

MONDAY, MARCH 23, 2026 AP CHEMISTRY

## Ch. 17 Aqueous Equilibria

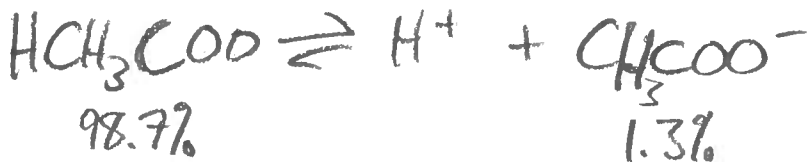
### 17.1 THE COMMON-ION EFFECT

COMMON IONS ARE IONS PRESENT IN DIFFERENT COMPOUNDS LIKE  $\text{Cl}^-$  IN  $\text{NaCl}$  AND  $\text{CaCl}_2$ .

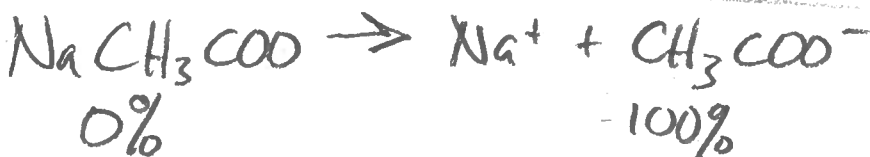
COMMON IONS IN STRONG ELECTROLYTES JUST INCREASE CONC. IF ADDED TO THE SAME SOLUTION.

BUT FOR WEAK ACIDS AND BASES, A COMMON ION WILL DISTURB AN EQUILIBRIUM.

WEAK ACID  
PARTIAL DISSOCIATION



STRONG  
ELECTROLYTE



LET'S MIX THESE TOGETHER:  $\text{HCH}_3\text{COO} \rightleftharpoons \text{H}^+ + \text{CH}_3\text{COO}^-$

0.1 M  $\text{HCH}_3\text{COO}$  ; 0.1 M  $\text{H}^+$  ; 0.1 M  $\text{CH}_3\text{COO}^-$

PLUS  
0.1 M  $\text{NaCH}_3\text{COO}$  ; c  
e

BY ADDING  $\text{CH}_3\text{COO}^-$  WE PUSH THIS EQUIL. TO THE LEFT, AS LE CHÂTELIER'S PRINCIPLE WOULD SAY.  $\text{pH} = 2.89$

FOR 0.1 M  $\text{HCH}_3\text{COO}$   $[\text{H}^+]_{\text{eq}} = 1.3 \times 10^{-3} \text{ M}$   $\text{pH} = 2.89$  Ch. 16

FOR 0.1 M  $\text{HCH}_3\text{COO}$

PLUS  
0.1 M  $\text{NaCH}_3\text{COO}$

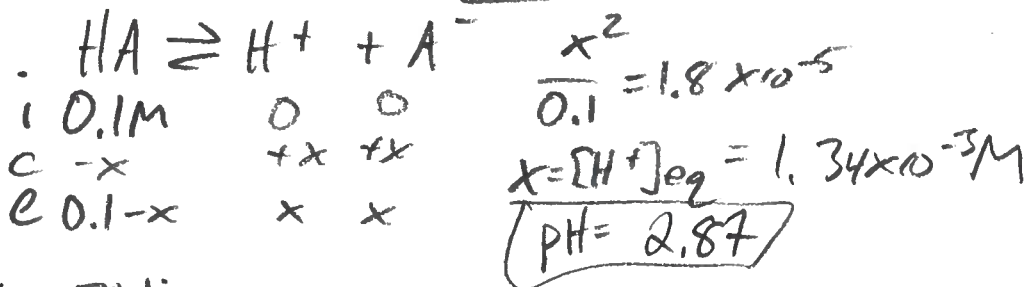
$[\text{H}^+]_{\text{eq}} = 1.8 \times 10^{-5} \text{ M}$   $\text{pH} = 4.74$

(1)

STOPPED AT BOTTOM OF PREV. PG. GROUP Y M 2026-03-23  
 — TRANSITIONED TO POGIL: COMMON ION EFFECT ON ACID IONIZATION

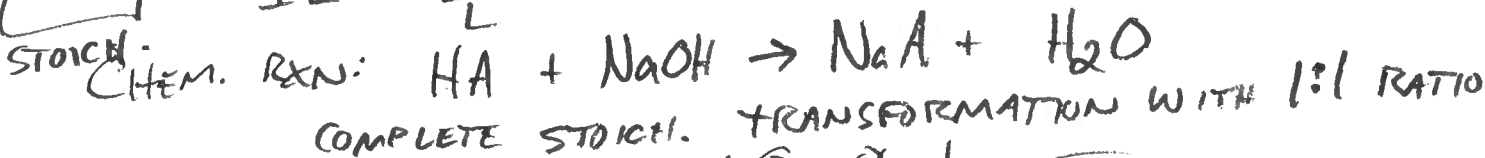
LET'S TALK STOICH. VS. EQUILIBRIUM

SCENARIO: HA = HCH<sub>3</sub>COO (0.1M)



FIRST VARIATION:

**I.** 1 L OF 0.1M HA ADD 0.05 mol NaOH  
 1 L x 0.1 mol/L = 0.1 mol HA ADD 0.05 mol NaOH

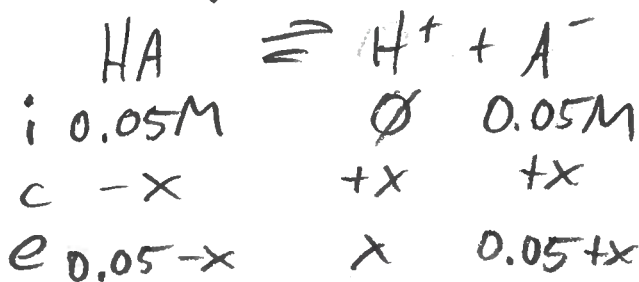


START 0.1 mol HA, 0.05 mol NaOH (LR), 0 mol NaA, 0 mol H<sub>2</sub>O  
 END 0.05 mol HA, 0 mol NaOH (LR), 0.05 mol NaA, 0.05 mol H<sub>2</sub>O

0.05 mol NaOH ·  $\frac{[HA]}{[NaOH]} = 0.05$  mol HA REACT

0.1 - 0.05 = 0.05 mol HA REMAIN

**II.** WHAT IS THE PH?



$$\frac{[H^+][A^-]}{[HA]} = \frac{(x)(0.05+x)}{(0.05-x)} = 1.8 \times 10^{-5}$$

ASSUME 0.05 ± x ≈ 0.05

$$\frac{x(0.05)}{(0.05)} = 1.8 \times 10^{-5}$$

$$x = [H^+]_{eq} = 1.8 \times 10^{-5}$$

PH = 4.74

17.2 BUFFERS

A BUFFER IS A SOLUTION OF A WEAK ACID MIXED WITH ITS CONJUGATE BASE. USUALLY,  $[HA]_0$  IS SIMILAR IN SIZE TO  $[A^-]_0$ .

THE KEY CHARACTERISTIC OF A BUFFER IS ITS RESISTANCE TO CHANGES IN THE pH OF THE SOLUTION WHEN SMALL AMOUNTS OF STRONG ACID OR BASE ARE ADDED.

COMPOSITION OF A BUFFER

① ADD HA TO SOLN. ADD NaA TO SOLN (TO PROVIDE  $A^-$ ).

②<sup>(a)</sup> ADD HA TO SOLN. ADD NaOH TO SOLN TO CONVERT HA INTO  $A^-$ .

(b) ADD  $A^-$  TO SOLN. ADD HCl TO SOLN TO CONVERT  $A^-$  INTO HA.

THERE IS A USEFUL SHORTCUT FOR CALC. pH FOR A SOLN. WE KNOW TO BE A BUFFER. YOU NEED:

①  $K_a$  ( $-\log K_a = pK_a$ ) OF THE WEAK ACID

②  $[HA]_0$

③  $[A^-]_0$

$$-\log \frac{A}{B} = \log \frac{B}{A}$$

BUFFER EQUATION A.K.A. HENDERSON-HASSELBALCH EQN.

(YOU DO NOT NEED TO DEMONSTRATE THIS DERIVATION)

①  $K_a = \frac{[H^+][A^-]}{[HA]}$

④  $pH = -(\log K_a + \log \frac{[HA]}{[A^-]})$

②  $[H^+] = \frac{K_a [HA]}{[A^-]}$

⑤  $pH = pK_a + \log \frac{[A^-]}{[HA]}$

③  $-\log [H^+] = -\left(\log \left(K_a \cdot \frac{[HA]}{[A^-]}\right)\right)$

MEMORIZE

③

(BTW, IN ORDER FOR THE MATH TO BE VALID BOTH  $[A^-]_0$  AND  $[HA]_0$  NEED TO BE  $\sim 10^3$  TIME BIGGER THAN  $K_a$ ).

USE THE BUFFER EQN. TO

① CALC. pH GIVEN  $[HA]_0$  AND  $[A^-]_0$   
(MAYBE YOU'LL HAVE TO DO A STOICH CALC. FIRST)

② CALC. A RATIO OF  $\frac{[A^-]_0}{[HA]_0}$  NEEDED TO  
GET A PARTICULAR pH.

$$pH = pK_a + \log \frac{A^-}{HA}$$

STOPPED HERE GROUP X W 2026-03-25  
AFTER THE CH. 16 QUIZ

THE BUFFER EQUATION CAN BE USED FORWARDS  
OR BACKWARDS.

FORWARDS: I WANT TO MAKE A BUFFER, WHAT  
HA/A<sup>-</sup> PAIR DO I NEED AND WHAT RATIO  
OF CONC.  $[A^-]_0/[HA]_0$  IS REQUIRED.

BACKWARDS: GIVEN A SOLN. WITH A STATED pH  
VALUE (FROM A STRONG ACID/BASE OR A  
BUFFER THAT WAS ALREADY DETERMINED) YOU  
CAN USE THE BUFFER EQUATION TO FIND OUT  
THE RATIO OF  $[A^-]/[HA]$  FOR A SMALL AMOUNT  
OF AN ADDED WEAK ACID/BASE. IT CAN'T  
AFFECT THE pH.

BUFFER EQN. FORWARDS

$$pH = pK_a + \log \frac{A^-}{HA}$$

LET'S SAY WE WANT A BUFFER WITH A  $pH = 4.00$ .  
ARBITRARILY, LET'S SAY WE WANT  $[HA]_0 = 0.1M$ .

FIRST, WE NEED A WEAK ACID WITH A  $pK_a$  NEAR 4.

THIS IS SO THE RATIO  $\frac{A^-}{HA}$  IS NOT MORE THAN  $\frac{10}{1}$   
OR LESS THAN  $\frac{1}{10}$  (LOGARITHMIC SCALE).

WE CHOOSE  $HNO_2$   $K_a = 4.5 \times 10^{-4}$   $pK_a = 3.35$

$$\text{CALC. } \frac{[A^-]_0}{[HA]_0} \text{ RATIO } 10^{(pH - pK_a)} = \frac{[A^-]_0}{[HA]_0} = 4.5$$

$$\frac{[A^-]_0}{[HA]_0} = 4.5 \quad \frac{[A^-]}{(0.1M)} = 4.5 \quad \text{so } [A^-]_0 = 0.45M$$

DOUBLE-CHECK

$$pH = 3.35 + \log \frac{0.45}{0.1} = 4.00 \quad \checkmark$$

BUFFER EQN. BACKWARDS

$$pH = pK_a + \log \frac{A^-}{HA}$$

PHENOLPHTHALEIN  $pK_a = 9.40$

$HP_h$  = COLORLESS  
PROTONATED FORM

$Ph^-$  = PINK

UNPROTONATED FORM

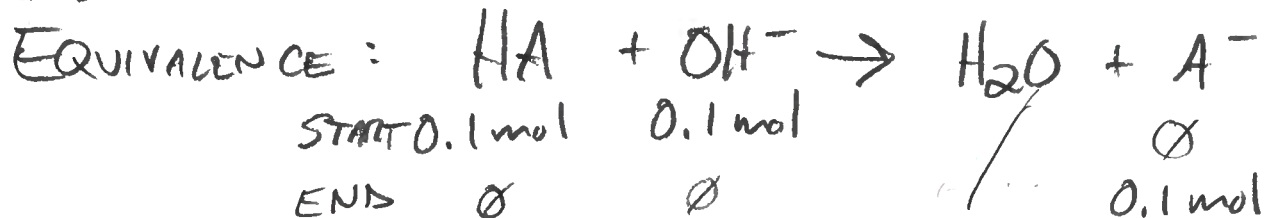
A) COLOR IS VISIBLE WHEN THAT FORM OUT NUMBERS  
THE OTHER BY A RATIO OF 10 TO 1.

$$pH = 9.40 + \log \frac{10}{1} = 10.40 \quad \text{ABOVE THIS } pH \text{ WE SEE PINK}$$

$$pH = 9.40 + \log \frac{1}{10} = 8.40 \quad \text{BELOW THIS } pH \text{ WE SEE CLEAR}$$

## 17.3 ACID-BASE TITRATIONS

TITRATION IS AN ANALYTICAL METHOD TO MEAS. THE CONC. OF A SOLN. BY MEASURING THE VOLUME OF A SOLN. WITH KNOWN CONC. NEEDED TO REACH STOICHIOMETRIC EQUIVALENCE WITH SOLN. BEING ANALYZED.



ENDPOINT: WHEN THE COLOR OF AN INDICATOR PERMANENTLY CHANGES

WE ARE GOING TO DISCUSS HOW TO UNDERSTAND WHAT METHOD IS APPROPRIATE FOR CALC. PH AT DIFFERENT STAGES DURING A TITRATION.

I. BEFORE ADDING ANYTHING!

STRONG ACID  $PH \Rightarrow [HX]_0$

BASE  $PH \Rightarrow [NaOH]_0$

WEAK ACID  $PH$  DEPENDS ON  $K_a$  OR  $K_b$   
BASE EQUIL. CALC. (CH. 16)

II. AFTER ADDING SOME TITRANT BUT BEFORE STOICH. EQUIVALENCE.

III. AT STOICH. EQUIV.

IV. EXCESS TITRANT

# I. BEFORE ADDING ANYTHING (TITRATION OF AN ACID WITH A STRONG BASE)

WEAK ACID

50.0 mL OF 0.10M HA

ACETIC ACID ( $\text{HCH}_3\text{COO}$ )  $K_a = 1.8 \times 10^{-5}$

TITRANT: 0.10M NaOH



$$i \quad 0.10 \quad \emptyset \quad \emptyset \quad \frac{x^2}{0.1} = 1.8 \times 10^{-5}$$

$$e \quad 0.10 - x \quad x \quad x$$

or  $\approx 0.10$

$$x = [\text{H}^+] = 1.3 \times 10^{-3} \text{M}$$

$$\text{pH} = 2.87$$

STRONG ACID

0.10M HCl SOLN

TITRANT 0.10M NaOH

$$[\text{HCl}]_0 = 0.10 \text{M}$$

so

$$[\text{H}^+]_{\text{eq}} = 0.10 \text{M}$$

$$\text{so pH} = 1.00$$

# II. BEFORE EQUIVALENCE

NaOH IS LR AND HA IS CONVERTED INTO  $\text{A}^-$   
AND  $\text{H}^+$  (FROM HCl) IS CONVERTED TO  $\text{H}_2\text{O}$

PREREQ: HOW MANY mL OF 0.10M NaOH ARE NEEDED TO REACH EQUIV?

$$50.0 \text{ mL} \cdot \left( \frac{1 \text{ L}}{1000 \text{ mL}} \right) \cdot \frac{0.10 \text{ mol HA}}{1 \text{ L}} \cdot \frac{1 \text{ NaOH}}{1 \text{ HA}} \cdot \frac{1 \text{ L}}{0.10 \text{ mol NaOH}} \cdot \left( \frac{1000 \text{ mL}}{1 \text{ L}} \right) =$$

SKIP

$$\left( \frac{\text{mol}}{\text{L}} = \frac{\text{mmol}}{\text{mL}} \right)$$

50.0 mL OF 0.10M NaOH  
WILL BE NEEDED TO REACH EQUIV.

EACH CALC. OF pH REQUIRES TWO STAGES:

① DO THE STOICH TO FIND OUT  $[\text{HA}]_0$  AND  $[\text{A}^-]_0$   
AS HA IS CONVERTED INTO  $\text{A}^-$ .

② CALC.  $[\text{H}^+]$  FOR THESE NEW INITIAL CONC.  
WHERE  $[\text{A}^-]_0 \neq \emptyset$  ( $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$  OR BUFFER EQN)

# WEAK ACID

LET'S SAY WE ADD 10.0ml OF

0.10 M NaOH  $10 \text{ mL} \left( \frac{1 \text{ L}}{1000 \text{ mL}} \right) \frac{0.1 \text{ mol}}{1 \text{ L}}$   
 $1.0 \times 10^{-3} \text{ mol}$

① DO STOICH. CALC.

mol HA =  $50.0 \text{ mL} \times \left( \frac{1 \text{ L}}{1000 \text{ mL}} \right) \frac{0.1 \text{ mol}}{1 \text{ L}}$   
 $0.005$  OR  $5.0 \times 10^{-3} \text{ mol HA}$   
 (OR 5 mmol)



S  $5 \times 10^{-3} \text{ mol}$   $1 \times 10^{-3} \text{ mol}$   $\emptyset$   
 $-1 \times 10^{-3}$   
 E  $4 \times 10^{-3} \text{ mol}$   $\emptyset$   $1 \times 10^{-3} \text{ mol}$

TOTAL VOL = 50 + 10 mL

② EQUIL. CALC.

$\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$   
 i  $\frac{4 \times 10^{-3} \text{ mol}}{0.060 \text{ L}}$   $\emptyset$   $\frac{1 \times 10^{-3} \text{ mol}}{0.060 \text{ L}}$

i  $6.7 \times 10^{-2} \text{ M}$   $\emptyset$   $1.7 \times 10^{-2} \text{ M}$

C  $-x$   $+x$   $+x$

E  $6.7 \times 10^{-2} - x$   $x$   $1.7 \times 10^{-2} + x$   
 $\approx 6.7 \times 10^{-2}$   $\approx 1.7 \times 10^{-2}$

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{(x)(1.7 \times 10^{-2})}{6.7 \times 10^{-2}}$$

$$x = 7.2 \times 10^{-5} \text{ M } [\text{H}^+]$$

$$\text{SO } \boxed{\text{pH} = 4.14}$$

SHORTCUT: BUFFER EQN.

$$\text{pH} = \text{p}K_a + \log \frac{\text{A}^-}{\text{HA}} \quad -\log 1.8 \times 10^{-5} = 4.74$$

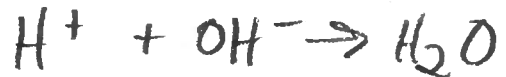
$$\text{pH} = 4.74 + \log \frac{0.017}{0.067} = 4.14$$

JUST mol NOT mol/L BC THE 60 mL CANCELS OUT ANYWAY

$$\text{pH} = 4.74 + \log \frac{1 \times 10^{-3}}{4 \times 10^{-3}} = 4.14$$

# STRONG ACID

① STOICH.



S  $5 \times 10^{-3} \text{ mol}$   $1 \times 10^{-3} \text{ mol}$

E  $4 \times 10^{-3} \text{ mol}$   $\emptyset$

$$\frac{4 \times 10^{-3} \text{ mol}}{0.060 \text{ L}} = 0.067 \text{ M} = [\text{H}^+]$$

$$\boxed{\text{pH} = 1.18}$$

STOPPED HERE GROUP X

F2026+03-27

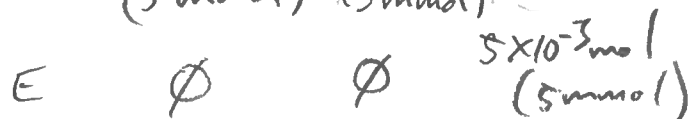
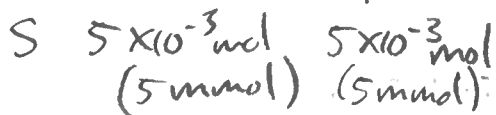
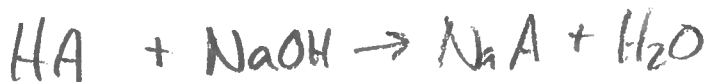
YOU CAN ONLY USE THE BUFFER EQN. WHILE IT IS A BUFFER! AT EQUIVALENCE ALL HA IS CONVERTED TO A<sup>-</sup> SO IT IS NO LONGER A BUFFER

### III. THE pH AT EQUIVALENCE

EQUIVALENCE IS WHEN THERE IS NO LIMITING REACTANT ANYMORE - YOU'VE ADDED THE SAME NO. OF MOLES OF NaOH AS MOLES OF HA THAT YOU HAD AT THE START.

#### WEAK ACID

① STOICH CALC.



( TO DO THIS WE ADDED 50 mL OF 0.1 M NaOH TO 50 mL OF 0.1 M HA - TOTAL VOL. 100 mL

$$\frac{5 \times 10^{-3} \text{ mol } A^-}{0.100 \text{ L}} = 5 \times 10^{-2} \text{ M} = [A^-] = 0.050$$

②  $[HA]_0$  IS NOW ZERO!

SO THIS IS A SOLN OF A WEAK BASE!

SO TO CALC pH AT EQUIVALENCE YOU DO THIS



$$0.05 - x \approx 0.05$$

$$\frac{x}{0.05} = \frac{K_w}{K_a} = K_b = 5.6 \times 10^{-10}$$

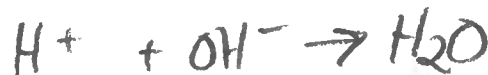
$$x = [OH^-]_{eq} = 5.3 \times 10^{-6} \text{ pH} = 5.28$$

THE pH AT EQUIVALENCE IN THE TITR. OF A WEAK ACID BY A STRONG BASE IS  $> 7.00$ .

#### STRONG ACID

THE pH AT EQUIV IN THE TITR. OF A STRONG ACID BY A STRONG BASE IS 7.00.

① STOICH



NO HCl IS LEFT

NO EXCESS NaOH HAS BEEN ADDED SO pH DEPENDS ON  $K_w$

$$K_w = [H^+][OH^-]$$

$$[H^+] = 1.0 \times 10^{-7}$$

$$\text{pH} = 7.00$$

so  $\boxed{\text{pH} = 8.72}$



BECAUSE INDICATORS CHANGE COLOR OVER THE RANGE  $\left(\frac{A^-}{HA} = \frac{1}{10}\right)$  TO  $\left(\frac{A^-}{HA} = \frac{10}{1}\right)$  THE

pH RANGE FOR THIS COLOR CHANGE IS

THE  $pK_a$  OF THE INDICATOR PLUS OR MINUS ONE.

REMEMBER, AN EXTERNALLY DETERMINED pH WILL DICTATE THE  $\frac{A^-}{HA}$  RATIO IN THE BUFFER EQN:  $pH = pK_a + \log \frac{A^-}{HA}$

$$pH = pK_a + 1 \quad \text{WHEN} \quad \frac{A^-}{HA} = \frac{10}{1} \quad (\log 10^1 = 1)$$

$$pH = pK_a - 1 \quad \text{WHEN} \quad \frac{A^-}{HA} = \frac{1}{10} \quad (\log 10^{-1} = -1)$$

FOR EXAMPLE: PHENOLPHTHALEIN  $pK_a = 9.40$

INTENSE PINK AT  $pH \geq 10.40$

COLORLESS AT  $pH \leq 8.40$

COLOR CHANGE RANGE: 8.4 - 10.4 (LIGHT PINK)

BROMOTHYMOLO BLUE  $pK_a = 7.10$

BLUE AT  $pH \geq 8.10$

YELLOW AT  $pH \leq 6.10$

$pH$  6.10 - 8.10 (GREEN)

METHYL RED  $pK_a = 4.95$

YELLOW AT  $pH \geq 5.95$

RED AT  $pH \leq 3.95$

$pH$  3.95 - 5.95 (ORANGE)

TO CHOOSE AN INDICATOR FOR A TITRATION, CHOOSE ONE WITH A  $pK_a$  WITHIN 1 pH UNIT OF THE CALCULATED pH AT THE EQUIVALENCE POINT.

STRONG ACID TITRATION  $pH = 7$  SO CHOOSE BROMOTHYMOLO BLUE

WEAK ACID  $pH > 7$  AT EQUIVALENCE SO (POSSIBLY) PHENOLPHTHALEIN

WEAK BASE  $pH < 7$  AT EQUIV. SO (POSSIBLY) METHYL RED

# How to MAKE A BUFFER

- ① CHOOSE A pH
- ② CHOOSE AN ACID/BASE PAIR WITH A  $pK_a$  NEAR THE TARGET pH ( $\pm 1$  UNIT PERHAPS)
- ③ CALC THE NECESSARY  $[A^-]/[HA]$  RATIO:  $pH = pK_a + \log \frac{A^-}{HA}$
- ④ BASED ON AVAIL. MATERIALS, EITHER:
  - a. USE TOTAL VOL. TO DECIDE HOW MANY MOL OF HA AND MOL OF  $A^-$  TO ADD, DISSOLVE, THEN DILUTE TO FINAL VOL.
  - b. USE TOTAL VOL. TO DECIDE MOL HA, INCL. THE AMOUNT YOU'LL NEED TO MAKE  $A^-$  BY ADDING NaOH TO CONVERT HA INTO  $A^-$ , THEN ADD NaOH, AND DILUTE TO FINAL VOL.

## BUFFER CAPACITY

TWO THINGS AFFECT A BUFFER'S RESISTANCE TO CHANGES IN pH: CONCENTRATION AND A BALANCED  $\frac{A^-}{HA}$  RATIO.

THE HIGHER THE CONC., THE MORE HA IS AVAIL TO REACT WITH  $OH^-$  OR  $A^-$  TO REACT WITH  $H^+$  AND SO A HIGHER CONC. HAS A HIGHER BUFFER CAPACITY.

THE CLOSER THE  $\frac{A^-}{HA}$  RATIO IS TO ONE, THE BETTER.

BUFFERS WORK BY CONVERTING ADDED  $OH^-$  TO  $A^-$  AND ADDED  $H^+$  TO HA. IF THE CONC. OF HA OR  $A^-$  IS TOO LOW, THERE WON'T BE ENOUGH TO TURN STRONG BASE (OR ACID) INTO WEAK.

SO  $\frac{1}{1}$  OR  $\frac{1}{10}$  OR  $\frac{10}{1}$  (WITHIN  $pK_a \pm 1$ ) IS BEST.

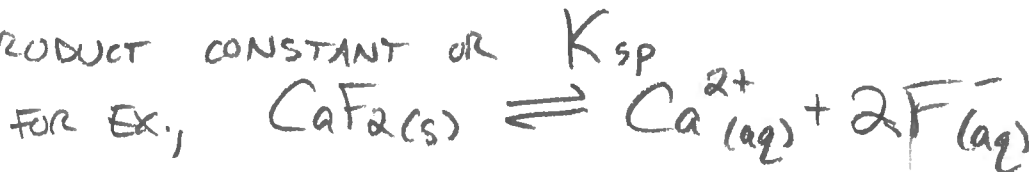
# 17.4 SOLUBILITY EQUILIBRIA

A SATURATED SOLUTION IS ONE WITH THE MAXIMUM POSSIBLE CONCENTRATION - SOLID IN CONTACT WITH THE SOLUTION REMAINS IN DYNAMIC EQUILIBRIUM BUT THE MASS OF SOLID IS CONSTANT OVER TIME.

SOLUBILITY IS A MEAS. OF CONC. FOR A SAT. SOLN.

UNITS  $\frac{\text{mol}}{\text{L}}$  OR  $\frac{\text{g}}{\text{L}}$  OR MASS%  $\frac{\text{g (SOLUTE)}}{\text{TOTAL g (SOLUTE + SOLVENT)}}$

A SOLUBILITY EQUILIBRIUM IS GOVERNED BY A SOLUBILITY PRODUCT CONSTANT OR  $K_{sp}$



$$K_{sp} = [\text{Ca}^{2+}][\text{F}^{-}]^2$$

NOTE:  $[\text{F}^{-}]^2$   
ALSO: NO SOLIDS IN  $K_{eq}$  EXPRESSIONS!

IT'S A PRODUCT IN THE SENSE OF AN ANSWER TO A MULTIPLICATION PROBLEM.

USE THE SOLUBILITY PRODUCT TO CALC. CONC. OF A SOLN THAT IS SATURATED.



i	$\emptyset$	$\emptyset$
c	+x	+x
e	x	x

$$K_{sp} = 1.1 \times 10^{-10}$$

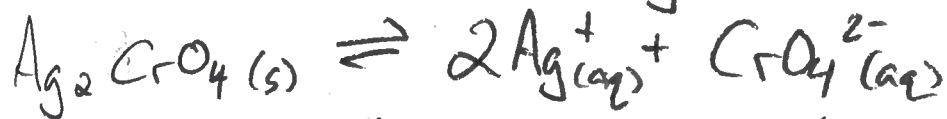
so  $(x)(x) = 1.1 \times 10^{-10}$

$$x = [\text{Ba}^{2+}] = [\text{SO}_4^{2-}]$$

$$x = 1.0 \times 10^{-5} \text{ M}$$

NOTE: SOLUBILITY IS NOT THE SAME AS  $K_{sp}$ !

EX. 2 CALC.  $K_{sp}$  GIVEN  $[Ag^+] = 1.3 \times 10^{-4} M$  IN  
A SAT. SOLN OF  $Ag_2CrO_4$ .



i	$\emptyset$	$\emptyset$
c	$+2x$	$+x$
e	$2x$	$x$

$$K_{sp} = [Ag^+]^2 [CrO_4^{2-}] = (2x)^2(x) = 4x^3$$

$$[Ag^+] = 2x = 1.3 \times 10^{-4} M \quad \text{so } x = 6.5 \times 10^{-5} M$$

$$K_{sp} = 4(6.5 \times 10^{-5})^3 = \boxed{1.1 \times 10^{-12}}$$

## 17.5 FACTORS THAT AFFECT SOLUBILITY

PREV. EX. LOOK AT SOLUBILITY IN PURE WATER.

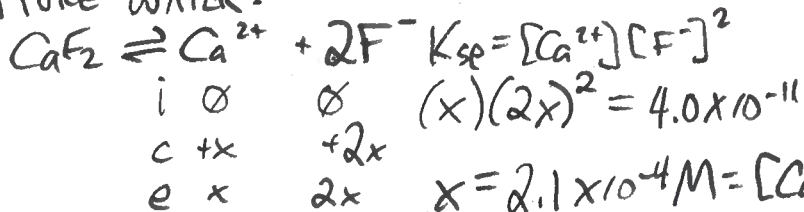
LET'S CHANGE THINGS UP BY

1. INTRODUCING COMMON IONS  
(FOR EX., ADD SOLUBLE NaF TO A  $CaF_2$  SOLN)
2. CHANGING THE pH  
(WHICH AFFECTS ANIONS WHICH ARE WEAK BASES)
3. CONSIDERING THE FORMATION OF COMPLEX IONS

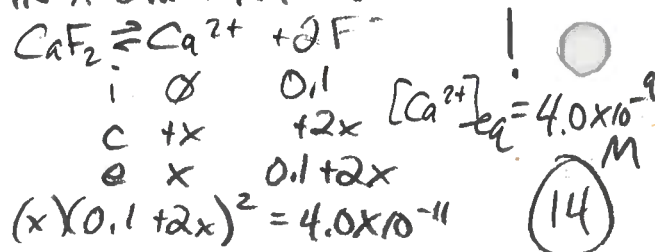
### COMMON IONS REDUCE SOLUBILITY

CONSIDER: IF YOU ADD SOLUBLE NaF TO A SAT. SOLN. OF  $CaF_2$   
THEN  $CaF_2$  WILL PRECIPITATE/CRYSTALLIZE. YOU PUSH  
THE SOLUBILITY EQUIL. TO THE LEFT.

IN PURE WATER:



IN A 0.1M NaF SOLN:



CHANGING THE pH MAY INCREASE OR DECREASE SOLUBILITY

For  $\text{OH}^-$  compounds a DECR. IN pH WILL MEAN INCREASED SOLUBILITY (ADD  $\text{H}^+$  AND IT REACTS WITH  $\text{OH}^-$ ).

For ex., THE SOLUBILITY OF  $\text{Mg}(\text{OH})_2$  IS INCR. WHEN ACID IS APPLIED B/C  $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$  GOES TO COMPLETION:  $\text{Mg}(\text{OH})_2 + 2\text{H}^+ \rightarrow \text{Mg}^{2+} + 2\text{H}_2\text{O}$  SO  $[\text{Mg}^{2+}]$  WILL JUST DEPEND ON THE ADDED ACID AND NOT ON ITS SOLUBILITY EQUILIBRIUM.

FOR COMPOUNDS IN WHICH THE ANION IS A WEAK BASE:



SOLUBILITY INCREASES AS  $\text{H}^+$  IS ADDED. THIS IS B/C STRONG ACID REACTS WITH WEAK BASE TO COMPLETION, FORMING THE WEAK ACID (WHICH REMOVES THE ANION FROM SOLUTION BY DECR. ITS CONC).



DO STOICH. CALC. BEFORE CONSIDERING WHETHER TO DO A  $K_{\text{SP}}$  CALC.

READ THE BOX ON pg 755 RE: TOOTH DECAY AND  $\text{F}^-$  IONS

( $\text{F}^-$  REPLACES  $\text{OH}^-$  IN TOOTH ENAMEL, WHICH MAKES IT LESS SOLUBLE IN ACID)

COMPLEX ION FORMATION INCREASES SOLUBILITY

METAL IONS CAN FORM VERY STRONG, SO-CALLED COORDINATE (NOT COVALENT) BONDS WITH MOLECULES OR IONS. THESE BONDS FORM WHEN A MOLECULE OR ION "DONATES" AN ELECTRON PAIR.

REMEMBER PRUSSIAN BLUE FROM THE PAINT LAB?

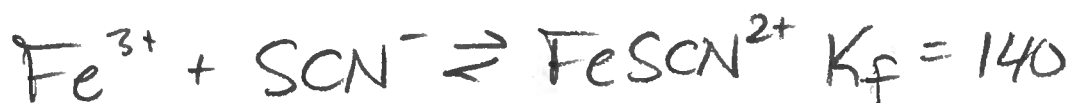
IT USED THE COMPLEX ION, HEXACYANOFERRATE(II)

$(Fe(CN)_6^{4-})$ . THIS ION FORMS WITH A

VERY LARGE COMPLEX-ION FORMATION CONSTANT ( $K_f$ ):



YOUR EQUILIBRIUM LAB MEASURED THE FORMATION CONSTANT OF  $FeSCN^{2+}$ :



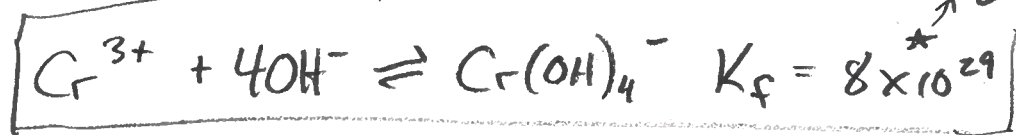
WHEN MAKING MIRRORS BY DEPOSITING SILVER ON GLASS, THE RATE OF REACTION FOR THE REDUCTION OF SILVER ( $Ag^+ + e^- \rightarrow Ag$ ) IS CONTROLLED BY MAKING A SOLUBLE COMPLEX DESPITE HIGH-PH CONDITIONS:



### 17.15 pg 758 PRACTICE EXERCISE 2

WHAT IS CONC. OF UNCOMPLEXED  $Cr^{3+}$  IN EQUIL. WITH  $Cr(OH)_4^-$  IN A SOLUTION WITH  $[Cr^{3+}]_0 = 0.010M$  WHICH IS BUFFERED AT  $pH = 10.0$ ?

SINCE  $pH = 10.0$ ,  $pOH = 4.0$  AND  $[OH^-]_{eq} = 1.0 \times 10^{-4}M$



TURN THIS AROUND:  $Cr(OH)_4^- \rightleftharpoons Cr^{3+} + 4OH^- \quad K = \frac{1}{K_f} = (8 \times 10^{29})^{-1}$

i	0.010M	$\emptyset$	$1 \times 10^{-4}M$
c	-x	+x	(+x) NOT VALID: BUFFER
e	0.01-x	x	$1 \times 10^{-4}$

$$\frac{[Cr^{3+}][OH^-]^4}{[Cr(OH)_4^-]} = (8 \times 10^{29})^{-1} = \frac{x(1 \times 10^{-4})^4}{(0.01)}$$

ASSUME  $0.01 - x \approx 0.01$

$$x = 1.25 \times 10^{-16} M = [Cr^{3+}]_{eq} \quad (16)$$

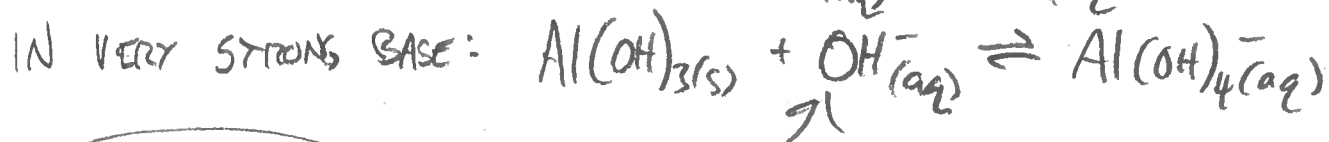
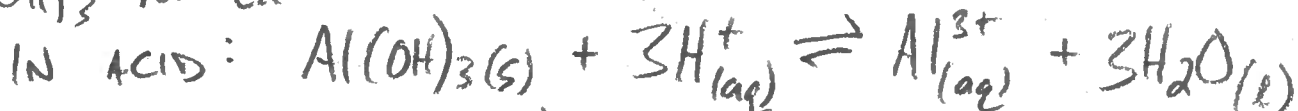
AMPHOTERISM

Oxides and hydroxides are basic and so naturally have increased solubility in acidic solution.

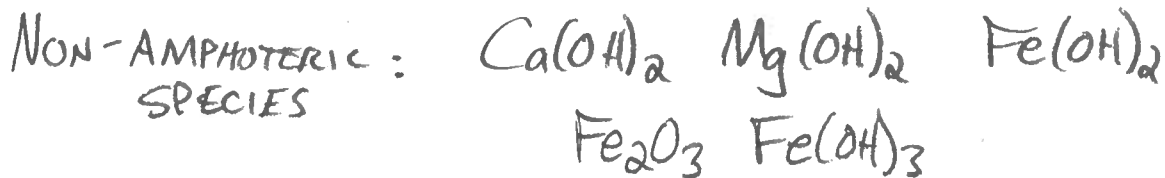
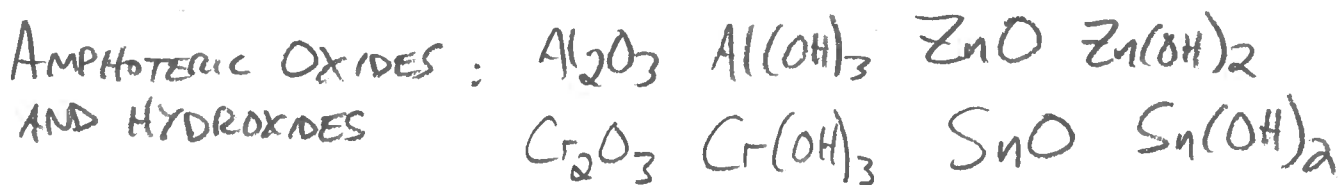
Counterintuitively, some also have increased solubility in basic solution, provided it is strongly basic, indeed.

This phenomenon, which is simply the formation of soluble hydroxide-complex ions, occurs when  $[\text{OH}^-]$  is well above the pH scale:  $[\text{OH}^-] > 1.0\text{M}$ .

$\text{Al}(\text{OH})_3$  for ex:



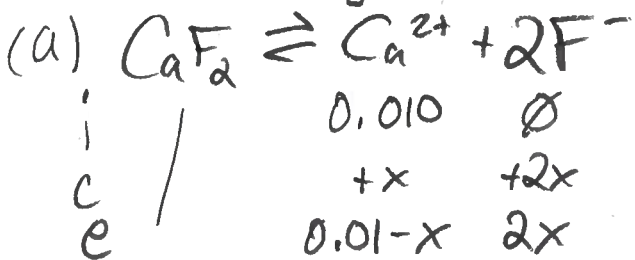
IT'S A 1:1 RATIO BUT  $[\text{OH}^-]$  MUST BE LARGE TO DRIVE THIS EQUIL. TO THE RIGHT.



SOME CALCULATIONS EXAMPLES FOR SOLUBILITY EQUILIBRIA  
SAMP. EX. 17.13 pg 752

$\text{CaF}_2$  HAS A SOLUBILITY OF  $2.1 \times 10^{-4} \text{ M}$  IN PURE WATER.

$\text{Ca}^{2+}$  IS SOLUBLE IN COMPOUNDS LIKE  $\text{CaCl}_2$  OR  $\text{Ca}(\text{NO}_3)_2$ . SO HOW DOES  $[\text{CaF}_2]_{\text{eq}}$  CHANGE IN A SOLUTION WITH AN INITIAL  $[\text{Ca}^{2+}] > 0$ ?



$$K_{\text{sp}} = 3.9 \times 10^{-11} = [\text{Ca}^{2+}][\text{F}^-]^2$$

ASSUME  $0.01 - x \approx 0.01$

$$3.9 \times 10^{-11} = (0.01)(2x)^2$$

$$= (0.01) \cdot 4x^2$$

$$x = \frac{\sqrt{(3.9 \times 10^{-11})}}{\sqrt{(0.01)(4)}} = 3.1 \times 10^{-5} \text{ M}$$

$$[\text{F}^-]_{\text{eq}} = 2(3.1 \times 10^{-5})$$

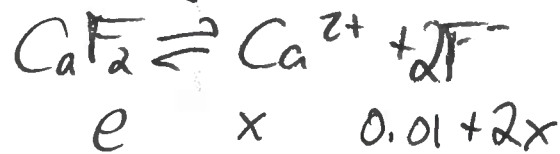
$$= 6.2 \times 10^{-5} \text{ M}$$

... WHICH IS LESS THAN  $2(2.1 \times 10^{-4}) =$

$4.2 \times 10^{-4} \text{ M}$  AS IT WOULD BE IN PURE WATER

$\text{NaF}$  IS A SOLUBLE COMPOUND. HOW DOES AN INITIAL  $\text{F}^-$  CONC. AFFECT SOLUBILITY OF  $\text{CaF}_2$ ?

LET  $[\text{F}^-]_0 = 0.010 \text{ M}$



$$3.9 \times 10^{-11} = (x)(0.01)^2$$

(B/C WE ASSUME  $0.01 + 2x \approx 0.01$ )

$$x = 3.9 \times 10^{-7} \text{ M}$$

AND  $[\text{Ca}^{2+}] = 3.9 \times 10^{-7} \text{ M}$ ,

WHICH IS MUCH LESS THAN  $2.1 \times 10^{-4} \text{ M}$  AS IT WOULD BE IN PURE WATER.

(NOTE:  $\text{F}^-$  LOWERS SOLUBILITY MORE B/C OF ITS COEFFICIENT OF 2 IN THE EQUILIBRIUM).