

# Basic Chemistry Concepts II

# Chemical equilibrium: acid-base equilibria

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- Ionization of water:  $H_2O + H_2O = H_3O^+ + OH^-$

$$K = \frac{\{H_3O^+\}\{OH^-\}}{\{H_2O\}^2}$$

$$\{H_2O\} = \gamma_{H_2O} \cdot [H_2O], \quad \gamma_{H_2O} \approx 1, \quad [H_2O] = 55.6 \text{ M}$$

- Dissociation constant of water,  $K_w$

$$K_w = K \cdot \{H_2O\}^2 = \{H_3O^+\}\{OH^-\}$$

# Chemical equilibrium: acid-base equilibria

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$$K_w = \{H_3O^+\}\{OH^-\} \quad \text{or} \quad K_w = \{H^+\}\{OH^-\}$$

$$pK_w = 14 \quad (\text{at } 25^\circ\text{C})$$

$$pH < 7 \longrightarrow \{H^+\} > \{OH^-\} \quad \text{acidic}$$

$$pH > 7 \longrightarrow \{H^+\} < \{OH^-\} \quad \text{basic}$$

# Acid dissociation constant

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- Acid dissociation constant,  $K_a$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

- Strong acid = strong tendency to dissociate = high  $K_a$  = low  $pK_a$
- Weak acid = only a small fraction dissociates = low  $K_a$  = high  $pK_a$

# Dissociation constants of some acids

Acid	Reaction	pK <sub>a</sub>	
Hydrochloric acid	$\text{HCl} = \text{H}^+ + \text{Cl}^-$	≈-3	} Strong
Nitric acid	$\text{HNO}_3 = \text{H}^+ + \text{NO}_3^-$	-1	
Sulfuric acid	$\text{H}_2\text{SO}_4 = \text{H}^+ + \text{HSO}_4^-$	≈-3	
Bisulfate	$\text{HSO}_4^- = \text{H}^+ + \text{SO}_4^{2-}$	1.9	
Acetic acid	$\text{CH}_3\text{COOH} = \text{H}^+ + \text{CH}_3\text{COO}^-$	4.75	} Weak
Carbonic acid	$\text{H}_2\text{CO}_3^* = \text{H}^+ + \text{HCO}_3^-$	6.35	
	$\text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{2-}$	10.33	
Phosphoric acid	$\text{H}_3\text{PO}_4 = \text{H}^+ + \text{H}_2\text{PO}_4^-$	2.12	
	$\text{H}_2\text{PO}_4^- = \text{H}^+ + \text{HPO}_4^{2-}$	7.20	
	$\text{HPO}_4^{2-} = \text{H}^+ + \text{PO}_4^{3-}$	12.32	

# Acid dissociation constant

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**Q:** A solution of HOCl is prepared in water by adding 15 mg HOCl to a volumetric flask, and adding water to the 1.0 L mark. The final pH is measured to be 7.0. What are the concentrations of HOCl and OCl<sup>-</sup>? (T = 25°C)

# Chemical equilibrium: gas dissolution

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- Henry's Law: partial pressure of a chemical in the gas phase is linearly proportional to the concentration of the chemical in the aqueous phase

$$P_{\text{gas}} = kC^*$$

where  $P_{\text{gas}}$  = partial pressure in the gas phase

$C^*$  = concentration in the water

$k$  = constant

# Caveat!

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- The equilibrium/solubility product constants do not tell anything about the reaction rate!
- Differentiate equilibrium and kinetics



# Reaction kinetics

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- Reaction kinetics: study of the speed at which reactions proceed



$$r_A = \frac{d[A]}{dt} = -k[A]^\alpha[B]^\beta$$

$r_A$  = reaction rate with respect to chemical A [conc./time]

$k$  = reaction rate constant

$\alpha + \beta$  = overall reaction order

# Reaction orders and half life

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Overall Reaction order	Rate expression	Units on $k$
Zero	$r_A = -k$	$(\text{conc.})(\text{time})^{-1}$
First	$r_A = -k[A]$	$(\text{time})^{-1}$
Second	$r_A = -k[A]^2$	$(\text{conc.})^{-1}(\text{time})^{-1}$
Second	$r_A = -k[A][B]$	$(\text{conc.})^{-1}(\text{time})^{-1}$

- Half-life ( $t_{1/2}$ ): time required for the concentration to reach  $\frac{1}{2}$  of its initial conc.
  - Defined for 1<sup>st</sup> order reactions only

# Concentration units in water

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- Weight percent,  $P$

$$P = \frac{W}{W + W_0} \times 100\%$$

$W = \text{mass of substance (g)}$

$W_0 = \text{mass of solvent (g)}$

- ppm, ppb, ppt
- Molarity,  $M$
- Normality,  $N$  (acid-base reaction)

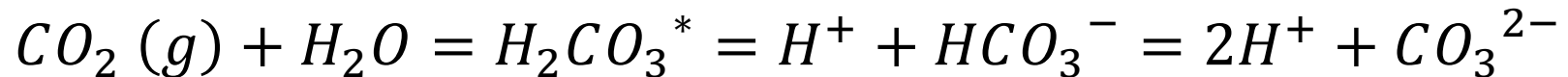
$$N = nM$$

$n = \text{no. of protons transferred}$

# Carbonate system – a natural buffer system

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- Buffer: a solution that resists large changes in pH
- A solution of weak acid and its salt is a buffer
- Atmospheric CO<sub>2</sub> produces a natural buffer:

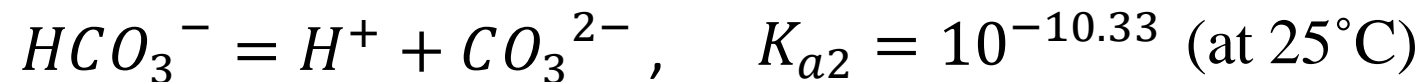
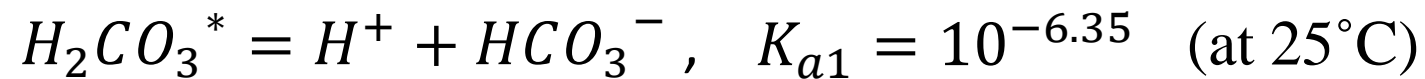


$H_2CO_3^*$  = sum of true  $H_2CO_3(aq)$  and  $CO_2(aq)$

# Carbonate system analysis

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Acid dissociation:



Define  $C_T$  as:

$$C_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}]$$

# Carbonate system analysis

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Now, recall the definition of the acid dissociation constant

$$K_{a1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3^*]}$$

$$pH - pK_{a1} = \log \frac{[HCO_3^-]}{[H_2CO_3^*]}$$

If  $pH < pK_{a1}$ ,  $[H_2CO_3^*] > [HCO_3^-]$

*(If  $pH - pK_{a1} = -2$ ,  $[H_2CO_3^*] = 100[HCO_3^-]$ )*

If  $pH > pK_{a1}$ ,  $[H_2CO_3^*] < [HCO_3^-]$

*(If  $pH - pK_{a1} = 2$ ,  $[HCO_3^-] = 100 [H_2CO_3^*]$ )*

# Carbonate system analysis

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This applies to  $\text{HCO}_3^-$  -  $\text{CO}_3^{2-}$  relationship as well:

$$K_{a2} = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$

If  $\text{pH} < \text{p}K_{a2}$ ,  $[\text{HCO}_3^-] > [\text{CO}_3^{2-}]$

If  $\text{pH} > \text{p}K_{a2}$ ,  $[\text{HCO}_3^-] < [\text{CO}_3^{2-}]$

Actually this principle applies to any acids:

If  $\text{pH} < \text{p}K_a$ , associated (protonated) form dominates

If  $\text{pH} > \text{p}K_a$ , dissociated (deprotonated) form dominates

# Carbonate species in a closed system

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Closed system  $\rightarrow C_T$  is constant

Solving for  $\text{pH} < \text{p}K_{a1}$  region as an example  
( $\text{pH}$  sufficiently lower than  $\text{p}K_{a1}$ )

At this  $\text{pH}$  range,  $\text{H}_2\text{CO}_3^*$  is dominant:

$$C_T \approx [\text{H}_2\text{CO}_3^*] \quad \rightarrow \quad \log[\text{H}_2\text{CO}_3^*] \approx \log C_T$$

$$[\text{HCO}_3^-] = \frac{K_{a1}}{[\text{H}^+]} \cdot [\text{H}_2\text{CO}_3^*] \quad \rightarrow \quad \log[\text{HCO}_3^-] = \log C_T - \text{p}K_{a1} + \text{pH}$$

$$[\text{CO}_3^{2-}] = \frac{K_{a1}K_{a2}}{[\text{H}^+]^2} \cdot [\text{H}_2\text{CO}_3^*] \quad \rightarrow \quad \log[\text{CO}_3^{2-}] = \log C_T - \text{p}K_{a1} - \text{p}K_{a2} + 2\text{pH}$$



# Carbonate species in a closed system

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What if  $pH = pK_{a1}$ ?

$$pH - pK_{a1} = \log \frac{[HCO_3^-]}{[H_2CO_3^*]} = 0$$

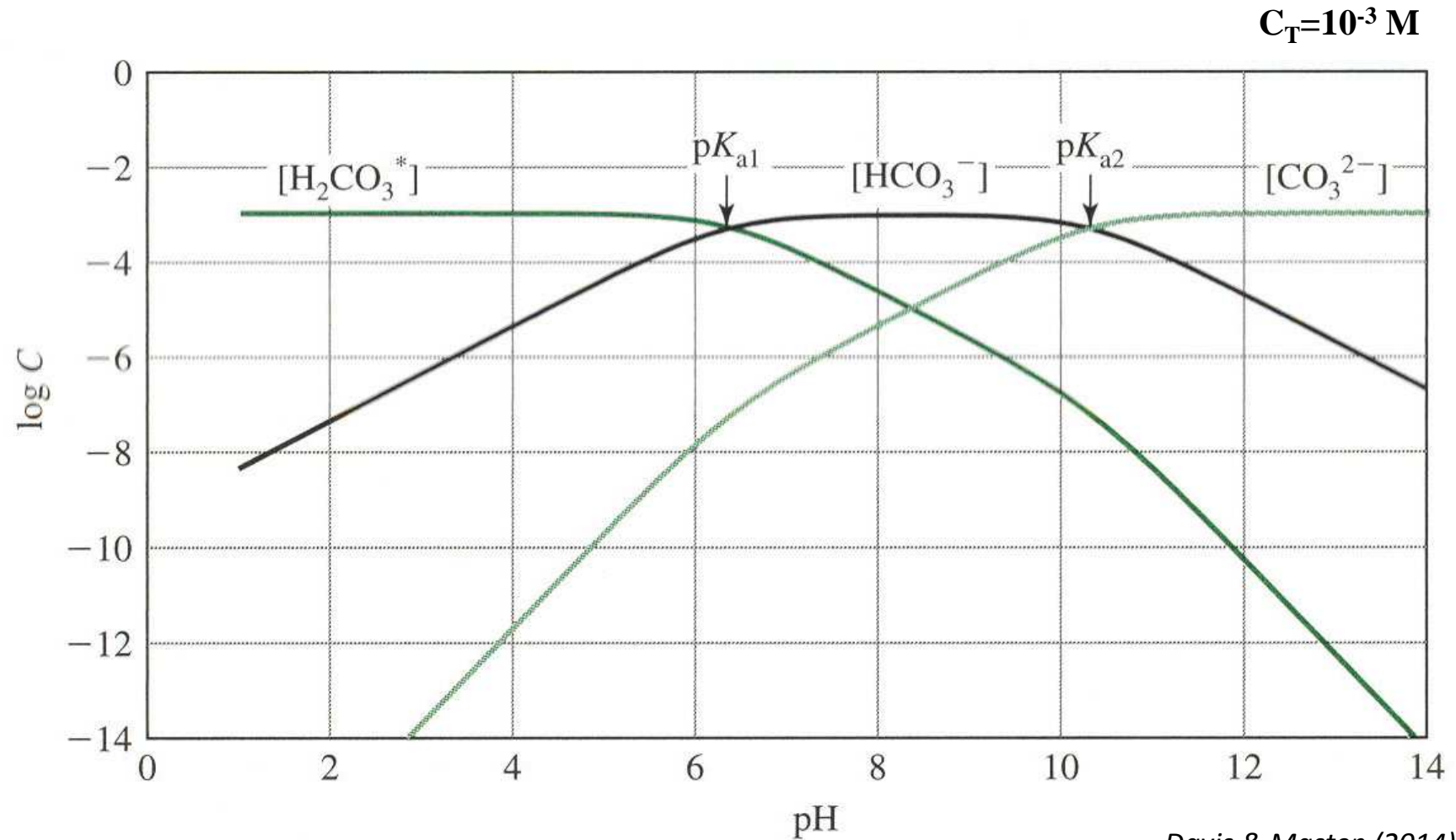
$$[H_2CO_3^*] = [HCO_3^-]$$

$$C_T \approx [H_2CO_3^*] + [HCO_3^-] \quad (\text{CO}_3^{2-} \text{ negligible because pH sufficiently lower than } pK_{a2})$$

$$[H_2CO_3^*] = [HCO_3^-] = \frac{C_T}{2}$$

  $\log[H_2CO_3^*] = \log[HCO_3^-] = \log C_T - 0.3$

# Carbonate speciation as f(pH) [Closed]



*Davis & Masten (2014)*

# Carbonate species in an open system

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Open system  $\rightarrow$  constant  $[H_2CO_3^*]$

$$[H_2CO_3^*] = K_H P_{CO_2} = (10^{-1.47} \text{ M/atm})(10^{-3.53} \text{ atm})$$

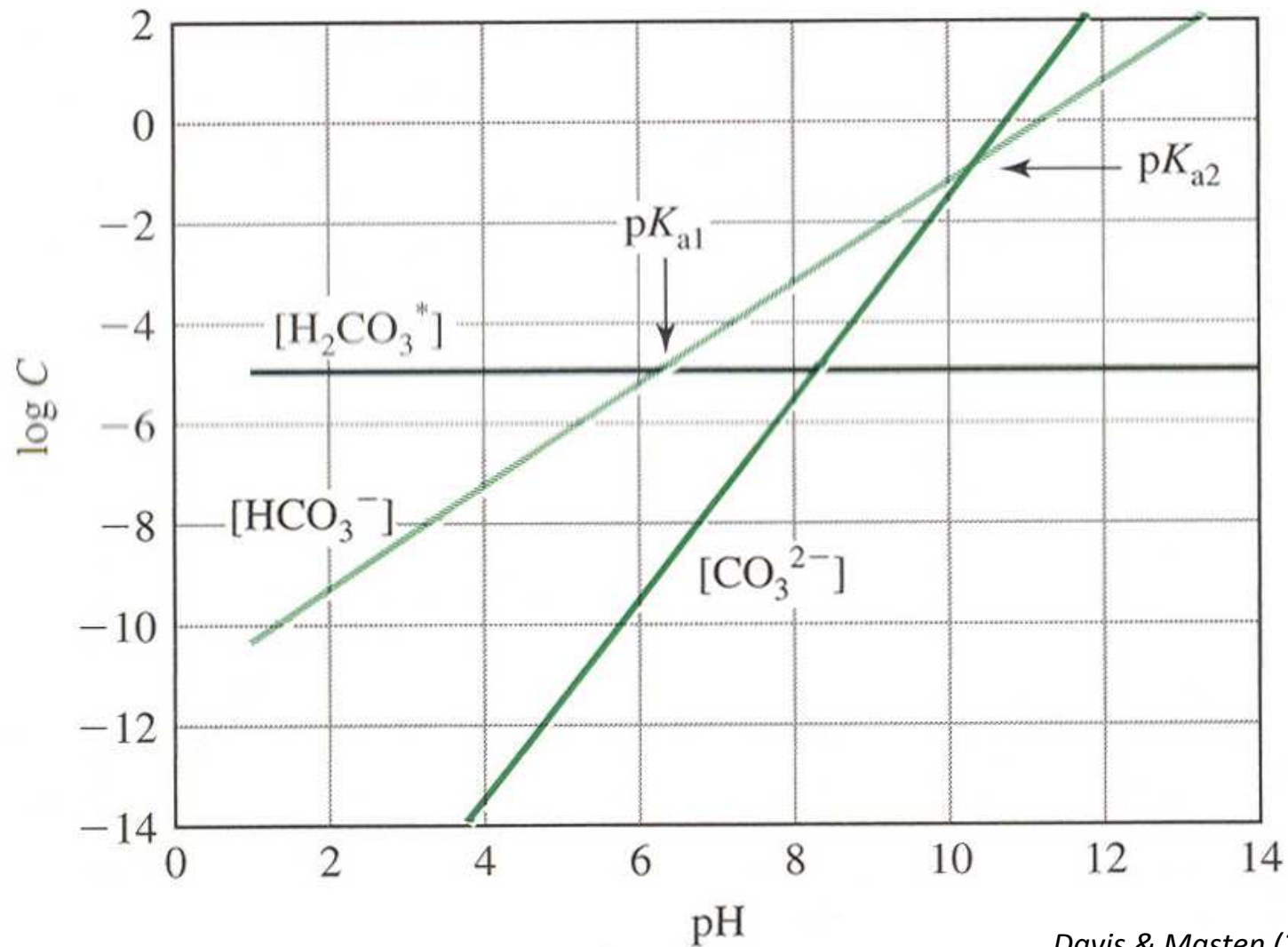
$$= 10^{-5.00} \text{ M} \quad (\text{at } 25^\circ\text{C}), \text{ ambient air}$$

$$[HCO_3^-] = \frac{K_{a1}}{[H^+]} \cdot [H_2CO_3^*] \quad \rightarrow \quad \log[HCO_3^-] = \log(K_H P_{CO_2}) - pK_{a1} + pH$$
$$= -11.35 + pH$$

$$[CO_3^{2-}] = \frac{K_{a1}K_{a2}}{[H^+]^2} \cdot [H_2CO_3^*]$$

$$\rightarrow \log[CO_3^{2-}] = \log(K_H P_{CO_2}) - pK_{a1} - pK_{a2} + pH = -21.68 + 2pH$$

# Carbonate speciation as f(pH) [Open]



# Alkalinity

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- Alkalinity: sum of all titratable bases to a pH of approximately 4.5

$$\text{Alkalinity} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + \dots + [\text{OH}^-] - [\text{H}^+]$$

Include  $\text{B}(\text{OH})_4^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{HPO}_4^{2-}$ ,  $\text{SiO}(\text{OH})_3^-$ , etc. if significant

$$\text{Carbonate alkalinity} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]$$

(bicarbonate and carbonate are major contributors of alkalinity in natural waters)

# Unit of alkalinity

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- Using molarity for each species, we get “eq/L”
- “eq”: equivalent, moles of H<sup>+</sup> ion in an acid-base solution or electrons in a redox reaction
- More common unit is “mg/L as CaCO<sub>3</sub>”
- Unit conversion: 1 meq/L = 10<sup>-3</sup> eq/L = 50 mg/L as CaCO<sub>3</sub>

# Reading assignment

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- Textbook Ch2 p. 51-75

# Acid dissociation

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## ***Slide#6 solution)***

*MW of HOCl = 52.46 g/mole*

*Unit conversion - mg/L to molarity:*

$$\frac{15 \text{ mg HOCl}}{1 \text{ L water}} \times \frac{1}{52.46 \text{ g HOCl/mole HOCl}} \times 10^{-3} \text{ g/mg} = 2.86 \times 10^{-4} \text{ M}$$



*weak acid → only a fraction dissociates*

$$K_a = 10^{-7.54} = \frac{[\text{H}^+][\text{OCl}^-]}{[\text{HOCl}]} = \frac{10^{-7} \cdot [\text{OCl}^-]}{[\text{HOCl}]}$$

$$[\text{HOCl}] = 3.47[\text{OCl}^-]$$

$$[\text{HOCl}] + [\text{OCl}^-] = 4.47[\text{OCl}^-] = 2.86 \times 10^{-4} \text{ M}$$

$$[\text{OCl}^-] = 0.64 \times 10^{-4} \text{ M}$$

$$[\text{HOCl}] = 2.22 \times 10^{-4} \text{ M}$$