CHEM 206 section 52

WEEK #13 Nov. 25th, 2014

FINAL LECTURE TOPICS:

Ch.17.8 & Ch.18 sections 1-2

(did 18.4-7 earlier, & 18.3 last week)

- **Final exam:**
  Tues. Dec. 16th, 7-10 pm @ SGW in Hall building
  H509 (A-GOL)
  H537 (GOR-LUI)
  H561 (LUO-Z)
- **Covers entire course:**
  Ch.5, 8.9, 19, 12, 14, 15, 16, 17, 18.1-7

Chapter 18: OTHER ASPECTS OF AQUEOUS EQUILIBRIA

- **Application of eqm concepts to control of pH (buffers), analysis of solutions (titrations), & understanding of solubility**

Outline (not done in this order…)

18.1 The Common ion effect
18.2 Controlling pH: buffer solutions

already done:
18.3 Acid-base titrations
18.4 Solubility of salts
18.5 Precipitation reactions
18.6 Equilibria involving complex ions
18.7 Solubility and complex ions

Chapter Goals

- Understand the common ion effect
- Understand the control of pH in aqueous solutions with buffers
- Evaluate the pH in the course of acid-base titrations
- Apply chemical equilibrium concepts to the solubility of ionic compounds

Common ion effect: reacting away an ion (pH effect; see 18.4)

$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$ $K_{sp} = 3.4\times10^{-9}$

Basic anion ⇨ eqm will shift right in acid!

Limestone dissolves in acid & bubbles of gas form. *WHY?*

$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$ $K_{sp} = 3.4\times10^{-9}$

$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$ $K_{b1} = 2.1\times10^{-4}$

$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$ $K_{b2} = 2.4\times10^{-8}$

$2[\,H_3O^+(aq) + OH^-(aq) \rightleftharpoons 2H_2O(l)\,]$ $K = [1/K_w]^2 = 10^{28}$

NET: $CaCO_3(s) + 2H_3O^+(aq) \rightleftharpoons Ca^{2+}(aq) + H_2CO_3(aq) + 2H_2O(l)$

When add rxns eqns ⇨ multiply *K*s: $K_{net} = K_{sp}K_{b1}K_{b2}K = 1.7\times10^8$

But recall: carbonic acid is unstable:

$H_2CO_3(aq) \rightleftharpoons H_2O(l) + CO_2(g)$ $K = \sim1\times10^5$

$CaCO_3(s) + 2H_3O^+(aq) \rightleftharpoons Ca^{2+}(aq) + CO_2(g) + 3H_2O(l)$

Large *K* ⇨ fully soluble in acid, + gaseous product. $K_{overall} = 2\times10^{13}$!

(…& gas leaves… ∴might never reach eqm, just keeps shifting right…)

18.1 The Common Ion Effect ⇨ *basis of all Ch.18, already seen…*

= shift in eqm position that occurs because of addition of an ion already involved in the equilibrium of interest (*cf* Le Châtelier…)

- ⇨ rxn initially speeds up in direction involving that ion…
- ⇨ when eqm re-established: mixture's composition ("position") changed

Adding HCl to a saturated sol'n of AgCl causes some AgCl to ppt out:

Related to solubility Kotz 18.4-5

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

← Same effect: Add another source of Ag^+ (*e.g.*, $AgNO_3$)

Adding $NaCH_3COO$ to an acetic acid sol'n inhibits the acid's dissociation:

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

Related to buffers Kotz 18.2

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

CLICKER Q: applying equilibrium knowledge

What effect will addition of sodium fluoride have on the pH of a solution of hydrofluoric acid?

A. increase pH
B. no effect
C. decrease pH
D. cannot tell from information given

(5)

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 ⇨ **verify** cause of indicator's response

Fig.18.2: Buffer *vs.* pure water:

How?

Before adding dilute acid

After adding dilute acid

(6)

Water itself cannot resist changes in pH

$$H_2O(l) + H_2O(l) \rightleftharpoons OH^-(aq) + H_3O^+(aq) \qquad K_w = 10^{-14}$$

Initial			10^{-7} M	10^{-7} M

- If add a strong **base**
  - ⇨ increase $[OH^-]$
  - ⇨ tiny $[H_3O^+]$ to shift left with
  - ⇨ large $[OH^-]$ remains…
  - ⇨ pH ↑↑↑

- If add a strong **acid**
  - ⇨ increase $[H_3O^+]$
  - ⇨ tiny $[OH^-]$ to shift left with
  - ⇨ large $[H_3O^+]$ remains…
  - ⇨ pH ↓↓↓

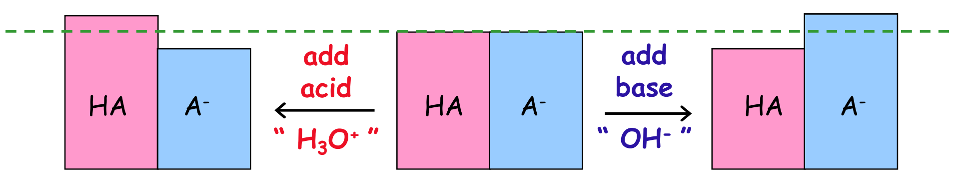
(7)

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** ⇨ consumes added base
- Conjugate base A^- = "**proton sink**" ⇨ consumes added acid
- **Solution's pH only changes significantly if HA or A^- runs out…**

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



Slight shift to more acidic pH
- eqm shifted left…
- some A^- consumed
- not all of added H_3O^+ used

1:1 $[HA]:[A^-]$
starting with $pH = pK_{a\,HA}$

Slight shift to more basic pH
- eqm shifted right…
- some HA consumed
- not all H_3O^+ replaced

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Understanding buffers: AN EFFECTIVE BUFFER HAS…

HA & A^-
BH^+ & B:

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 → 1:10 works very well**
- **Implication: a buffer will maintain a pH close to HA's pK_a…**

pK_a ± 1-2 pH units

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} → 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!

(9)

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: CO_2 dissolves to yield H_2CO_3… ∴H^+

Blood is naturally buffered by bicarbonate/carbonate

- Constant amount of **CO_2 dissolved** in blood from air/metabolism

⇨ **$H_2CO_{3(aq)}$** pK_a = 6.4

Blood pH 7.4 ⇨ [HCO_3^-]:[H_2CO_3]
≈ 10.8 : 1

SOME SIMPLE BUFFERS USED IN BIOLOGY LABS:

- H_2CO_3 / HCO_3^- pH ~ 6.4 with 1:1 initial ratio
- $H_2PO_4^-$ / HPO_4^{2-} pH ~ 7.2 with 1:1 initial ratio

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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 = 5.6x10^{-10}).

$$NH_4^+(aq) + H_2O(l) \overset{K_a}{\rightleftharpoons} NH_3(aq) + H_3O^+(aq)$$

	$NH_4^+(aq)$	$H_2O(l)$	$NH_3(aq)$	$H_3O^+(aq)$
Initial	0.250 M	---	0.500 M	0
Change	- x	---	+ x	+ x
Eqm	0.250-x	---	0.500+x	+ x

$$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]} \Rightarrow 5.6\text{x}10^{-10} = \frac{(0.500+x)x}{0.250-x}$$

K << 1000x smaller than **BOTH** large initial [ ]'s
⇨ **double approximation** (top & bottom!)

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

x = (0.250 x 5.6x10^{-10})/0.500
x = 2.80x10^{-10} M = $[H_3O^+]$

pH = $-\log[H_3O^+]$
= $-\log(2.80\text{x}10^{-10})$]
= 9.55 *(2SF)*

& Adding H_3O^+ or OH^- (exogenous acid/base) will change pH only SLIGHTLY…

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

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

double approx'n ⇨ $K_a \approx \frac{[A^-]_0\,[H_3O^+]_{eq}}{[HA]_0}$

⇨ $[H_3O^+] \approx K_a \frac{[HA]_0}{[A^-]_0}$

⇨ $-\log[H_3O^+] \approx -\log K_a + -\log\frac{[HA]_0}{[A^-]_0}$

Flip quotient to reverse log's sign ⇨

Henderson-Hasselbalch Eq'n

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

IF SOLUTION CONTAINS:
1) **Weak** acid & conj.base
2) **High** concentrations
3) **$[HA] \approx [A^-]$**

THEN: it is a buffer
double approx'n works

User's manual for Henderson-Hasselbalch equation:
- **HOW:** use initial $[A^-]$:[HA] ratio (= double approximation)
- **WHEN:** if $[A^-]_o$:$[HA]_o$= 10:1 → 1:10… (but not outside this range)
- **NOTE:** do NOT use for other solutions (must be ~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, *i.e.,* the short-cut!)
(b) Find the pH after bubbling 0.0100 mol of HCl gas through the buffer.

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

$$NH_4^+(aq) + H_2O(l) \overset{K_a}{\rightleftharpoons} NH_3(aq) + H_3O^+(aq)$$

NH_4^+:
V = 0.500 L
n = 0.125 mol
C = 0.125mol/0.500L
= 0.2500M *(1 extra SF…)*

NH_3:
V = 0.500 L
C = 0.500 M
n = (0.500mol/L)(0.500L) *for (b)*
= 0.2500mol *(1 extra SF…)*

Solution has ~1:1 ratio of $[\text{weak acid}]_o$ to $[\text{conj.base}]_o$ (actual ratio = 1:2),
⇨ **can be safely treated as a buffer:**

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

⇨ $pH = -\log(5.6 \times 10^{-10}) + \log([0.500M]/[0.250M])$
= 9.252 + 0.301
= 9.55 *(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

	HCl(aq) +	NH_3(aq) →	NH_4Cl(aq)
Initial:	$\#n_{HCl}$ = 0.0100 mol	$\#n_{NH3}$ = 0.2500 mol	$\#n_{NH4+}$ = 0.125 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)

$$NH_4^+(aq) + H_2O(l) \overset{K_a}{\rightleftharpoons} NH_3(aq) + H_3O^+(aq)$$

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

⇨ $pH = -\log(5.6 \times 10^{-10}) + \log \frac{[0.2400\text{mol}]}{[0.135\text{ mol}]}$
= 9.252 + 0.250
= 9.50 *(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)

(14)

Summary: Attacking quantitative buffer problems

For calculations: simplest to consider conj. A/B pair as HA & A^-

⇨ use acid-dissociation rxn (eqm constant K_a), even for basic buffers:

$$NH_4^+(aq) + H_2O(l) \overset{K_a}{\rightleftharpoons} NH_3(aq) + H_3O^+(aq)$$

↙ *"ammonia buffer" suitable for pH @ $pK_a(NH_4^+)$ 9.3 ± 2.0*

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)

TO CALCULATE pH AFTER ADDING ACID/BASE: *2 steps…*

1. Deal with stoichiometry 1st: to find new $[HA]_o$ & $[A^-]_o$ — using $HA + OH^- \rightarrow A^- + H_2O$ *OR* $A^- + H_3O^+ \rightarrow HA + H_2O$
2. Then "let system come to eqm": or use H.-H. eq'n (short-cut) — $HA + H_2O \rightleftharpoons A^- + H_3O^+$

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How to choose & prepare a buffer solution

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 ±1-2**
2. Acid & salt must be highly soluble: **high conc. ~0.1 < [ ] < 10 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 → 10:1 working range…
2. Dissolve appropriate quantities of acid & salt
   (or, dissolve acid only & add NaOH to make desired ratio)
3. Accurately measure pH with pH meter
4. Adjust to exact pH by adding strong acid or base

(Steps 1–2: LAB BOOK; steps 2–4: LAB BENCH)

CLICKER Q: choosing buffer components

Which pair would be <u>best</u> to buffer a solution at pH ~ 3 ?

A. HCl & NaCl
B. CH_3COOH & CH_3COONa
C. Na_3PO_4 & NaH_2PO_4
D. NaH_2PO_4 & Na_2HPO_4
E. NaH_2PO_4 & H_3PO_4

DATA:	K_a
CH_3COOH	$1.8x10^{-5}$
H_3PO_4	$7.5x10^{-3}$
$H_2PO_4^-$	$6.2x10^{-8}$
HPO_4^{2-}	$4.8x10^{-13}$

CLICKER Q: choosing your buffer-component ratio

For the buffer chosen in the previous example, what ratio of conjugate acid to conjugate base is needed to maintain pH = 3.00 ?

HA : A^-

A. 1 : 7.5
B. 1 : 3
C. 1 : 1
D. 3 : 1
E. 7.5 : 1

Ex.3: Choosing & understanding a buffer… (on your own)

For the buffer used in the previous two problems:

1) Describe how to prepare 1.0 L of buffer that contains 0.100 M of the less abundant buffer component (hint: also figure out the concentration of the other component). Specify the quantities (in g) of each of the substances you will need to dissolve in water.

2) Then, determine the pH of this buffer BEFORE and AFTER adding 1.0 mL of… (use a fresh sample of buffer for each)
   (a) 10.0 M HCl ("conc. HCl" – a sat'd solution of HCl(g) - is 12 M)
   (b) 10.0 M NaOH

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

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FINAL EXAM INFORMATION

- **Final exam:**
  Tues. Dec. 16th, 7-10 pm @ SGW in Hall building
  H509 (A-GOL)
  H537 (GOR-LUI)
  H561 (LUO-Z)
- **Covers entire course:**
  Ch.5, 8.9, 19, 12, 14, 15, 16, 17, 18
- The examination room invigilators are VERY STRICT:
  - Student ID card mandatory
  - No programmable calculators
  - **No electronic dictionaries, cell phones, pagers, blackberries, *etc***
  - Book-format translation dictionaries (word-to-word only) allowed, but they will be inspected.
  - Arrive to the exam room early !

FINAL EXAMS FROM PREVIOUS YEARS ON MOODLE:
& Moodle site has link to: http://faculty.concordia.ca/rogers

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EXAM REVIEW

Sample exam questions from Ch.17-18

(see website for solutions…)

Sample exam question **Winter 2004 section 02**

 # 7. (__/ 9 marks) You are asked to prepare a 100.0 mL sample of a solution with pH of 5.50 by dissolving the appropriate amount of a solute in pure water (pH 7.00). Which ONE of the following solutes would you use, and in what quantity? EXPLAIN YOUR CHOICE, AND SHOW ALL RELEVANT CALCULATIONS.

CIRCLE YOUR CHOICE:

a) 15 M NH_3(aq)
b) 12 M HCl(aq)
c) NH_4Cl(s)
d) Pure ("glacial") acetic acid, $HC_2H_3O_2$

SUBSTANCE	K_a
HCl	very large
$HC_2H_3O_2$	1.8×10^{-5}
NH_4^+	5.6×10^{-10}
H_2O	$K_w = 1\times10^{-14}$

Sample exam question **Winter 2004 section 51**

 # 10. (__/ 9 Marks) The ancient Romans added calcium sulfate to wine to clarify it (*i.e.,* to remove cloudiness). They didn't know it at the time, but this treatment also removed any dissolved lead in the wine. [Note: Roman water pipes were made of lead, and wealthy people drank from lead cups….]

a) What is the <u>maximum</u> concentration of dissolved lead (II) ions, in molarity, that might be present in wine to which excess calcium sulfate has been added? [K_{sp} $PbSO_4$ = 1.6x10^{-8}; K_{sp} $CaSO_4$ = 6.1x10^{-5}]

a) Chronic exposure to lead is dangerous, particularly to children, because lead is a poison that builds up in the bloodstream. Even very low concentrations of lead in the blood (50 parts per billion, = 0.050 ppm) causes increased blood pressure; above 100 ppb, intelligence is affected, and coma or death can result above 800 ppb. **Convert the concentration of Pb^{2+} ions in the wine from part (a) to parts per <u>billion</u>, ppb**, and comment on whether or not you think the fall of the Roman Empire might have been related to lead poisoning.

Sample exam question **Fall 2004 section 52**

 # 10. (__/ 12 Marks) You are working in a biology lab and are asked to prepare a pH 7.40 buffer that mimics human blood. You will use KH_2PO_4 and Na_2HPO_4. The K_a of $H_2PO_4^-$ is 6.3×10^{-8}; the K_a of HPO_4^{2-} is 4.2×10^{-13}.

a) **(3 marks)** Briefly explain why HPO_4^{2-} and $H_2PO_4^-$ are a good pair of substances to use.

a) **(3 marks)** What should be the ratio of $[HPO_4^{2-}]$ / $[H_2PO_4^-]$ in this buffer?

a) **(6 marks)** To mimic blood, the buffer must exert an osmotic pressure of π = 8.00 atm at 37°C. Using this information, calculate the masses of KH_2PO_4 and Na_2HPO_4 you should use to prepare 1.0 L of buffer.

THIS IS THE END OF GENERAL CHEMISTRY II.

Best of luck with your studies!

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