Notes: Chapter 18

Tuesday, January 09, 2007
11:39 AM

Chapter 18
Acid-Base Equilibria

Homework:

Auto Ionization of Water

$H_2O + H_2O \text{--->} H_3O^+ + OH^-$

Note: For purposes of brevity the hydronium ion, H_3O^+ , will be represented by H^+. In neutral water there are equal amounts of H^+ and OH^-. The quantities of H+ and OH- in the solution are equal at a concentration of $1x10^{-7}$ M each. The equilibrium constant for this is:

$K_{eq} = [H^+][OH^-]/[H_2O]$

where the concentration of water is 55.5 M and is essentially a constant. You should verify that the concentration of water in water is 55.5M. If we include the $[H_2O]$ constant into the K_{eq}, the constant becomes K_w or the autoionization constant for water and has the value of $1x10^{-14}$, that is: $K_w=[H^+][OH^-]$

In solutions of acids and bases the equilibrium of the autoionization is shifted to the left when either an acid or base are added to water.

Addition of a base increases the concentration of hydroxide and decreases the concentration of hydronium. Addition of an acid increases the concentration of hydronium and decreases the concentration of the hydroxide ion. A system used to measure the concentration of hydronium ion is called pH.

$pH = - \log[H^+]$

or

$[H^+] = 10^{-pH}$

From the point of view of the hydroxide:

$pOH = - \log[OH^-]$

or

$[OH^-] = 10^{-pOH}$

$[H^+]$	pH	$[OH^-]$	pOH	K_w
$1x10^{+1}$	-1	$1x10^{-15}$	15	$1x10^{-14}$
$1x10^{-0}$	0	$1x10^{-14}$	14	$1x10^{-14}$
$1x10^{-1}$	1	$1x10^{-13}$	13	$1x10^{-14}$
$1x10^{-2}$	2	$1x10^{-12}$	12	$1x10^{-14}$
$1x10^{-3}$	3	$1x10^{-11}$	11	$1x10^{-14}$
$1x10^{-4}$	4	$1x10^{-10}$	10	$1x10^{-14}$
$1x10^{-5}$	5	$1x10^{-9}$	9	$1x10^{-14}$
$1x10^{-6}$	6	$1x10^{-8}$	8	$1x10^{-14}$
$1x10^{-7}$	7	$1x10^{-7}$	7	$1x10^{-14}$
$1x10^{-8}$	8	$1x10^{-6}$	6	$1x10^{-14}$
$1x10^{-9}$	9	$1x10^{-5}$	5	$1x10^{-14}$
$1x10^{-10}$	10	$1x10^{-4}$	4	$1x10^{-14}$
$1x10^{-11}$	11	$1x10^{-3}$	3	$1x10^{-14}$
$1x10^{-12}$	12	$1x10^{-2}$	2	$1x10^{-14}$
$1x10^{-13}$	13	$1x10^{-1}$	1	$1x10^{-14}$
$1x10^{-14}$	14	$1x10^{-0}$	0	$1x10^{-14}$
$1x10^{-15}$	15	$1x10^{+1}$	-1	$1x10^{-14}$

From this table it is clear that

$pH + pOH = 14$ and $K_w = [H^+][OH^-] = 1x10^{-14}$.

Solutions of Strong Acids and Bases

Strong acids and bases are 100% ionized. The concentration of H^+ is always equal to the concentration of strong acid present in a solution and the concentration of OH^- is always equal to the concentration of strong base present in solution.

Problem:
Calculate the pH and pOH for a 2M solution of HCl.

Problem:
Calculate the pH, and pOH for a 6M solution of NaOH.

Solutions of Weak Acids and Bases

Weak acids and bases are only partially dissociated and give comparatively low concentrations of H^+ and OH^- respectively.

When weak acid dissociates:

$HX \leftrightarrow H^+ + X^-$

we can write an equilibrium constant for the dissociation.

$K_a = [H^+][X^-]/[HX]$

These equilibrium constants can be found in the book or in references such as the Handbook of Chemistry and Physics, CRC Press.

Problem:
Calculate the pH of a 1M solution of HOAc. $K_a = 1.8x10^{-5}$

Calculate the pH of a 1M solution of NH_3 $K_b=1.8x10^{-5}$

Polyprotic Acids

A polyprotic acid is an acid with more than one acidic hydrogen; H_2SO_4, H_3PO_4 and H_2CO_3 are three common examples.

The dissociation of these acids takes place in a stepwise fashion and each step has its own K value; K_{a1}, K_{a2}, and K_{a3} for the first three sequential dissociations.

Consider the dissociation of phosphoric acid:

H_3PO_4 ---> $H^+ + H_2PO_4^-$ $K_{a1} = 7.2x10^{-3}$

$H_2PO_4^-$ ---> $H^+ + HPO_4^{-2}$ $K_{a2} = 6.3x10^{-8}$

HPO_4^{-2} ---> $H^+ + PO_4^{-3}$ $K_{a3} = 4.2x10^{-13}$

We can see that the successive dissociations of the acid have successively smaller K values (by about 10^{-5} for each successive dissociation).
Problem:
Calculate the concentration of PO_4^{-3} in a 1 M solution of phosphoric acid.

Is there an easier way?

Simply add the reactions and you get

$K_{a1,2,3} = K_{a1}K_{a2}K_{a3} = [H^+]^3[PO_4^{-3}]/[H_3PO_4]$

IONS OF WEAK ACIDS AND BASES

From the Brønstead Lowrey theory of acids and bases, we know that an acid gives a conjugate base and a base gives a conjugate acid. Salts of weak acids and bases have their conjugate effect on solutions made from them.
For example: Sodium acetate contains the acetate ion, which is the conjugate base of acetic acid. We therefore expect acetate to have less acidic character than acetic acid (which is another way of saying more basic character). The acetate ion reacts with water to form acetic acid and hydroxide.

$OAc^- + H_2O \text{--->} HOAc + OH^-$

The equilibrium expression for this is :
$Kb = [OH^-][HOAc]/[OAc^-]$

The question is how can we find the K_b for this reaction, it is not published data.

If we examine the K_w for water and the K_a for the acid, it is easy to see how we could derive the numeric quantity for the K_b of the ion of a weak base.

Problem:
Calculate the pH of a solution made by adding 1.00 moles of NaOAc to 500 ml of water.

The same goes for the ions of weak bases:

Problem:
Calculate the pH of a solution made by adding 2 M of NH_4Cl to 500 ml of water.

Problem:
Calculate the product of the $K_a x K_b$ for any acid-conjugate base system.

Review the Brønstead-Lowrey theory and Lewis Acid-Base Theory.

Pasted from <http://fp.academic.venturacollege.edu/doliver/chem1b/notes/Chap18new.htm>