Aqueous Equilibrium 1

CHEM 102

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Mixed Solutions

- Most (not all) of Chapter 17 of your text deals with how various solutions of a single acid or base affect the pH.
- Chapter 18 deals mixtures of acids, bases, and salts.
- A key concept to keep in mind involves conjugate acids and bases.

Acid plus Salt w/conjugate Base

Example: what is the pH of a solution that is 0.1M in HF in HF and 0.05 M NaF? For hydrofluoric acid, pK_a = 3.46.

$$HF(aq) + H_2O \rightleftharpoons H_3O^+(aq) + F^-(aq)$$

initial	0.1 M	0	0.05 M
equil.	0.1 – x	x	0.05 + x
Ans.	x = 6.79 × 10^{-4} (exact)	6.93 × 10^{-4} (approx)	

Conclusions from last example

- HF is an acid that is only moderately weak, but in the presence of added F^- the net dissociation of HF is strongly suppressed.
- The 2% error in the approximate answer will only get smaller for this kind of situation with weaker acids.

The Common Ion Effect

- In chapter 17, the behavior of weak acids and bases are examined in terms of equilibrium involving conjugate pairs.
- The pH of a solution was found via K_a or K_b.
- In the last example, we saw what happens if you start with a solution of acid that is mixed with a solution of its conjugate base.
- The change of pH when a significant amount of conjugate base is present is an example of the "Common Ion Effect".

The Common Ion Effect – Another Example

What is the pH of a solution made by adding 0.10 mol NH_4Cl(s) to 0.25 M NH_3(aq) to yield 1.0 L of solution?

$$NH_3(aq) + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

NH_4^+ is an ion that is COMMON to the equilibrium.

Le Chatelier predicts that the equilibrium will shift to the *left* to reduce the disturbance.

This results in a reduciton of the hydroxide ion concentration, which will lower the pH.

Hint: *NH_4^+ is an acid!*

Controlling pH: Buffer Solutions

HCl is added to pure water.

HCl is added to a solution of a weak acid $H_2PO_4^-$ and its conjugate base HPO_4^{2-}.

Controlling pH: Buffer Solutions

- A "Buffer Solution" is an example of the common ion effect.
- From an acid/base standpoint, buffers are solutions that resist changes to pH.
- A buffer solution requires two components that do not react with one another:

1. An acid capable of consuming OH^-
2. The acid's conjugate base capable of consuming H_3O^+

Controlling pH: Buffer Solutions

Consider the acetic acid / acetate buffer system.

- The ability for the acid to consume OH^- is seen from the reverse of the base hydrolysis:

$$CH_3CO_2^-(aq) + H_2O(l) \rightleftharpoons CH_3CO_2H(aq) + OH^-(aq)$$

$$K_b = 5.6 \times 10^{-10}$$

- K_{rev} is >> 1, indicating that the reaction is product favored.

$$K_{rev} = \frac{1}{K_b} = 1.8 \times 10^9$$

- An hydroxide added will immediately react with the acid so long as it is present.

Controlling pH: Buffer Solutions

Consider the acetic acid / acetate buffer system.

- Similarly, the conjugate base (acetate) is readily capable of consuming H_3O^+
- K_{rev} is >> 1, indicating that the reaction is product favored.

$$K_{rev} = \frac{1}{K_a} = 5.6 \times 10^4$$

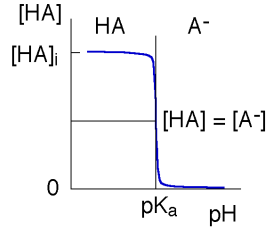
- An hydronium ion added will immediately react wit the acid so long as it is present.

Buffer Solutions

Problem:

What is the pH of a buffer that has $[CH_3CO_2H]$ = 0.700 M and $[CH_3CO_2^-]$ = 0.600 M?

The buffer effect



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

When appreciable amounts of both HA and A^- are present, pH will be near pK_a of the acid.

Henderson-Hasselbalch Eqn.

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \Rightarrow [H_3O^+] = K_a \times \frac{[HA]}{[A^-]}$$

take "-log" of both sides of the right-hand eqn,

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

When appreciable amounts of both HA and A^- are present, $[HA] \approx [HA]_{initial}$, $[A^-] \approx [A^-]_{initial}$

$$pH \approx pK_a + \log\frac{[A^-]_{initial}}{[HA]_{initial}}$$

Henderson-Hasselbalch Eqn.

- Remember where the eqn. comes from or how it must work, otherwise you're likely to get the logarithm mixed up!
- Alternatively, just get used to playing with the equilibrium const. expression, and don't try to memorize "H-H" eqn. at all.

Base buffers

- Work in a manner analogous to the acid case, e.g., what is the pH of a solution that is 0.15M in NH_3 and 0.10 M NH_4Cl? For NH_3, $pK_b = 4.74$.

$$NH_3(aq) + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

initial	0.15 M	0.10 M	0
equil.	0.15 - x	0.1 + x	x

Ans. $x = [OH^-] = 2.73 \times 10^{-5}$ (approx = exact to 3 digits)

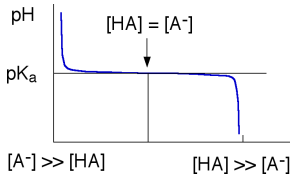
Buffer effect, "H-H" for bases

$$B + H_2O \rightleftharpoons BH^+(aq) + OH^-(aq)$$

$$pOH \approx pK_b + \log\frac{[BH^+]_{initial}}{[B]_{initial}}$$

Alternatively, use the acid equation and the pK_a of the conjugate acid: $pK_a = 14 - pK_b$

How a buffer works



pH changes relatively slowly over a fairly wide range of concentration ratios $[HA]:[A^-]$.

How to prepare a buffer

Composition	pK_a
Acid buffers	
$CH_3COOH/CH_3CO_2^-$	4.75
HNO_2/NO_2^-	3.37
$HClO_2/ClO_2^-$	2.00
Base buffers	
NH_4^+/NH_3	9.25
$(CH_3)_3NH^+/(CH_3)_3N$	9.81
$H_2PO_4^-/HPO_4^{2-}$	7.21

(1) Find an acid (or conjugate acid) with a pK_a within ~ 0.5 of the desired pH.

(2) Adjust HA to A^- ratio.

Example: How do we prepare a buffer for pH = 5?

Buffer Capacity

Compare two cases:

(1) Add 50 ml of 0.1M HCl to 50 ml of pure H_2O. Find final pH.

(2) Add 50 ml of 0.1M HCl to 50 ml of a buffer solution that is 0.2 M in CH_3COOH and 0.2 M in $Na[CH_3COO]$. Find initial and final pH.

Preparing a Buffer – Another Example

- Suppose you wish to prepare a buffer a solution at pH of 4.30. How would you proceed?

Preparing a Buffer

Buffer prepared from

8.4 g $NaHCO_3$

weak acid

16.0 g Na_2CO_3

conjugate base

What is the pH?

Adding an Acid to a Buffer

What is the pH when 1.00 mL of 1.00 M HCl is added to:

a) 1.00 L of pure water

b) 1.00 L of buffer that has $[CH_3CO_2H] = 0.700$ M and $[CH_3CO_2^-] = 0.600$ M (pH = 4.68)

Commercial Buffers

- The solid acid and conjugate base in the packet are mixed with water to give the specified pH.
- Note that the quantity of water does not affect the pH of the buffer.