Updated: 18 September 2019

Print version

CEE 370 Environmental Engineering Principles

Lecture #7

Environmental Chemistry V: Thermodynamics, Henry's Law, Acids-bases II

Reading: Mihelcic & Zimmerman, Chapter 3

Davis & Masten, Chapter 2
Mihelcic, Chapt 3

Henry’s Law

Henry's Law states that the amount of a gas that dissolves into a liquid is proportional to the partial pressure that gas exerts on the surface of the liquid. In equation form, that is:

$$C_A = K_H \; p_A$$

where,

C_A = concentration of A, [mol/L] or [mg/L]

K_H = equilibrium constant (often called Henry's Law constant), [mol/L-atm] or [mg/L-atm]

p_A = partial pressure of A, [atm]

Henry's Law Constants

Reaction	Name	K_h, mol/L-atm	$pK_h = -\log K_h$
$CO_2(g)$ _ $CO_2(aq)$	Carbon dioxide	3.41×10^{-2}	1.47
$NH_3(g)$ _ $NH_3(aq)$	Ammonia	57.6	-1.76
$H_2S(g)$ _ $H_2S(aq)$	Hydrogen sulfide	1.02×10^{-1}	0.99
$CH_4(g)$ _ $CH_4(aq)$	Methane	1.50×10^{-3}	2.82
$O_2(g)$ _ $O_2(aq)$	Oxygen	1.26×10^{-3}	2.90

Example: Solubility of O_2 in Water

- Background
  - Although the atmosphere we breathe is comprised of approximately 20.9 percent oxygen, oxygen is only slightly soluble in water. In addition, the solubility decreases as the temperature increases. Thus, oxygen availability to aquatic life decreases during the summer months when the biological processes which consume oxygen are most active.
- Summer water temperatures of 25 to 30°C are typical for many surface waters in the U.S. Henry's Law constant for oxygen in water is 61.2 mg/L-atm at 5°C and 40.2 mg/L-atm at 25°C.
  - What is the solubility of oxygen at 5°C and at 25°C?

Example 4.1 from Ray

Solution O_2 Solubility Ex.

At 5^0C the solubility is:

$$C_{O_2}(5°C) = K_{H,O_2} P_{O_2} = 61.2 \frac{mg}{L\text{-}atm} \text{ x } 0.209 \text{ atm}$$

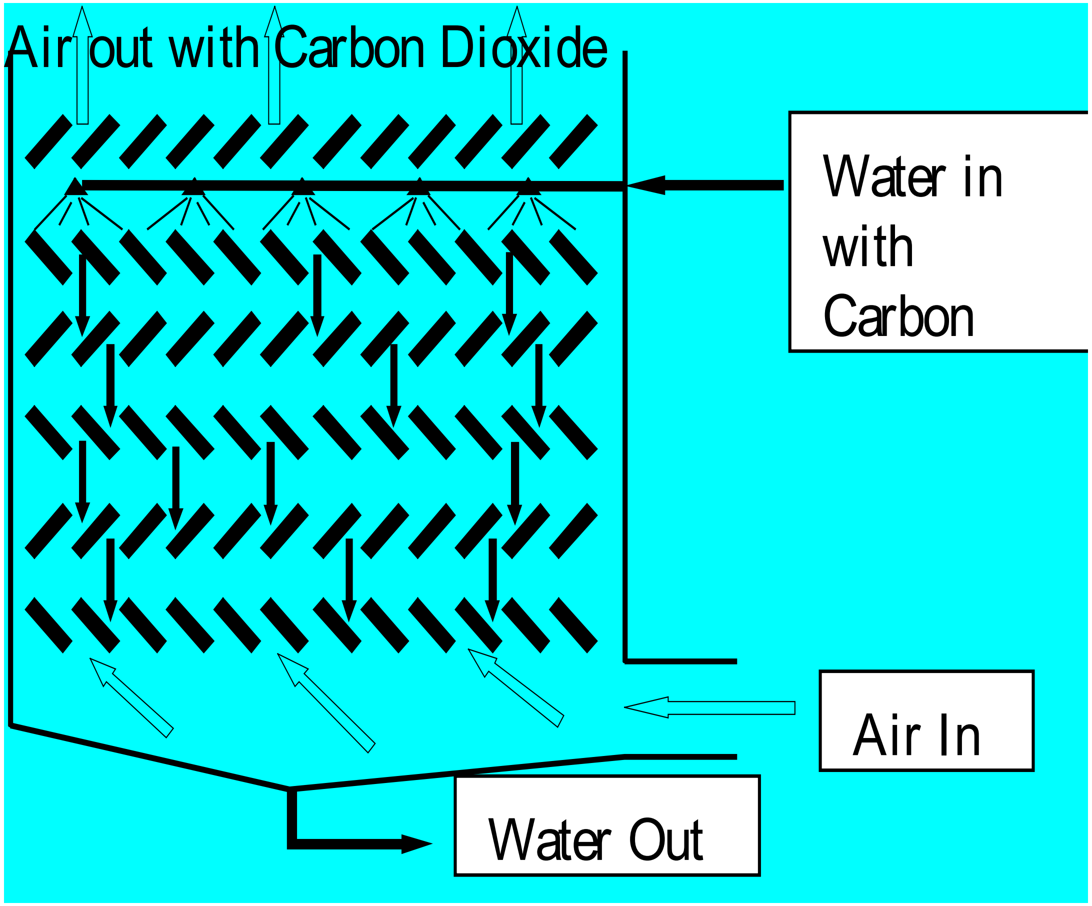
$$C_{O_2}(5°C) = 12.8 \frac{mg}{L}$$

At 25^0C the solubility is:

$$C_{O_2}(25°C) = K_{H,O_2} P_{O_2} = 40.2 \frac{mg}{L\text{-}atm} \text{ x } 0.209 \text{ atm}$$

$$C_{O_2}(25°C) = 8.40 \frac{mg}{L}$$

Air Stripping Tower



Air Stripping Example

An air stripping tower, similar to that shown in the previous slide , is to be used to remove dissolved carbon dioxide gas from a groundwater supply. If the tower lowers the level to twice the equilibrium concentration, what amount of dissolved gas will remain in the water after treatment? The partial pressure is about 350 ppm or 0.00035. The log of 0.00035 is about -3.5. Therefore the partial pressure of carbon dioxide in the atmosphere is $10^{-3.5}$ atm.

Example 4.2 from Ray

Solution to Air Stripping Ex.

The first step is to determine Henry's Law constant for carbon dioxide. From the table it is $10^{-1.5}$. The equilibrium solubility is then:

$$C_{CO_2} = K_{H,CO_2} p_{CO_2} = 10^{-1.5} \frac{\text{mole}}{\text{L-atm}} 10^{-3.5} \text{atm} = 10^{-5}\, mole/L$$

$$C_{CO_2} = 10^{-5}\ \text{M} = 10^{-5} \frac{\text{mole}}{\text{L}} \times \frac{44\ \text{g}}{\text{mole}} \times \frac{10^{3}\ \text{mg}}{\text{g}}$$

At equilibrium: $C_{CO_2} = 0.44\ \text{mg/L}$

After treatment: $C_{CO_2} = 0.88\ \text{mg/L}$

Ideal Gas Law

The Ideal Gas Law states that the product of the absolute pressure and the volume is proportional to the product of the mass and the absolute temperature. In equation form this is usually written:

$$PV = nRT$$

where,

P = absolute pressure, [atm]
V = volume, [L]
n = mass, [mol]
T = absolute temperature, [K]
R = proportionality constant or ideal gas constant, [0.0821 L-atm/K-mol]

Ideal Gas Law Example

Anaerobic microorganisms metabolize organic matter to carbon dioxide and methane gas. Estimate the volume of gas produced (at atmospheric pressure and 25°C) from the anaerobic decomposition of one mole of glucose. The reaction is:

$$C_6H_{12}O_6 \rightarrow 3CH_4 + 3CO_2$$

Example 4.3 from Ray

Solution to Ideal Gas Law Ex.

Each mole of glucose produces three moles of methane and three moles of carbon dioxide gases, a total of six moles. The total volume is then:

$$V = \frac{nRT}{P} = \frac{(6\ \text{mol})(0.0821\frac{\text{L-atm}}{\text{K-mol}})(298\ \text{K})}{(1\ \text{atm})}$$

$$V = 147\ \text{L}$$

Dalton’s Law of Partial Pressure

Dalton's Law of partial pressures states that the total pressure of a mixture of several gases is the sum of the partial pressures of the individual gases. In equation form this is simply:

$$P_t = \sum_{i=1}^{n} P_i$$

where,

P_t = total pressure of the gases, [atm]
P_i = pressure of the ith gas, [atm]

Anaerobic Digester Example

Anaerobic digesters are commonly used in wastewater treatment. The biological process produces both carbon dioxide and methane gases. A laboratory worker plans to make a "synthetic" digester gas. There is currently 2 L of methane gas at 1.5 atm and 1 L of carbon dioxide gas at 1 atm in the lab. If these two samples are mixed in a 4 L tank, what will be the partial pressures of the individual gases? The total pressure?

Example 4.4 from Ray

Solution to Anaerobic Digester Ex.

First, we must find the partial pressures of the individual gases using the ideal gas law:

$$P_1 V_1 = nRT = P_2 V_2$$

or

$$P_2 = P_1 \left(\frac{V_1}{V_2} \right)$$

For methane gas

$$P_2 = 1.5 \text{ atm} \left(\frac{2 \text{ L}}{4 \text{ L}} \right) = 0.75 \text{ atm}$$

For carbon dioxide gas:

$$P_2 = 1 \text{ atm} \left(\frac{1 \text{ L}}{4 \text{ L}} \right) = 0.25 \text{ atm}$$

And the total is:

$$P_t = P_{CH_4} + P_{CO_2} = 1 \text{ atm}$$

Equilibrium Reactions

$$aA + bB \leftrightarrow pP + rR$$

$$K_{eq} = \frac{\{C\}^c \{D\}^d}{\{A\}^a \{B\}^b}$$

thermodynamics

a, b, p, r = stoichiometric coefficients of the respective reactants

{A}, {B}, {P}, {R} = activity of the reactants and products

Chemical Activity

$$\{A\} = \gamma_A [A]$$

$\{A\}$ = activity of species A, [mol/liter]
$[A]$ = concentration of species A, [mol/liter]
γ_A = activity coefficient of A, unitless

γ is dependent on ionic strength -- the concentration of ions in solution. For dilute aqueous solutions γ is near unity. Thus, the activity and concentration are approximately the same. For most freshwater systems, γ may be neglected.

Activity conventions

- the activity of the **solvent**, water is set equal to unity
- the activity of a **solid** in equilibrium with a solution is unity
- the activity of a **gas** is the partial pressure the gas exerts on the liquid surface
- the activity of a **solute** is related to the concentration by $\{A\} = \gamma_A[A]$, where γ_A is the activity coefficient of species A

Auto-dissociation of Water

$$H_2O \leftrightarrow H^+ + OH^-$$

$$K_w = \frac{[H^+][OH^-]}{[H_2O]} = [H^+][OH^-]$$

At 25°C the value of K_w is 10^{-14}

Example 4.12

Find the pH and pOH of water at 25°C if the concentration of H^+ ions is 10^{-5} M.

Solution

$$pH = -\log\{H^+\} = -\log(10^{-5}) = 5$$

$$\{OH^-\} = \frac{K_w}{\{H^+\}} = \frac{10^{-14}}{10^{-5}} = 10^{-9}$$

$$pOH = -\log\{OH^-\} = -\log(10^{-9}) = 9$$

Acids & Bases

- Which is the strongest acid
  A. H_3PO_4
  B. H_2CO_3
  C. HNO_3
  D. CH_3COOH
  E. HF

Acid:Base Equilibria

Monoprotic Acid

$$HA \leftrightarrow H^+ + A^-$$

$$K_A = \frac{\{H^+\}\{A^-\}}{\{HA\}}$$

Diprotic Acid

$$H_2A = H^+ + HA^-$$

$$K_A1 = \frac{\{H^+\}\{HA^-\}}{\{H_2A\}}$$

$$HA^- \leftrightarrow H^+ + A^{2-}$$

$$K_A2 = \frac{\{H^+\}\{A^{2-}\}}{\{HA^-\}}$$

Similar to Table 3.5 in M&Z

Acidity Constants

Reaction	Name	K_a	$pK_a = –\log K_a$
$HCl = H^+ + Cl^–$	Hydrochloric	1000	-3
$H_2SO_4 = H^+ + HSO_4^-$	Sulfuric, H1	1000	-3
$HNO_3 = H^+ + NO_3^-$	Nitric	~1	~0
$HSO_4^- = H^+ + SO_4^-$	Sulfuric, H2	1×10^{-2}	2
$H_3PO_4 = H^+ + H_2PO_4^-$	Phosphoric, H1	7.94×10^{-3}	2.1
$HAc = H^+ + Ac^-$	Acetic	2.00×10^{-5}	4.7
$H_2CO_3 = H^+ + HCO_3^-$	Carbonic, H1	5.01×10^{-7}	6.3
$H_2S = H^+ + HS^-$	Hydrosulfuric, H1	7.94×10^{-8}	7.1
$H_2PO_4^- = H^+ + HPO_4^{–2}$	Phosphoric, H2	6.31×10^{-8}	7.2
$HOCl = H^+ + OCl^-$	Hypochlorous	3.16×10^{-8}	7.5
$NH_4^+ = H^+ + NH_3$	Ammonium	5.01×10^{-10}	9.3
$HCO_3^- = H^+ + CO_3^{–2}$	Carbonic, H2	5.01×10^{-11}	10.3
$HPO_4^{–2} = H^+ + PO_4^{–3}$	Phosphoric, H3	5.01×10^{-13}	12.3

NAME	EQUILIBRIA	pKa
Perchloric acid	$HClO_4 = H^+ + ClO_4^-$	-7 STRONG
Hydrochloric acid	$HCl = H^+ + Cl^-$	-3
Sulfuric acid	$H_2SO_4 = H^+ + HSO_4^-$	-3 (&2) ACIDS
Nitric acid	$HNO_3 = H^+ + NO_3^-$	-0
Hydronium ion	$H_3O^+ = H^+ + H_2O$	0
Trichloroacetic acid	$CCl_3COOH = H^+ + CCl_3COO^-$	0.70
Iodic acid	$HIO_3 = H^+ + IO_3^-$	0.8
Dichloroacetic acid	$CHCl_2COOH = H^+ + CHCl_2COO^-$	1.48
Bisulfate ion	$HSO_4^- = H^+ + SO_4^{-2}$	2
Phosphoric acid	$H_3PO_4 = H^+ + H_2PO_4^-$	2.15 (&7.2, 12.3)
Ferric ion	$Fe(H_2O)_6^{+3} = H^+ + Fe(OH)(H_2O)_5^{+2}$	2.2 (&4.6)
Chloroacetic acid	$CH_2ClCOOH = H^+ + CH_2ClCOO^-$	2.85
o-Phthalic acid	$C_6H_4(COOH)_2 = H^+ + C_6H_4(COOH)COO^-$	2.89 (&5.51)
Citric acid	$C_3H_5O(COOH)_3 = H^+ + C_3H_5O(COOH)_2COO^-$	3.14 (&4.77, 6.4)
Hydrofluoric acid	$HF = H^+ + F^-$	3.2
Formic Acid	$HCOOH = H^+ + HCOO^-$	3.75
Aspartic acid	$C_2H_6N(COOH)_2 = H^+ + C_2H_6N(COOH)COO^-$	3.86 (&9.82)
m-Hydroxybenzoic acid	$C_6H_4(OH)COOH = H^+ + C_6H_4(OH)COO^-$	4.06 (&9.92)
Succinic acid	$C_2H_4(COOH)_2 = H^+ + C_2H_4(COOH)COO^-$	4.16 (&5.61)
p-Hydroxybenzoic acid	$C_6H_4(OH)COOH = H^+ + C_6H_4(OH)COO^-$	4.48 (&9.32)
Nitrous acid	$HNO_2 = H^+ + NO_2^-$	4.5
Ferric Monohydroxide	$FeOH(H_2O)_5^{+2} + H^+ + Fe(OH)_2(H_2O)_4^+$	4.6
Acetic acid	$CH_3COOH = H^+ + CH_3COO^-$	4.75
Aluminum ion	$Al(H_2O)_6^{+3} = H^+ + Al(OH)(H_2O)_5^{+2}$	4.8

NAME	FORMULA	pKa
Propionic acid	$C_2H_5COOH = H^+ + C_2H_5COO^-$	4.87
Carbonic acid	$H_2CO_3 = H^+ + HCO_3^-$	6.35 (& 10.33)
Hydrogen sulfide	$H_2S = H^+ + HS^-$	7.02 (& 13.9)
Dihydrogen phosphate	$H_2PO_4^- = H^+ + HPO_4^{-2}$	7.2
Hypochlorous acid	$HOCl = H^+ + OCl^-$	7.5
Copper ion	$Cu(H_2O)_6^{+2} = H^+ + CuOH(H_2O)_5^+$	8.0
Zinc ion	$Zn(H_2O)_6^{+2} = H^+ + ZnOH(H_2O)_5^+$	8.96
Boric acid	$B(OH)_3 + H_2O = H^+ + B(OH)_4^-$	9.2 (& 12.7, 13.8)
Ammonium ion	$NH_4^+ = H^+ + NH_3$	9.24
Hydrocyanic acid	$HCN = H^+ + CN^-$	9.3
p-Hydroxybenzoic acid	$C_6H_4(OH)COO^- = H^+ + C_6H_4(O)COO^{-2}$	9.32
Orthosilicic acid	$H_4SiO_4 = H^+ + H_3SiO_4^-$	9.86 (& 13.1)
Phenol	$C_6H_5OH = H^+ + C_6H_5O^-$	9.9
m-Hydroxybenzoic acid	$C_6H_4(OH)COO^- = H^+ + C_6H_4(O)COO^{-2}$	9.92
Cadmium ion	$Cd(H_2O)_6^{+2} = H^+ + CdOH(H_2O)_5^+$	10.2
Bicarbonate ion	$HCO_3^- = H^+ + CO_3^{-2}$	10.33
Magnesium ion	$Mg(H_2O)_6^{+2} = H^+ + MgOH(H_2O)_5^+$	11.4
Monohydrogen phosphate	$HPO_4^{-2} = H^+ + PO_4^{-3}$	12.3
Calcium ion	$Ca(H_2O)_6^{+2} = H^+ + CaOH(H_2O)_5^+$	12.5
Trihydrogen silicate	$H_3SiO_4^- = H^+ + H_2SiO_4^{-2}$	12.6
Bisulfide ion	$HS^- = H^+ + S^{-2}$	13.9
Water	$H_2O = H^+ + OH^-$	14.00
Ammonia	$NH_3 = H^+ + NH_2^-$	23
Hydroxide	$OH^- = H^+ + O^{-2}$	24
Methane	$CH_4 = H^+ + CH_3^-$	34

Acidity Constants, #1

Reaction	Name	K_a	pK_a
$HCl = H^+ + Cl^-$	Hydrochloric	1000	-3
$H_2SO_4 = H^+ + HSO_4^-$	Sulfuric, H1	1000	-3
$HNO_3 = H^+ + NO_3^-$	Nitric	~1	~0
$HSO_4^- = H^+ + SO_4^{-2}$	Sulfuric, H2	1×10^{-2}	2
$H_3PO_4 = H^+ + H_2PO_4^-$	Phosphoric, H1	7.9×10^{-3}	2.1
$HAc = H^+ + Ac^-$	Acetic	2.0×10^{-5}	4.7
$H_2CO_3 = H^+ + HCO_3^-$	Carbonic, H1	5.0×10^{-7}	6.3

Acidity Constants, #2

Reaction	**Name**	**K_a**	**pK_a**
$H_2S = H^+ + HS^-$	Hydrosulfuric, H1	7.9×10^{-8}	7.1
$H_2PO_4^- = H^+ + HPO_4^{-2}$	Phosphoric, H2	6.3×10^{-8}	7.2
$HOCl = H^+ + OCl^-$	Hypochlorous	2.5×10^{-8}	7.6
$NH_4^+ = H^+ + NH_3$	Ammonium	5×10^{-10}	9.3
$HCO_3^- = H^+ + CO_3^{-2}$	Carbonic, H2	5×10^{-11}	10.3
$HPO_4^{-2} = H^+ + PO_4^{-3}$	Phosphoric, H3	5×10^{-13}	12.3

Example

What fraction of the following acids are ionized at pH 7?

a) Nitric
b) Hydrochloric
c) Sulfuric
d) Hypochlorous

Solution to Example a)

$$K_a = \frac{[H^+][NO_3^-]}{[HNO_3]}$$

$$\frac{[HNO_3]}{[NO_3^-]} = \frac{[H^+]}{K_a} = \frac{10^{-7}}{1} = 10^{-7}$$

$$F = \frac{[NO_3^-]}{[HNO_3] + [NO_3^-]} = \frac{[NO_3^-]}{10^{-7}[NO_3^-] + [NO_3^-]} \cong 1$$

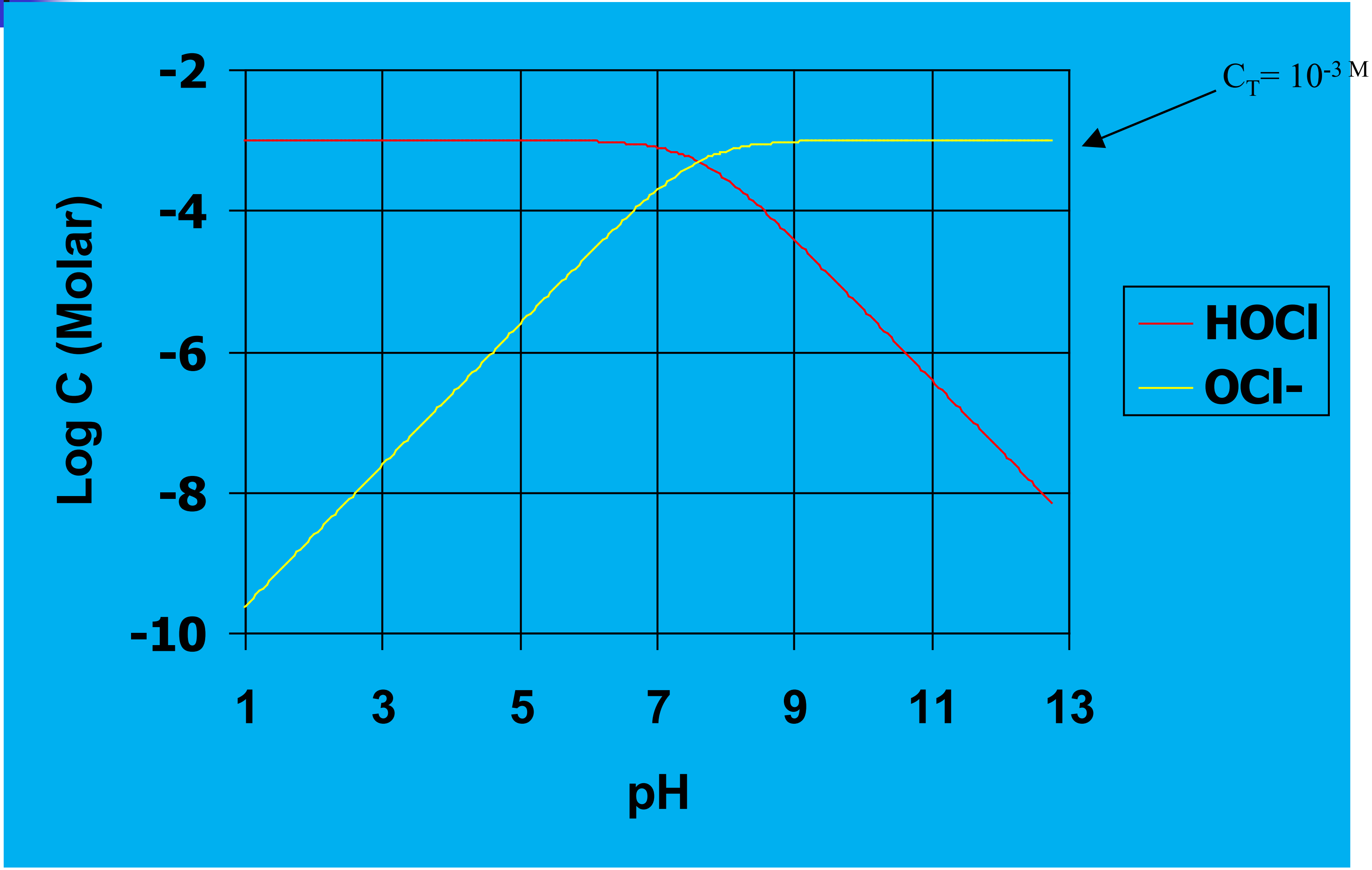
Solution to Example d)

$$K_a = \frac{[H^+][OCl^-]}{[HOCl]}$$

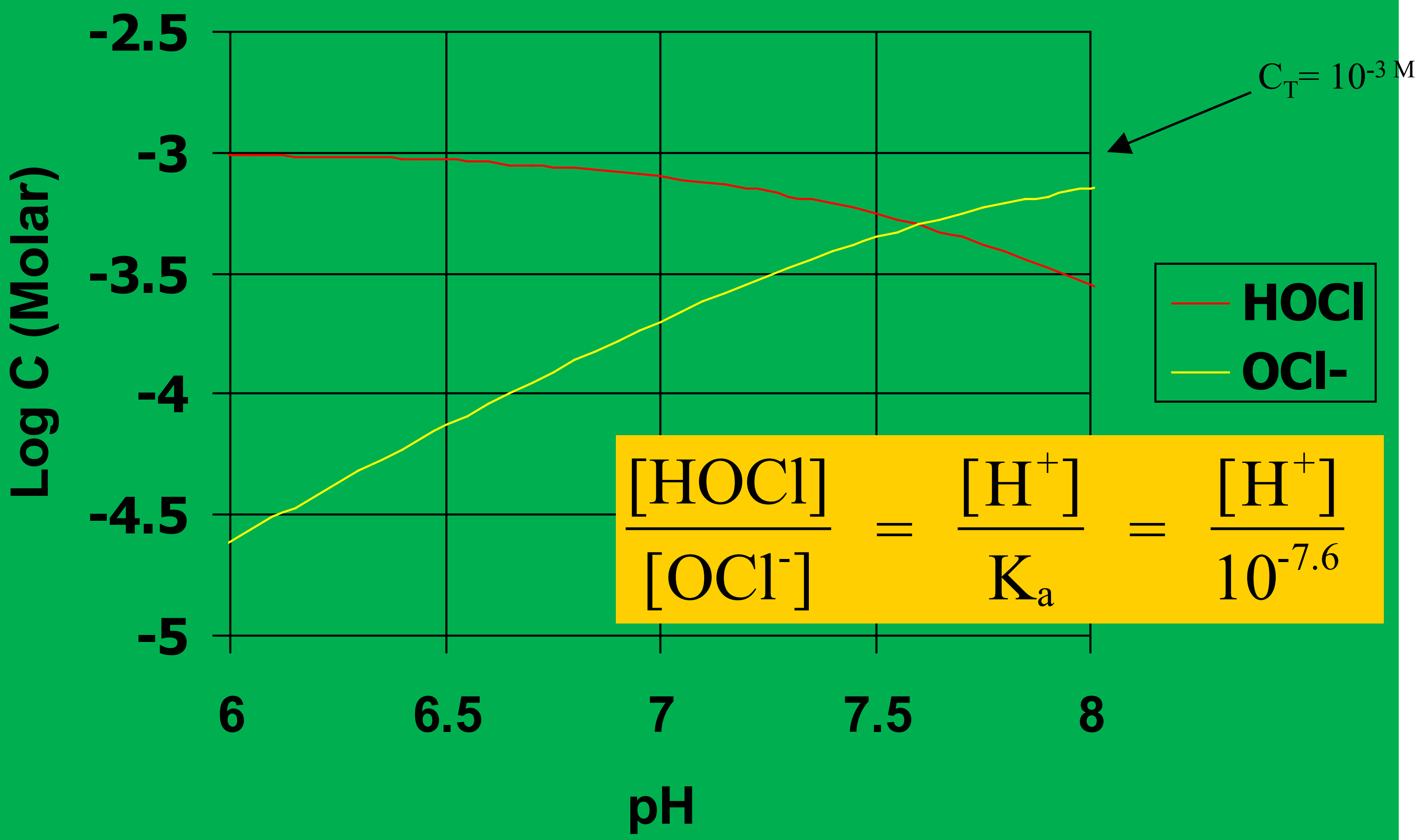
$$\frac{[HOCl]}{[OCl^-]} = \frac{[H^+]}{K_a} = \frac{10^{-7}}{10^{-7.6}} = 4.0$$

$$F = \frac{[OCl^-]}{[HOCl] + [OCl^-]} = \frac{[OCl^-]}{4[OCl^-] + [OCl^-]} = 0.20$$

Log C vs pH Diagram for Hypochlorous Acid



Log C vs pH Diagram for Hypochlorous Acid



$C_T = 10^{-3}$ M

$$\frac{[HOCl]}{[OCl^-]} = \frac{[H^+]}{K_a} = \frac{[H^+]}{10^{-7.6}}$$

Definitions

- Bronsted-Lowry (1923)
  - Acids: (proton donor)
    - any substance that can donate a proton to any other substance
  - Bases: (proton acceptor)
    - any substance that accepts a proton from any other substance

$Acid_1$	+	$Base_2$	=	$Acid_2$	+	$Base_1$
HNO_3	+	H_2O	=	H_3O^+	+	NO_3^-
$HOCl$	+	H_2O	=	H_3O^+	+	OCl^-
NH_4^+	+	H_2O	=	H_3O^+	+	NH_3
H_2O	+	H_2O	=	H_3O^+	+	OH^-

- Acid strength of a conjugate acid-base pair is measured relative to the other pair
- the stronger the acid, the weaker the conjugate base, and vice versa

- To next lecture