Effective Henry's Law Constant

Henry's Law

The amount of a gas, X, in equilibrium with aqueous-phase concentration of the gas, X_{aq}, is proportional to the gas-phase partial pressure, pX.

$$\begin{aligned} X_{\mathrm{aq}} &= K_H \; pX \\ [K_H] &= \mathrm{moles} X/\mathrm{liter\ of\ air/atm} \\ \left[X_{\mathrm{aq}}\right] &= \mathrm{moles} X/\mathrm{liter\ of\ liquid\ H_2O} \\ [p_X] &= \mathrm{atm} \end{aligned}$$

where K_H is the Henry's Law constant. The temperature dependence of the Henry's Law constant is often parameterized.

$$K_H = \mathrm{kh}_{298} \; \exp\left(\mathrm{dh}_r \; \left(\frac{1}{T} - \frac{1}{298}\right)\right)$$

Acid

For an acid, where the compound and its anions are in equilibrium,

$$\begin{aligned} H_{eff} &= K_H \left(1 + \frac{K_1}{[H+]}\left(1 + \frac{K_2}{[H+]}\right)\right) \\ K_1 &= \mathrm{k1}_{298} \; \exp(\mathrm{dh1}_r \; (\frac{1}{T} - \frac{1}{298})) \\ K_2 &= \mathrm{k2}_{298} \; \exp(\mathrm{dh2}_r \; (\frac{1}{T} - \frac{1}{298})) \\ [H+] &= 10^{-pH} \end{aligned}$$

Base

For a base, where the compound and its cations are in equilibrium

$$H_{eff} = K_H \left(1 + \frac{K_1}{K_w}[H+]\right)$$

$$
\begin{aligned}
K_1 &= \mathrm{k1}_{298}\ \exp(\mathrm{dh1}_r\ (\frac{1}{T} - \frac{1}{298})) \\
K_w &= \mathrm{kw}_{298}\ \exp(\mathrm{dh2}_w\ (\frac{1}{T} - \frac{1}{298})) \\
K_w &= \left[H^+\right]\left[OH^-\right]
\end{aligned}
$$

Example Derivation of H_{eff} for an acid

Assume the compound and its anions are in equilibrium. Define a family for that species, in this case, CO_2 For example,

$$C(IV) = H_2CO_3 + HCO_3^- + CO_3^=$$

Find the effective Henry's Law for that family,

$$H_{eff} = \frac{[C(IV)]}{p_{CO_2}}$$

where p_{CO_2} is the partial pressure of CO_2. Based on the equilibria,

$$
\begin{aligned}
[H_2CO_3] &= K_H\ p_{CO_2} \\
\left[HCO_3^-\right] &= K_1\ \frac{[H_2CO_3]}{[H+]} \\
[CO_3^=] &= K_2\ \frac{[HCO_3-]}{[H+]}
\end{aligned}
$$

substitute those equilibria into the $C(IV)$ equation giving

$$H_{eff} = \left(K_H p_{CO_2} + K_1 \frac{[H_2CO_3]}{[H+]} + K_2 \frac{[HCO_3^-]}{[H+]}\right) / p_{CO_2}$$

and further substitution gives

$$H_{eff} = K_H + K_H \frac{K_1}{[H+]} + K_H \frac{K_1 K_2}{[H+]^2}$$

resulting in

$$H_{eff} = K_H \left(1 + \frac{K_1}{[H+]}\left(1 + \frac{K_2}{[H+]}\right)\right)$$

Example derivation of H_{eff} for a base

For a gas that hydrolyzes and dissociates into a cation such as NH_3,

$$NH_3\text{aq} = K_H\ pNH_3$$

NH_3 hydrolyzes to make $NH_3 - H_2O = NH_4OH$ which dissociates:

$$\begin{aligned} NH_4OH &\leftrightarrow NH_4^+ + OH^- \\ K_1 &= \left[NH4^+\right]\left[OH^-\right]/\left[NH_4OH\right] \end{aligned}$$

with an equilibrium constant K_1.

Water also dissociates

$$\begin{aligned} H_2O &\leftrightarrow H^+ + OH^- \\ K_w &= \left[H^+\right]\left[OH^-\right] \end{aligned}$$

with an equilibrium constant K_w.

The algebraic derivation follows as:

$$\begin{aligned} \left[NH_4OH\right] &= K_H\ \ pNH3 \\ \left[NH_4^+\right]\left[OH^-\right] &= K_1\left[NH_4OH\right] \\ \therefore \left[NH_4^+\right] &= K_1\left[H^+\right]\left[NH_4OH\right]/K_w \end{aligned}$$

Or using the same derivation as the acid above, for NH_3 define the family, $N(-III)$, as

$$N(-III) = NH_4OH + NH4^+$$

It follows that

$$\begin{aligned} N(-III) &= K_H\ \ pNH_3 + \frac{K_1}{\left[OH^-\right]}\left[NH_4OH\right] \\ N(-III) &= K_H\ \ pNH_3 + \frac{K_1 * [H+]}{K_w}\ K_H\ \ pNH_3 \end{aligned}$$

but by the definition $[N(-III)] = H_{eff}\ \ pNH_3$ we can identify

$$H_{eff} = K_H\left(1 + \frac{K_1}{K_w}\ \left[H^+\right]\right)$$