Unit 8: Acids and Bases

Chapter 15
Applications of Aqueous Equilibria
March 4th, 2020

Percent ionization

Salts that produce basic solutions and acidic solutions 14.8 (find your notes)

Alka Seltzer- labette

15.2 Buffer Solutions

Buffering capacity

2017 FRQ Qu 3.
Percent ionization question

\[ \text{HNO}_2(aq) \rightleftharpoons \text{H}^+(aq) + \text{NO}_2^-(aq) \quad K_a = 4.0 \times 10^{-4} \]

On the basis of the information above, what is the approximate percent ionization of HNO\(_2\) in a 1.0 \(M\) HNO\(_2\)(aq) solution?

0.00040%
0.020%
0.040%
2.0%
Percent ionization question

\[ \text{HNO}_2(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{NO}_2^-(\text{aq}) \quad K_\alpha = 4.0 \times 10^{-4} \]

\[
\begin{array}{ccc}
1.0 M & 0 & 0 \\
-x & +x & +x \\
1.0 - x & x & x \\
\end{array}
\]

\[ K_\alpha = 4.0 \times 10^{-4} = [\text{H}^+] [\text{NO}_2^-] = x^2 \quad \text{approx} = x^2 \]

\[ [\text{HNO}_2] \quad 1.0 - x \quad 1.0 \]
Percent ionization question

\[ \text{HNO}_2(aq) \rightleftharpoons \text{H}^+(aq) + \text{NO}_2^-(aq) \quad K_a = 4.0 \times 10^{-4} \]

\[ K_a = 4.0 \times 10^{-4} = [\text{H}^+] [\text{NO}_2^-] = x^2 \quad \text{approx} = x^2 \]

\[
\frac{[\text{HNO}_2]}{1.0-x} = 1.0
\]

\[ \sqrt{4.0 \times 10^{-4}} = x \quad x = [\text{H}^+] = 2.0 \times 10^{-2} \text{ M} \]

\[ \frac{x}{[\text{HNO}_2]} \times 100 = 2.0 \times 10^{-2} \times 100 = 2\% \quad 5\% \text{ approx. is valid} \]
Percent ionization question

\[ \text{HNO}_2(aq) \rightleftharpoons \text{H}^+(aq) + \text{NO}_2^-(aq) \quad K_\alpha=4.0 \times 10^{-4} \]

\[ K_\alpha=4.0 \times 10^{-4} = \frac{[\text{H}^+][\text{NO}_2^-]}{[\text{HNO}_2]} \approx x^2 \]

\[ \sqrt{4.0 \times 10^{-4}} = x \quad x = [\text{H}^+] = 2.0 \times 10^{-2} \text{ M} \]

\[ \frac{x}{[\text{HNO}_2]} \times 100 = 2.0 \times 10^{-2} \times 100 = 2\% \text{, percent of acid dissociated} \]
Percent ionization question

\[
\text{HNO}_2(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{NO}_2^-(\text{aq})
\]

\[
K_a = 4.0 \times 10^{-4} = \frac{[\text{H}^+][\text{NO}_2^-]}{[\text{HNO}_2]} = \frac{x}{1.0}
\]

\[
\sqrt{4.0 \times 10^{-4}} = x \quad x = [\text{H}^+] = 2.0 \times 10^{-2} \text{ M}
\]

\[
\frac{x}{[\text{HNO}_2]} \times 100 = 2.0 \times 10^{-2} \times 100 = 2\% \text{, percent of acid dissociated}
\]

Notice this is the same step as checking the 5% rule is a valid approximation.
Percent ionization question

\[ \text{HNO}_2(aq) \rightleftharpoons \text{H}^+(aq) + \text{NO}_2^-(aq) \quad K_\alpha = 4.0 \times 10^{-4} \]

On the basis of the information above, what is the approximate percent ionization of \( \text{HNO}_2 \) in a 1.0 \( M \) \( \text{HNO}_2(aq) \) solution?

- 0.00040%
- 0.020%
- 0.040%
- 0.40%
- 2.0%
14.8 Salts that produce basic solutions - find your notes

The ionization constant for acetic acid is \(1.8 \times 10^{-5}\); that for hydrocyanic acid is \(4 \times 10^{-10}\). In 0.1 \(M\) solutions of sodium acetate and sodium cyanide, it is true that

A. \([H^+]\) equals \([OH^-]\) in each solution
B. \([H^+]\) exceeds \([OH^-]\) in each solution
C. \([H^+]\) of the sodium acetate solution is less than that of the sodium cyanide solution
D. \([OH^-]\) of the sodium acetate solution is less than that of the sodium cyanide solution
E. \([OH^-]\) for the two solutions is the same
The ionization constant for acetic acid is $1.8 \times 10^{-5}$; that for hydrocyanic acid is $4 \times 10^{-10}$. In 0.1 $M$ solutions of sodium acetate and sodium cyanide, it is true that:

Sodium salts are very soluble so equilibria to the right:

$$C_2H_3O_2Na(aq) \rightleftharpoons Na^+(aq) + C_2H_3O_2^-(aq)$$

$$NaCN(aq) \rightleftharpoons Na^+(aq) + CN^-(aq)$$

$Na^+$ ions have neither acid nor base properties
14.8 Salts that produce basic solutions - find your notes

The ionization constant for acetic acid is $1.8 \times 10^{-5}$; that for hydrocyanic acid is $4 \times 10^{-10}$. In 0.1 M solutions of sodium acetate and sodium cyanide, it is true that:

Sodium salts are very soluble so equilibria to the right:

$$C_2H_3O_2Na(aq) \rightleftharpoons Na^+(aq) + C_2H_3O_2^-(aq)$$

$$NaCN(aq) \rightleftharpoons Na^+(aq) + CN^-(aq)$$

BUT, the ionization constants (or Ka) values for acetic acid and hydrocyanic acid tell us that they are both weak acids (not very ionized) and that the hydrocyanic acid is a weaker acid than the acetic.
14.8 Salts that produce basic solutions - find your notes

The conjugate bases of weak acids, will therefore be strong bases with a significant affinity for a proton (available from water molecules).

\[
\text{C}_2\text{H}_3\text{O}_2^- (aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{C}_2\text{H}_3\text{O}_2\text{H} (aq) + \text{OH}^- (aq)
\]
\[
\text{CN}^- (aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCN} + \text{OH}^- (aq)
\]

Since the HCN was the weakest acid, it will have the strongest conjugate base, and so the second equilibrium will have an equilibrium favoring the RHS most; so highest \([\text{OH}^-]\) at equilibrium.
Salts that produce basic solutions - find your notes

The ionization constant for acetic acid is $1.8 \times 10^{-5}$; that for hydrocyanic acid is $4 \times 10^{-10}$. In 0.1 $M$ solutions of sodium acetate and sodium cyanide, it is true that

A. $[H^+]$ equals $[OH^-]$ in each solution
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C. $[H^+]$ of the sodium acetate solution is less than that of the sodium cyanide solution
D. $[OH^-]$ of the sodium acetate solution is less than that of the sodium cyanide solution
E. $[OH^-]$ for the two solutions is the same
14.8 Salts that produce basic solutions - find your notes

The ionization constant for acetic acid is $1.8 \times 10^{-5}$; that for hydrocyanic acid is $4 \times 10^{-10}$. In $0.1 \text{ M}$ solutions of sodium acetate and sodium cyanide, it is true that

A. $[\text{H}^+]$ equals $[\text{OH}^-]$ in each solution
B. $[\text{H}^+]$ exceeds $[\text{OH}^-]$ in each solution
C. $[\text{H}^+]$ of the sodium acetate solution is less than that of the sodium cyanide solution
D. $[\text{OH}^-]$ of the sodium acetate solution is less than that of the sodium cyanide solution
E. $[\text{OH}^-]$ for the two solutions is the same
14.8 Salts that produce acidic solutions - find your notes

Samples of NaF(s) and NH₄Cl(s) are dissolved in separate beakers that each contain 100mL of water. One of the salts produces a slightly acidic solution.

Which one and why?

“In general, salts in which the anion (−ve) is NOT a base and the cation (+ve) is the conjugate acid of a weak base produce acidic solutions.”
14.8 Salts that produce acidic solutions - find your notes

Samples of NaF(s) and NH₄Cl(s) are dissolved in separate beakers that each contain 100mL of water. One of the salts produces a slightly acidic solution.

\[ \text{NH}_4^+ (aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_3(aq) + \text{H}_3\text{O}^+ (aq) \]

“In general, salts in which the anion (-ve) is NOT a base and the cation (+ve) is the conjugate acid of a weak base produce acidic solutions.”
14.8 Salts that produce acidic solutions - find your notes

\[
\text{Al(H}_2\text{O)}_6^{3+} \text{(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{Al(OH)(H}_2\text{O)}_5^{2+} + \text{H}_3\text{O}^+ \text{(aq)}
\]

Also look out for salts with a highly charged metal ion as above. The 3+ charge on the aluminum ion polarizes (distorts in one direction the electrons in the bonds) the O-H bonds in the attached water molecules, making the hydrogens in the water molecules more acidic than those in free water molecules. Typically, the higher the charge on the metal ion, the stronger the acidity of the hydrated ion.
Alka-seltzer labette  20 mins
15.2 Buffered Solutions

A buffered solution is one that resists a change in the pH when either hydroxide ions or protons are added. (Alka-seltzer label)

Eg. Our blood - can absorb acids and bases produced in biological reactions without changing pH. Constant pH necessary because cells can only survive in a narrow pH range.
Types of buffered solutions

Weak acid and its salt (eg. HF and NaF)

Weak base and its salt (eg. NH$_3$ and NH$_4$Cl)
pH of a buffered solution (1)

0.5 M acetic acid (HC$_2$H$_3$O$_2$, $K_a = 1.8 \times 10^{-5}$)

0.5 M sodium acetate (NaC$_2$H$_3$O$_2$)

Major species in the solution are:

HC$_2$H$_3$O$_2$(aq), Na$^+$ (aq), C$_2$H$_3$O$_2^-$ (aq) and H$_2$O

Weak acid, neither acid nor base, very weak, Base, acid or base

(quickly draw the structural formula for acetic acid - see where the acidic proton is - attached to an O)
\[ \text{HC}_2\text{H}_3\text{O}_2\text{(aq)} \rightleftharpoons \text{H}^+ \text{(aq)} + \text{C}_2\text{H}_3\text{O}_2^- \text{(aq)} \]

Initial 0.50 0 0.50 (from salt)

Change -x x x

Equilibrium 0.50 - x x 0.50 + x

\[ K_a = 1.8 \times 10^{-5} = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} \approx \frac{(x)(0.5 + x)}{0.5 - x} \approx x(0.5) \]

(assuming the x is small compared with \([\text{HA}]_0\), valid by 5% rule)

Thus \[ x \approx 1.8 \times 10^{-5} \]
So $[H^+] = x = 1.8 \times 10^{-5}$ M

$pH = -\log(1.8 \times 10^{-5})$

$pH = 4.74$
So $[H^+] = x = 1.8 \times 10^{-5}$ M

$pH = -\log(1.8 \times 10^{-5})$

$pH = 4.74$

Now calculate the change in pH that occurs when 0.010 mole of solid NaOH is added to 1.0L of the buffered solution above.

NaOH will be completely dissociated, so the major species will be:

$H_2C_2H_3O_2(aq) \quad Na^+(aq) \quad OH^-(aq) \quad C_2H_3O_2^-(aq) \quad$ and $H_2O$
So \([H^+] = x = 1.8 \times 10^{-5}\) M

\[
pH = -\log(1.8 \times 10^{-5})
\]

\[pH = 4.74\]

Now calculate the change in pH that occurs when 0.010 mole of solid NaOH is added to 1.0L of the buffered solution above.

NaOH will be completely dissociated, so the major species will be:

\(\text{HC}_2\text{H}_3\text{O}_2(\text{aq})\)  \(\text{Na}^+(\text{aq})\)  \(\text{OH}-(\text{aq})\)  \(\text{C}_2\text{H}_3\text{O}_2^-(\text{aq})\)  and \(\text{H}_2\text{O}\)

Source of protons  strong base
\[ \text{HC}_2\text{H}_3\text{O}_2\text{(aq)} + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O(l)} + \text{C}_2\text{H}_3\text{O}_2^-\text{(aq)} \]

The hydroxide ion is such a strong base (proton acceptor) that the reaction will proceed essentially to completion - or until all the hydroxide ions are consumed.

So assume this reaction goes to completion and deal with it first and then carry out the equilibrium calculations.
Stoichiometry problem

\[ \text{HC}_2\text{H}_3\text{O}_2(aq) + \text{OH}^-(aq) \rightarrow \text{H}_2\text{O}(l) + \text{C}_2\text{H}_3\text{O}_2^-(aq) \]

\[ 1.0 \text{ L} \times 0.50\text{mol/L} = 0.5\text{mol} \]
Stoichiometry problem

\[ \text{HC}_2\text{H}_3\text{O}_2(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O(l)} + \text{C}_2\text{H}_3\text{O}_2^-(\text{aq}) \]

1.0 L \times 0.50\text{M} = 0.5\text{mol} \quad \text{1.0 L \times 0.50\text{M} = 0.5\text{mol}}

0.01 \text{ mol}
Stoichiometry problem

\[ \text{HC}_2\text{H}_3\text{O}_2(aq) + \text{OH}^-(aq) \rightarrow \text{H}_2\text{O}(l) + \text{C}_2\text{H}_3\text{O}_2^-(aq) \]

\[ 1.0 \text{ L} \times 0.50\text{M} = 0.5\text{mol} \quad 1.0 \text{ L} \times 0.50\text{M} = 0.5\text{mol} \]

\[ 0.01 \text{ mol} \]

After reaction

\[ 0.5 \text{ mol} - 0.01 \text{ mol} \quad (\text{OH}^- \text{ all gone}) \quad 0.5 \text{ mol} + 0.01\text{mol} \]

\[ 0.49\text{mol} \quad 0.51 \text{ mol} \]
Now treat the Equilibrium part of the problem

$$\text{HC}_2\text{H}_3\text{O}_2(\text{aq}) + \text{OH}-(\text{aq}) \rightarrow \text{H}_2\text{O(1)} + \text{C}_2\text{H}_3\text{O}_2^-(\text{aq})$$

After this reaction is complete

The major species in solution are

$$\text{HC}_2\text{H}_3\text{O}_2, \text{Na}^+, \text{C}_2\text{H}_3\text{O}_2^- \text{ and } \text{H}_2\text{O}$$

Dominant equilibrium involves dissociation of acetic acid
\[ \text{HC}_2\text{H}_3\text{O}_2(aq) \rightleftharpoons \text{H}^+ (aq) + \text{C}_2\text{H}_3\text{O}_2^- (aq) \]

Initial $\begin{array}{c} 0.49 \\ 0 \\ 0.51 \end{array}$

Change $\begin{array}{c} -x \\ x \\ x \end{array}$

Equilibrium $\begin{array}{c} 0.49 - x \\ x \\ 0.51 + x \end{array}$

\[ K_a = 1.8 \times 10^{-5} = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} \approx \frac{(x)(0.51 + x)}{x(0.51)} \frac{0.49 - x}{0.49} \]

(assuming the $x$ is small compared with $[\text{HA}]_0$, valid by 5% rule)

Thus $x \approx 1.7 \times 10^{-5}$
So $[H+] = x = 1.7 \times 10^{-5}$ M

$pH = -\log(1.7 \times 10^{-5})$

$pH = 4.76$

The change in pH produced by the addition of 0.01 mole of OH$^-$ to this buffered solution is then

$4.76 - 4.74 = 0.02$

The pH has increased by only 0.02 pH units.

Now compare that to what happens when 0.01 mole of solid NaOH is added to 1.0L of water to give 0.01M NaOH.
\[ [\text{OH}^-] = 0.01 \text{ M} \]
\[ [\text{H}^+] = \text{Kw} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-2}} = 1.0 \times 10^{-12} \]

\[ \text{pH} = 12.00 \]

Change in pH is from pure water to this
\[ 12.00 - 7.00 = 5.00 \]

pH has gone up by 5 pH units.

**Notice how well the buffer resists a change in pH compared to water.**
\[ K_a = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = \frac{[H^+][A^-]}{[HA]} \]

We often know the concentration of the acid and its conjugate base so

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

will be helpful
Then taking negative logs we can generate another useful form

\[- \log[H^+] = - \log Ka - \log \frac{[HA]}{[A^-]}\]

\[\text{pH} = pKa + \log \frac{[A^-]}{[HA]}\]

Believe it or not, this is called the Henderson-Hasselbach Equation (Topic 8.9)
Then

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

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

If we know the ratio of the concentrations of the Acid and its conjugate base, then we can find the pH of the buffered solution.
Then

\[-\log[H^+] = -\log Ka - \log \frac{[HA]}{[A^-]}\]

\[\text{pH} = pKa + \log \frac{[A^-]}{[HA]}\]

Or stated another way, the pH of the buffered solution will depend on the \([A^-]\) to \([HA]\) ratio. When this ratio is least affected by added protons or hydroxide ions, the solution is most resistant to change in pH.
Then

\[-\log[H^+] = -\log Ka - \log \frac{[HA]}{[A^-]}\]

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

For the most effective buffering we want to avoid large changes in the [A-] to [HA] ratio. This will be when their concentrations are equal.
Then

\[-\log[H^+] = -\log Ka - \log \left[ HA \right] \]

For most effective buffering:

\[pH = pKa + \log (1)\]

\[pH = pKa\]

For the most effective buffering, we want to avoid large changes in the [A-] to [HA] ratio. This will be when their concentrations are equal.
Then

\[-\log[H^+] = -\log Ka - \log \frac{[HA]}{[A^-]}\]

For most effective buffering:

\[\text{pH} = \text{pKa} + \log (1)\]

\[\text{pH} = \text{pKa}\]

So the pKa of the weak acid to be used in the buffer should be as close as possible to the desired pH.
Note that to use
\[ \text{pH} = \text{pKa} + \log \left( \frac{[A^-]}{[HA]} \right) \]

We assume that the equilibrium concentrations of A- and HA are equal to the initial concentrations (the amount of acid that dissociates is small compared to the initial concentration of the acid). Since the initial concentrations of HA and A- are relatively large in a buffered solution, this is generally acceptable.
15.3 Buffering Capacity

represents amount of protons or hydroxide ions the buffer can absorb without a significant change in pH.

pH of a buffered solution is determined by the ratio $[\text{A-}]/[\text{HA}]$.

The capacity of a buffered solution is determined by the magnitudes of $[\text{HA}]$ and $[\text{A-}]$ - increasing the concentration of the buffer components (while keeping the ratio of these concentrations constant) keeps the pH of the buffer the same but increases the capacity of the buffer to neutralize added acid or base.
When a buffer has more conjugate acid than base, it has greater buffer capacity for addition of base than acid.

When a buffer has more conjugate base than acid, it has greater buffer capacity for addition of acid than base.
AP Classroom 8.4 Quiz Acids, bases and buffers
FRQ 2017 Qu. 3.

\[ \text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{NO}(\text{g}) \]

At high temperatures \( \text{N}_2(\text{g}) \) and \( \text{O}_2(\text{g}) \) can react to produce nitrogen monoxide, \( \text{NO}(\text{g}) \), as represented by the equation above.

a) Write the expression for the equilibrium constant, \( K_p \), for the forward reaction.
FRQ 2017 Qu. 3.

\[ \text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{NO}(\text{g}) \]

a) Write the expression for the equilibrium constant, \( K_p \), for the forward reaction.

\[ K_p = \frac{(P_{\text{NO}})^2}{(P_{\text{N}_2})(P_{\text{O}_2})} \]
b) A student injects \(N_2\) and \(O_2\) into a previously evacuated, rigid vessel and raises the temperature of the vessel to 2000\(^\circ\)C. At this temperature the initial partial pressures of \(N_2\) and \(O_2\) are 6.01 atm and 1.61 atm respectively. The system is allowed to reach equilibrium. The partial pressure of NO at equilibrium is 0.122 atm. Calculate the value of \(K_p\).

\[
N_2(g) + O_2(g) \rightleftharpoons 2 \text{ NO(g)}
\]

<table>
<thead>
<tr>
<th></th>
<th>(6.01) atm</th>
<th>1.61 atm</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>-x</td>
<td>-x</td>
<td>+ 2x</td>
</tr>
<tr>
<td>E</td>
<td>6.01 - x</td>
<td>1.61 - x</td>
<td>0.122 atm</td>
</tr>
</tbody>
</table>
\[
\begin{align*}
\text{N}_2(g) + \text{O}_2(g) & \rightleftharpoons 2 \text{NO}(g) \\
\text{I} & \quad 6.01 \text{ atm} \quad 1.61 \text{ atm} \quad 0 \\
\text{C} & \quad -x \quad -x \quad + 2x \\
\text{E} & \quad 6.01 - x \quad 1.61 - x \quad 0.122 \text{ atm} \\
2x &= 0.122 \text{ atm} \text{ hence } x = 0.061 \text{ atm} \\
\text{At equilibrium P nitrogen} &= (6.01 - 0.061) = 5.95 \text{ atm} \\
\text{P oxygen} &= 1.61 - 0.061 = 1.55 \text{ atm}
\end{align*}
\]
\[
\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{NO}(g)
\]

At equilibrium P nitrogen = (6.01 - 0.061) = 5.95 atm

P oxygen = 1.61 - 0.061 = 1.55 atm

\[
K_p = \frac{(0.122)^2}{(5.95)(1.55)}
\]

= 0.00161

Finish rest of the question for next class meeting.