

CHEM 206 section 01

LECTURE #25

Wed. April 9, 2008

LECTURE TOPICS:

TODAY'S CLASS: 18.1-18.2

NEXT CLASS: finish Ch.18 (up to 18.5)

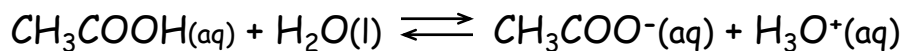
(1)

18.1 The Common Ion Effect \Rightarrow basis of all Ch.18

= shift in eqm position that occurs because of addition of an ion already involved in the equilibrium of interest (*cf* Le Châtelier...)
 \Rightarrow rxn initially speeds up in direction involving that ion...



Adding HCl(aq) to a sat'd solution of AgCl causes some AgCl to precipitate out



Adding CH_3COONa to a solution of acetic acid "inhibits" the acid's dissociation

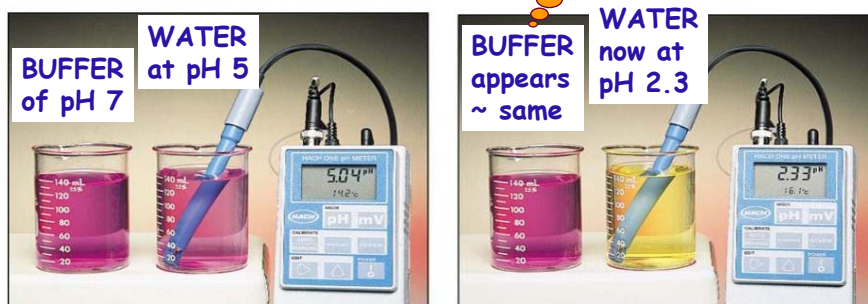
Same effect: Add another source of H_3O^+ (*e.g.*, HCl ...)

(2)

18.2 Buffer solutions resist changes in pH...

- Compare how pH changes when add 5 mL of dilute HCl (0.01 M)
- Both beakers contain alizarin = indicator that is pink at neutral pH but yellow in acidic solution
- Use pH meter: monitor pH \Rightarrow verify cause of indicator's response

Fig.18.2: Buffer vs. pure water:



(3) Before adding dilute acid

After adding dilute acid

Water itself cannot resist changes in pH



Initial			10^{-7} M	10^{-7} M
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- If add a strong base
 - \Rightarrow increase $[\text{OH}^-]$
 - \Rightarrow tiny $[\text{H}_3\text{O}^+]$ to shift left with
 - \Rightarrow large $[\text{OH}^-]$ remains...
 - \Rightarrow pH $\uparrow\uparrow\uparrow$

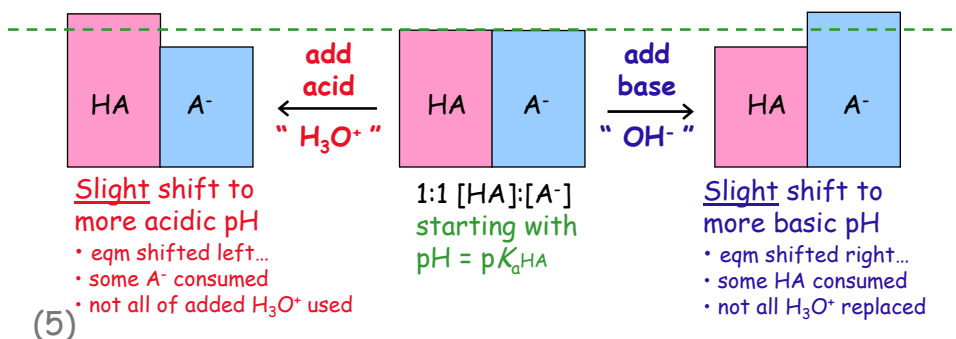
- If add a strong acid
 - \Rightarrow increase $[\text{H}_3\text{O}^+]$
 - \Rightarrow tiny $[\text{OH}^-]$ to shift left with
 - \Rightarrow large $[\text{H}_3\text{O}^+]$ remains...
 - \Rightarrow pH $\downarrow\downarrow\downarrow$

(4)

How does a buffer resist changes in pH?

A **BUFFER** = solution containing a mixture of a weak acid/base & its salt
i.e., a weak acid-base conjugate pair together in solution!

- Weak acid HA = **proton donor** \Rightarrow consumes added base
- Conjugate base A⁻ = "**proton sink**" \Rightarrow consumes added acid
- **Solution's pH only changes significantly if HA or A⁻ runs out...**



Understanding buffers: AN EFFECTIVE BUFFER HAS...

1. Roughly 1:1 ratio of weak conjugate A/B pair

- Want ability to react with random additions of acid or base
- [HA]:[A⁻] from 10:1 \rightarrow 1:10 works very well
- **Implication: a buffer will maintain a pH close to HA's pK_a...**
pK_a \pm 1-2 pH units

HA & A⁻
 BH⁺ & B:

2. Relatively large concentrations of both HA & A⁻

- So that do not run out of either HA or A⁻
- Usually see concentrations in 10⁻² \rightarrow 1 M range
- Provides high **buffer capacity** to counteract added acid/base
 = amount of strong HA or B needed to change pH of 1L by 1 unit

3. No reactivity/toxicity towards substances/organisms you are trying to study!

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Ex.1: What is the pH of this buffer? (the long way...)

Imagine you prepare a buffer by adding 0.125 mol of ammonium chloride to 500.mL of 0.500M aqueous ammonia (NH_4^+ $K_a = 5.6 \times 10^{-10}$).

$$\text{NH}_4^+(\text{aq}) + \text{H}_2\text{O}(\text{l}) \xrightleftharpoons{K_a} \text{NH}_3(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$$

Initial	0.250 M	built into K_a	0.500 M	0
Change	- x	---	+ x	+ x
Eqm	0.250-x	---	0.500+x	+ x

$$K_a = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} \Rightarrow 5.6 \times 10^{-10} = \frac{(0.500+x)x}{0.250-x}$$

pH = $-\log[\text{H}_3\text{O}^+]$
 = $-\log(1.18 \times 10^{-5})$
 = 9.55 (2SF)

$K \ll 1000x$ smaller than BOTH large initial []'s
 \Rightarrow double approximation (top & bottom!)

So: $5.6 \times 10^{-10} \approx \frac{0.500x}{0.250}$

Adding H_3O^+ or OH^- will change pH only very SLIGHTLY...

$x = (0.250 \times 5.6 \times 10^{-10}) / 0.500$
 $x = 2.80 \times 10^{-10} \text{ M} = [\text{H}_3\text{O}^+]$

Estimating the pH of a BUFFER: the Henderson-Hasselbalch Eq'n



double approx'n $\Rightarrow K_a \approx \frac{[\text{A}^-]_0 [\text{H}_3\text{O}^+]_{\text{eq}}}{[\text{HA}]_0}$

$\Rightarrow [\text{H}_3\text{O}^+] \approx K_a \frac{[\text{HA}]_0}{[\text{A}^-]_0}$

$\Rightarrow -\log[\text{H}_3\text{O}^+] \approx -\log K_a + -\log \frac{[\text{HA}]_0}{[\text{A}^-]_0}$

IF SOLUTION CONTAINS:

- 1) Weak acid & conj. base
- 2) High concentrations
- 3) $[\text{HA}] \approx [\text{A}^-]$

THEN: it is a buffer
 double approx'n works

Henderson-Hasselbalch Eq'n

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]_0}{[\text{HA}]_0}$$

User's manual for Henderson-Hasselbalch equation:

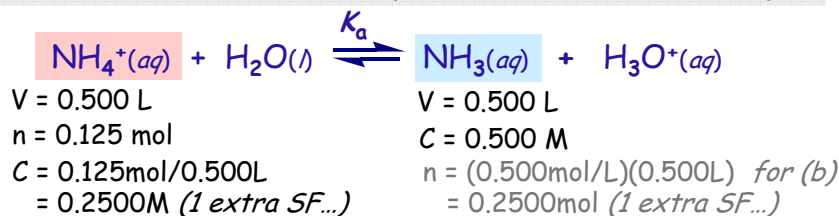
- **HOW:** use initial $[\text{A}^-]:[\text{HA}]$ ratio (= double approximation)
- **WHEN:** if $[\text{A}^-]_0:[\text{HA}]_0 = 10:1 \rightarrow 1:10...$ (but not outside this range)
- **NOTE:** do NOT use for other solutions (must be $\sim 1:1$ weak conj. pair...)

Ex.2: How much does our buffer's pH change if...?

Same buffer as before: 0.125 mol of ammonium chloride in 500.mL of 0.500M aqueous ammonia (NH_4^+ K_a 5.6×10^{-10}).

- (a) Estimate the pH of this buffer (using H-H eqn)
 (b) Find the pH after bubbling 0.0100 mol of HCl gas through the buffer.

(a) Use Henderson-Hasselbalch equation to estimate initial pH:



Solution has ~1:1 ratio of [weak acid]_o to [conj.base]_o (actual ratio = 1:2),
 ⇒ can be safely treated as a buffer:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]} \Rightarrow \text{pH} = -\log(5.6 \times 10^{-10}) + \log\left(\frac{[0.500 \text{ M}]}{[0.250 \text{ M}]}\right)$$

$$= 9.252 + 0.301$$

$$= 9.55 \text{ (2SF)}$$

same as long way

Note: A⁻ & HA in same volume, so can just use mole ratio!

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(b) Calculate the pH of the buffer after rxn with HCl

1st: stoichiometry: rxn of strong acid with conj.base: NH_3

	$\text{HCl}(\text{aq})$	+	$\text{NH}_3(\text{aq})$	→	$\text{NH}_4\text{Cl}(\text{aq})$
Initial:	$\#n_{\text{HCl}} = 0.0100 \text{ mol}$		$\#n_{\text{NH}_3} = 0.2500 \text{ mol}$		$\#n_{\text{NH}_4^+} = 0.125 \text{ mol}$
100% rxn:	- 0.0100		+ 0.0100		+ 0.0100
After rxn:	0		= 0.2400 mol		= 0.135 mol

2nd: new analysis of buffer's pH (eqm calc. or using H-H eqn)



$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]} \Rightarrow \text{pH} = -\log(5.6 \times 10^{-10}) + \log \frac{[0.2400 \text{ mol}]}{[0.135 \text{ mol}]}$$

$$= 9.252 + 0.250$$

$$= 9.50 \text{ (2SF) SLIGHTLY more acidic}$$

pH 9.55 before HCl added

Note: if we'd added the same # of moles of strong base:
 pH would have changed by same amount, but in opposite direction
 (to become very slightly more alkaline)

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Summary: Attacking quantitative buffer problems

TO CALCULATE pH OF BUFFER: *two acceptable approaches...*

- Full equilibrium calculation: using $HA + H_2O \rightleftharpoons A^- + H_3O^+$
- Henderson-Hasselbalch eq'n (double approximation short-cut)

For calculations: simplest to consider conj. A/B pair as HA & A⁻
⇒ use acid-dissociation rxn (eqm constant K_a) even for basic buffers:



TO CALCULATE pH AFTER ADDING ACID/BASE:

1. Deal with stoichiometry 1st: using $HA + OH^- \rightarrow A^- + H_2O$
OR $A^- + H_3O^+ \rightarrow HA + H_2O$

to determine new starting concentrations of HA & A⁻

2. Then "allow system to come to eqm": $HA + H_2O \rightleftharpoons A^- + H_3O^+$
or use Henderson-Hasselbalch eq'n

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A buffer is used when your system is sensitive to pH

Biological molecules only work properly at pH they evolved at!

- **Gaining or losing a H⁺ affects molecule's:**
 - charge, # lone pairs, e⁻s location (localized/resonance-delocalized)
 - ⇒ **influences interactions with other molecules!!**
- If studying an enzyme-catalyzed rxn, *in vivo* organisms, etc...
- & acid or base may be released into your system
 - in a living system: most metabolism releases H⁺
 - solution exposed to air: CO₂ dissolves to yield H₂CO₃... ∴ H⁺

Blood is naturally buffered by bicarbonate/carbonate

- Constant amount of **CO₂ dissolved** in blood from air/metabolism



$$\text{Blood pH } 7.4 \Rightarrow [HCO_3^-]:[H_2CO_3] \\ \approx 10.8 : 1$$

SOME SIMPLE BUFFERS USED IN BIOLOGY LABS:

- H₂CO₃ / HCO₃⁻ pH ~ 6.4 with 1:1 initial ratio
- H₂PO₄⁻ / HPO₄²⁻ pH ~ 7.2 with 1:1 initial ratio

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How to choose & prepare a buffer

Table 18.1 • Some Commonly Used Buffer Systems

Weak Acid	Conjugate Base	HA's pK_a	Useful pH Range
Phthalic acid, $C_6H_4(CO_2H)_2$	Hydrogen phthalate ion $C_6H_4(CO_2H)(CO_2)^-$	(2.89)	1.9–3.9
Acetic acid, CH_3CO_2H	Acetate ion, $CH_3CO_2^-$	(4.74)	3.7–5.7
Dihydrogen phosphate ion, $H_2PO_4^-$	Hydrogen phosphate ion, HPO_4^{2-}	(7.21)	6.2–8.2
Hydrogen phosphate ion, HPO_4^{2-}	Phosphate ion, PO_4^{3-}	(12.44)	11.3–13.3

DECIDING ON A BUFFER SYSTEM TO USE:

1. Select acid with pK_a near required pH: **maintain pH of $pK_a \pm 1-2$**
2. Acid & salt must be highly soluble: **high conc. $\sim 0.1 < [] < 10 \text{ M}$**
3. For biological applications: **minimize toxicity etc...**

PREPARATION OF A BUFFER IN THE LAB:

1. Calculate $[A^-]/[HA]$ ratio needed for desired pH
ensure within 1:10 \rightarrow 10:1 working range...
2. Dissolve appropriate quantities of acid & salt
3. Accurately measure pH with pH meter
4. Adjust to exact pH by adding strong acid or base

}

LAB BOOK

LAB BENCH

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Ex.3: Choosing & understanding a buffer...

Which pair would be best to keep a solution at pH ~ 3 ?

- (a) HCl and NaCl
- (b) NH_3 and NH_4Cl
- (c) CH_3COOH and CH_3COONa
- (d) Na_3PO_4 and NaH_2PO_4
- (e) NaH_2PO_4 and Na_2HPO_4
- (f) NaH_2PO_4 and H_3PO_4

DATA:	K_a
NH_4^+	5.5×10^{-10}
CH_3COOH	1.8×10^{-5}
H_3PO_4	7.5×10^{-3}
$H_2PO_4^-$	6.2×10^{-8}
HPO_4^{2-}	4.8×10^{-13}

For this buffer: (on your own)

Describe how to prepare 1.0 L of buffer that is 1.00M in both species, & estimate (by calculation) its pH.

Then determine the pH after you add 25mL of...

- (a) 0.20M HCl
- (b) 0.20M NaOH

Strategy:

1. Identify initial $[HA]$ & $[A^-]$, and pH
2. Deal with 100% rxn with H^+ or OH^-
3. Calculate pH for new $[HA]:[A^-]$ ratio

(14)

ASSIGNED READINGS:

BEFORE NEXT CLASS:

Read: sections 18.1-18.2

Practice: identifying buffer solutions
calculating pH of buffers
calculating pH changes if add acid/base

Review: ionic compound solubilities from Ch.5

+ WORK ON Problems from Ch.17 & 18.1-18.3

(15)