Chemistry BC2001x: General Chemistry I

Lecture 14: Tuesday October 27, 2009
Topic: BUFFERS

Pick up (1) graded problem set 6

(2) Chemistry program planning for spring term.

A word to the wise: Come during office hours to pick up old graded problems and (especially) exams. Not doing so (in this and other courses) sends the message to your Professor that you are not interested in learning from your mistakes. All old papers are kept in my office, 811 Altschul.

BUFFERS

A buffer is a solution whose pH changes little when acid or base is added.

Buffers are very important: many processes are very sensitive to pH, so maintaining pH is critical.

Experiments done in biochemistry and biology are almost always done with careful buffering of pH.

Living biological systems are naturally buffered.

But if H^+ or OH^- is added, how does pH remain steady?

You need something to absorb the added acid or base.

BUFFERS

Weak acid HA

$HA \rightleftarrows H^+ + A^-$ $\quad K_a = [H^+][A^-] / [HA]$

Weak Acid	pK_a	Conjugate Base
HOAc	4.76	OAc^-
$H_2PO_4^-$	7.20	HPO_4^{2-}
NH_4^+	9.24	NH_3
HCO_3^-	10.33	CO_3^{2-}

Buffers

Buffer solutions contain both a weak acid and its conjugate base.
(The acid can react with added base, the base with added acid).
The ratio of concentrations of acid and conjugate base is adjusted to fine-tune the pH:

$K_a = [H^+][A^-]/[HA]$ so $[H^+] = K_a\,[HA]/[A^-]$

Take $-\log_{10}$ of both sides: $pH = pK_a - \log [HA]/[A^-]$

Since $\log (x/y) = -\log (y/x)$, $pH = pK_a + \log [A^-]/[HA]$

Sometimes written $pH = pK_a + \log [base]/[acid]$

Henderson-Hasselbalch equation.

I urge you NOT to use HH for buffer problems!

Instead, use the equation in red: why? (1) nothing new to learn, (2) no signs to get wrong, (3) no confusion about *which* acid, *which* base.

Buffers

For a buffer to function well there must be enough of both the acid and its conjugate base. As a rule-of-thumb, we say that the ratio $[HA]/[A^-]$ must be larger than 1/10, smaller than 10/1.

Thus $[H^+]$ and K_a differ by no more than a factor of 10, so the pK_a of the weak acid must be within 1 unit of the desired pH.

$$[H^+] = K_a\,[HA]/[A^-]$$

If $[HA] = [A^-]$	then $[H^+] = K_a$	and $pH = pK_a$
If $[HA] = 10\,[A^-]$	then $[H^+] = 10\,K_a$	and $pH = pK_a - 1$
If $[HA] = [A^-]/10$	then $[H^+] = K_a/10$	and $pH = pK_a + 1$

To make a buffer with a desired pH:

1) Choose an appropriate acid-base pair

2) Determine the ratio of acid to base needed

3) Based on available reagents, prepare solution with these concentrations.

While you sometimes may add HA and A^- directly, one or the other may be generated by reacting excess HA with strong base (e.g. NaOH,) or excess A^- with strong acid (e.g. HCl).