} \leftrightarrow \text{Fe}^{2+} \)

b. **Bond partner oxidation state**: high charge → **stiff** bonds
   
   \( \text{Si} \text{O}_2 \leftrightarrow \text{Al}_2 \text{O}_3 \leftrightarrow \text{CaO} \)

c. **Bond partners**: “hard”, low atomic # → **stiff** bonds
   
   \( \text{Si} \text{O}_2 \leftrightarrow \text{Ti} \text{O}_2 \leftrightarrow \text{UO}_2 \)

d. **Bond type**: covalent → **stiff** bonds

e. **Coordination number**: fewer bonds, smaller site → **stiff** bonds
   
   1-fold < 2-fold < 3-fold > 4-fold > 6-fold > 8-fold coordination