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"Mass-Dependent Fractionation *from Urey to Bigeleisen*"

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1. Urey's formula *(The Theory of the Equilibrium Constants of Exchange Reactions)*

$$aA_1 + bB_2 \leftrightarrow aA_2 + bB_1$$

(Initial material → $aA_1 + bB_2 + aA_2 + bB_1$)

where A and B are molecules which have some one element as a common constituent. Subscripts 1 and 2 indicate that the molecule contains only the light or heavy isotope respectively

(For example, volcanic sulfur containing gas → $H_2{}^{32}S + {}^{34}SO_4 \leftrightarrow {}^{32}SO_4 + H_2{}^{34}S$)

According to Mayer and Mayer, "Statistical Mechanics," equilibrium constant would be

$$K(T) = \left[\left(\frac{Q_{A_2}}{Q_{A_1}}\right)^a \Big/ \left(\frac{Q_{B_2}}{Q_{B_1}}\right)^b\right]$$

(which is constant under the same temperature)

$$G^0 = -RTlnQ \quad (\mathrm{K(T)} = e^{-\Delta G^0/RT})$$

(G^0 *is standard Gibbs Free Energy*)

where Qs are the partition functions of the molecules

$$Q = Q_{trans} * Q_{vibration} * Q_{rotation} * Q_{electronic}$$

However, we don't have to think about $Q_{electronic}$, since it will mostly be in the ground state only. If it's under sun's temperature, then we might have to care about it. So, we can assume that $Q_{electronic}$ as 1.

$$Q = Q_{trans} * Q_{vibn} * Q_{rot}$$

Each of the partition functions is statistically mechanically defined as below

$Q_{trans} = \mathrm{V}_{*}(\frac{2\pi M k_B T}{h^2})^{3/2}$ (not quantized)

Q_{rot}[1]$= \frac{1}{\sigma}\sum_{J=0}^{\infty} g_J \cdot e^{-\frac{hcB_e J(J+1)}{k_B T}}$ (quantized)

$Q_{vibn} = \sum_{i}^{\infty} e^{-\frac{\left(\frac{1}{2}+i\right)hv}{k_B T}}$ (quantized)

([1] σ is a symmetry term. For homonuclei, σ is 1 while for heteronuclei, σ is 2. g_J is degeneracy due to same angular momentum but having different magnetic quantum numbers. $g_J = 2\mathrm{J}+1$)

Okay. Let's break down each of the partition functions.
First, it would be Q_{rot}.

$$Q_{rot} = \frac{1}{\sigma}\sum_{J=0}^{\infty} g_J \cdot e^{-\frac{hcB_e J(J+1)}{k_B T}} = \frac{1}{\sigma}\int_0^{\infty} dJ(2J+1)\, e^{-\frac{hcB_e J(J+1)}{k_B T}}$$

If we put $\tau = J(J+1)$, $d\tau = dJ(2J+1)$. So we can change the equation above into

$$Q_{rot} = \frac{1}{\sigma}\int_0^{\infty} d\tau\ e^{-\frac{hcB_e}{k_B T}\tau} = \frac{1}{\sigma}\frac{k_B T}{hcB_e}$$

You might be curious about what is B_e. Well, that is actually derived from moment of Inertia. If we reduce two body rotating problem into one body problem, we have angular momentum equation

$$L = \mu r^2 \omega = I\,\omega$$

Momentum $P=mv$ corresponds to $L=I\,\omega$. As you can see I is such a thing like the mass m. Scientists call this property as the *moment of Inertia*.

In the same way, Kinetic Energy of rigid rotator system can be expressed by L and I.

$$\text{Kinetic Energy} = \frac{P^2}{2m} = \frac{(\mu r\omega)^2}{2\mu} = \frac{L^2}{2\mu r^2} = \frac{L^2}{2I}$$

In quantum mechanics, angular momentum operator L^2 has an eigenvalue of $\hbar^2 J(J+1)$ based on the mathematical solutions to Legendre equation. So Kinetic Energy of rigid rotator system is

$$\text{Kinetic Energy} = \frac{L^2}{2I} = \frac{\hbar^2}{2I} J(J+1) = B_e\, J(J+1)$$

$$\text{So } Q_{rot} = \frac{1}{\sigma}\frac{k_B T}{hcB_e} \propto \frac{I}{\sigma} \text{ (since } B_e \propto \frac{1}{I})$$

Next, it would be Q_{vibn}

$$Q_{vibn} = \sum_i^\infty e^{-\frac{\left(\frac{1}{2}+i\right)hv}{k_B T}} = e^{-\frac{hv}{2k_B T}} + e^{-\frac{3hv}{2k_B T}} + e^{-\frac{5hv}{2k_B T}} + \ldots$$

$$= e^{-\frac{hv}{2k_B T}} * (1 + e^{-\frac{hv}{k_B T}} + e^{-\frac{2hv}{k_B T}} + e^{-\frac{3hv}{k_B T}} + e^{-\frac{4hv}{k_B T}} + \ldots)$$

$$= \lim_{n\to\infty} \frac{e^{-\frac{hv}{2k_B T}}\left(1 - e^{-\frac{nhv}{2k_B T}}\right)}{1 - e^{-\frac{hv}{k_B T}}} = \frac{e^{-\frac{hv}{2k_B T}}}{1 - e^{-\frac{hv}{k_B T}}} = \frac{e^{-\frac{u}{2}}}{1-e^{-u}} \quad \text{(where u} = \frac{hv}{k_B T})$$

$$\text{So } Q_{vibn} = \frac{e^{-\frac{u}{2}}}{1-e^{-u}}$$

We don't have to do special actions on Q_{trans} since it will be just

$$Q_{trans} = \mathrm{V}*\left(\frac{2\pi M k_B T}{h^2}\right)^{3/2} \propto M^{3/2}$$

So we are ready to combine all these partition functions.

$$Q = Q_{trans} * Q_{vibn} * Q_{rot} \propto (M^{3/2}) * \left(\frac{e^{-\frac{u}{2}}}{1-e^{-u}}\right) * \left(\frac{I}{\sigma}\right)$$

Now, recall the equilibrium constant K.

$$K(T) = \left[\left(\frac{Q_{A_2}}{Q_{A_1}}\right)^a \Big/ \left(\frac{Q_{B_2}}{Q_{B_1}}\right)^b\right] \text{ and let us only think about highlighted part!}$$

$$\frac{Q_{A_2}}{Q_{A_1}} \;!!$$

For easier notation, let's take

$$\frac{Q_{A_2}}{Q_{A_1}} = \frac{Q_2}{Q_1}$$

Then,

$$\frac{Q_2}{Q_1} = (\frac{M_2}{M_1})^{\frac{3}{2}}(\frac{\sigma_1}{\sigma_2})(\frac{I_2}{I_1})\ (\frac{e^{-\frac{u_2}{2}}}{1-e^{-u_2}})\ (\frac{1-e^{-u_1}}{e^{-\frac{u_1}{2}}})$$

The first term is from translational term, the next two terms are from rotational terms and the last two terms are from vibrational terms. This ratio is partition function ratio of two diatomic molecules. In order to make this equation general, we have to think about polyatomic molecule's partition function.

For polyatomic molecule, it would be

$$\frac{Q_2}{Q_1} = (\frac{M_2}{M_1})^{\frac{3}{2}}(\frac{\sigma_1}{\sigma_2})(\frac{A_2B_2\ldots Z_2}{A_1B_1\ldots Z_1})^{\frac{1}{2}}\ \prod_i(\frac{e^{-\frac{u_{2i}}{2}}}{e^{-\frac{u_{1i}}{2}}})\ (\frac{1-e^{-u_{1i}}}{1-e^{-u_{2i}}})$$

(Where A_x, B_x are principle moments of inertia of the polyatomic molecules, respectively and i is indicating dimension of freedom of Harmonic Oscillators)

According to a theorem of Teller and Redlich,

$$(\frac{A_2B_2\ldots Z_2}{A_1B_1\ldots Z_1})^{\frac{1}{2}}(\frac{M_2}{M_1})^{\frac{3}{2}}(\frac{m_1}{m_2})^{\frac{3}{2}n}\ \prod_i^N\frac{u_{1i}}{u_{2i}} = 1$$

So if we use this theorem, we can get…

$$f = \frac{Q_2}{Q_1}\ (\frac{m_1}{m_2})^{\frac{3}{2}n} = (\frac{A_2B_2\ldots Z_2}{A_1B_1\ldots Z_1})^{\frac{1}{2}}(\frac{M_2}{M_1})^{\frac{3}{2}}(\frac{m_1}{m_2})^{\frac{3}{2}n}\ \prod_i^N\frac{u_{1i}}{u_{2i}}\ (\frac{\sigma_1}{\sigma_2})\ \prod_i^N(\frac{u_{2i}}{u_{1i}})(\frac{e^{-\frac{u_{2i}}{2}}}{e^{-\frac{u_{1i}}{2}}})\ (\frac{1-e^{-u_{1i}}}{1-e^{-u_{2i}}})$$

since highlighted part is 1, with trivial arrangement

$$\frac{Q_2}{Q_1}\ (\frac{m_1}{m_2})^{\frac{3}{2}n}(\frac{\sigma_2}{\sigma_1}) = \frac{Q_2'}{Q_1'} = \prod_i^N(\frac{u_{2i}}{u_{1i}})(\frac{e^{-\frac{u_{2i}}{2}}}{e^{-\frac{u_{1i}}{2}}})\ (\frac{1-e^{-u_{1i}}}{1-e^{-u_{2i}}})$$

From above, we are now able to express partition functions only with frequencies.
By the way,

$$\frac{Q_2'}{Q_1'} = (\frac{\sigma_2}{\sigma_1})\ \frac{Q_2}{Q_1}\ (\frac{m_1}{m_2})^{\frac{3}{2}n} = \frac{s}{s\prime}f$$

$$(\text{where } \frac{s}{s\prime} = \frac{\sigma_2}{\sigma_1})$$

is called Reduced Partition Function Ratio (RPFR) originally used in Urey,1947.

2. Bigeleisen's formula *(Calculation of equilibrium constants for isotopic exchange reactions)*

$$\frac{s}{s\prime} f = \frac{Q_2}{Q_1} (\frac{m_1}{m_2})^{\frac{3}{2}n} (\frac{\sigma_2}{\sigma_1}) = \frac{Q_2'}{Q_1'} = \prod_i^N (\frac{u_{2i}}{u_{1i}}) (\frac{e^{-\frac{u_{2i}}{2}}}{e^{-\frac{u_{1i}}{2}}}) (\frac{1-e^{-u_{1i}}}{1-e^{-u_{2i}}})$$

So,

$$\frac{s}{s\prime} f = \prod_i^N (\frac{u_{2i}}{u_{1i}}) (\frac{e^{-\frac{u_{2i}}{2}}}{e^{-\frac{u_{1i}}{2}}}) (\frac{1-e^{-u_{1i}}}{1-e^{-u_{2i}}}) \qquad \text{Eq (1)}$$

Equation (1) is the most exact equation when it comes to calculate the equilibrium constant.

According to Bigeleisen and Mayor.,1947, the ratio of the masses of the isotopes will cancel in any chemical reaction and the ratio of the symmetry numbers, no matter what its value, will not lead to isotopic enrichment since it merely represents the relative probabilities of forming symmetrical and unsymmetrical molecules. So in calculating the equilibrium constant of isotopic exchanges the useless classical ratio of $(m_1/m_2)^{3/2}$ is best omitted (treated as 1).

So,

$$\frac{\sigma_2 Q_2}{\sigma_1 Q_1} = \prod_i^N (\frac{u_{2i}}{u_{1i}}) (\frac{e^{-\frac{u_{2i}}{2}}}{e^{-\frac{u_{1i}}{2}}}) (\frac{1 - e^{-u_{1i}}}{1 - e^{-u_{2i}}})$$

Recall that

$$K(T) = [\left(\frac{Q_{A_2}}{Q_{A_1}}\right)^a \Big/ \left(\frac{Q_{B_2}}{Q_{B_1}}\right)^b]$$

Let's apply this equation to calculate the equilibrium constant of isotope exchange of the reaction

$$H_2 + 2DI = D_2 + 2HI$$

Molecule	$\omega_e\ [cm^{-1}]$	$\omega_e x_e\ [cm^{-1}]$	$v_i = \omega_e - {}^1\!/_2\, \omega_e x_e\ [cm^{-1}]$
H_2	4405.3	125.325	4263.75
D_2	3117.05	63.034	3085.53
HI	2309.53	39.73	2289.67
DI	1640.18	20.04	1630.16

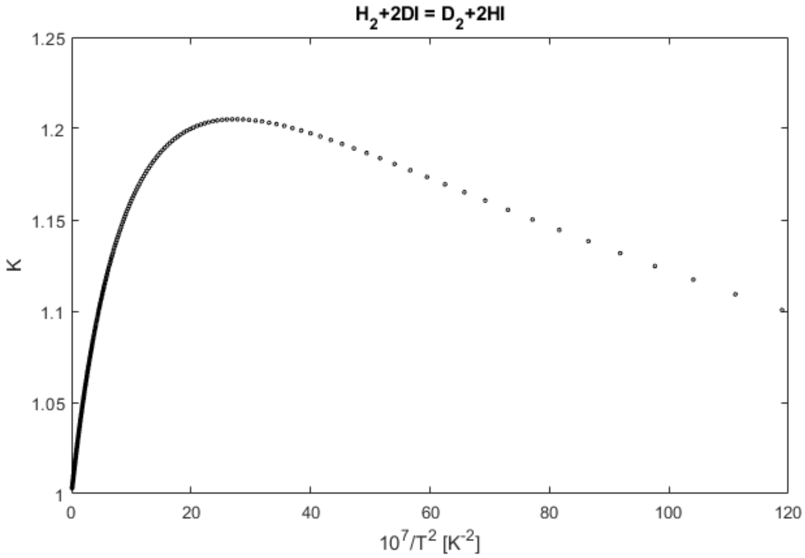
(Reported by G.K. Teal and G.E.Macwood, J.Chem .Phys.3,760 (1935))

Assuming the rigid rotor and since both H_2 and D_2 have same symmetry number of 1 and HI and DI have the same symmetry number of 2, all these symmetry number will cancel out, we will have…

$$K(T) = [(\frac{Q_{D_2}}{Q_{H_2}}) \Big/ \left(\frac{Q_{DI}}{Q_{HI}}\right)^2]$$

When it comes to calculation, it is important to check out the units and frequency. (e.g. $u_i = \frac{hcv_i}{k_B T}$)

And if we plot this K_{eq} with regard to *1/T*, we will get the graph below.



(We can see that at the high temperature, equilibrium constant K becomes linear.)

Now, it is over! Like this, we were able to get equilibrium constant and since…

Wait.. No. There is a lot more to go…

When this quantum calculation was done, there wasn't any good computer nor calculating program like ~~Matlab~~. So Bigeleisen and Mayor tried to make this equation as much simple as possible. So, let's go further to make this MDF simpler!

$$\frac{s}{s\prime}f = \frac{\sigma_2 Q_2}{\sigma_1 Q_1} = \frac{Q_2'}{Q_1'} = \prod_i^N (\frac{u_{2i}}{u_{1i}})(\frac{e^{-\frac{u_{2i}}{2}}}{e^{-\frac{u_{1i}}{2}}})\ (\frac{1-e^{-u_{1i}}}{1-e^{-u_{2i}}}) = \prod_i^N q_i = q_{1*}\, q_{2*}\, q_{3\ldots}\, q_N$$

(where N is the dimension of freedom of Harmonic Oscillator)

For convenience in calculation, $u_{1i} = u_i'$ (lighter isotope) and $u_{2i} = u_i$, which means $u_i = \frac{hcv_i}{k_B T}$

For each Harmonic Oscillator, $\Delta u_i = u_i' - u_i$

$$q_i = (\frac{u_i}{u_i+\Delta u_i})(e^{\frac{\Delta u_i}{2}})(\frac{1-e^{-(u_i+\Delta u_i)}}{1-e^{-u_i}})$$

and thus,

$$\frac{s}{s'}f = \prod_i^N (\frac{u_i}{u_i+\Delta u_i})(e^{\frac{\Delta u_i}{2}})(\frac{1-e^{-(u_i+\Delta u_i)}}{1-e^{-u_i}})$$

Actually, at this point, we have two ways to make an approximation.

The first one starts from the definition of Gibbs free energy.

Recall that

$$G^0 = -RTlnQ$$

So, we can arrange that

$$G^{0\prime} = -RTlnQ'$$

(where Q' means partition function of lighter isotope)

&

$$G^0 = -RTlnQ$$

Then, from equation (1),

$$\frac{G^{0'} - G^0}{RT} = -ln\frac{Q}{Q'} = -lnf = -ln\left[\frac{s'}{s}\prod_i^N\left(\frac{u_i}{u_i+\Delta u_i}\right)\left(e^{\frac{\Delta u_i}{2}}\right)\left(\frac{1-e^{-(u_i+\Delta u_i)}}{1-e^{-u_i}}\right)\right]$$

$$= ln\frac{s}{s'} + \sum_i^N\left[ln\left(1+\frac{\Delta u_i}{u_i}\right) + ln\left(\frac{1-e^{-u_i}}{1-e^{-(u_i+\Delta u_i)}}\right) - \frac{\Delta u_i}{2}\right]$$

Since $\Delta u_i \sim 0$ for every isotope except for hydrogen isotope,

$$= ln\frac{s}{s'} + \sum_i^N\left[\frac{\Delta u_i}{u_i} - \frac{\Delta u_i}{2} + ln\left(\frac{1-e^{-u_i}}{1-e^{-(u_i+\Delta u_i)}}\right)\right]$$

$$*** \quad ln\left(\frac{1-e^{-u_i}}{1-e^{-(u_i+\Delta u_i)}}\right) = ln\left(\frac{\frac{e^{u_i}-1}{e^{u_i}}}{\frac{e^{(u_i+\Delta u_i)}-1}{e^{(u_i+\Delta u_i)}}}\right) = ln\left(\frac{e^{u_i}-1}{e^{u_i}} * \frac{e^{(u_i+\Delta u_i)}}{e^{(u_i+\Delta u_i)}-1}\right)$$

$$= \ ln\frac{e^{u_i}(e^{u_i}-1)}{e^{(u_i+\Delta u_i)}-1} = \ ln\frac{e^{(u_i+\Delta u_i)}-1+1-e^{\Delta u_i}}{e^{(u_i+\Delta u_i)}-1}$$

$$= ln\left(1+\frac{1-e^{\Delta u_i}}{e^{(u_i+\Delta u_i)}-1}\right) \approx \frac{1-e^{\Delta u_i}}{e^{(u_i+\Delta u_i)}-1} \qquad (\text{since } 1-e^{\Delta u_i} \sim 0 \ when \ \Delta u_i \ \rightarrow 0)$$

Also, $e^{\Delta u_i} = 1 + \Delta u_i + \frac{\Delta {u_i}^2}{2} + \frac{\Delta {u_i}^3}{6} + \cdots \approx 1 + \Delta u_i \qquad \therefore \ \frac{1-e^{\Delta u_i}}{e^{(u_i+\Delta u_i)}-1} \sim \frac{-\Delta u_i}{e^{u_i}-1}$

Eventually,

$$\frac{G^{0'}-G^{0}}{RT} = -ln\frac{Q}{Q'} = -lnf = ln\frac{s}{s'} + \sum_{i}^{N}\left[\frac{\Delta u_i}{u_i} - \frac{\Delta u_i}{2} + ln\left(\frac{1-e^{-u_i}}{1-e^{-(u_i+\Delta u_i)}}\right)\right]$$

$$= ln\frac{s}{s'} + \sum_{i}^{N}\left[\frac{\Delta u_i}{u_i} - \frac{\Delta u_i}{2} + \frac{-\Delta u_i}{e^{u_i}-1}\right]$$

In turn,

$$ln\frac{s}{s'}f = \sum_{i}^{N}\left[\frac{1}{2} - \frac{1}{u_i} + \frac{1}{e^{u_i}-1}\right]\Delta u_i$$

$$\frac{s}{s'}f = e^{\sum_{i}^{N}\left[\frac{1}{2}-\frac{1}{u_i}+\frac{1}{e^{u_i}-1}\right]\Delta u_i} \qquad \text{Eq (2)}$$

Equation (2) is the approximation derived from Gibbs Free Energy equation.

Now, let us move on to the second approximation. This approximation also starts from equation (1).

$$\frac{s}{s'}f = \prod_{i}^{N}\left(\frac{u_i}{u_i+\Delta u_i}\right)\left(e^{\frac{\Delta u_i}{2}}\right)\left(\frac{1-e^{-(u_i+\Delta u_i)}}{1-e^{-u_i}}\right) = \prod_{i}^{N} q_i = q_{1}* q_{2}* q_{3}\ldots q_{N}$$

where

$$q_i = \left(\frac{u_i}{u_i+\Delta u_i}\right)\left(e^{\frac{\Delta u_i}{2}}\right)\left(\frac{1-e^{-(u_i+\Delta u_i)}}{1-e^{-u_i}}\right)$$

Again, since $\Delta u_i \sim 0$ for every isotope except for hydrogen isotope, we can do taylor expansions for all three terms which would be tedious and horrible…

Anyway, it would be…

$$q_i = \left(1 - \frac{\Delta u_i}{u_i} + \left(\frac{\Delta u_i}{u_i}\right)^2 + \cdots\right)\left(1 + \frac{\Delta u_i}{2} + \frac{(\Delta u_i)^2}{8} + \cdots\right)\left(1 + \frac{\Delta u_i * e^{-u_i}}{1-e^{-u_i}} + \cdots\right)$$

Ignore $(\Delta u_i)^2$ >>, since $\Delta u_i \sim 0$, then…

$$q_i \approx \left(1 - \frac{\Delta u_i}{u_i}\right)\left(1 + \frac{\Delta u_i}{2}\right)\left(1 + \frac{\Delta u_i * e^{-u_i}}{1-e^{-u_i}}\right)$$

Expand all the terms and ignore the term higher than $(\Delta u_i)^2$ again, then…

$$q_i = 1 + (\frac{1}{2} - \frac{1}{u_i} + \frac{1}{e^{u_i-1}})\Delta u_i$$

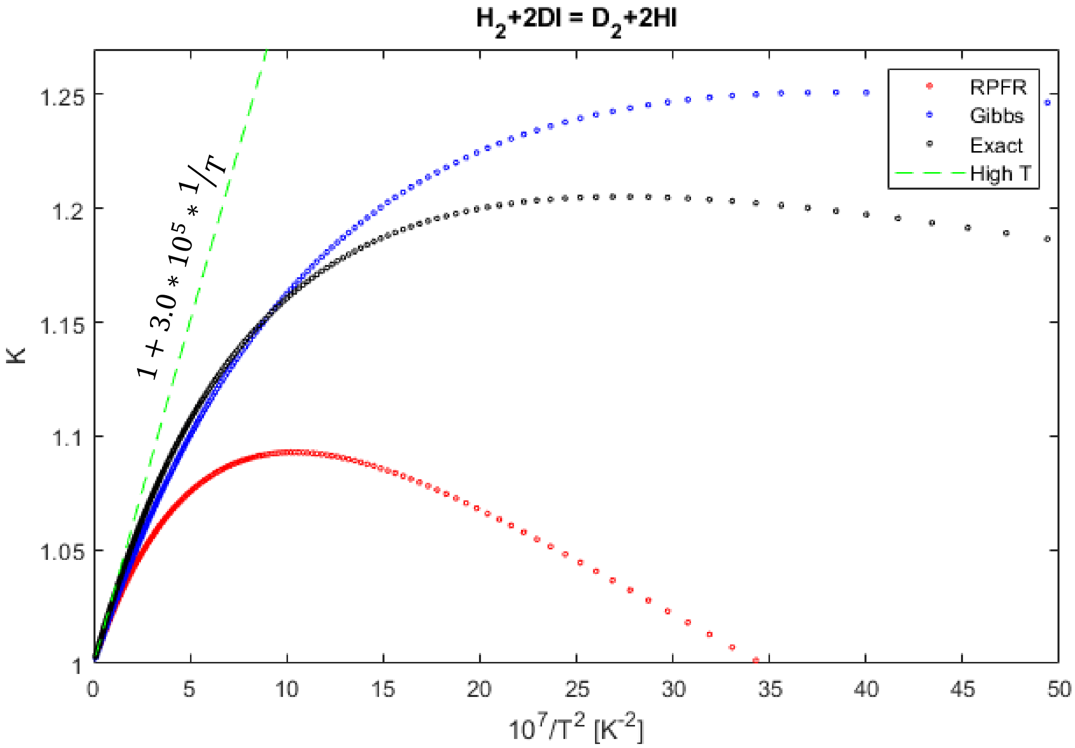
Following…

$$\prod_i^N q_i \approx 1 + \sum_i(\frac{1}{2} - \frac{1}{u_i} + \frac{1}{e^{u_i-1}})\Delta u_i$$

$$\frac{s}{s\prime} f = 1 + \sum_i(\frac{1}{2} - \frac{1}{u_i} + \frac{1}{e^{u_i-1}})\Delta u_i \qquad \text{Eq (3)}$$

Equation (3) is derived via ignoring lots of terms higher than $(\Delta u_i)^2$. For this reason, this approximation would be the least precise approximation when going down to lower temperature.

If I calculate these equation 1,2,3 and plot in one plot in order to compare each other, the result will be below in case of $H_2 + 2DI = D_2 + 2HI$.



(The red circle is eqn (3), the blue circle is eqn (2) and the black circle is eqn (1) which is the exact calculation. You can see that the blue circles are better approximation comparing to the red circles.)

Wait… is this all? We haven’t seen any kind of equation related to the Mass Dependent Fractionation law. What have we done so far?

Calm down. Now we are at the final stage. In the next section, we will talk about the main dish, “the Mass Dependent Fractionation Law.”

3. Mass Dependent Isotope Fractionation Law

We have to start from equation (3)

$$\frac{s}{s\prime}f =1 + \sum_i \left(\frac{1}{2} - \frac{1}{u_i} + \frac{1}{e^{u_i - 1}}\right)\Delta u_i \qquad \text{Eq (3)}$$

Let's say $u_i \equiv \gamma\, u_i'$(i.e. $\Delta u_i \equiv u_i'(1-\gamma)$), then…

$$\sum_i \left(\frac{1}{2} - \frac{1}{u_i} + \frac{1}{e^{u_i - 1}}\right)\Delta u_i = \sum_i^N \left(\frac{1}{2} - \frac{1}{\gamma u_i'} + \frac{1}{e^{\gamma u_i' - 1}}\right) u_i'(1-\ \gamma)$$

$$= \sum\nolimits_i^N \left(1 - \frac{1}{\gamma}\right) + \frac{1}{2}(1-\gamma)u_i' + \frac{1-\gamma}{e^{\gamma u_i'} - 1}u_i'$$

At high temperature so we can say $u_i = \frac{hcv_i}{k_B T} = \gamma\, u_i' \sim 0,$

we can expand $e^{\gamma u'_i} \sim 1 + \gamma u'_i + \frac{(\gamma u'_i)^2}{2} + \frac{(\gamma u'_i)^3}{6} + \frac{(\gamma u'_i)^4}{24} \ldots$

$$\therefore \frac{1-\gamma}{e^{\gamma u'_i - 1}}u'_i = \frac{(1-\gamma)u'_i}{\gamma u'_i + \frac{(\gamma u'_i)^2}{2} + \frac{(\gamma u'_i)^3}{6} + \frac{(\gamma u'_i)^4}{24} + \cdots} = \frac{(1-\gamma)}{\gamma\left(1 + \frac{\gamma u'_i}{2} + \frac{(\gamma u'_i)^2}{6} + \frac{(\gamma u'_i)^3}{24} + \cdots\right)}$$

$$= \frac{(1-\gamma)}{\gamma}\left(1 + \frac{\gamma u'_i}{2} + \frac{(\gamma u'_i)^2}{6} + \frac{(\gamma u'_i)^3}{24} + \cdots\right)^{-1}$$

If we replace $f(u'_i) = \left(1 + \frac{\gamma u'_i}{2} + \frac{(\gamma u'_i)^2}{6} + \frac{(\gamma u'_i)^3}{24} + \cdots\right)^{-1}$,

$$\frac{1-\gamma}{e^{\gamma u'_i} - 1}u'_i = \frac{(1-\gamma)}{\gamma}\left(f(0) + f'(0)u'_i + f''(0)\frac{{u'_i}^2}{2} + \cdots\right)$$

$$= \frac{(1-\gamma)}{\gamma}\left(1 - \frac{\gamma u'_i}{2} + \frac{\gamma^2 {u'_i}^2}{12} + \ldots\right)$$

So finally…

$$\sum_i \left(\frac{1}{2} - \frac{1}{u_i} + \frac{1}{e^{u_i - 1}}\right)\Delta u_i = \sum_i \left(1 - \frac{1}{\gamma}\right) + \frac{1}{2}(1-\gamma)u'_i + \frac{1-\gamma}{e^{\gamma u'_i - 1}}u'_i$$

$$= \sum_i \left(1 - \frac{1}{\gamma}\right) + \frac{1}{2}(1-\gamma)u'_i + \frac{(1-\gamma)}{\gamma}\left(1 - \frac{\gamma u'_i}{2} + \frac{\gamma^2 {u'_i}^2}{12} + \cdots\right)$$

$$= \sum_i \frac{\gamma u'_i{}^2}{12} - \frac{\gamma^2 u'_i{}^2}{12} + \cdots \text{ (ignore } u'_i{}^3 < \text{ terms)} = \sum_i \frac{\gamma u'_i(u'_i - \gamma u'_i)}{12}$$

$$= \sum_i^N \frac{u_i \Delta u_i}{12}$$

Now, equation (3) has been reduced into

$$\frac{s}{s'} f = 1 + \sum_i \left(\frac{1}{2} - \frac{1}{u_i} + \frac{1}{e^{u_i} - 1}\right) \Delta u_i = 1 + \sum_i^N \frac{u_i \Delta u_i}{12}$$

Since,

$$u'_i{}^2 - u_i^2 = (u_i + \Delta u_i)^2 - u_i{}^2 \sim 2u_i \Delta u_i \qquad (\text{ignore } \Delta u_i{}^2 \sim 0)$$

$$\frac{s}{s'} f = 1 + \sum_i \frac{u_i \Delta u_i}{12} = 1 + \sum_i \frac{2u'_i \Delta u_i}{24} = 1 + \sum_i \frac{u'^2_i - u_i^2}{24}$$

$$\frac{s}{s'} f = 1 + \sum_i \frac{u'^2_i - u_i^2}{24} \qquad \text{Eq (4)}$$

(This is called high temperature approximation)

Recall that $u_i = \frac{hc v_i}{k_B T}$,

$$\frac{u'^2_i - u_i^2}{24} = \frac{1}{24} \left(\frac{hc}{k_B T}\right)^2 (v_i'^2 - v_i{}^2)$$

In classical Harmonic Oscillator,

$$\text{frequency } v = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

Thus,

$$\frac{s}{s'} f = 1 + \sum_i \frac{1}{24} \left(\frac{hc}{2\pi k_B T}\right)^2 \left(\frac{k_i}{\mu'} - \frac{k_i}{\mu}\right) = 1 + C * \frac{\mu - \mu'}{\mu' \mu} \quad \text{where } C \text{ is the constant}$$

Recall that

$$\left(\frac{s}{s'} f\right)_A = \frac{Q'_2}{Q'_1} = \frac{\sigma_2 Q_{A_2}}{\sigma_1 Q_{A_1}}$$

Thus, the isotope fractionation factor

$$\alpha_{A-B} = \frac{\left(\frac{s}{s'}f\right)_A}{\left(\frac{s}{s'}f\right)_B} = \frac{R_A}{R_B}$$

where

$$\left(\frac{s}{s'}f\right)_A = 1 + C_A * \frac{\mu-\mu'}{\mu'\mu}$$

$$\left(\frac{s}{s'}f\right)_B = 1 + C_B * \frac{\mu-\mu'}{\mu'\mu}$$

Finally…!

$$ln\alpha_{A-B} = l\,n(\delta+1) = l\,n\left(1 \,+\, C_A \,*\, \frac{\mu-\mu'}{\mu'\mu}\right) - l\,n\left(1 \,+\, C_B \,*\, \frac{\mu-\mu'}{\mu'\mu}\right)$$

$$\approx \ \delta$$

Since δ, $C_A \, * \, \frac{\mu-\mu'}{\mu'\mu}$ and $C_B \, * \, \frac{\mu-\mu'}{\mu'\mu}$ are small, we can make an approximation.

$$\delta = (C_A - C_B) \, * \, \frac{\mu-\mu'}{\mu'\mu} \approx \tilde{E} * \frac{\mu-\mu'}{\mu'\mu}$$

(where $\tilde{E}$ is a constant)

More generally, if we think about multiple isotopes, (μ_1 is the most abundant isotope.)

$$\delta^x = \tilde{E} * \frac{\mu_x-\mu_1}{\mu_1\mu_x}$$

Someone might worry about the mass of different elements affecting the isotope fractionation factor. For example, in case of $^{12}C^{16}O$, $^{12}C^{17}O$, $^{12}C^{18}O$, we might have to worry about ^{12}C. Let's test it!

First step, we have to derive the reduced mass of each diatomic molecules.

$$\mu_{ab} = \frac{m_a * m_b}{m_a + m_b}$$

$$\therefore \quad \mu_{1216} = \frac{12*16}{12+16}, \qquad \mu_{1217} = \frac{12*17}{12+17}, \qquad \mu_{1218} = \frac{12*18}{12+18}$$

$$\delta^{17} = \tilde{E} * \frac{\mu_{1217}-\mu_{1216}}{\mu_{1216}\mu_{1217}}$$

$$\delta^{18} = \tilde{E} * \frac{\mu_{1218}-\mu_{1216}}{\mu_{1216}\mu_{1218}}$$

$$\frac{\delta^{17}}{\delta^{18}} = {\frac{\mu_{1217}-\mu_{1216}}{\mu_{1216}\mu_{1217}}}\Bigg/{\frac{\mu_{1218}-\mu_{1216}}{\mu_{1216}\mu_{1218}}} = {\frac{\frac{12*17}{12+17}-\frac{12*16}{12+16}}{\frac{12*17}{12+17}*\frac{12*16}{12+16}}}\Bigg/{\frac{\frac{12*18}{12+18}-\frac{12*16}{12+16}}{\frac{12*18}{12+18}*\frac{12*16}{12+16}}}$$

$$= \frac{\frac{12*17*(12+16)-12*16*(12+17)}{(12+17)*(12+16)} * \frac{(12+17)*(12+16)}{12*17*12*16}}{\frac{12*18*(12+16)-12*16*(12+18)}{(12+18)*(12+16)} * \frac{(12+18)*(12+16)}{12*18*12*16}}$$

$$= \frac{\frac{12*17*12-12*12*16}{12*12*16*17}}{\frac{12*18*12-12*12*16}{12*12*16*18}} = \frac{{}^{17-16}\!/_{16*17}}{{}^{18-16}\!/_{16*18}} = 0.529$$

As you can see in the yellow part, the mass of carbon 12 has gone away with remaining oxygen isotope terms in case of diatomic molecules. For polyatomic molecules, it would be lot much more complicated to prove it but same.

So we can say that

$$\delta^{x} = \tilde{E} * \frac{m_x - m_1}{m_1 m_x}\,!!$$

Now we can apply this idea to real world. In 2000, there was a historical discovery about Sulfur Mass Independent Fractionation by Farquhar et al.,2000. In this paper, they found out that Archean rock samples (Barite, Pyrite, Gypsum and etc) were showing notable deviation from Mass Dependent Fractionation signals of multiple Sulfur isotopes which are…

$$\delta^{33}S = 0.515 * \delta^{34}S$$

$$\delta^{36}S = 1.89 * \delta^{34}S$$

Let’s use our *MDF* (Mass Dependent Fractionation) formula derived from Urey to Bigeleisen!

$$\delta^{x}{}_{A} = \tilde{E} * \frac{m_x - m_1}{m_1 m_x}$$

$$\delta^{33}{}_{sample} = \tilde{E} * \frac{33-32}{32*33} \cong 0.000947\tilde{E}$$

$$\delta^{34}{}_{sample} = \tilde{E} * \frac{34-32}{32*34} \cong 0.001840\tilde{E}$$

$$\delta^{36}{}_{sample} = \tilde{E} * \frac{36-32}{32*36} \cong 0.003470\tilde{E}$$

so…

$$\boldsymbol{\delta^{33}S = 0.514673913\ldots * \delta^{34}S \cong 0.515 * \delta^{34}S}$$

$$\boldsymbol{\delta^{36}S = 1.885869565\ldots * \delta^{34}S = 1.89 * \delta^{34}S}$$

Mass Independent Fractionation of Sulfur, thus, can be expressed as the deviation from this MDF relationship

$$\Delta^{33}\boldsymbol{S} = \boldsymbol{\delta^{33}S - 0.515 * \delta^{34}S}$$

$$\Delta^{36}\boldsymbol{S} = \boldsymbol{\delta^{36}S - 1.89 * \delta^{34}S}$$

Mark Thiemens group is also famous for Oxygen stable isotope chemistry! Let’s apply *MDF* (Mass Dependent Fractionation) formula into oxygen isotope.

$$\delta^{x}{}_{A} = \tilde{E} * \frac{m_x - m_1}{m_1 m_x}$$

$$\delta^{17}{}_{sample} = \tilde{E} * \frac{17-16}{17*16} \cong 0.003676\tilde{E}$$

$$\delta^{18}{}_{sample} = \tilde{E} * \frac{18-16}{18*16} \cong 0.006944\tilde{E}$$

so…

$$\delta^{17}O \cong 0.529 * \delta^{18}O$$

4. References

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