Isotope Fractionation Reactions: Do Questions 1, 5, 6, 9, 10, 11

Remember MID TERM NEXT WEEK FEBUARY 15, 2008

1. Atmospheric water vapor is seldom sampled and measured for isotopes, but assume that for a given time and place it is found to have a $\delta^{18}O$ value of $-18‰$. What would be the $\delta^{18}O$ value for rain that fell with a condensation temperature of 15°C?

   Condensation of rain is generally an equilibrium process and the equilibrium enrichment factor, ε, is used to find the $\delta^{18}O$ of the water. The value for $\varepsilon^{18}O_{water-vapor}$ is calculated from the equation found in :
   $$\varepsilon^{18}O_{water-vapor} = 1.137(10^6/T^2) - 0.4156(10^3/T) - 2.0667$$

   At 15°C, $\varepsilon^{18}O_{water-vapor} = 10.2‰$.

   Considering that this problem is formulated with vapor as the reactant and water as the product (unlike the example 2-11), we can express the enrichment factor in this sequence:
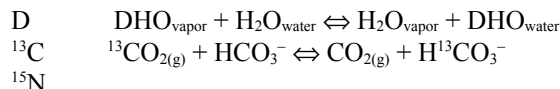 $$\varepsilon^{18}O_{vapor-water} = -\varepsilon^{18}O_{water-vapor}$$
   $$= \delta^{18}O_{wapor} - \delta^{18}O_{water}$$
   $$= -10.2‰$$

   The $\delta^{18}O$ of rain is then:
   $$\delta^{18}O_{water} = \delta^{18}O_{wapor} - \varepsilon^{18}O_{vapor-water}$$
   $$= -18 - (-10.2) = -7.8‰$$

2. Write an example of an equilibrium isotope exchange reaction involving each of the isotopes and associated samples in Table 1-4.

   For this question, it is important to use a reaction for which a chemical equilibrium can exist, such as evaporation, or CO_2 dissolution. Biologically-mediated reactions, for which equilibrium cannot be established, cannot have an equilibrium isotope exchange.

D	$DHO_{vapor} + H_2O_{water} \Leftrightarrow H_2O_{vapor} + DHO_{water}$
^{13}C	$^{13}CO_{2(g)} + HCO_3^- \Leftrightarrow CO_{2(g)} + H^{13}CO_3^-$
^{15}N	

3. The analysis of ^{18}O in water is done by equilibrating the sample with CO_2 and then measuring $\delta^{18}O_{CO_2}$. The fractionation factor for this exchange of ^{18}O between CO_2 and H_2O is $\alpha^{18}O_{CO_2-H_2O} = 1.0415$ at 25°C (and so $\varepsilon^{18}O_{CO_2-H_2O} = (\alpha-1) \cdot 1000$). For $\delta^{18}O_{CO_2}$ measurements of +35.5‰ and +32.1‰ VPDB (samples A and B), what are the values for $\delta^{18}O_{H_2O}$ for A and B?

   $$\varepsilon^{18}O_{reactant-product} = \delta^{18}O_{reactant} - \delta^{18}O_{product}$$
   $$\varepsilon^{18}O_{CO_2-H_2O} = (\alpha^{18}O_{CO_2-H_2O} - 1) \cdot 1000$$
   $$= (1.0415 - 1) \cdot 1000$$
   $$= 41.5‰$$
   $$\varepsilon^{18}O_{CO_2-H_2O} = \delta^{18}O_{CO_2} - \delta^{18}O_{H_2O}$$
   $$\delta^{18}O_{H_2O} = \delta^{18}O_{CO_2} - \varepsilon^{18}O_{CO_2-H_2O}$$

   A: For $\delta^{18}O_{CO_2} = +35.5‰$,
   $$\delta^{18}O_{H_2O-A} = \delta^{18}O_{CO_2} - \varepsilon^{18}O_{H_2O-CO_2}$$
   $$= 35.5 - 41.5$$

$$= -6.0‰$$

B: For $\delta^{18}O_{CO_2} = +32.1‰$,

$$\delta^{18}O_{H_2O-B} = 32.1 - 41.5$$
$$= -9.4‰$$

This is a standard method for analysis of waters, as it is relatively easy to equilibrate CO_2 under isothermal conditions in the lab (an important consideration) and CO_2 is a clean, non-reactive and non-condensing gas at room temperature.

4. The enrichment factor for isotopes, α, particularly for kinetic reactions, can be calculated from isotope measurements of the two reacting phases, such as for, or ^{18}O in water and evaporated vapor. Determine the fractionation factor, α, and the enrichment factor, ϵ, for the following two isotope exchange reactions (hint: first derive the fractionation factor, α in terms of δ values).
   - ^{18}O during strong evaporation under low humidity conditions, $H_2O_{water} \rightarrow H_2O_{vapor}$
     $$\delta^{18}O_{water} = -10‰ \quad \text{and} \quad \delta^{18}O_{vapor} = -25‰$$
   - ^{13}C during photosynthesis: $CO_2 + H_2O \rightarrow CH_2O + O_2$
     $$\delta^{13}C_{CO_2} = -8‰ \quad \text{and} \quad \delta^{13}C_{CH2O} = -26‰$$

First, derive the fractionation factor, α, in terms of δ values:

$$\alpha^{18}O_{water\text{-}vapor} = \frac{(^{18}O/^{16}O)_{water}}{(^{18}O/^{16}O)_{vapor}}$$

$$\delta^{18}O_{water} = \left(\frac{(^{18}O/^{16}O)_{water}}{(^{18}O/^{16}O)_{VSMOW}} - 1 \right) \cdot 1000$$

$$(^{18}O/^{16}O)_{water} = \left(\frac{\delta^{18}O_{water}}{1000} + 1 \right) \cdot (^{18}O/^{16}O)_{VSMOW}$$

$$\alpha^{18}O_{water\text{-}vapor} = \frac{\left(\frac{\delta^{18}O_{water}}{1000} + 1 \right) \cdot (^{18}O/^{16}O)_{VSMOW}}{\left(\frac{\delta^{18}O_{vapor}}{1000} + 1 \right) \cdot (^{18}O/^{16}O)_{VSMOW}} = \frac{\left(\frac{\delta^{18}O_{water}}{1000} + 1 \right)}{\left(\frac{\delta^{18}O_{vapor}}{1000} + 1 \right)}$$

$$= \frac{\delta^{18}O_{water} + 1000}{\delta^{18}O_{vapor} + 1000}$$

Now substitute in the values for each case to determine the fractionation factor, α.
   - ^{18}O during strong evaporation:

   $$\alpha^{18}O_{water\text{-}vapor} = \frac{\delta^{18}O_{water} + 1000}{\delta^{18}O_{vapor} + 1000} = \frac{-10 + 1000}{-25 + 1000} = \frac{990}{975} = 1.0154$$

   The enrichment factor, is then $\epsilon^{18}O_{water\text{-}vapor} = (\alpha^{18}O_{water\text{-}vapor} - 1) \cdot 1000 = 15.4‰$
   The enrichment factor compares with an equilibrium value of 9.3‰ at 25°C. It is much higher, showing that under conditions of low humidity and strong evaporation, the vapor is much more depleted than the water.

   - ^{13}C during photosynthesis:

   $$\alpha^{13}C_{CO2\text{-}CH2O} = \frac{\delta^{13}C_{CO_2} + 1000}{\delta^{13}C_{CH_2O} + 1000} = \frac{-8 + 1000}{-26 + 1000} = \frac{992}{974} = 1.0185$$

   The enrichment factor, is then $\epsilon^{13}C_{CO2\text{-}CH2O} = (\alpha^{13}C_{CO2\text{-}CH2O} - 1) \cdot 1000 = 18.5‰$.
   There is no equilibrium fractionation factor, as photosynthesis nor the reverse reaction, respiration, are biologically mediated reactions that function independent of each other.

5. A pond of water, with $\delta^{18}O = -10‰$ starts to evaporate to dryness. Given an enrichment factor for isotope exchange between water and vapor of $\varepsilon^{18}O_{vapor-water} = -9.3‰$, $(\alpha^{18}O_{water-vapor} = 1.0093)$ determine the isotopic composition of the pond water when it has evaporated to residual fractions $f = 0.5$, $f = 0.15$, $f = 0.05$ and $f = 0.01$. What would be the effect on your calculations if you used a kinetic enrichment factor which was less than $-9.3‰$ (say $-13‰$).

Using the simplified Rayleigh distillation equation:

$$\delta^{18}O_{pond(f)} = \delta^{18}O_{o\text{-}pond} + \varepsilon^{18}O_{vapor-water} \cdot \ln f$$

$$\varepsilon^{18}O_{water\text{-}vapor} = (1.009 - 1)\ 1000$$
$$= 9.3‰$$

$f=0.5$ $\delta^{18}O_{pond(f)} = -10.0 - 9.3 \cdot \ln(0.5)$
         $= -3.6$

$f=0.15$ $\delta^{18}O_{pond(f)} = -10.0 - 9.3 \cdot \ln(0.15)$
         $= +7.6$

$f=0.05$ $\delta^{18}O_{pond(f)} = -10.0 - 9.3 \cdot \ln(0.05)$
         $= +17.9$

$f=0.01$ $\delta^{18}O_{pond(f)} = -10.0 - 9.3 \cdot \ln(0.01)$
         $= +32.8$

With a kinetic enrichment factor, $\varepsilon^{18}O_{vapor\text{-}water} = -13‰$, the $\delta^{18}O$ values of the residual water would be even greater.

$f=0.5$ $\delta^{18}O_{pond(f)} = -10 - 13 \cdot \ln(0.5)$
         $= -0.99$

$f=0.15$ $\delta^{18}O_{pond(f)} = -10 - 13 \cdot \ln(0.15)$
         $= +14.66$

$f=0.05$ $\delta^{18}O_{pond(f)} = -10 - 13 \cdot \ln(0.05)$
         $= +28.94$

$f=0.01$ $\delta^{18}O_{pond(f)} = -10 - 13 \cdot \ln(0.01)$
         $= +49.87$

Note that at high humidity and with small residual fractions, the effect of exchange with the atmospheric water vapor becomes important and limits this exponential increase in the $\delta^{18}O$ of the residual water.

6. A sample of water in a partially filled container has a $\delta^{18}O$ value of $-7.0‰$. The temperature is 25°C. What will be the $\delta^{18}O$ value of the water vapor in isotopic equilibrium with this water?

$$\delta^{18}O_{vapor} = \delta^{18}O_{water} + \varepsilon^{18}O_{vapor\text{-}water}$$
$$= -7.0 + (-9.3)$$
$$= -16.3‰$$

7. What are the ^{18}O fractionation factors and the ^{18}O enrichment factors for water in equilibrium with vapor at 0°C and at 50°C? At which temperature will there be a greater difference between measurements of $\delta^{18}O_{water}$ and $\delta^{18}O_{vapor}$, and what are the differences?

$$
\begin{aligned}
\text{Fractionation factor, } \alpha^{18}O_{water\text{-}vapor} \quad &= \quad 1.0116 \text{ @ 0°C} \\
&= \quad 1.0075 \text{ @ 50°C} \\
\text{Enrichment factor, } \varepsilon^{18}O_{water\text{-}vapor} \quad &= 11.6 \text{ ‰ @ 0°C} \\
&= \quad 7.5 \text{ ‰ @ 50°C}
\end{aligned}
$$

Difference between $\delta^{18}O_{water}$ and $\delta^{18}O_{vapor}$, is greater at the lower temperature:
11.6 ‰ @ 0°C versus 7.5 % @ 50°C,
because fractionation is greater at lower temperature.

8. Write the fractionation factor, $\alpha^{18}O_{water\text{-}vapor}$ in terms of an isotope ratio for these compounds.

$$
\alpha^{18}O_{water\text{-}vapor} = \frac{R_{water}}{R_{vapor}} = \frac{\left(\dfrac{^{18}O}{^{16}O}\right)_{water}}{\left(\dfrac{^{18}O}{^{16}O}\right)_{vapor}}
$$

9. A small lake was profiled for dissolved oxygen (DO as O_2) as well as for temperature and pH. Calculate the percent saturation for DO at each measurement depth. (Note that Henry's constant at different temperatures can be calculated from: $K_{H\text{-}O2} = 5E\text{-}07\ T^2 - 5E\text{-}05\ T + 0.0022$).
   With reference to the pH, account for the anomaly at 2 m depth and the decrease in DO below this depth.

Depth (m)	Temp (Celsius)	DO (mg/L)	Cond ms/cm	pH
0.5	23.70	6.82	320	8.23
1.0	23.53	6.80	319	8.13
1.5	22.12	9.92	332	7.88
2.0	18.12	18.20	334	9.16
2.5	14.29	1.29	345	7.32
3.0	9.85	0.82	348	6.85
3.5	7.24	0.70	347	6.68
4.0	5.90	0.62	348	6.57
4.5	4.92	0.53	354	6.47
5.0	4.41	0.46	358	6.41
5.5	4.15	0.39	368	6.30

Depth	Temp	DO		Cond	pH	K_{O2}	P(total)		Saturation

(m)	(Celsius)	(mg/L)	(mol/L)	ms/cm			atm	mol/l	%
0.5	23.70	6.82	2.13E-04	320	8.23	1.30E-03	0.26	3.35E-04	**63.62**
1.0	23.53	6.80	2.13E-04	319	8.13	1.30E-03	0.31	4.00E-04	**53.13**
1.5	22.12	9.92	3.10E-04	332	7.88	1.34E-03	0.36	4.77E-04	**64.94**
2.0	18.12	18.20	5.69E-04	334	9.16	1.46E-03	0.41	5.92E-04	**96.15**
2.5	14.29	1.29	4.03E-05	345	7.32	1.59E-03	0.45	7.22E-04	**5.58**
3.0	9.85	0.82	2.56E-05	348	6.85	1.76E-03	0.50	8.85E-04	**2.90**
3.5	7.24	0.70	2.19E-05	347	6.68	1.86E-03	0.55	1.03E-03	**2.12**
4.0	5.90	0.62	1.94E-05	348	6.57	1.92E-03	0.60	1.16E-03	**1.67**
4.5	4.92	0.53	1.66E-05	354	6.47	1.97E-03	0.65	1.28E-03	**1.29**
5.0	4.41	0.46	1.44E-05	358	6.41	1.99E-03	0.70	1.39E-03	**1.03**
5.5	4.15	0.39	1.22E-05	368	6.30	2.00E-03	0.75	1.50E-03	**0.81**

Air Saturation vs Depth

ph vs Depth
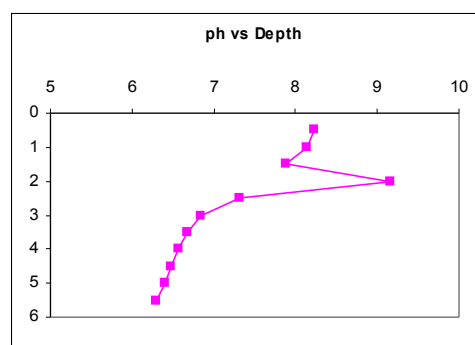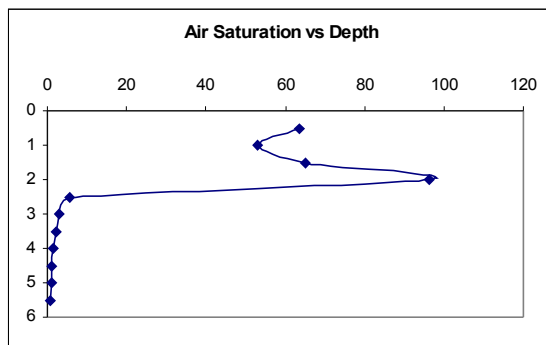
The pH and O_2 is the highest at 2m depth. This lake is stratified, the upper 2 m is productive with photosynthesis occurring, which removes CO_2 and increases pH. Below 2 m depth respiration dominates and O_2 is used up, and CO_2 produced, decreasing the pH.

10. How much methane can be produced at 10 m below the water table before you produce a separate gas phase (@25°C)?

$K_{CH4} = 0.0014$ mol/L/atm

$$K_{CH4} = \frac{m_{CH4}}{P_{CH4}}$$

Pressure at 10 m is
$$\Delta p = \rho gh$$
p_o=1 atm = 101.32 kPa
ρ= 1kg/m³ g= 9.81 m/s², h = 10m
$p_{@10m}$=0.96 atm
$$m_{CH4} = K_{CH4} \times \Delta p$$
m_{CH4}= 1.73E-06 mol/kg

11. Compare and contrast the solubility's of the different noble gases? What explains the difference in solubility's?

The solubility's of the noble gases are controlled by the mass of gas. Xenon has the highest solubility, while helium has the lowest.   The noble gases are none reactive, making them a useful tracer. The use of this tracer is complicated by the difficulty of analysis, and complications in noble gas concentrations in groundwater.