Air-Water Exchange

At full equilibrium: Henry's Law governs:

\[
\frac{C_A}{C_w} = H
\]

\[
C_{eq} = H C_w
\]

\[
C_w = \frac{C_A}{H}
\]

But what if system not at equilibrium?

\[
C_A < H C_w
\]

Will be net loss of volatilization from water into air

Flux density that results:

\[
J = -k_w [C_w - C_{eq}] = -k_w [C_w - \frac{C_A}{H}]
\]

Analyse that eqn a bit...

At Equilibrium

\[
\frac{C_A}{H} = C_{eq}
\]

Conc's at Equilibrium

Hence no net flux

Actual Air

Actual Water Conc.

At equilibrium

\[
C_A = C_{eq}
\]

Not at equilibrium

\[
C_A = C_{eq}
\]

\[
J = -D \frac{dc}{dx} = -\frac{D}{A} \frac{dc}{dx}
\]

Conc's not equal (at equil).

Hence net flux outward

Call \[
\frac{D}{A} = k_w \left[ L \frac{L}{m} \right]
\]

\[
J = -k_w [C_w - C_q] = -k_w [C_w - \frac{C_A}{H}]
\]

"Piston velocity"
In General

\[ J = - \left[ \frac{\delta n}{\delta x} + \frac{\delta n}{\delta H} \right] [c_w - \frac{c_a}{H}] \]

Can use this
1. For general case of no one phase controlling
2. To inspect possible (advance) simplifications

Estimating \( k_w \)

\[ \frac{k_a}{k_b} = \frac{D_a}{D_b} \approx \frac{\sqrt{M_w}}{\sqrt{M_b}} \]

E.g. use propane in a river or lake & convert to gas of interest

For an IDEAL GAS:

\[ \text{K.E.} = \frac{1}{2} m v^2 \]

And TEMPERATURE is defined as a measure of the mean kinetic energy of molecules

\[ \therefore \text{K.E.} \propto T \]

So if two gases at same \( T \), they have same K.E.

\[ \overline{\text{KE}}_1 = \overline{\text{KE}}_2 \Rightarrow \frac{1}{2} m_1 v_1^2 = \frac{1}{2} m_2 v_2^2 \]

\[ \frac{v_1^2}{v_2^2} = \frac{m_2}{m_1} \]

\[ \therefore \frac{v_1}{v_2} = \sqrt{\frac{m_2}{m_1}} \]

Graham Law

HCl: \( \text{FW} = 36.5 \)
NH\textsubscript{3}: \( \text{FW} = 17.0 \)

\[ \frac{v_{\text{NH}_3}}{v_{\text{HCl}}} = \sqrt{\frac{36.5}{17.0}} = 1.46 \]
VOLATILIZATION FROM PURE PHASE

E.g. a spill of liquid

\[ J = \frac{D_v}{\delta_s} C_s^5 \]

VAPOR PRESSURE CONVERTED TO CONC (say, mg/L)

\[ \nu = 0.029 \nu_{\text{wind}} L^{-0.17} \text{ Sc}^{-0.62} \]

Schmidt No. = \( \frac{D_v}{\nu} \) = Kin. viscosity

Diffusion coeff.

But exponents are small so often neglect \( \nu \) & Sc factors