Computing HOCl

Cyanuric Acid

- Reference other CYA species to $[H_3Cy]$
- $[H_2Cy^-]$

$$H_3Cy \leftrightarrow H_2Cy^- + H^+$$
$$[H_2Cy^-] = [H_3Cy]\,K_{H_3Cy,a}/[H^+]$$

- $[HCy^{2-}]$

$$H_2Cy^- \leftrightarrow HCy^{2-} + H^+$$
$$[HCy^{2-}] = [H_2Cy^-]\,K_{H_2Cy^-,a}/[H^+]$$

- $[Cy^{3-}]$

$$HCy^{2-} \leftrightarrow Cy^{3-} + H^+$$
$$[Cy^{3-}] = [HCy^{2-}]\,K_{HCy^{2-},a}/[H^+]$$

Cyanuric Acid (cont.)

- Combine into single formula factoring out $[H_3Cy]$ and removing other species

$$[H_3Cy] + [H_2Cy^-] + [HCy^{2-}] + [Cy^{3-}] =$$

$$[H_3Cy]\Big(\mathbf{1} + \left(\boldsymbol{K_{H_3Cy,a}/[H^+]}\right)\Big(\mathbf{1} + \left(\boldsymbol{K_{H_2Cy^-,a}/[H^+]}\right)\left(\mathbf{1} + \left(\boldsymbol{K_{HCy^{2-},a}/[H^+]}\right)\right)\Big)\Big)$$

$$= \boldsymbol{a}[H_3Cy]$$

Cl-CYA

- Reference Cl-CYA species to $[H_3Cy][HOCl]$
- $[H_2ClCy]$

$$H_2ClCy + H_2O \leftrightarrow H_3Cy + HOCl$$
$$[H_2ClCy] = [H_3Cy][HOCl]/K_{H_2ClCy,h}$$

- $[HClCy^-]$

$$H_2ClCy \leftrightarrow HClCy^- + H^+$$
$$[HClCy^-] = [H_2ClCy]K_{H_2ClCy,a}/[H^+]$$

- $[ClCy^{2-}]$

$$HClCy^- \leftrightarrow ClCy^{2-} + H^+$$
$$[ClCy^{2-}] = [HClCy^-]K_{HClCy^-,a}/[H^+]$$

Cl-CYA (cont.)

- Combine into single formula factoring out $[H_3Cy][HOCl]$ and removing other species

$$[H_2ClCy] + [HClCy^-] + [ClCy^{2-}] =$$

$$[H_3Cy][HOCl] \times$$

$$\frac{\left(\mathbf{1} + \left(\frac{\boldsymbol{K_{H_2ClCy,a}}}{[\boldsymbol{H^+}]}\right)\left(\mathbf{1} + \left(\frac{\boldsymbol{K_{HClCy^-,a}}}{[\boldsymbol{H^+}]}\right)\right)\right)}{\boldsymbol{K_{H_2ClCy,h}}}$$

$$= \boldsymbol{b}[H_3Cy][HOCl]$$

Cl_2-CYA

- Reference Cl_2-CYA species to $[H_3Cy][HOCl]^2$
- $[HCl_2Cy]$

$$HCl_2Cy + H_2O \leftrightarrow H_2ClCy + HOCl$$
$$[HCl_2Cy] = [H_2ClCy][HOCl]/K_{HCl_2Cy,h}$$

$$[HCl_2Cy] = [H_3Cy][HOCl]^2/\left(K_{HCl_2Cy,h}K_{H_2ClCy,h}\right)$$

- $[Cl_2Cy^-]$

$$HCl_2Cy \leftrightarrow Cl_2Cy^- + H^+$$
$$[Cl_2Cy^-] = [HCl_2Cy]\left(K_{HCl_2Cy,a}/[H^+]\right)$$

Cl_2-CYA (cont.)

- Combine into single formula factoring out $[H_3Cy][HOCl]^2$ and removing other species

$$[HCl_2Cy] + [Cl_2Cy^-] =$$

$$[H_3Cy][HOCl]^2 \left(\frac{\left(\mathbf{1} + \boldsymbol{K_{HCl_2Cy,a}}/[\boldsymbol{H^+}]\right)}{\boldsymbol{K_{HCl_2Cy,h}}\boldsymbol{K_{H_2ClCy,h}}} \right)$$

$$= \boldsymbol{c}[H_3Cy][HOCl]^2$$

Cl_3-CYA

- Reference Cl_3-CYA species to $[H_3Cy][HOCl]^3$
- $[Cl_3Cy]$

$$Cl_3Cy + H_2O \leftrightarrow HCl_2Cy + HOCl$$
$$[Cl_3Cy] = [HCl_2Cy][HOCl]/K_{Cl_3Cy,h}$$

$$[Cl_3Cy] =$$

$$[H_3Cy][HOCl]^3 \left(\frac{\mathbf{1}}{\boldsymbol{K_{Cl_3Cy,h} K_{HCl_2Cy,h} K_{H_2ClCy,h}}} \right)$$

$$= \boldsymbol{d}[H_3Cy][HOCl]^3$$

Total Cyanuric Acid

- Total Cyanuric Acid is the sum of all cyanurate species both with and without chlorine
- $CYA_{TOT} = [H_3Cy] + [H_2Cy^-] + [HCy^{2-}] + [Cy^{3-}] +$
$[H_2ClCy] + [HClCy^-] + [ClCy^{2-}] +$
$[HCl_2Cy] + [Cl_2Cy^-] +$
$[Cl_3Cy]$

Total Free Chlorine

- Total Free Chlorine is the sum of all chlorinated species with and without CYA accounting for multiple chlorine
- FC_{TOT} = [HOCl] + [OCl^-] + [H_2ClCy] + [$HClCy^-$] + [$ClCy^{2-}$] + 2*([HCl_2Cy] + [Cl_2Cy^-]) + 3*[Cl_3Cy]

$$HOCl \leftrightarrow OCl^- + H^+$$
$$[OCl^-] = [HOCl]K_{HOCl}/[H^+]$$

Net Equations

- We now have two equations with two unknowns ($[H_3Cy]$, [HOCl]) but whereas $[H_3Cy]$ is linear, [HOCl] is not.
- We can iterate on [HOCl] and to make the iterations converge quickly we can use derivatives of the two equations in the following form:
  - $CYA_{TOT} = [H_3Cy] * f([HOCl])$
  - $FC_{TOT} = h([HOCl]) + [H_3Cy]*g([HOCl])$

Net Equations (cont.)

- We can solve for $[H_3Cy]$ in the first equation and substitute into the second equation
  - $[H_3Cy] = CYA_{TOT} / f([HOCl])$
  - **$FC_{TOT} = h([HOCl]) + CYA_{TOT}*g([HOCl])/f([HOCl])$**
- We take the derivative to get an error term

$$\frac{d(FC_{TOT})}{d[HOCl]} =$$

$$\frac{dh}{d[HOCl]} + \frac{CYA_{TOT}}{f}\left(\frac{dg}{d[HOCl]} - \frac{g}{f}\frac{df}{d[HOCl]}\right)$$

Details of f,g,h

- With a,b,c,d defined in the previous slides, then we have for f, g and h
- **$f = a + b*[HOCl] + c*[HOCl]^2 + d*[HOCl]^3$**
- $g = b*[HOCl] + 2*c*[HOCl]^2 + 3*d*[HOCl]^3$
- $h = [HOCl] + [OCl^-] = [HOCl](1+K_{HOCl}/[H+])$

Derivatives of f,g,h

- Then we have for f, g and h derivatives

$$\frac{df}{d[HOCl]} = b + 2c[HOCl] + 3d[HOCl]^2$$

$$\frac{dg}{d[HOCl]} = b + 4c[HOCl] + 9d[HOCl]^2$$

$$\frac{dh}{d[HOCl]} = 1 + K_{HOCl}/[H^+]$$

- Note simpler formulas for g and h:

$$g = [HOCl]\frac{df}{d[HOCl]}$$

$$h = [HOCl]\frac{dh}{d[HOCl]}$$

Iteration

- We can now calculate $d(FC_{TOT})/d(HOCl)$ with only an initial guess or previous [HOCl] as input.
- We then calculate FC_{TOT} and subtract our actual known FC from it to get the amount of error in FC.
- Take the negative of that error and divide by $d(FC_{TOT})/d(HOCl)$ to get d(HOCl) which we add to our HOCl estimate (with limit checks).
- Repeat the above until convergence.