Acids and Bases IV

Silberberg 2nd Ed, Chapter 18 & 19
www.chem.usyd.edu.au/hpage3.htm (login “chem”, passwd “chem@usyd”)
http://www.science.ubc.ca/~chem/tutorials/pH/launch.html
Any questions or requests - email to c.kepert@chem.usyd.edu.au
Revision: Buffers

– Solutions containing both
  a weak acid + its salt  OR  a weak base + its salt

that withstand pH changes when (limited) amounts of acid or base are added.
Revision:
Henderson - Hasselbalch Equation

For a buffer solution, which contains similar concentrations of a conjugate acid/base pair of a weak acid:

\[ K_a = \frac{[H^+][A^-]}{[HA]} \approx \frac{[H^+][\text{added base}]}{[\text{added acid}]} \]

since the dissociation of HA or protonation of A\(^-\) doesn’t lead to a significant change in the concentrations of these species.

Rearranging:

\[ pH \approx pK_a + \log \frac{[\text{added base}]}{[\text{added acid}]} \]
Example

- Find pH of solution which is 0.1 M in NH$_4^+$ and 0.2 M in NH$_3$ where pK$_a$ of NH$_4^+$ = 9.2

$$\text{NH}_3 + \text{H}_2\text{O} \leftrightharpoons \text{NH}_4^+ + \text{OH}^-$$

before: \hspace{1em} 0.2 \hspace{1em} 0.1 \hspace{1em} 0
after: \hspace{1em} 0.2 - x \hspace{1em} 0.1 + x \hspace{1em} x

\[ pK_b = 14 - 9.2 = 4.8 \]

\[ K_b = 10^{-4.8} = \frac{(0.1 + x)x}{0.2 - x} \approx \frac{0.1x}{0.2} \Rightarrow \text{pH} = 9.5 \]

Using Henderson-Hasselbalch:

\[ \text{pH} \approx pK_a + \log \frac{[\text{added base}]}{[\text{added acid}]} \]
Example

Consider a buffer solution with 0.1 M each of sodium acetate (NaA) & acetic acid (HA):

(found earlier that pH = 4.7)

What is the pH when $10^{-3}$ M HCl is added?

Using the Henderson-Hasselbalch Equation:

$$\text{pH} \approx \text{pK}_a + \log \frac{[\text{added base}]}{[\text{added acid}]}$$
Buffer Preparation and Capacity

Buffer Preparation

- If the pH of a required buffer is $pK_a$ of available acid then use equimolar amounts of acid and conjugate base.

- If the required pH differs from the $pK_a$ then use the Henderson-Hasselbalch equation.

Buffer Capacity

Buffer capacity is related to the amount of strong acid or base that can be added without causing significant pH change.

Depends on amount of acid & conjugate base in solution:

- highest when [HA] and [A$^-$] are large

- highest when $[HA] \approx [A^-]$ (most effective buffers have acid/base ratio less than 10 and more than 0.1 $\Rightarrow$ pH range is $\pm 1$)
Buffers in Natural Systems

• Biological systems, e.g. blood, contain buffers: pH control essential because biochemical reactions are very sensitive to pH

• Human blood is slightly basic, pH ≈ 7.39 – 7.45

• In a healthy person, blood pH is never more than 0.2 pH units from its average value

• pH < 7.2, “acidosis”; pH > 7.6, “alkalosis”

• Death if pH < 6.8 or > 7.8
Buffer System in Blood

- “Extracellular” buffer (outside cell)

\[
\begin{align*}
\text{H}^+ + \text{HCO}_3^- & \leftrightarrow \text{H}_2\text{CO}_3 \\
\text{H}_2\text{CO}_3 & \leftrightarrow \text{H}_2\text{O} + \text{CO}_2 (g)
\end{align*}
\]

- Removal of CO\textsubscript{2} shifts equilibria to right, reducing [H\textsuperscript{+}], i.e., raising the pH

- The pH can be reduced by:

\[
\text{H}_2\text{CO}_3 + \text{OH}^- \leftrightarrow \text{HCO}_3^- + \text{H}_2\text{O}
\]
Another Blood Buffer

- Phosphate buffer, present **inside** cells (“intracellular” buffer)
- $\text{H}_2\text{PO}_4^-$ and $\text{HPO}_4^{2-}$:

$$\text{H}_2\text{PO}_4^- \Leftrightarrow \text{H}^+ + \text{HPO}_4^{2-}$$

from $\text{H}_3\text{PO}_4$, a tribasic (triprotic) acid
In the \( \text{H}_3\text{PO}_4 / \text{NaH}_2\text{PO}_4 / \text{Na}_2\text{HPO}_4 / \text{Na}_3\text{PO}_4 \) system, how could you make up a buffer with a pH of 7.40?

**DATA:** \( K_{a1} = 7.2 \times 10^{-3}, \ K_{a2} = 6.3 \times 10^{-8}, \ K_{a3} = 4.2 \times 10^{-13} \)
Titrations

• **Equivalence Point:**
  - when number of moles of added base = original number of moles of acid
    – Strong acid/strong base pH = 7
    – Weak acid/strong base pH > 7
    – Strong acid/weak base pH < 7

• **End Point:**
  - when a colour change in the indicator is observed

⇒ Choose an indicator that changes colour close to the equivalence point
**Indicators**

weak acid ⇌ base

– each form has a different colour

• The pH at which acid → base depends on the pK$_a$ of the indicator
Demonstration: Organic Molecules as Indicators

- Nitrogen and oxygen in a molecule may intensify colour
- If a conjugate base has a different colour to the acid form, the pair may be used as an indicator in titrations
Titrations: Strong Acid / Strong Base

**Table:**

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<th>pH</th>
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<td>12.43</td>
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<td>80.00</td>
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**Graph:**

- **Titration of 40.00 mL of 0.1000 M HCl with 0.1000 M NaOH**
- **Equivalence point at pH 7**

Fig 19.6
Titrations: Weak Acid / Strong Base

- equivalence point pH > 7 (value depends on starting concentrations)
- change is more gradual
Titrations:
Weak Base / Strong Acid

Fig 19.8

- equivalence point pH < 7
  (value depends on starting concentrations)
Titrations:
Strong Base/Weak Acid

Fig 19.9

Titrations of 40.00 mL of 0.1000 \( M \) \( H_2SO_3 \) with 0.1000 \( M \) \( NaOH \)

\[ pK_{a1} = 1.85 \]
\[ pK_{a2} = 7.19 \]

\[ [HSO_3^-] = [SO_3^{2-}] \quad \text{at second equivalence point} \]

\[ [H_2SO_3] = [HSO_3^-] \quad \text{pH = 4.25 at first equivalence point} \]

\[ \text{Buffer region} \]

\( \text{pH} = 9.86 \)`
Question 19 from this week’s problem sheet

– 1.00 mL of acid taken from a lead storage battery was pipetted into a flask. Deionised water and phenolphthalein were added and the solution titrated with 0.50 M NaOH until a pink colour appeared. 12.0 mL were required. What mass (to within 5%) of H$_2$SO$_4$ is present in 1.00 L of the battery acid?