Monoprotic Acid/Base Equilibria_____ H Ch 8-4, 9

SWITCHED TO HARRIS TEXT

THIS WEEK IS THE LAST WEEK FOR IN-PERSON LABS

9-2 Weak Acids and Bases
9-3 Weak Acid Equilibria
9-4 Weak Base Equilibria
9-5 Buffers (Friday)

FRIDAY QUIZ ON ACIDS/BASES
include systematic for strong

Acid/Base Strengths

acid strength – determined by extent of reaction of acid with water to form $H_3O^+(aq)$, or the extent of its ionization or dissociation, as shown by the magnitude of its equilibrium constant, K_a – then for any hydrogen-containing compound, HA
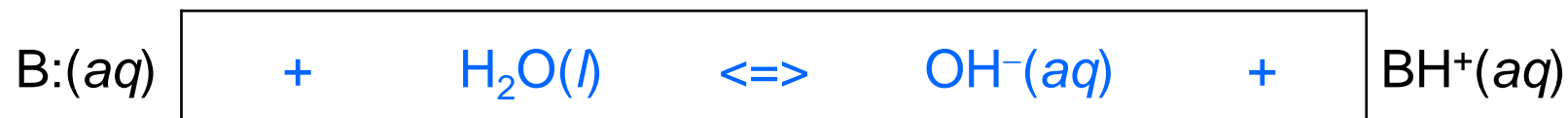
HA(*aq*) | + H_2O(*l*)   <=> H_3O^+(*aq*)   + | A^-(*aq*)
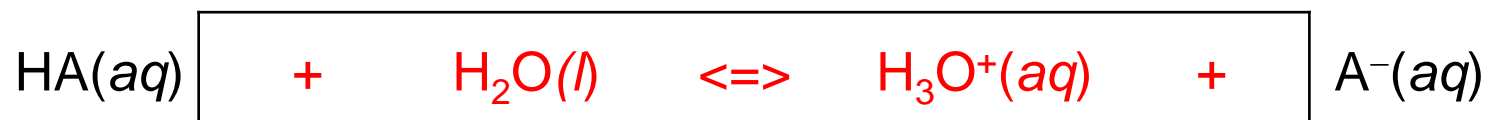
EQUATION FOR ACIDITY FOR ANY HA

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

EQUILIBRIUM CONSTANT

base strength – (aside from Group I and II hydroxides) determined by extent of reaction of base with water to form $OH^-(aq)$, or extent of its ionization, as shown by the magnitude of its equilibrium constant, K_b – then for any base B:

B:(*aq*) | + H_2O(*l*)   <=> OH^-(*aq*)   + | BH^+(*aq*)

EQUATION FOR BASICITY FOR ANY B:

$$K_b = \frac{[OH^-][BH^+]}{[B:]}$$

EQUILIBRIUM CONSTANT

Conjugate Acid/Base Pairs

The conjugate base of a weak acid is a weak base. The weaker the acid, the stronger the base. However, if one member of a conjugate pair is weak, so is its conjugate.

The relation between K_a for an acid and K_b for its conjugate base in aqueous solution is $K_w = K_a \times K_b$.

When a strong acid (or base) is added to a weak base (or acid), they react nearly completely.
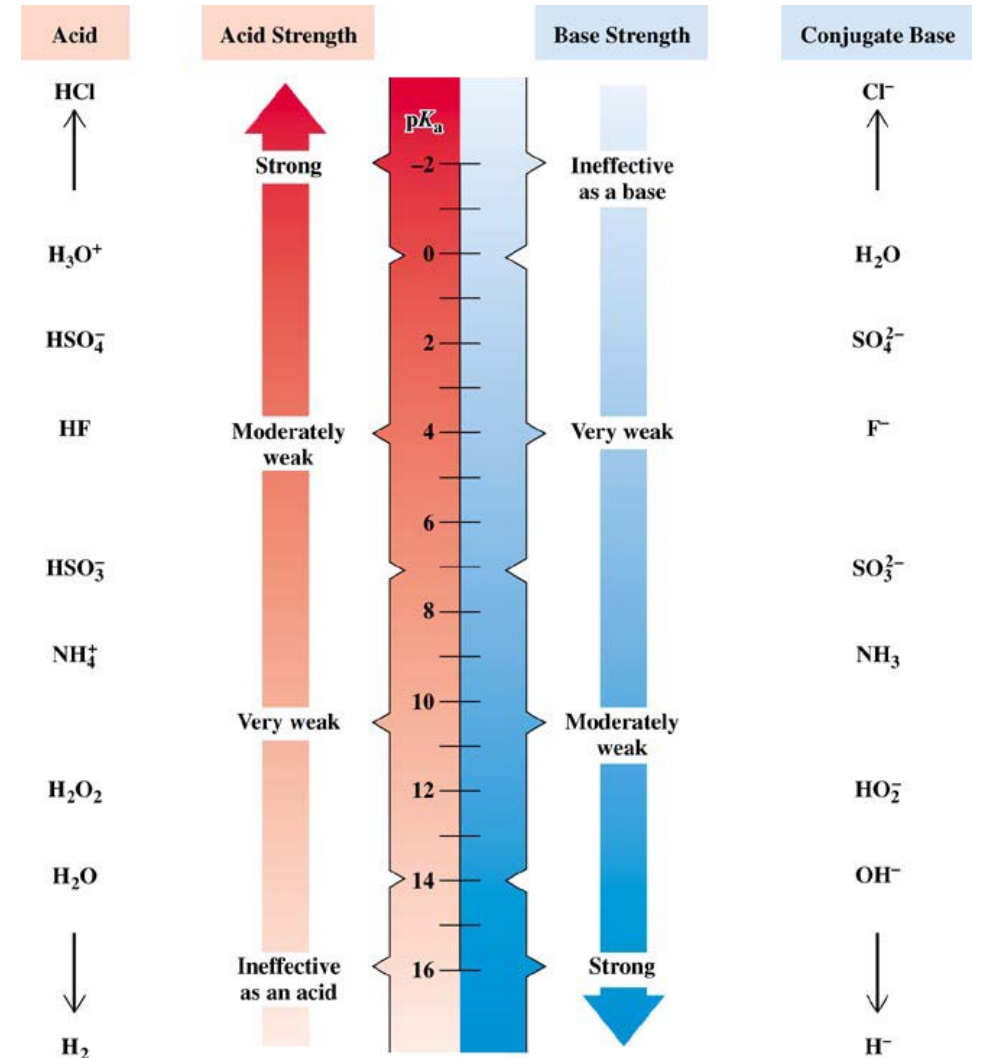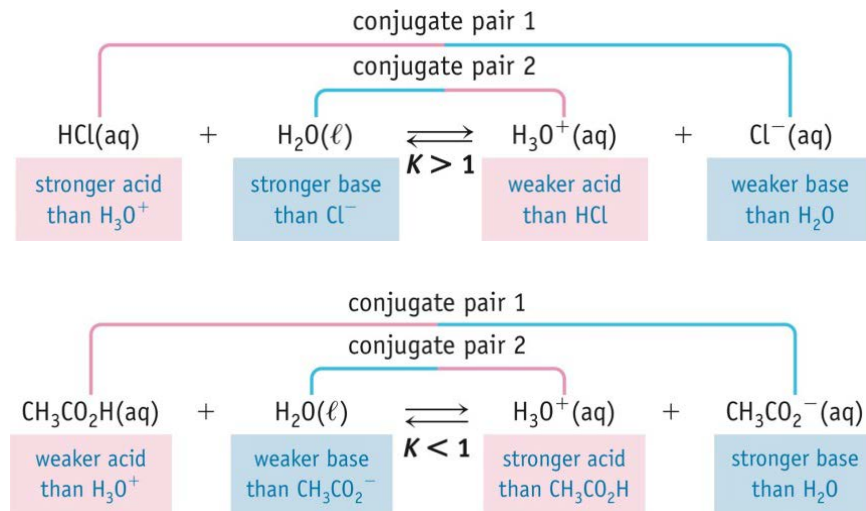
Systematic Treatment of Equilibrium

GOAL - account for the concentration of all species present in a solution once equilibrium has been reached. The equations to do this derive from

1. **charge balance** - solution must be electrically neutral

2. **material balance** - conservation of matter; what happens to initial concentrations

3. equilibrium expressions and their equilibrium constants

# Systematic Treatment of Equilibrium – Charge Balance

salt

EX 2. Write the charge balance for a solution containing $(NH_4)_3PO_4$. Be sure to consider all possible equilibrium reactions.

NH_4^+ is an acid but its equilibrium reaction produces its neutral conjugate base, NH_3; PO_4^{3-} is a base whose equilibrium reactions produce

$$PO_4^{3-} + H_2O \iff OH^- + HPO_4^{2-}$$
$$HPO_4^{2-} + H_2O \iff OH^- + H_2PO_4^-$$
$$H_2PO_4^- + H_2O \iff OH^- + H_3PO_4$$

in aqueous solution autoionization of water must always be considered:
$$H_2O + H_2O \iff H_3O^+ + OH^-$$

$$[NH_4^+] + [H^+] = [OH^-] + [H_2PO_4^-] + 2\,[HPO_4^{2-}] + 3\,[PO_4^{3-}]$$
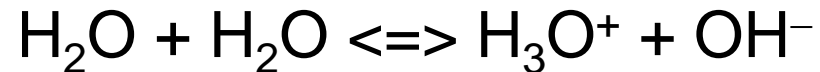
Molarity and Formality

These two types of concentration are identical for a species which does not dissociate into ions in solution or does not react with water to produce ions

**Molarity** is the concentration of the species that is actually present in solution such as 1.0 M Cl^-.

Consider a species which forms ions in solution such as acetic acid, CH_3COOH. You might try to place exactly 1.0 mole in a liter of water to form a 1.0 M solution but the solution will have partially dissociated into CH_3COO^-. Such a solution is 1.0 F = $[CH_3COOH]$ + $[CH_3COO^-]$. So **formality** represents the concentration of the different "pieces" that acetic acid forms in solution or the concentration originally placed in water (before dissociation).

Harris uses formality

Systematic Treatment of Equilibrium – Mass Balance

EX 3. What is the mass balance equation for a solution prepared by adding 0.100 moles of ammonia to 1.000 L?

NH_3 is a weak base and reacts with water:

$$NH_3(aq) + H_2O\ (l)\ \ <=>\ \ OH^-(aq)\ +\ NH_4^+(aq)$$
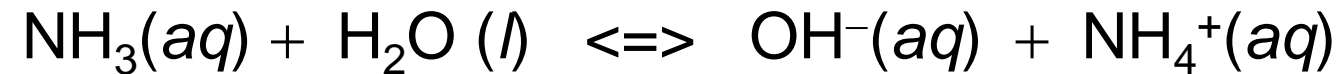
so the mass balance is

$$0.100\ F\ =\ [NH_3]_o\ =\ [NH_3]\ +\ [NH_4^+]$$

Systematic Treatment of Equilibrium

equations needed for solution for unknown

General approach includes

1. write down the pertinent chemical reactions and their equilibrium constant expressions

2. write down all species present in solution according to #1

3. set up the charge balance equation (the solution must be electrically neutral so the number of positive charges = the number of negative charges)

4. apply the material balance equation (conservation of matter) – may be more than one

5. are there enough equations to solve for the unknowns?

Systematic Treatment – Dilute Strong Acid

EX 4. What is the pH of a 1.0×10^{-8} M solution of HBr?

1. reactions, K (HBr $\rightarrow$ H$^+$ + Br$^-$)   2. species: H$^+$, OH$^-$, Br$^-$
   $H_2O \iff H^+ + OH^-$ $K_w = [H^+][OH^-]$

3. **charge balance**: **[H$^+$] = [OH$^-$] + [Br$^-$]**   4. **mass balance**: **[Br$^-$] = 1.0 $\times$ 10^{-8}**

   substitute for [OH$^-$]   substitute for [Br$^-$]

$$K_w = [H^+][OH^-] = [H^+]\{ [H^+] - [Br^-] \} = [H^+]^2 - [H^+][Br^-]$$

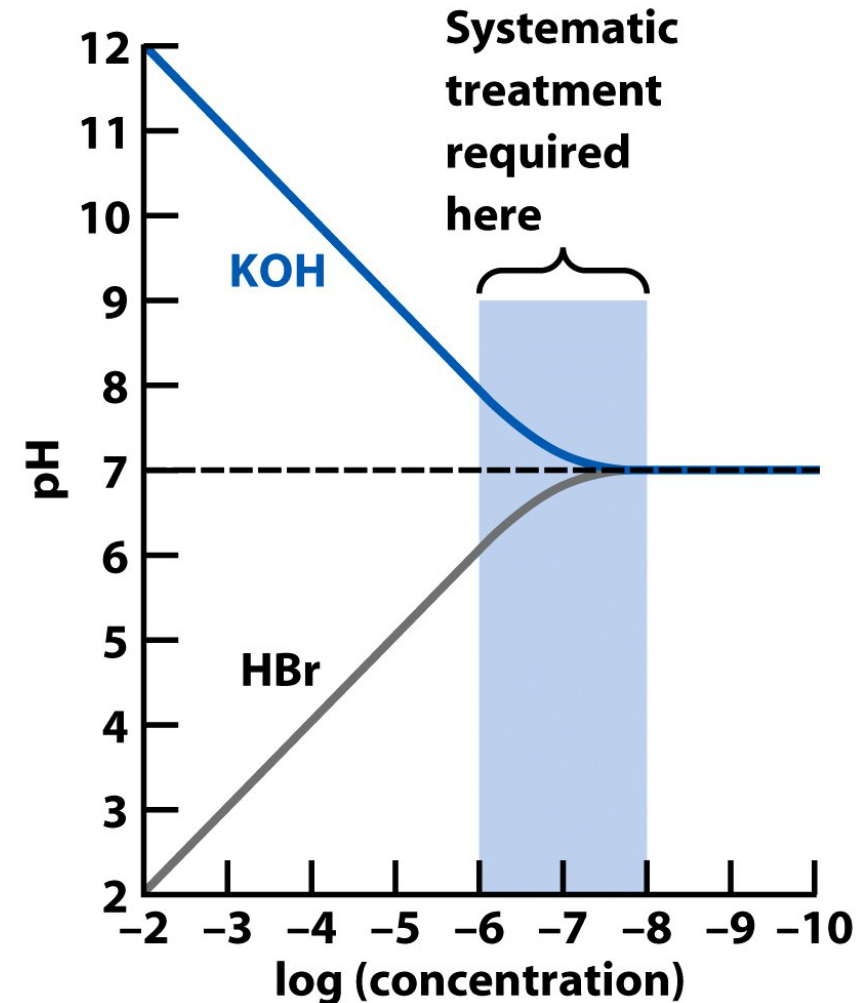$$\text{quadratic: } [H^+]^2 - [H^+](1.0 \times 10^{-8}) - K_w = 0$$

$$[H^+] = \{ -10^{-8} \pm \sqrt{[(10^{-8})^2 + 4(1.01 \times 10^{-14})]} \} / 2$$

$$= 1.05 \times 10^{-8} \text{ M}$$

$$\Rightarrow \text{pH} = 6.978 \Rightarrow \mathbf{6.98}$$

Systematic Treatment – Dilute Strong Acid/Base

For dilute strong acids or bases a systematic treatment is only re-quired when the concentration is between ~ 10^{-8} and 10^{-6} M. Above 10^{-8} one cannot practically make such a dilute solution and below 10^{-6} H^+ from K_w is too small a con-tribution.

Systematic Treatment – Weak Acid/Base

The acidity of an aqueous solution of CH_3COOH is determined by its reaction with water:

$$CH_3COOH(aq) + H_2O(l) <=> H_3O^+(aq) + CH_3COO^-(aq)$$
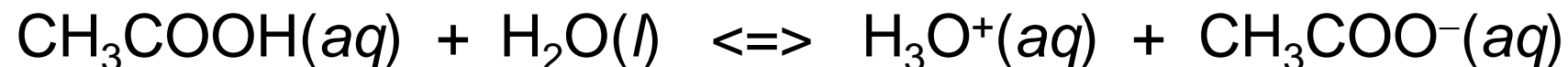
and quantitatively measured by its acid dissociation constant, K_a
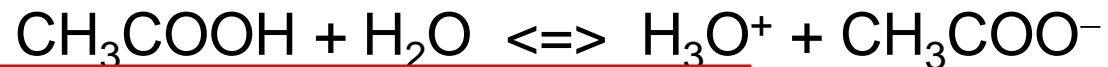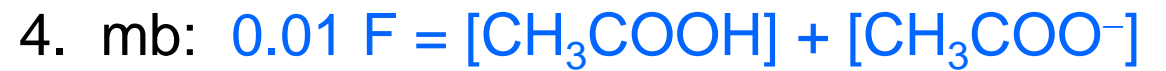
$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

where all concentrations are obtained at equilibrium.

Systematic Treatment – Weak Acid/Base

1. reactions

$H_2O \iff H^+ + OH^-$ $K_w = [H^+][OH^-]$

$CH_3COOH + H_2O \iff H_3O^+ + CH_3COO^-$

2. species: CH_3COOH, CH_3COO^-, H^+, OH^-

3. cb: $[H^+] = [OH^-] + [CH_3COO^-]$

4. mb: $0.01\ F = [CH_3COOH] + [CH_3COO^-]$

$$\boxed{K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}} = \frac{[H^+][CH_3COO^-]}{0.01 - [CH_3COO^-]}$$

$$= \frac{[H^+]\{[H^+] - [OH^-]\}}{0.01 - \{[H^+] - [OH^-]\}}$$

CH_3COOH is an acid so $[OH^-] \ll [H^+]$

$$= \frac{[H^+]\{[H^+] - K_w/[H^+]\}}{0.01 - \{[H^+] - K_w/[H^+]\}}$$

$$= \frac{[H^+]^2}{0.01 - [H^+]} \quad \Rightarrow \quad \boxed{K = \frac{x^2}{F - x}}$$

Weak Acid - $K_a = x^2 / (F - x)$

EX 6. What is the pH of 0.050 M solution of a weak acid, $K_a = 1.59 \times 10^{-10}$?

$$HA(aq) + H_2O(l) \iff H_3O^+(aq) + A^-(aq)$$

	HA		H_3O^+	A^-
I	0.050 M		~ 0	0
C	$-x$		$+x$	$+x$
E	$0.050 - x$		x	x

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{x^2}{0.050 - x}$$

quadratic: $x^2 + K_a x - 0.050 K_a = 0$

$$x = \{ -1.59 \times 10^{-10} \pm \sqrt{[(1.59 \times 10^{-10})^2 + 4(0.050)(1.59 \times 10^{-10})]} \} / 2$$

$= 2.819 \times 10^{-6}$ M

$\Rightarrow$ pH $= 5.5498 \Rightarrow$ **5.55**

$(2.819 \times 10^{-6}) / 0.050$

$< 1\%$

$x = \sqrt{(0.050\, K_a)}$

1% (5%) Rule

Weak Acid Dissociation - $K_a = x^2 / (F - x)$

EX 7. What is the pH of 0.010 and 0.0010 M acetic acid, $K_a = 1.76 \times 10^{-5}$, and its fraction of dissociation

$$CH_3COOH(aq) + H_2O(l) \iff H_3O^+(aq) + CH_3COO^-(aq)$$

I	M	~ 0	0
C	$-x$	$+x$	$+x$
E	$M - x$	x	x
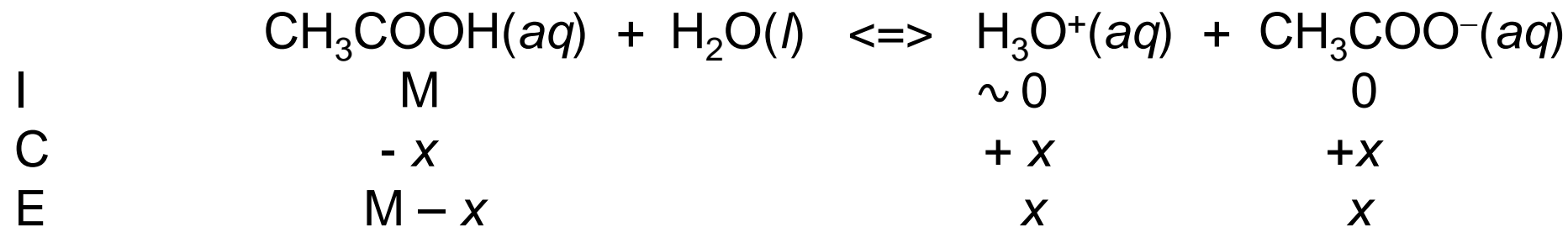
$$K_a = \frac{x^2}{M - x} \qquad \text{quadratic: } x^2 + K_a\, x - M\, K_a = 0$$

a) 0.010 M

[H$^+$] = 4.108×10^{-4} M

pH = **3.396**

α = **0.04**

b) 0.0010

1.241×10^{-4} M

3.906

0.1241

fraction dissociation (acids)

$\alpha = [A^-]/[HA]_o$

fraction of association (bases)

$\alpha = [BH^+]/[B:]_o$

Weak Acid Dissociation - $K_a = x^2 / (F - x)$

$$CH_3COOH(aq) + H_2O(l) \iff H_3O^+(aq) + CH_3COO^-(aq)$$
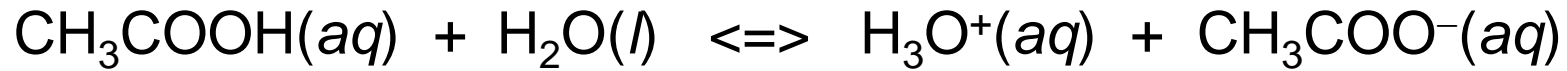
a) 0.010 M
$[H^+] = 4.108 \times 10^{-4}$ M
pH = **3.396**
α = **0.04**

b) 0.0010 M
1.241×10^{-4} M
3.906
0.1241

fraction dissociation (acids)
$\alpha = [A^-]/[HA]_o$
fraction of association (bases)
$\alpha = [BH^+]/[B:]_o$

dilution effect on
1. equilibrium
2. $[H^+]$
3. pH
4. ionization

$[H_3O^+] = n_{H3O+} / $ L of solution

More concentrated   More dilute

Acid concentration

Percent dissociation

H^+ concentration

Weak Base Dissociation - $K_b = x^2 / (F - x)$

EX 8. What is the pH of 0.25 M solution of ammonia, $K_b = 1.8 \times 10^{-5}$

$$NH_3(aq) + H_2O(l) <=> OH^-(aq) + NH_4^+(aq)$$

I	M	~ 0	0
C	- x	+ x	+x
E	M – x	x	x
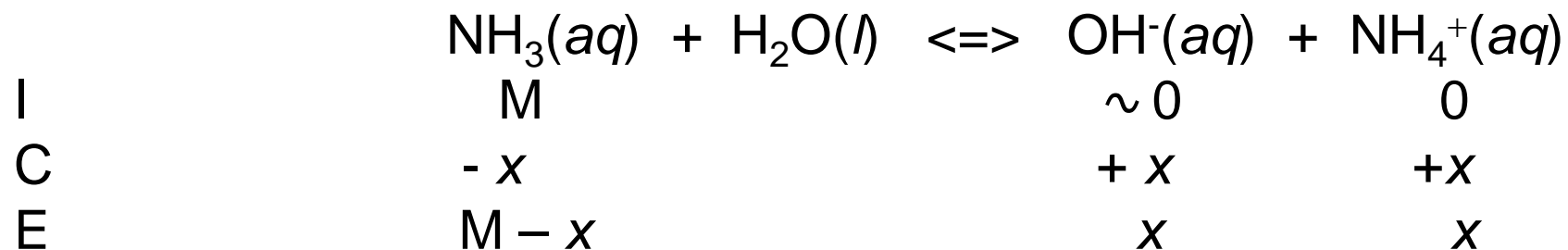
$K_b = \dfrac{x^2}{M - x}$ quadratic: $x^2 + K_b\, x - M\, K_b = 0$

$[OH^-] = 0.00211$ => $[H^+] = K_w / [OH^-] = 4.7811 \times 10^{-12}$ M

pH = 11.32

Acid/Base Properties of Salt Solutions

cation*	anion**	example	pH of solution
from strong base	from strong acid (conjugate base of)	MgI_2, $KClO_4$	neutral
from strong base	from weak acid (conjugate base of)	KF, AgCN	basic
from weak base (conjugate acid of)	from strong acid (conjugate base of)	NH_4Br	acidic
from weak base (conjugate acid of)	from weak acid (conjugate base of)	NH_4NO_2	acidic if $K_a > K_b$ basic if $K_b > K_a$ neutral if $K_a = K_b$
highly charged metal ion (hydrated in water)	from strong acid (conjugate base of)	$Al(NO_3)_3$, $Cr(H_2O)_6^{3+}$	acidic

*cation from strong base (Group I and II hydroxides, excluding Be) and silver:

   Li^+, Na^+, K^+, Rb^+, Cs^+ Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} Ag^+

**anion from strong acid: conjugate base of six of the seven common strong acids

   Cl-, Br-, I- ClO_4^-, ClO_3^-, NO_3^- (not HSO_4^-) **WHY? HSO_4^- is the conjugate base of a strong acid => ineffective base but it does have an acidic proton => solutions are acidic**

Acidity of Aqueous Solutions of Metal Ions

$$Al(H_2O)_6{}^{3+}(aq) \quad + \quad H_2O(aq) \quad \rightleftharpoons \quad Al(H_2O)_5(OH)^{2+}(aq) + H_3O^+(aq)$$