Ch. 17 Additional Aqueous Equilibria

- "we've considered solutions where one thing (acid, base, or salt) is put in water"
- real solutions often have >1 solute
  - ⇒ more complex equilibria, pH calcs.
  - ⇒ extra solute impacts degree to which first chemical dissociates

3 cases

① buffers: weak acid + weak base

② titrations: mixing acid + base

③ partially soluble solids: impact of pH or other salts

17.1 Buffer Solutions: resist change in pH when either acid or base added

- crucial in nature: blood pH, lake pH, must be tightly controlled, ~~lake pH~~ for people, animals, & fish to survive

1 L pure water pH = 7

add 0.1 mol NaOH → pOH = 1, pH = 13

add 0.1 mol HCl → $[H^+] = 0.1$ pH = 1

blood ~7.40 ± .05

<7.35 acidosis

>7.45 alkalosis

Unbuffered, unacceptable!!

Need buffer to stabilize pH

A. Buffer Action: a buffer must contain both
a weak acid (to neutralize $^{\ominus}OH$) and
a weak base (to " $H^{\oplus}$)

- normally conjugates
- normally ~ equal quantities

☆ Fact: a weak acid react completely with strong ba
" base " " aci

For an $HA/A^{\ominus}$ weak acid/base buffer:

① Reaction with strong acid

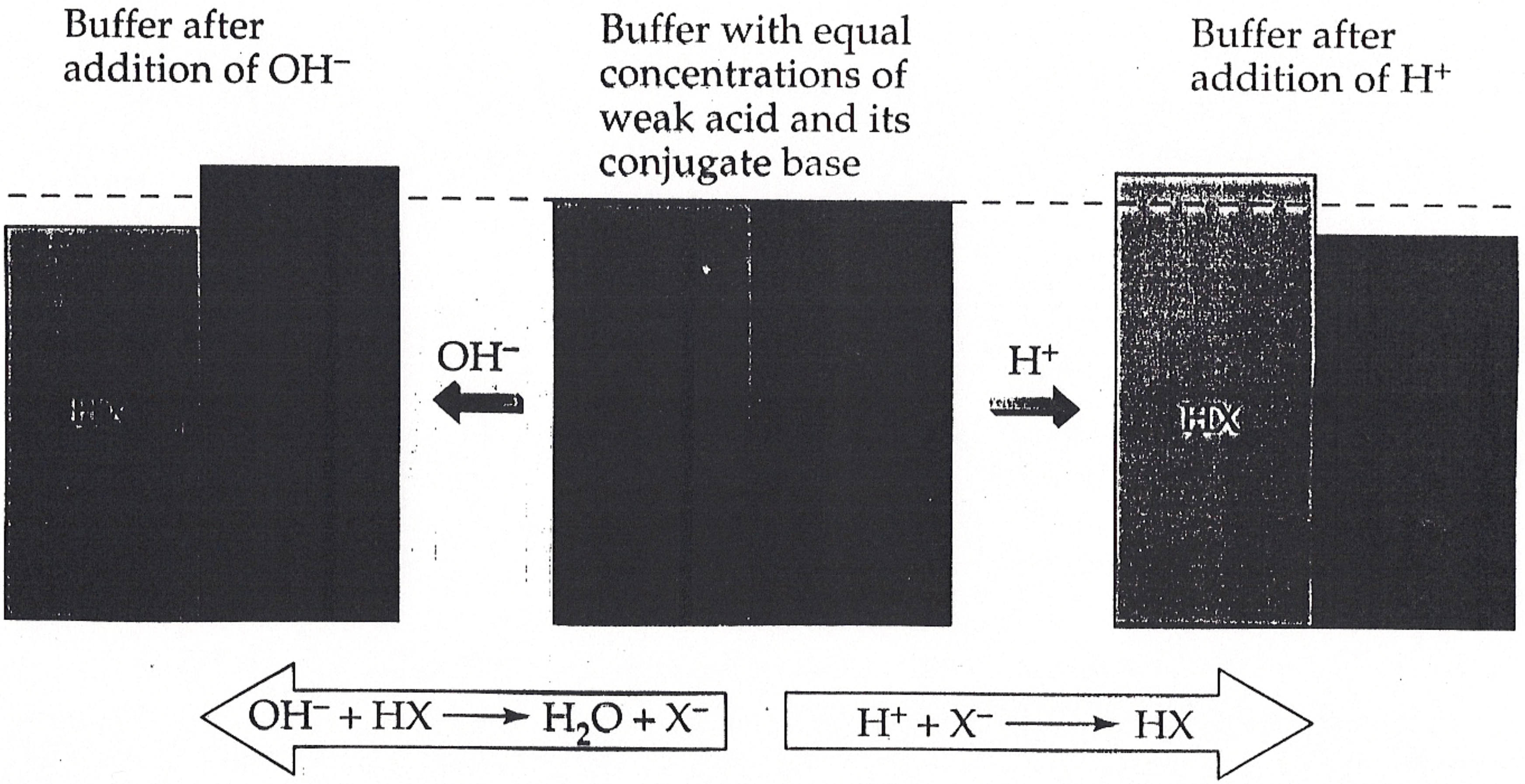
$$HCl + A^{\ominus} \longrightarrow HA + Cl^{\ominus}$$

② " " base

$$^{\ominus}OH + HA \longrightarrow A^{\ominus}$$

When weak reacts with strong, conjugate
is produced: strong acid → weak acid
strong base → weak base

Fig. 17.2 Buffer Action



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1. Unbuffered: Find pH

a. 1.0 L pure water $[H^+] = 10^{-7}$ $\boxed{pH = 7.0}$

b. 1.0 L water + 0.1 mol HCl $[H^+] = 0.1$ $\boxed{pH = 1.0}$

c. 1.0 L water + 0.1 mol NaOH $[OH^-] = 0.1$ $pOH = 1.0$ $\boxed{pH = 13.0}$

$\boxed{\text{0.1 mol HCl or NaOH makes big difference!}}$

2. Buffer: 1.0 L water with 0.5 mol HF ($K_a = 6.8 \times 10^{-4}$) and 0.5 mol NaF.

$\downarrow$

$pK_a = 3.1$

a. No extra acid or base added:

$$pH = pK_a + \log\left(\frac{base}{acid}\right)$$
$$= 3.17 + \log\left(\frac{.5}{.5}\right)$$
$$\boxed{pH = 3.17}$$

b. Add 0.1 mol HCl

Reaction: $HCl + NaF \rightleftharpoons HF + NaCl$

I	.1	$\overset{.05}{.5}$	.5
C	-.1	-.1	+.1
E	~	.4	.6

$pH = 3.17 + \log\left(\frac{.4}{.6}\right) = \boxed{2.99}$

c. Add 0.1 mol NaOH

Reaction: $NaOH + HF \rightarrow H_2O + NaF$

I	.1	$\overset{.05}{.5}$	.5
C	-.1	-.1	+.1
E	—	.4	.6

$pH = 3.17 + \log($

$\boxed{pH = 3.35}$

B. The pH of Buffer Solutions: K_a, pK_a, H^+, pH

1. Formula

$$\underset{\text{weak acid}}{HA} \rightleftharpoons H^+ + \underset{\text{weak base}}{A^-} \qquad K_a = \frac{[H^+][A^-]}{[HA]}$$

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

math

$$\boxed{pH = pK_a + \log \frac{[\text{base}]}{[\text{acid}]}}$$ Henderson-Hasselbalch Equation

$$\boxed{pK_a = -\log K_a}$$

2. Dual

a. buffer pH depends on ① K_a/pK_a (acid streng

② base/acid ratio

"choose the acid to fit desired pH"

b. if ratio = 1, ⇒ $\boxed{pH = pK_a}$ ratio same whether $\frac{\text{mol}}{\text{mol}}$ or $\frac{M}{M}$

c. Adding H^+ ⇒ reduces ratio ⇒ lower pH

OH^- ⇒ increases ⇒ raises pH

C. Buffer Capacity: determined by the quantity of weak acid/base
- dictates how much strong acid/base is consumed before buffer exhausted
- if more strong acid (base) is added than there is weak base (acid), the capacity is exceeded.

D. Creating/Recognizing a buffer
- must end with weak $\boxed{\text{acid}}/\boxed{\text{base}}$ pair

1. Combine directly

2. Start with one of conj. pair, and add strong acid or strong base to create other

Begin	Add (~½ as much)	Result
Weak acid	Strong base	= weak acid + conj base
weak base	Strong acid	→ " "

Ex: $HF + NaOH \longrightarrow H_2O + NaF$

	HF	$NaOH$	NaF
I	0.4 moles	0.20 moles	0
C	−.2	−.2	+.2
E	.2 mol	−	.2 mol

Ex: $NH_3 + HCl \longrightarrow NH_4^{\oplus}Cl^{\ominus}$

	NH_3	HCl	$NH_4^{\oplus}Cl^{\ominus}$
I	0.6 mol	0.3 mol	0
C	−.3	−.3	+.3
E	.3 mol	−	.3 mol

Note: doesn't work if you add too much strong acid/base (ex ≥ .6 mc HCl

17-6

① which combos would make a buffer soln?

[✓ a.] HF, $KF^{\ominus}$
WA WB

[✓ b.] $\overset{\oplus}{NH_4}Cl$, NH_3
WA WB

[✓ c.] HCl, (0.2 M),
NaN_3 (0.4 M)

↓

$0.2\ HN_3 + 0.2\ N_3^{\ominus}$

~~d.~~ HCl (0.2 mol)
NaN_3 (0.1 mol)

↓

$0.1\ HN_3$ WA
+
$0.1\ HCl$ SA

e. HN_3, $NaCl$

f. KF, NaF

g. KF, $NaOH$

h. HF, HCl

i. NH_3, KF

g. HF (0.2 mol)
$NaOH$ (0.1 mol)

② which could be added to 0.4 mol $NaCN$ to give a buffer?

a. HCN b. 0.2 mol HCl c. 0.2 mol $NaOH$

③ which could be added to 0.4 mol H_3PO_4 to give a buffer?

a. NaH_2PO_4 b. 0.2 mol $NaOH$

c. 0.4 mol $NaOH$ d. 0.2 mol HCl e. KCl

17-6

① Which combos would make a buffer soln?

[✓ a.] HF, KF

[✓ b.] NH_4Cl, NH_3

[✓ c.] HCl (0.2 M), NaN_3 (0.4 M)

↓

0.2 HN_3
0.2 NaN_3

~~d.~~ HCl (0.2 mol) NaN_3 (0.1 mol)

↓

0.1 HN_3
0.1 HCl

~~e.~~ HN_3, $NaCl$
no base

~~f.~~ KF, NaF
no acid

~~g.~~ KF, $NaOH$
no acid

~~h.~~ HF, HCl
no base

~~i.~~ NH_3, KF
no acid

[✓ g.] HF (0.2 mol) $NaOH$ (0.1 mol)

↓

0.1 NaF
0.1 HF

② Which could be added to 0.4 mol $NaCN$ to give a buffer?

[✓ a.] HCN [✓ b.] 0.2 mol HCl c. 0.2 mol $NaOH$

③ Which could be added to 0.4 mol H_3PO_4 to give a buffer?

[✓ a.] NaH_2PO_4 [✓ b.] 0.2 mol $NaOH$

c. 0.4 mol $NaOH$ d. 0.2 mol HCl e. KCl

E. Simple Buffer Calcs
- a. find pH
- b. find Ka
- c. solve for quantity of acid or base needed for target pH

F. pH Changes after Acid or Base is Added to a Buffer

① Write acid/base eqn by which strong would react with weak
② fill in ICE (use moles)
③ Assess situation (buffer? some strong acid/base left? complete conversion to weak?)
④ if buffer at end, use HH (using moles)
⑤ if not, calculate ala Ch. 16 (using molarity)

Finding pH after Strong Acid or base is Added to buffer

① Write Acid/Base Reaction of Strong with weak

② Fill out ICE (using moles)

③ Assess whats left

- a. weak acid + weak base ⇒ Use HH
- b. only weak acid or weak base ⇒ see Ch.16
- c. strong acid + weak acid ⇒ use strong acid only

buffer capacity exceeded

④ Assuming buffer capacity was <u>not</u> exceeded, use "E" values and Henderson-Hasselbalch

General: finding pH after Acid or base is added, whether to a buffer, a strong acid, a weak acid, a strong base, or a weak base

① Write acid-base reaction
- helps to recognize strong/weak/acid/base/neutral

② Calculate Initial Moles

#moles = molarity × volume (in Liters)

③ Use ICE to Determine Final Moles.

④ Assess situation

⑤ Solve pH from there
- sometimes convert back to molarity
- Key is Recognizing Final Situation!!

17-8

1. Find pH for buffer 0.12 M HNO_2, 0.16 M $NaNO_2$.

$K_a(HNO_2) = 4.5 \times 10^{-4}$

2. ~~An acid~~ HA [HA] = 0.11 M [NaA] = 0.13 M

What is K_a for HA if pH = 5.18?

3. How much NaF (42g/mol) should be added to 612 mL solution of 0.4 M HF ($K_a = 6.8 \times 10^{-4}$) to produce a pH = 3.10 buffer?

(17-8)

1. Find pH for buffer 0.12 M HNO_2, 0.16 M $NaNO_2$.

$K_a(HNO_2) = 4.5\times10^{-4}$ $pK_a = 3.35$

HH: $pH = pK_a + \log\left(\frac{base}{acid}\right)$

$$pH = 3.35 + \log\left(\frac{.16}{.12}\right) = 3.35 + 0.12 = \boxed{3.47}$$

2. ~~An acid~~ HA $[HA] = 0.11\ M$ $[NaA] = 0.13\ M$

What is K_a for HA if $pH = 5.18$?

HH: $5.18 = pK_a + \log\left(\frac{.13}{.11}\right)$ or $\underset{.11}{HA} \rightleftharpoons H^+ + \underset{.13}{A^-}$ $[H^+] = 6.61\times10^{-6}$

$5.18 = pK_a + 0.07$

$pK_a = 5.11$

$K_a = 10^{-5.11} = \boxed{7.81\times10^{-6}}$

$$K_a = \frac{(6.61\times10^{-6})(.13)}{.11} = \boxed{7.81\times10^{-6}}$$

3. How much NaF (42g/mol) should be added to 612 mL solution of 0.4 M HF ($K_a = 6.8\times10^{-4}$) to produce a $pH = 3.10$ buffer? $pK_a = 3.17$

Logic: ① Use HH to find needed (base/acid) ratio
② Calculate moles acid
③ Find moles base
④ Convert to grams base

$$mol\ HF = \frac{0.612L \mid 0.4\ mol}{\mid L} = 0.245\ mol$$

$3.10 = 3.17 + \log\left(\frac{base}{acid}\right)$

$-0.07 = \log\left(F^-/HF\right)$

$$\frac{F^-}{HF} = 10^{-0.07} = 0.851 = \frac{x\ mol\ NaF}{0.245\ mol\ HF}$$

$$x\ g\ NaF = \frac{0.209\ mol\ NaF \mid 42g}{\mid 1\ mol} = \boxed{8.76\ g\ NaF}$$

(17-9)

① Given a 1.0L solution that i's initially 0.2 M in both HF and KF assess the situation and find the pH after the following acids or bases are added.

K_a(HF) $= 6.8 \times 10^{-4}$

$pK_a = 3.17$

a. 0.1 mol HCl added

Assess:

Reaction:

I
C
E

b. 0.2 mol HCl added

Assess:

Reaction:

I
C
E

c. 0.3 mol HCl added

Assess:

Reaction:

I
C
E

d. 0.1 mol NaOH added

Assess:

Reaction:

I
C
E

e. 0.2 mol NaOH added

Assess:

Reaction:

I
C
E

17-9

① Given a 1.0L solution that is initially 0.2 M in both HF and KF assess the situation and find the pH after the following acids or bases are added.

$K_a(HF) = 6.8\times10^{-4}$

$pK_a = 3.17$

a. 0.1 mol HCl added

Reaction: $HCl + KF \rightarrow HF + KCl$

	HCl	KF	HF	KCl
I	.1	.2	.2	
C	-.1	-.1	+.1	
E	-	+.1	+.3	

Assess: WA/WB ⇒ buffer

$pH = 3.17 + \log(.1/.3) = \boxed{2.69}$

b. 0.2 mol HCl added

Reaction: $HCl + KF \rightarrow HF + KCl$

	HCl	KF	HF	KCl
I	.2	.2	.2	
C	-.2	-.2	+.2	
E			.4	

Assess: Weak Acid

$[H^+] = \sqrt{(.4)(6.8\times10^{-4})}$

$= 0.016$

$\boxed{pH = 1.78}$

c. 0.3 mol HCl added

Reaction: $HCl + KF \rightarrow HF + KCl$

	HCl	KF	HF	KCl
I	.3	.2	.2	
C	-.2	-.2	+.2	
E	.1		.4	

Assess: WA + Strong Acid

Strong acid dominates pH

$[H^+] = 0.1$ $\boxed{pH = 1.0}$

d. 0.1 mol NaOH added

Reaction: $NaOH + HF \rightarrow H_2O + NaF$

	NaOH	HF	H_2O	NaF
I	.1	.2		.2
C	-.1	-.1		+.1
E		.1		.3

Assess: WA/WB $\boxed{\text{Buffer}}$

$pH = 3.17 + \log\left(\frac{.3}{.1}\right)$

$\boxed{= 3.65}$

e. 0.2 mol NaOH added

Reaction: $NaOH + HF \rightarrow H_2O + NaF$

	NaOH	HF	H_2O	NaF
I	.2	.2		.2
C	-.2	-.2		+.2
–	–	–	–	.4

Assess: $\boxed{\text{Weak Base}}$

$K_b = 1.47\times10^{-11}$ $[OH^-] = 2.43\times10$

$pOH = 5.62$ $\boxed{pH = 8.35}$

17.2 Acid-Base Titrations

- acid + base mixed, at least one being strong
- "equivalence point" or "end point": equal moles of acid/base
- indicator often used to turn color, a pH meter used to give "titration curve"
- unlike buffer, pH changes fast near endpoint

A. General: finding pH after Acids or bases Added
- handout

B. Endpoint Situations:

		End	pH
SA/SB	$HCl + NaOH \rightarrow H_2O + NaCl$	neutral	$pH = 7$
WA/SB	$HF + NaOH \rightarrow H_2O + \underset{\text{basic}}{NaF}$	basic	$pH > 7$

For quantitative pH:

$$K_a \rightarrow \underbrace{\underset{\text{for } F^{\ominus}}{K_b}} \rightarrow [OH^-] \rightarrow pOH \rightarrow pH$$

would need $[OH^-] = \sqrt{K_b \cdot [F^{\ominus}]}$ ← needs to be correct, combined volumes

SA/WB	$HCl + NaCN \rightarrow \underset{\text{acid}}{HCN} + NaCl$		$pH < 7$

For exact pH, $K_a \rightarrow [H^+] \rightarrow pH$

$[H^+] = \sqrt{K_a [HCN]}$ ← combined volume

17-7b

Final Situation + pH Solution

1. Strong Acid only	$[H^+] = [SA]$	
2. Strong Acid plus weak Acid	$[H^+] = [SA]$	ignore WA, which makes insignificant contribution
3. Strong base only	$[OH^-] = [SB]$	
4. Strong base plus weak base	$[OH^-] = [SB]$	ignore WB, which makes insignificant contribution
5. Weak Acid only - qual: pH < 7	$[H^+] = \sqrt{K_a \cdot [WA]}$	
6. Weak Base only - qual: pH > 7	$[OH^-] = \sqrt{K_b \cdot [WB]}$	May need to find K_b from K_a of conjugate acid
7. Weak Acid plus weak base	$pH = pK_a + \log \frac{WB}{WA}$	Buffer!! Henderson-Hasselbalch
8. No acids or bases; only neutral salts	$pH = 7.0$	

Key: Recognizing Final Situation!

17-11

● what is pH after:

① 22 mL of 0.10 M NaOH is added to 22 mL of 0.10 M HClO ($K_a = 3.0\times10^{-8}$).

② 20 mL of 0.10 M NaOH is added to 10 mL of 0.10 M HClO?

③ 20 mL of 0.10 M NaOH is added to 30 mL of 0.10 M HClO? ($K_a = 3.0\times10^{-8}$)

⓪ What is pH after:

① 22 mL of 0.10 M NaOH is added to 22 mL of 0.10 M HClO ($K_a = 3.0\times10^{-8}$).

① Convert to moles for ICE
② back to M for pH
③ Factor combined volume

$\boxed{\text{Weak base}}$

	$NaOH +$	$HClO \longrightarrow$	$H_2O +$	$NaClO$
I	2.2×10^{-3}	2.2×10^{-3} mol		
C	− "			$+2.2\times10^{-3}$
E				2.2×10^{-3} mol

$$[ClO^-] = \frac{2.2\times10^{-3}\text{ mol}}{(22+22\text{ mL})}\left|\frac{1000\text{ mL}}{\text{L}}\right. = 0.050\ M$$

$$K_b = \frac{1\times10^{-14}}{3.0\times10^{-8}} = 3.33\times10^{-7}$$

$$[OH^-] = \sqrt{(0.050)(3.33\times10^{-7})}$$
$$= 1.29\times10^{-4}$$

$pOH = 3.89$ $\boxed{pH = 10.11}$

② 20 mL of 0.10 M NaOH is added to 10 mL of 0.10 M HClO?

$\boxed{\text{Weak base + Strong Base}}$

	$NaOH +$	$HClO \longrightarrow$	$H_2O +$	$NaClO$
I	2.0×10^{-3}	1.0×10^{-3} mol		0
C	−1	−1		$+1.0\times10^{-3}$ mol
E	1.0×10^{-3} mol			1.0×10^{-3} mol

$$[OH^-] = \frac{1\times10^{-3}\text{ mol}}{30\text{ mL}}\left|\frac{1000\text{ mL}}{1\text{ L}}\right.$$
$$= 0.033\ M$$

$pOH = 1.48$

$\boxed{\text{Weak base dominates}}$ $\boxed{pH = 12.52}$

③ 20 mL of 0.10 M NaOH is added to 30 mL of 0.10 M HClO? ($K_a = 3.0\times10^{-8}$) $pK_a = 7.52$

$\boxed{\text{Weak acid/weak base}}$

	$NaOH +$	$HClO \longrightarrow$	$H_2O +$	$NaClO$
I	2×10^{-3}	3×10^{-3}		0
C	-2×10^{-3}	-2×10^{-3}		$+2\times10^{-3}$
E		1×10^{-3}		2×10^{-3}

Buffer.

$$pH = 7.52 + \underbrace{\log\frac{2\times10^{-3}}{1\times10^{-3}}}_{0.30}$$

$\boxed{pH = 7.82}$

(17-12)

① Would pH at endpoint be acidic, basic, or neutral when titrated with NaOH?

a. HCN

b. HNO_3

c. HF

② Would pH at endpoint be acidic, basic, or neutral when titrated with HCl?

a. NaOH

b. NaF

③ An initial pH = 1.3 and an equivalence point of 7 corresponds to a titration curve in which a ☐ base is added to a ☐ acid.

④ An initial pH = 9.3 and an edpoint of pH = 4.7 corresponds to a titration curve in which a ☐ is added to a ☐.

① Would pH at endpoint be acidic, basic, or neutral when titrated with NaOH? (17-12)

a. $HCN + {}^{\ominus}OH \rightarrow H_2O + {}^{\ominus}CN$ $\boxed{\text{basic}}$

w.b

b. $HNO_3 + {}^{\ominus}OH \rightarrow H_2O + {}^{\ominus}NO_3$ nonbasic $\boxed{\text{neutral}}$

c. $HF + {}^{\ominus}OH \rightarrow H_2O + F^{\ominus}$ $\boxed{\text{basic}}$

② Would pH at endpoint be acidic, basic, or neutral when titrated with HCl?

a. $NaOH + HCl \rightarrow H_2O + NaCl$ $\boxed{\text{neutral}}$

b. $NaF + HCl \rightarrow HF + NaCl$ $\boxed{\text{acidic}}$

③ An initial pH = 1.3 and an equivalence point of 7 corresponds to a titration curve in which a $\boxed{\text{strong}}$ base is added to a $\boxed{\text{strong}}$ acid.

④ An initial pH = 9.3 and an edpoint of pH = 4.7 corresponds to a titration curve in which a $\boxed{\text{strong acid}}$ is added to a $\boxed{\text{weak base}}$.

(always add a strong acid/base to whatever you started with)

C. Titration Curves

Recognition Factors

1. Initial pH ⇒ initial solution

$pH < 2$	strong acid
$2 < pH < 7$	weak acid
$7 < pH < 12$	weak base
$pH > 12$	strong base

2. Endpoint pH

7	SA/SB
<7	SA/WB (so only WA left at endpoint)
>7	WA/SB (so only WB left at endpoint)

Odds n ends

- endpoint pH where pH changes most steeply, rapidly

- weak/strong often go through "buffer zone", where pH changes little

- at halfway, $[HA]=[A^-]$ so $pH = pK_a$

T-131

Fig. 17.11 Weak Acid-Strong Base Titration Curve

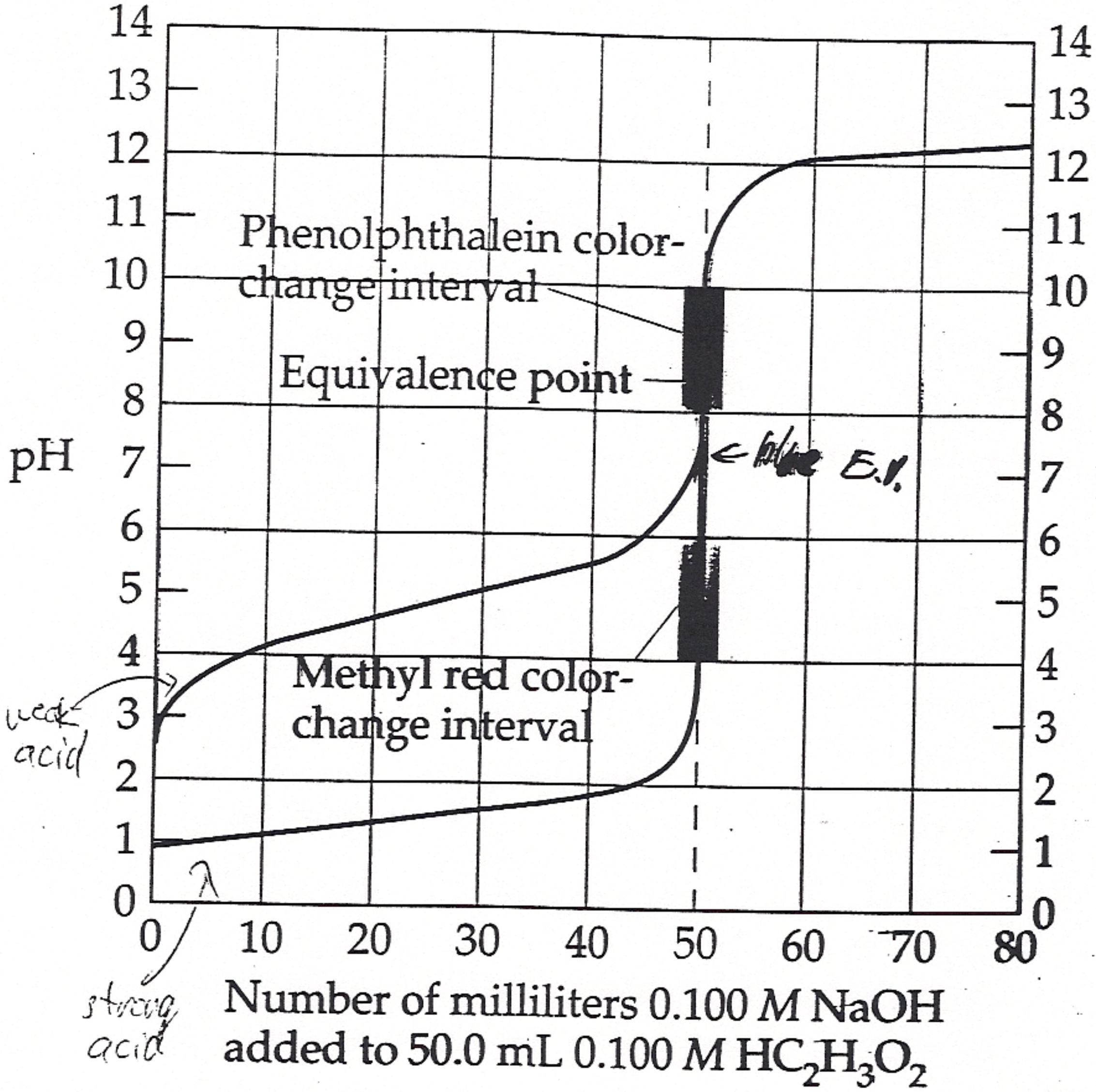

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Fig. 17.13 Strong Acid-Weak Base Titration Curve

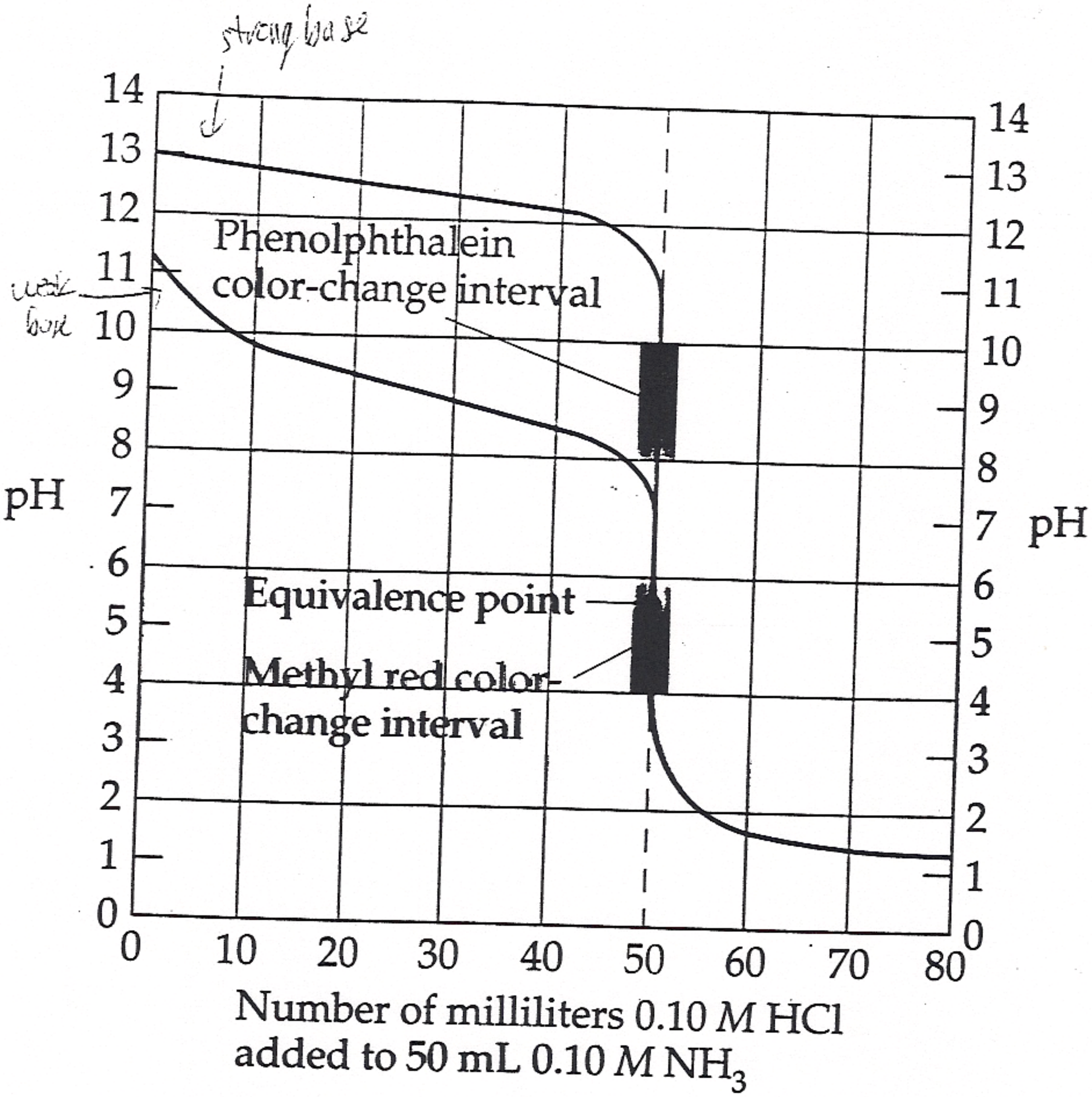

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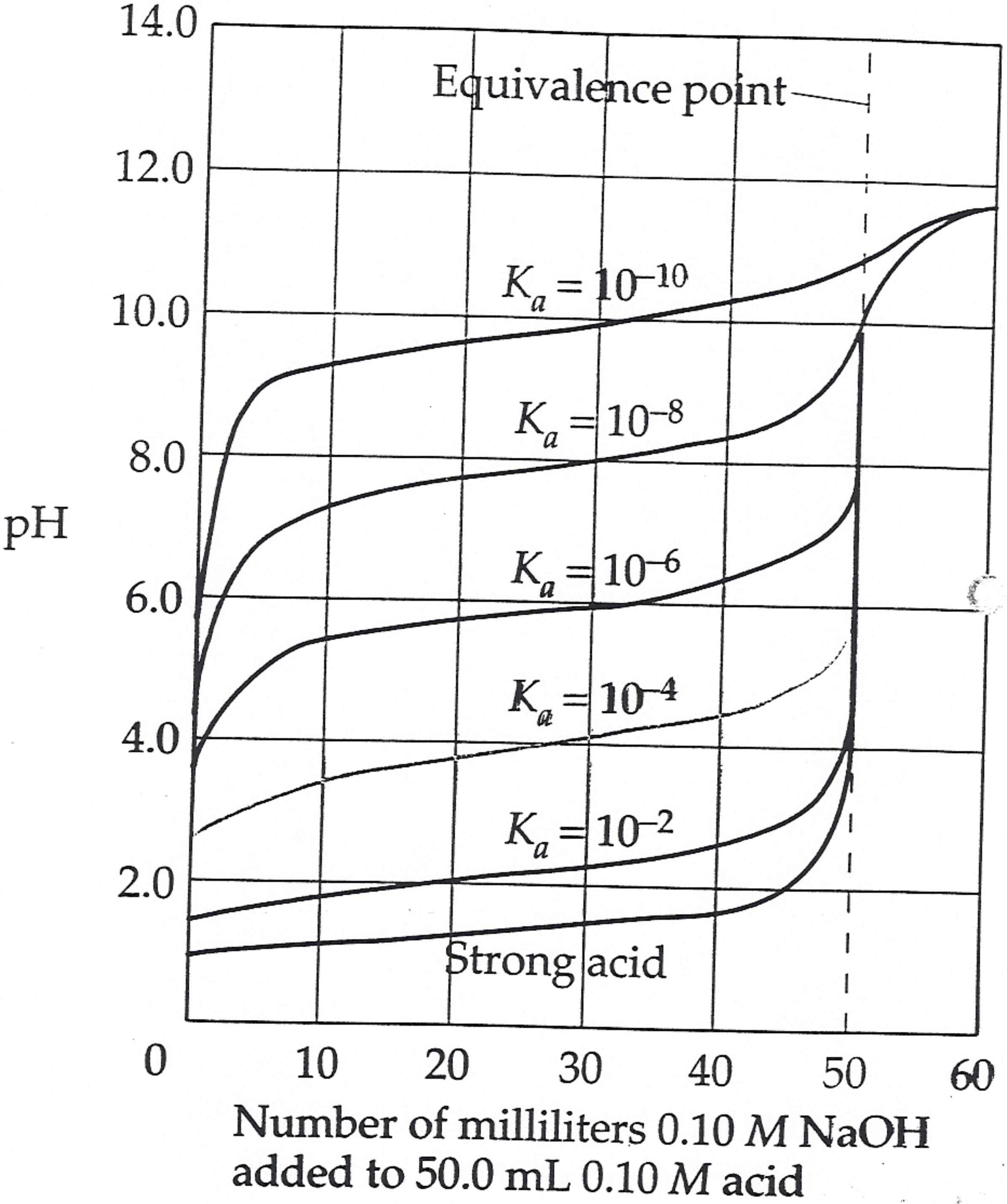
Fig. 17.12 Effect of Ka on Titration Curve



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D. Titration Calculations

Key: At equivalence point, $\boxed{\text{moles acid} = \text{moles base}}$

- know one ⇒ know other

Applications

① Find volume required

② Determine unknown concentration

③ " " grams

E. Weak acid + strong acid
(or Weak base + strong base)

Prob: A solution contains 1 L of 0.40 M acetic acid ($K_a = 1.80 \times 10^{-5}$). 0.016 mol of HCl is added.
a) find pH before HCl, and $[CH_3COO^-]$
b) find pH after HCl
c) find $[CH_3COO^{\ominus}]$ after HCl.

Weak Acid + Strong Acid (Weak base/strong base analogous)

① 0.10 mol HCl is added to 1.0 L of 0.20 M weak acid HA ($K_a = 5.3 \times 10^{-5}$). (Assume no volume change).

a. Determine $[H^+]$, $[A^-]$, and pH before HCl.

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

I
C
E

b. Determine $[H^+]$, $[A^-]$, and pH after HCl.

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

I
C
E

17-15

1. What volume of 0.12 M NaOH is needed to titrate 36 mL of 0.14 M HCl?

2. When 42 mL of aqueous HCl is titrated by 0.10 M NaOH, it takes 25 mL of the NaOH solution to reach the endpoint.
What is the [HCl] of the original solution?

3. How many grams of KOH (56 g/mol) would it take to neutralize
86 mL of 1.2 M HNO_3?

17-15

1. What volume of 0.12 M NaOH is needed to titrate 36 mL of 0.14 M HCl?

$1HCl + 1NaOH \rightarrow H_2O + NaCl$

① find mols acid
② that equals mols base
③ $\frac{\text{moles base}}{\text{volume base}}$ = concentration

$\boxed{\text{volume} = \frac{\text{moles}}{\text{Molarity}}}$

$\text{mol HCl} = \frac{0.036\,L \mid 0.14\,mol}{\mid 1\,L} = 5.04 \times 10^{-3}\ \text{mol HCl}$

$\text{mol } OH^- = \text{mol } H^+ = 5.04 \times 10^{-3}\ \text{mol}$

$x\ mL = \frac{5.04 \times 10^{-3}\ \text{mol NaOH} \mid 1000\ mL}{\mid 0.12\ \text{mol}} = \boxed{42\ mL}$

2. When 42 mL of aqueous HCl is titrated by 0.10 M NaOH, it takes 25 mL of the NaOH solution to reach the endpoint.
What is the [HCl] of the original solution?

① Find moles NaOH
② Equals moles HCl
③ $\frac{\text{moles}}{\text{volume}}$ = concentration

$x\ \text{mol HCl} = x\ \text{mol NaOH} = \frac{.025\,L \mid 0.10\,mol}{\mid L} = 2.5 \times 10^{-3}\ \text{mol}$

$M = \frac{2.5 \times 10^{-3}\ \text{mol HCl}}{.042\,L} = \boxed{.0595\ M}$

3. How many grams of KOH (56 g/mol) would it take to neutralize 86 mL of 1.2 M HNO_3?

① Find moles acid
② Equals moles KOH
③ Convert to grams

$x\ \text{mol KOH} = \text{mol } HNO_3 = \frac{1.2\,mol \mid .086\,L}{L \mid} = 0.103\ \text{mol}$

$x\,g\ KOH = \frac{0.103\ \text{mol} \mid 56\,g}{\mid 1\ \text{mol}} = \boxed{5.78\,g}$

17.14 Solubility Equilibria + K_{sp}

- solubility of ionics is a big deal, from kidney stones to drinking water to caves

A. K_{sp} "Solubility Product Constant"

- in a "saturated soln", insoluble solid in equilibrium with aqueous ions
- easy to write K expressions

	$PbCl_2(s)$	$\rightleftharpoons$	$Pb^{2+}(aq)$	+	$2Cl^-(aq)$	$K = [Pb^{2+}][Cl^-]$
I	0.20		0		0	
C			x		2x	
E	(doesn't matter, not in K!!)		x		2x	

B. Solubility: g/L of solid that dissolves

Molar solubility: mol/L of solid " "

Interconverting:

$$\boxed{K_{sp} \rightleftharpoons \underset{\text{(ions)}}{\text{mol/L}} \rightleftharpoons \underset{\text{(solid)}}{\text{mol/L}} \rightleftharpoons \underset{\text{(of solid)}}{\text{g/L}}}$$

Calculator job: $x^3 = 100$, (means $x = 100^{1/3}$) $x^4 = 100$

$0.26^3 = x$ $0.14^4 = x$

enter .26,
hit y^x (x^y for Casio)
enter 3

Various K_{sp} Setups, Depending on Formulas and Number of Cations / Anions Produced:

① $AB(s) \rightleftharpoons A^+(aq) + B^-(aq) \qquad K = x^2$

$\qquad - \qquad\qquad x \qquad\qquad x$

② $AB_2(s) \rightleftharpoons A^{2+}(aq) + 2B^-(aq) \qquad K = x(2x)^2$

$\qquad\qquad\qquad x \qquad\qquad 2x \qquad\qquad = 4x^3$

③ $AB_3(s) \rightleftharpoons A^{3+} + 3B^- \qquad K = x(3x)^3$

$\qquad\qquad\qquad x \qquad\quad 3x \qquad\qquad = 27x^4$

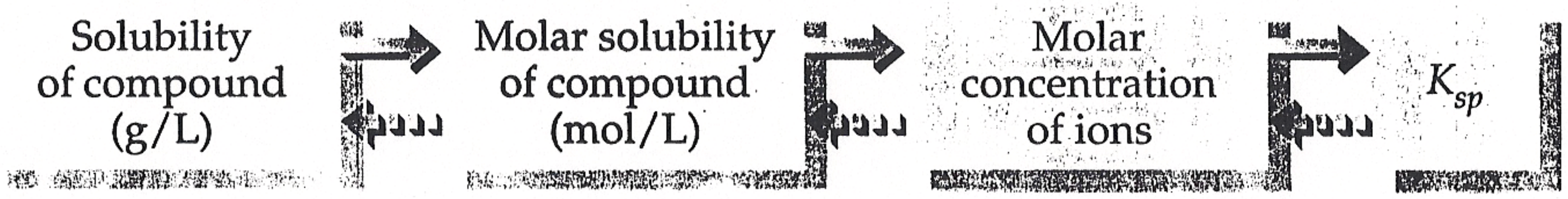
④ $A_2B_3(s) \rightleftharpoons 2A^{3+} + 3B^{2-} \qquad K = (2x)^2(3x)^3$

$\qquad\qquad\qquad 2x \qquad\quad 3x \qquad\qquad = 108x^5$

Point: ① manipulating things more complex than x^2 is common!!

② While the solid itself doesn't appear in the K expression, the value of x does tell how many moles/L of the original solid can dissolve.

Fig. 17.15 Interconverting Solubility and K_{sp}



Solubility of compound (g/L)

Molar solubility of compound (mol/L)

Molar concentration of ions

K_{sp}

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(17-17)

Calculator Practice

	x equals		x equals
$x^3 = 125$		$12^3 = x$	
$x^3 = 100$		$8^4 = x$	
$x^4 = 12.7$		$3.2^3 = x$	

1. $K_{sp} \rightarrow$ mol/L $\rightarrow$ g/L

$PbCl_2$ (278 g/mol) $K_{sp} = 1.6 \times 10^{-5}$

a) Calculate $[Pb^{2+}]$ and $[Cl^-]$ for saturated soln.

b) " " molar solubility (mol/L)

c) " " solubility (g/L)

d) what mass is dissolved in 140 mL?

17-17

Calculator Practice

	x equals		x equals
$x^{3'} = 125$	5.00	$12^3 = x$	1728
$x^3 = 100$	4.64	$8^4 = x$	4096
$x^4 = 12.7$	1.59	$3.2^3 = x$	32.768

1. $K_{sp} \rightarrow mol/L \rightarrow g/L$

$PbCl_2$ (278 g/mol) $K_{sp} = 1.6 \times 10^{-5}$

a) Calculate $[Pb^{2+}]$ and $[Cl^-]$ for saturated soln.

b) " " molar solubility (mol/L)

c) " " solubility (g/L)

d) what mass is dissolved in 140 mL?

a. $PbCl_2(s) \rightleftarrows Pb^{2+} + 2Cl^-$ $K = 1.6 \times 10^{-5} = x(2x)^2 = 4x^3$

	$PbCl_2(s)$	Pb^{2+}	$2Cl^-$
I	whatever	0	0
C	$-x$	$+x$	$2x$
E		x	$2x$

$x^3 = 4.0 \times 10^{-6}$

$x = 1.59 \times 10^{-2}$

$\boxed{[Pb^{2+}] = 1.59 \times 10^{-2}}$ $\boxed{[Cl^-] = 2x = 3.17 \times 10^{-2}}$

b. Solubility = "x" $\boxed{1.59 \times 10^{-2} \text{ mol/L}}$

c. $x\ g/L = \frac{1.59 \times 10^{-2} \text{ mol}}{L} \Big| \frac{278\ g}{1 \text{ mol}} = \boxed{4.42\ g/L}$

d. $x\ g = \frac{.140\ L}{} \Big| \frac{4.42\ g}{1\ L} = \boxed{0.619\ g}$

$$\boxed{K \longrightarrow \underset{\text{solubility}}{\text{molar/L}} \longrightarrow \underset{\text{solubility}}{g/L} \longrightarrow \underset{\text{per actual volume}}{\text{actual g}}}$$

17-18

1. Molar solubitity → Ksp

Find K_{sp} for CaF_2 whose molar solubility is 2.1×10^{-4} mol/L.

2. Gram solubility → molar sol → Ksp

$BaCO_3$ has a solubility of 0.014 g/L. Find K_{sp}.
(197 g/mol)

(17-18)

1. Molar solubility → K_{sp}

Find K_{sp} for CaF_2 whose molar solubility is 2.1×10^{-4} mol/L.

$$\underset{}{CaF_2(s)} \rightleftharpoons \underset{2.1\times10^{-4}\,M}{Ca^{2+}(aq)} + \underset{4.2\times10^{-4}\,M}{2F^-(aq)}$$

$$K = (2.1\times10^{-4})(4.2\times10^{-4})^2$$

$$\boxed{K_{sp} = 3.70\times10^{-11}}$$

Molar solubility plus stoichiometry tell what the ion concentrations are

2. Gram solubility → molar sol → K_{sp}

$BaCO_3$ has a solubility of 0.014 g/L. Find K_{sp}. (197 g/mol)

$$\frac{x \text{ mol}}{L} = \frac{0.014\,g}{L}\left|\frac{\text{mol}}{197\,g}\right. = 7.11\times10^{-5}\ \frac{\text{mol } BaCO_3}{L}$$

$$BaCO_3(s) \rightleftharpoons \underset{7.11\times10^{-5}}{1Ba^{2+}(aq)} + \underset{7.11\times10^{-5}}{1\,CO_3^{2-}(aq)}$$

$$\boxed{K = (7.11\times10^{-5})^2 = 5.05\times10^{-9}}$$

17.5 Factors that affect Solubility of Ionic Compounds (Le Chatelier)

A. pH If anion is basic, solubility $\boxed{\text{increases}}$ at low pH (high $[H^+]$)
- via selective removal of anion!

OH^-, F^-, CO_3^{2-}, SO_4^{2-}, PO_4^{3-} ---

ex: $Cu(OH)_2\,(s) \rightleftharpoons Cu^{2+}(aq) + 2OH^-(aq)$

$\downarrow 2H^+$

H_2O

- by selective removal of $[OH^-]$, $Q<K$, so solid keeps dissolving, $[Cu^{2+}]$ keeps rising

$PbF_2\,(s) \rightleftharpoons Pb^{2+}(aq) + 2F^-(aq)$ $K=[Pb^{2+}][F^-]$

$\downarrow 2H^+$

$2HF$

- by keeping $[F^-]$ low, low pH forces $[Pb^{2+}]$ to be high!!

B. Common Ion Effect: A "common ion" $\boxed{\text{decreases}}$ solubility.

$BaSO_4\,(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$

Used to remove undesired ions

- if Ba^{2+} or SO_4^{2-} is present, from a different source, that pushes eq. to left, so less dissolves

① can measure max solubility

② can calc. molar concentration

Fig. 17.18 Effect of pH on Solubility of CaF_2

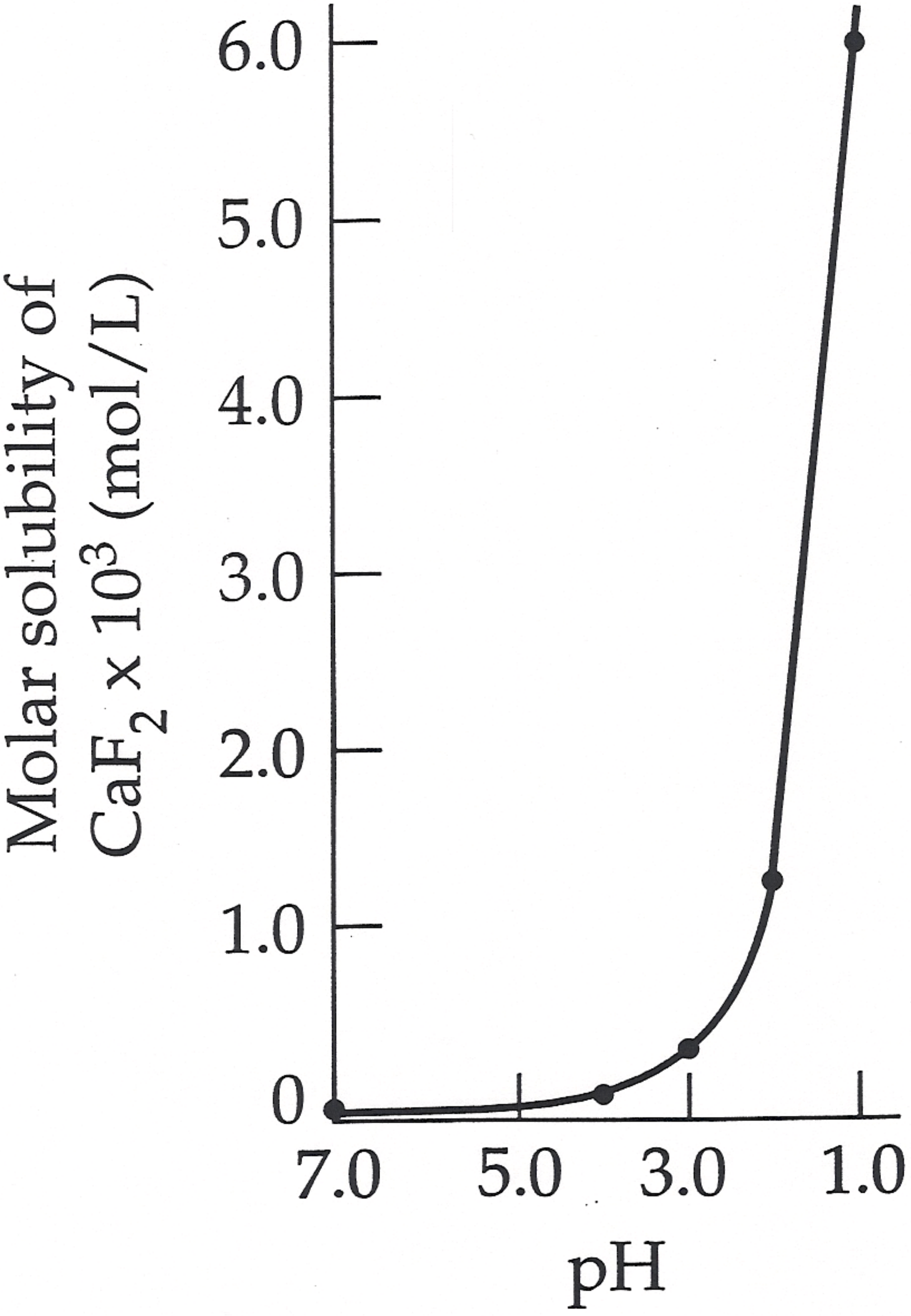

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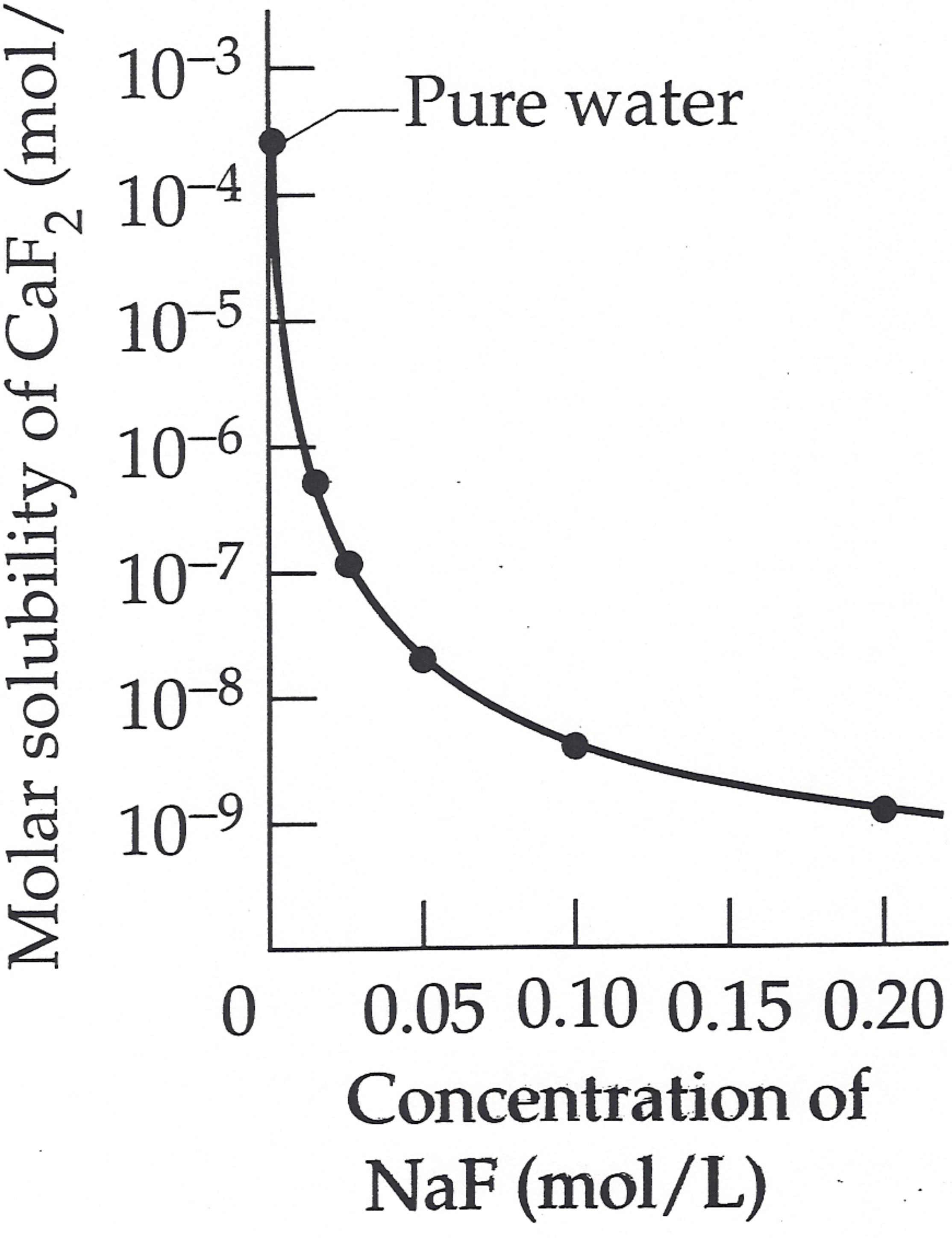
Fig. 17.16 Effect of NaF on Solubility of CaF_2

Common Ion Effect



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(17-20)

How Would Solubility be Affected?

	Added $Ca(NO_3)_2$	Added NaF	Added HNO_3	More Soluble at Low or High pH?
CaF_2				
$CaCO_3$				
$Ca(OH)_2$				
ZnF_2				
$PbCl_2$				
AgI				
$ZnSO_4$				

(17-20)

How Would Solubility be Affected?

	Added $Ca(NO_3)_2$	Added NaF	Added HNO_3	More Soluble at Low or High pH?
CaF_2	↓	↓	↑	low
$CaCO_3$	↓	—	↑	low
$Ca(OH)_2$	↓	—	↑	low
ZnF_2	—	↓	↑	low
$PbCl_2$	—	—	—	—
AgI	—	—	—	—
$ZnSO_4$	—	—	↑	low

Common ion reduces solubility, No common ion, no impact.

If anion is basic, solubility increases at high acid/low pH.

17-21

1. What is molar solubility of AgBr ($K_{sp}=3.3\times10^{-13}$) in a solution with 0.20 M NaBr?

dissolves fully

(what would AgBr solubility be without NaBr present?)

2. Determine molar solubility for $Mg(OH)_2$ ($K_{sp}=1.5\times10^{-11}$) at the following pH's:

a. pH= 12.00

b. pH= 6.00

Common Ion Effect on Acids

3. What is $[CNO^-]$ for a solution that is 0.22 M in HCNO (a weak acid) and also contain 0.25 M HCl?

17-21

1. What is molar solubility of AgBr ($K_{sp} = 3.3 \times 10^{-13}$) in a solution with 0.20 M NaBr?

$AgBr(s) \rightleftarrows Ag^+ + Br^-$

dissolves fully

I	[illegible]	0	.20
C	$-x$	$+x$	x
E		x	$.20+x$
E*		x	$.20$

$K = 3.3 \times 10^{-13} = (x)(.20)$

$\boxed{x = 1.65 \times 10^{-12} \text{ mol/L}}$

(what would AgBr solubility be without NaBr present?)

$AgBr \rightleftarrows Ag^+ + Br^-$

$x \quad x$

$K = 3.3 \times 10^{-13} = x^2$

$\boxed{x = 5.74 \times 10^{-7}}$

① Common ion: greatly reduces solubility

② simplifies calc!!

2. Determine molar solubility for $Mg(OH)_2$ ($K_{sp} = 1.5 \times 10^{-11}$) at the following pH's:

$Mg(OH)_2 \rightleftarrows Mg^{2+}(aq) + 2OH^-(aq)$

a. pH = 12.00

pOH = 2 $[OH^-] = 0.010$

E	x	$2x + 0.010$
E*	x	$.010$

$1.5 \times 10^{-11} = x(.010)^2$

$\boxed{x = 1.5 \times 10^{-7} \text{ mol/L}}$

b. pH = 6.00

$[OH^-] =$

$1.5 \times 10^{-11} = x(1 \times 10^{-8})^2$

$x = 1.5 \times 10^{5} \text{ mol/L}$

150,000 moles per Liter ≡ infini

Common Ion Effect on Acids

3. What is $[CNO^-]$ for a solution that is 0.22 M in HCNO (a weak acid) and also contain 0.25 M HCl?

(17-22)

C. Complex Ion Formation

- many Lewis bases can increase the solubility of a solid by irreversible removal of a product cation
- NH_3, $^{\ominus}CN$ common

$$CuBr(s) \rightleftharpoons Cu^{+}(aq) + Br^{-}(aq)$$

$$\Big\downarrow 4NH_3$$

$$Cu(NH_3)_4^{\ominus}$$