Additional Aspects of Aqueous Equilibria
Chapter 17

17.1 The Common-Ion Effect

17.2 Buffered Solutions

The Common-Ion Effect

The shift in equilibrium caused by the addition of a compound having an ion in common with the dissolved substance.

$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$

$CH_3COONa(s) \rightarrow Na^+(aq) + CH_3COO^-(aq)$

$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$ **Common ion**

The presence of a common ion <u>suppresses</u> the ionization of a weak acid or a weak base

The Common-Ion Effect

Calculate the [H⁺] in a 0.10 *M* chlorous acid (HOCl) solution. $K_a = 3.0 \times 10^{-8}$

	$HOCl(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$OCl^-(aq)$
i	0.10		0.00		0.00
Δ	- x		+ x		+ x
eq	0.10 - x		x		x

$$K_a = \frac{[H^+][OCl^-]}{[HOCl]} \qquad 3.0 \times 10^{-8} = \frac{x^2}{0.10 - x}$$

The Common-Ion Effect

$$3.0 \times 10^{-8} = \frac{x^2}{0.10 - x} \qquad 0.10 - x \approx 0.10$$

$x = 5.5 \times 10^{-5}\ M$ **0.06%**

$[H^+] = 5.5 \times 10^{-5}\ M$

pH = 4.26

The Common-Ion Effect

Calculate the $[H^+]$ in a 0.10 *M* HOCl and 0.10 *M* NaOCl solution.

	NaOCl(s)	→	Na^+(aq)	+	OCl^-(aq)
			0.10 *M*		0.10 *M*
	HOCl(aq)	⇌	H^+(aq)	+	OCl^-(aq)
i	0.10		0.00		0.10
Δ	- x		+ x		+ x
eq	0.10 - x		x		0.10 + x

The Common-Ion Effect

$$K_a = \frac{[H^+][OCl^-]}{[HOCl]}$$

$$3.0 \times 10^{-8} = \frac{x\,(0.10 + x)}{0.10 - x} \qquad 0.10 \pm x \approx 0.10$$

$x = [H^+] = 3.0 \times 10^{-8}$ *M*

$[H^+] = 5.5 \times 10^{-5}$ *M* For 0.10 M HOCl

Presence of the common ion (OCl^-) decreases the ionization of the weak electrolyte

The Common-Ion Effect

Calculate the pH and $[OCl^-]$ in a 0.20 *M* HOCl and 0.10 *M* HCl solution.

	HCl(aq)	→	H^+(aq)	+	Cl^-(aq)
			0.10 *M*		0.10 *M*
	HOCl(aq)	⇌	H^+(aq)	+	OCl^-(aq)
i	0.20		0.10		0.00
Δ	- x		+ x		+ x
eq	0.20 - x		0.10 + x		x

The Common-Ion Effect

$$K_a = \frac{[H^+][OCl^-]}{[HOCl]}$$

$$3.0 \times 10^{-8} = \frac{(0.10 + x)\,x}{0.20 - x} \qquad \begin{array}{l} 0.10 + x \approx 0.10 \\ 0.20 - x \approx 0.20 \end{array}$$

$x = [OCl^-] = 6.0 \times 10^{-8}$ *M*

$[H^+] = 0.1 + x = 0.1 + 6.0 \times 10^{-8}$ *M*

$= 0.1$ *M*

pH = - log 0.1 = 1.0

Buffered Solutions

Buffer: a solution that contains <u>substantial</u> amounts of <u>both</u> a <u>weak</u> acid and its <u>conjugate</u> base (HA/A$^-$), or a <u>weak</u> base and its <u>conjugate</u> acid (B/BH$^+$).

Acidic Buffers	Basic Buffers
CH_3COOH/CH_3COO^-	NH_3/NH_4^+
HF/F^-	CO_3^{2-}/HCO_3^-
HCN/CN^-	$HPO_4^{2-}/H_2PO_4^-$
~~HCl/Cl^-~~ strong acid	

Important Property of Buffers:

Resist <u>drastic</u> changes in pH upon <u>dilution</u> and upon <u>addition of small</u> amounts of either a strong acid or strong base.

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

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

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

Henderson-Hasselbalch equation

Dilution:

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

$$pH = pK_a + \log \frac{\frac{\text{mol } A^-}{\cancel{V}}}{\frac{\text{mol HA}}{\cancel{V}}}$$

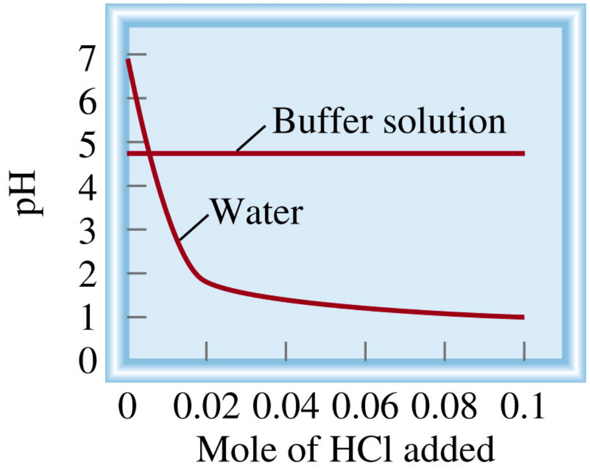
$$pH = pK_a + \log \frac{\text{mol } A^-}{\text{mol HA}}$$

Addition of Strong Acid

In buffer: HA/A$^-$

$$HCl + A^- \rightarrow HA + Cl^-$$

The weak base part of the buffer neutralizes the added acid to form HA.



Addition of Strong Base

In buffer: HA/A^-

$OH^- + HA \rightarrow H_2O + A^-$

The weak acid part of the buffer neutralizes the added base to form A^-.

Buffer Capacity and pH

Buffer Capacity:

Amount of strong acid or strong base the buffer can neutralize without significant change in pH.

Effective pH Range:

The usable range of the buffer

$pH = pK_a \pm 1$

Buffer A: $[HA] = [A^-] = 0.30\ M$

Buffer B: $[HA] = [A^-] = 1.0\ M$

K_a (HA) = 6.8×10^{-4} at 25°C

	pH		
1.0 L solution	no addition	+ 0.10 mol H^+	ΔpH
H_2O	7	1	-6
Buffer A	3.17	2.87	-0.3
Buffer B	3.17	3.08	-0.09

	HA	$\rightleftharpoons$	H^+	+	A^-
i	0.30		0.0		0.30
Δ	-x		+x		+x
eq	0.30 - x		+x		0.30 + x

$$pH = pK_a + \log\frac{[A^-]}{[HA]} = 3.17 + \log\frac{0.30 + \cancel{x}}{0.30 - \cancel{x}}$$

pH = 3.17

In buffer problems:

> Always ignore x $[HA] = [HA]_i$ $[A^-] = [A^-]_i$

> If $[HA] = [A^-]$, then $pH = pK_a$

Addition of 0.10 M H^+

	H^+	+	A^-	$\rightarrow$	HA
i	0.10		0.30		0.30
Δ	-0.10		-0.10		+0.10
fnl	0.00		0.20		0.40

	HA	$\rightleftharpoons$	H^+	+	A^-
i	0.40		0.0		0.20
Δ	-x		+x		+x
eq	0.40 - x		x		0.20 + x

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

$$pH = 3.17 + \log\frac{0.20 + x}{0.40 - x}$$ Ignore x

pH = 2.87

	pH		
1.0 L solution	no addition	+ 0.10 mol H^+	ΔpH
H_2O	7	1	-6
Buffer A	3.17	2.87	-0.3
Buffer B	3.17	3.08	-0.09

Capacity: Buffer B > Buffer A

pH of a buffer solution depends $[A^-]/[HA]$ ratio

Capacity of a buffered solution depends on the amounts (concentration) of [HA] and $[A^-]$.

Buffer Capacity: maximum when $[HA] = [A^-]$ i.e. $pH = pK_a$.

How to Prepare a Buffer?

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

Choose a weak acid whose pK_a close to required pH.

Calculate $[A^-]/[HA]$ required to adjust to required pH.

If both HA and A^- available, mix calculated quantities.

If only HA available:

Generate A^- in solution using strong base.

	HA	+	OH^-	$\rightarrow$	A^-	+	H_2O	
i	0.50		0.20		0.00			
Δ	-0.20		-0.20		+0.20			
Final	0.30		0		0.20			buffer

If only A^- available:

Generate HA in solution using strong acid.

	A^-	+	H^+	$\rightarrow$	HA	
i	0.60		0.30		0.00	
Δ	-0.30		-0.30		+0.30	
Final	0.30		0.00		0.30	buffer

Calculate the pH of a solution containing 0.30 M HCOOH and 0.52 M HCOOK

$K_a = 1.7 \times 10^{-4}$ $pK_a = 3.77$

Mixture of weak acid and conjugate base = buffer

	HCOOH	$\rightleftharpoons$	H^+	+	$HCOO^-$
i	0.30		0.00		0.52
Δ	-x		+x		+x
eq	0.30 - x		x		0.52 + x

	HCOOH	⇌	H^+	+	$HCOO^-$
i	0.30		0.00		0.52
Δ	-x		+x		+x
eq	0.30 - x		+x		0.52 + x

$$pH = pK_a + \log \frac{[HCOO^-]}{[HCOOH]}$$

$$pH = 3.77 + \log \frac{0.52 + \cancel{x}}{0.30 - \cancel{x}}$$

$$pH = 3.77 + \log \frac{0.52}{0.30}$$

pH = 4.01

Calculate the pH of a solution containing 0.30 *M* HCOOH and 0.52 *M* HCOOK after the addition of 0.10 mol HCl gas to 1.0 L of solution

	H^+	+	$HCOO^-$	→	HCOOH
i	0.10		0.52		0.30
Δ	-0.10		-0.10		+0.10
Final	0.00		0.42		0.40

	HCOOH	⇌	H^+	+	$HCOO^-$
i	0.40		0.00		0.42
Δ	-x		+x		+x
eq	0.40 - x		x		0.42 + x

$$pH = pK_a + \log \frac{0.42 + \cancel{x}}{0.40 - \cancel{x}}$$

$$pH = 3.77 + \log \frac{0.42}{0.40}$$

pH = 3.79

Calculate the pH of a 0.30 *M* NH_3/0.36 *M* NH_4Cl buffer system. What is the pH after the addition of 20.0 mL of 0.050 *M* NaOH to 80.0 mL of the buffer solution?

$NH_4^+ (aq) \rightleftharpoons H^+ (aq) + NH_3 (aq)$ $\quad pK_a = 9.25$

$$pH = pK_a + \log \frac{[NH_3]}{[NH_4^+]}$$

$$pH = 9.25 + \log \frac{[0.30]}{[0.36]}$$

pH = 9.17

	NH_4^+ +	OH^- →	H_2O +	NH_3
mmol *i*	0.36 x 80	0.050 x 20		0.30 x 80
mmol *i*	28.8	1.0		24
Δ	- 1.0	- 1.0		+ 1.0
Final	27.8	0.0		25

$$pH = pK_a + \log \frac{\text{mmol } NH_3}{\text{mmol } NH_4^+} = 9.25 + \log \frac{25}{27.8}$$

pH = 9.20 vs 9.17 before addition of base

Calculate the concentration of sodium benzoate that must be present in a 0.20 M solution of benzoic acid to produce pH of 4.00. $K_a = 6.5 \times 10^{-5}$. *Answer:* 0.13 *M*

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

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

$$4.00 = 4.19 + \log \frac{[A^-]}{0.20} \qquad -0.19 = \log \frac{[A^-]}{0.20}$$

$$10^{-0.19} = \frac{[A^-]}{0.20} \qquad [A^-] = 0.13\ M$$

Calculate the pH of a solution formed by mixing 55 mL of 0.20 M $NaHCO_3$ with 65 mL of 0.15 M Na_2CO_3. *Answer*: 10.20

$K_{a1} = 4.3 \times 10^{-7}$; $K_{a2} = 5.6 \times 10^{-11}$.

$NaHCO_3 \rightarrow Na^+ + HCO_3^-$

55 x 0.20 = 11 mmol

buffer

$Na_2CO_3 \rightarrow 2Na^+ + CO_3^{2-}$

65 x 0.15 = 9.75 mmol

$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$ $\quad K_{a2}$

11 mmol $\quad$ 9.75 mmol

$$pH = pK_{a2} + \log \frac{\text{mmol } CO_3^{2-}}{\text{mmol } HCO_3^-}$$

$$pH = 10.25 + \log \frac{9.75}{11}$$

pH = 10.20