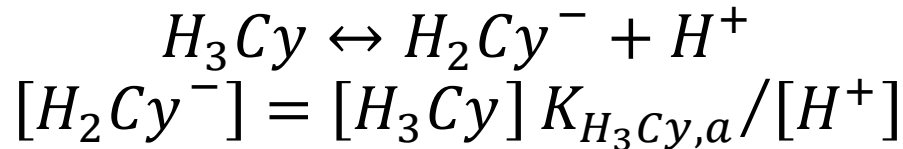


Computing HOCl

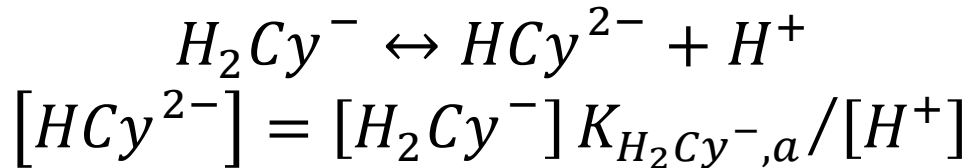
Cyanuric Acid

- Reference other CYA species to $[H_3Cy]$

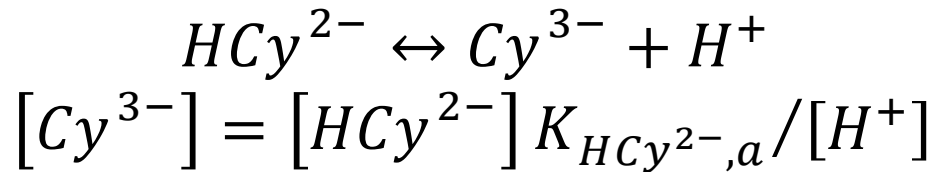
- $[H_2Cy^-]$



- $[HCy^{2-}]$



- $[Cy^{3-}]$



Cyanuric Acid (cont.)

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

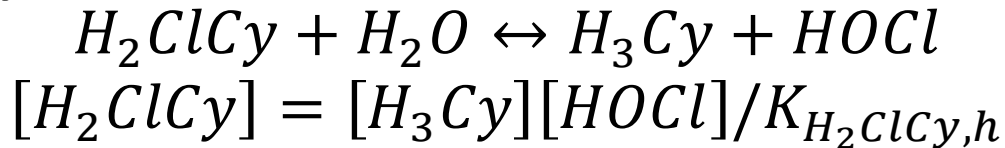
$$[H_3Cy] + [H_2Cy^-] + [HCy^{2-}] + [Cy^{3-}] =$$

$$\begin{aligned} [H_3Cy] & \left(1 \right. \\ & \quad + \left(K_{H_3Cy,a} / [H^+] \right) \left(1 \right. \\ & \quad \left. \left. + \left(K_{H_2Cy^-,a} / [H^+] \right) \left(1 + \left(K_{HCy^{2-},a} / [H^+] \right) \right) \right) \right) \\ & = a [H_3Cy] \end{aligned}$$

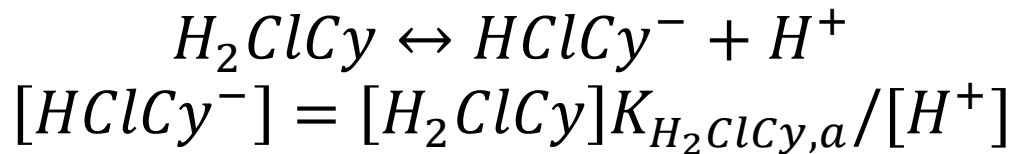
Cl-CYA

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

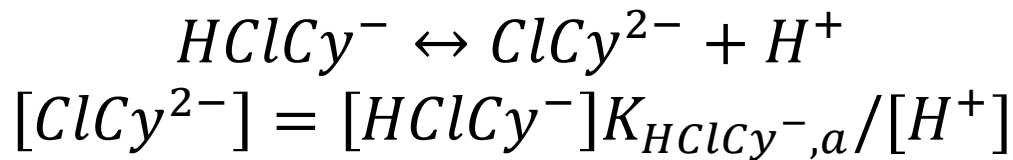
- $[H_2ClCy]$



- $[HClCy^-]$



- $[ClCy^{2-}]$



Cl-CYA (cont.)

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

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

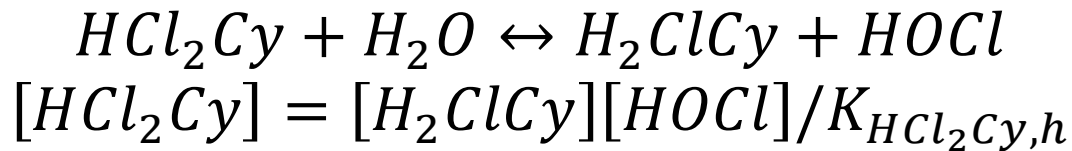
$$[H_3Cy][HOCl] \times$$

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

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

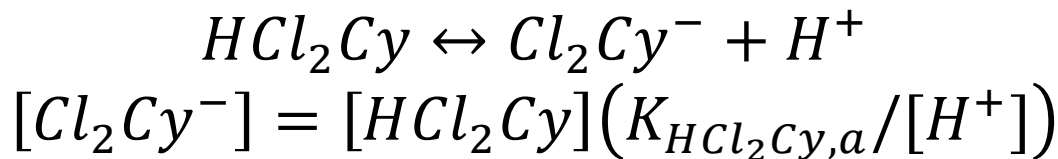
Cl₂-CYA

- Reference Cl₂-CYA species to [H₃Cy][HOCl]²
- [HCl₂Cy]



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

- [Cl₂Cy⁻]



Cl₂-CYA (cont.)

- Combine into single formula factoring out [H₃Cy][HOCl]² and removing other species

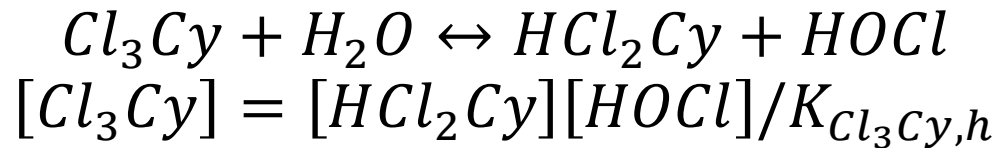
$$[HCl_2Cy] + [Cl_2Cy^-] =$$

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

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

Cl₃-CYA

- Reference Cl₃-CYA species to [H₃Cy][HOCl]³
- [Cl₃Cy]



$$[Cl_3Cy] =$$

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

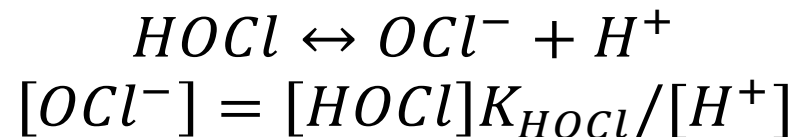
$$= \textcolor{red}{d}[H_3Cy][HOCl]^3$$

Total Cyanuric Acid

- Total Cyanuric Acid is the sum of all cyanurate species both with and without chlorine
- $$\text{CYA}_{\text{TOT}} = [\text{H}_3\text{Cy}] + [\text{H}_2\text{Cy}^-] + [\text{HCy}^{2-}] + [\text{Cy}^{3-}] +$$
$$[\text{H}_2\text{ClCy}] + [\text{HClCy}^-] + [\text{ClCy}^{2-}] +$$
$$[\text{HCl}_2\text{Cy}] + [\text{Cl}_2\text{Cy}^-] +$$
$$[\text{Cl}_3\text{Cy}]$$

Total Free Chlorine

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



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 $d(\text{FC}_{\text{TOT}})/d(\text{HOCl})$ with only an initial guess or previous $[\text{HOCl}]$ 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 $d(\text{FC}_{\text{TOT}})/d(\text{HOCl})$ to get $d(\text{HOCl})$ which we add to our HOCl estimate (with limit checks).
- Repeat the above until convergence.