Equilibrium stable isotope fractionation

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Notation for fractionation factors:

$$\alpha_{XA\text{-}XB} = R_{XA}/R_{XB}$$

$$\delta_{XA} - \delta_{XB} \approx 1000 \bullet (\alpha_{XA\text{-}XB} - 1) \approx 1000 \bullet ln(\alpha_{XA\text{-}XB})$$

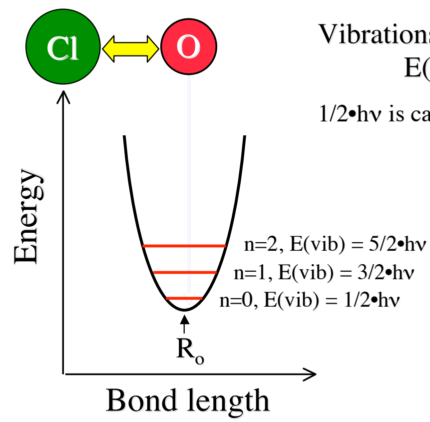
For equilibrium isotopic fractionation, α is related to the equilibrium constant of a one-atom exchange reaction:

$$^{light}XA + {}^{heavy}XB \leftrightarrow {}^{heavy}XA + {}^{light}XB$$

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

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

Theory of equilibrium isotopic fractionation



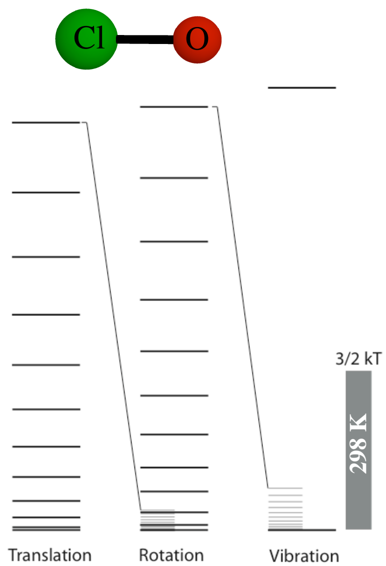
Vibrations are quantized,

$$E(vib) = h\nu(n+1/2) \quad n=0,1,2,3\ldots$$

1/2•hν is called the Zero-Point Energy (ZPE)

Rotation and Translation:

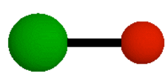
Both types of motion are also quantized, but there is no zero-point energy, and the quanta are much smaller than for vibrations.
Rotational and translational quanta are much smaller than thermal energy at room temperature.

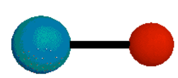


Rotational and translational quanta are so small relative to relevant thermal energies that classical mechanics gives a reasonably accurate description of non-vibrational motion.

^{35}ClO $\nu = 853.72$ cm^{-1}
(25.59•10^{12} Hz)

^{37}ClO $\nu = 846.45$ cm^{-1}
(25.38•10^{12} Hz)





E(vib) = 1/2•hν
≈ 5106 J/mol

E(vib) = 1/2•hν
≈ 5063 J/mol

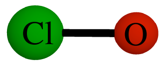
At Equilibrium, for Cl-isotope exchange between monoatomic Cl and ClO:

$$^{37}\text{Cl} + {}^{35}\text{ClO} \leftrightarrow {}^{35}\text{Cl} + {}^{37}\text{ClO}$$

$\Delta G_0 \approx \Delta E_{(vib)} = E_{(vib)}$ *products* – $E_{(vib)}$ *reactants*

$E_{(vib)}$ *products* = 5063 J/mol (^{37}ClO)
$E_{(vib)}$ *reactants* = 5106 J/mol (^{35}ClO)

ΔE(vib) = –43 J/mol, driving the reaction to the right and concentrating ^{37}Cl in ClO!



To get from ΔG_0 to a fractionation factor, we can use the standard thermodynamic formula:

$$\Delta G_0 = -kT \bullet ln(K_{eq}) = -kT \bullet ln(\alpha_{ClO\text{-}Cl})$$

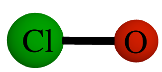
$$\alpha_{ClO\text{-}Cl} = exp(-\Delta G_0/kT)$$

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

$$\alpha_{ClO\text{-}Cl} = exp(-\Delta G_0/kT) = exp(-\Delta E_{vib}/kT)$$

$$\approx exp(-\{1/2 \bullet h\nu_{37ClO} - 1/2 \bullet h\nu_{35ClO}\}/kT)$$

$$= exp(\frac{h}{2kT}\{\nu_{35ClO} - \nu_{37ClO}\}) \quad = 1.017 \text{ at } 298 \text{ K}$$



In reality, some molecules will be vibrationally excited:

$$\alpha_{ClO\text{-}Cl} = exp(-\Delta G_0/kT) = exp(-\Delta E_{vib}/kT)$$

$$E_{vib} = -kTln(Q_{vib})$$

$$Q_{vib} = \Sigma_{n=0}^{\infty} exp(-E_n/kT)$$

$$Q_{vib} = \Sigma_{n=0}^{\infty} exp(-h\nu(n+1/2)/kT)$$

$$= \Sigma_{n=0}^{\infty} exp(-h\nu/2kT) \bullet exp(-h\nu n/kT)$$

$$= exp(-h\nu/2kT) \bullet \Sigma_{n=0}^{\infty} exp(-h\nu/kT)^n$$

$$\Sigma_{n=0}^{\infty} y^n = 1/(1-y)$$

$$= \underbrace{exp(-h\nu/2kT)}_{\text{ZPE}} \bullet 1/\{1 - \underbrace{exp(-h\nu/kT)}_{\text{Excited states}}\}$$

So by including excited vibrational states,

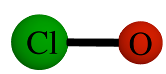
$$\alpha_{ClO\text{-}Cl} = \frac{exp(-h\nu_{^{37}ClO}/2kT)/\{1-exp(-h\nu_{^{37}ClO}/kT)\}}{exp(-h\nu_{^{35}ClO}/2kT)/\{1-exp(-h\nu_{^{35}ClO}/kT)\}}$$

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

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

Rotation and translation

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



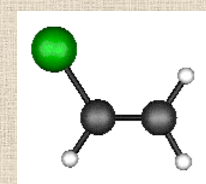
$\alpha_{ClO\text{-}Cl} = 1.0096$ *at 298 K*

(the difference is due mainly to excited rotation & translation)

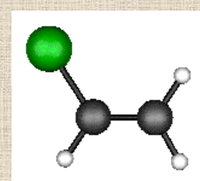
It is necessary to know vibrational frequencies of all relevant isotopic forms of a molecule or mineral (i.e. Na^{35}Cl *and* Na^{37}Cl).

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.



93.53 THz w/^{35}Cl, no shift when ^{37}Cl is substituted

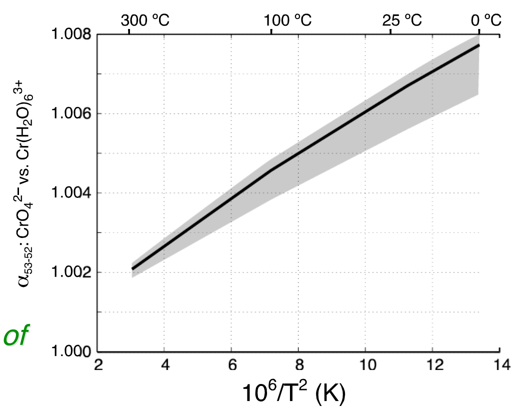


11.78 THz w/^{35}Cl, 0.07 THz shift when ^{37}Cl is substituted

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 $(m_{heavy}-m_{light})/m^2$*

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*
      $C^{4+} \leftrightarrow C \leftrightarrow C^{4-}$, $S^{6+} \leftrightarrow S^{2-}$, $Fe^{3+} \leftrightarrow Fe^{2+}$

   b. *Bond partner oxidation state: high charge →* ***stiff*** *bonds*
      $SiO_2 \leftrightarrow Al_2O_3 \leftrightarrow CaO$

   c. *Bond partners: "hard", low atomic # →* ***stiff*** *bonds*
      $SiO_2 \leftrightarrow TiO_2 \leftrightarrow UO_2$

   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