Review of Simple Acid/Base Properties

Where HA is used to represent any generic Bronsted acid:

$$HA\,(aq) \quad + \quad H_2O(l) \quad ========== \quad H_3O^+(aq) \quad + \quad A^-(aq)$$

$$K_a = \{[H_3O^+][A^-]/[HA]\}$$

STRONG ACIDS completely dissociate and therefore have very large values of K_a. Examples include HCl, HNO_3, $HClO_4$ and H_2SO_4. The conjugate base of strong acids are very weak bases. Therefore, Cl^-, NO_3^-, ClO_4^- and SO_4^{2-} are examples of weak bases and are said to be neutral anions.

WEAK ACIDS remain largely undissociated and have relatively small values of K_a. Examples include HF, HNO_2, HOCl and H_2S. The conjugate bases of weak acids are relatively strong bases. Therefore, F^-, NO_2^-, OCl^- and S^{2-} are examples of basic anions.

STRONG BASES are quantitatively converted into hydroxide ion in aqueous solution.
NaOH, KOH, $Ca(OH)_2$ and $Mg(OH)_2$ are examples of strong bases, although the latter two have limited solubility in water.

WEAK BASES partially react with water to produce hydroxide ions.

$$NH_3(aq) \quad + \quad H_2O(l) \quad ========== \quad NH_4^+(aq) \quad + \quad OH^-(aq)$$

$$K_b = \{[NH_4^+][OH^-]/[NH_3]\}$$

Water is amphoteric . It can both donate and accept a proton, thus it has the ability to act either as an acid or a base.

$$H_2O \quad + \quad H_2O \quad ======== \quad H_3O^+ \quad + \quad OH^-$$

$$K_w = [H_3O^+][OH^-] \qquad K_w = 1.0 \times 10^{-14} \text{ at } 25^oC$$

In general: K_b (base) = K_w/K_a(conjugate acid) and K_a(acid) = K_w/ K_b(conjugate base)

Thus, $K_a\,(NH_4^+) = K_w/K_b(NH_3)$

$pH = -\log a_{H+} \approx -\log [H^+]$

In general: $pH + pOH = pK_w$
In pure water at 25^oC; $pH = pOH = 7.0$

Rules for Predicting the pH of Aqueous Solutions

In general: Aqueous solutions of covalent oxides are acidic (i.e., CO_2, SO_2, SO_3 and NO_2)
Note: rainwater is naturally acidic (pH ~ 5.8 - 6.2) due to the presence of atmospheric CO_2

Aqueous solutions of ionic oxides are basic (i.e., CaO, MgO and K_2O)

Neutral ions: All Group 1A and 2A cations (e.g., Na^+, Ca^{2+} etc)
Anions which are conjugates of strong acids (Cl^-, NO_3^- etc)

Acids: Uncharged strong or weak acids (e.g., HCl, H_2CO_3 etc.)
Metal cations other than those of Groups 1A nad 2A
Cationic conjugates of nitrogen bases (e.g., NH_4^+, C_5H_5NH+ etc)
The two anions HSO_4^- and $H_2PO_4^-$

Bases: All anions not listed above
Uncharged nitrogen bases, such as NH_3, C_5H_5N etc

Sample Exercises:

1. State whether the following aqueous solutions are expected to be acidic, basic or neutral

a) $CuCl_2$
b) Na_3PO_4
c) NH_4Br
d) MgS

2. Calculate the concentration of ammonium chloride in a solution whose pH is measured as 5.13, given that the K_a for the ammonium ion is 5.6×10^{-10} **M**.

3. Calculate the value of K_b for cyanide ion, given that a 1.6×10^{-2} **M** solution of potassium cyanide has a pH of 10.76. (Compare your answer with that obtained using the K_a for HCN).

4. Commercial bleach is a 5% (wt/wt) solution of sodium hypochlorite. The value of K_a for hypochlorous acid (HOCl) is 2.8×10^{-8}.

a) Do you expect bleach to be acidic or basic?
b) Calculate the K_b of hypochlorite ion.
c) Calculate the pH of a 5% bleach solution.

Solutions:

1. Using the rules for predicting the pH of aqueous solutions.
a) acidic (Cu^{2+} metal cations other than alkali and alkali earth metals are slightly acidic, Cl^- is neutral)
b) basic (Na^+ is an alkali metal, therefore neutral and PO_4^{3-} is the conjugate base of HPO_4^{2-}, which is a weak acid. Therefore the solution is basic)
c) acidic (ammonium ion is acidic, chloride is neutral)
d) basic (Mg^{2+} is an alkali earth metal, therefore neutral and S^{2-} is the conjugate base of a weak acid HS^-. Therefore the solution is basic)

2. The relevant equilibria are potentially:

$NH_4^+ \;+\; H_2O \;====\; NH_3 \;+\; H_3O^+$ $\qquad K_a = 5.6 \times 10^{-10}$

$Cl^- \;+\; H_2O \;\leftarrow\; HCl \;+\; OH^-$

$2\,H_2O \;====\; H_3O^+ \;+\; OH^-$ $\qquad K_w = 1.0 \times 10^{-14}$

Using the first and last of these, we can set up an equilibrium table as follows.
Where $x = 7.31 \times 10^{-6}$, since pH = 5.13, the $[H^+] = 10^{-5.13} = 7.41 \times 10^{-6}$ M

	NH_4^{+-} + H_2O ====	NH_3 +	H_3O^+	K_a
I	i	0	10^{-7}	
C	$-x$	x	x	
E	$i - x$	x	$x + 10^{-7}$	
	$i - 7.31 \times 10^{-6}$	7.31×10^{-6}	7.41×10^{-6}	

Using the expression for $K_a(NH_4^+)$
$K_a = [NH_3]\,[H_3O^+]/[NH_4^+] = 5.6 \times 10^{-10}$
So, $(7.41 \times 10^{-6})\,(7.31 \times 10^{-6})/(i - 7.31 \times 10^{-6}) = 5.6 \times 10^{-10}$
Solving for i yields, $i = 0.0097$ M

(this is the initial concentration of NH_4^+, which corresponds to the number of moles of NH_4Cl dissolved per liter. In grams, this is 0.52 g/L)

3. The potentially relevant equilbria are:

$CN^- + H_2O$ ==== $HCN + OH^-$ $K_b(CN^-)$ {= $K_w/K_a(HCN)$}

$K^+ + H_2O \leftarrow KOH + H^+$

$2\ H_2O$ ==== $H_3O^+ + OH^-$ $K_w = 1.0 \times 10^{-14}$

Using the first and last of these, we can set up an equilibrium table as follows.
Where $x = 5.75 \times 10^{-4}$ M, since pH = 10.76, the pOH = 3.24 and $[OH^-] = 10^{-3.24} = 5.75 \times 10^{-4}$ M,

	CN^- + H_2O ====	HCN +	OH^-	K_b
I	1.6×10^{-2} M	0	10^{-7}	
C	$-x$	x	x	
	-5.75×10^{-4} M	5.75×10^{-4}	5.75×10^{-4}	
E	$1.6 \times 10^{-2} - 5.75 \times 10^{-4}$	5.75×10^{-4}	$10^{-7} + 5.75 \times 10^{-4}$	
	1.54×10^{-2} M	5.75×10^{-4}	$\tilde{}5.75 \times 10^{-4}$	

$K_b = [HCN]\,[OH^-]/[CN^-] = (5.75 \times 10^{-4})^2/(1.54 \times 10^{-2}) = 2.1 \times 10^{-5}$

(From reference tables of K_a values $K_a(HCN) = 4.9 \times 10^{-10}$, so $K_b(CN^-) = K_w/K_a = 2.0 \times 10^{-5}$)

4. a) Sodium hypochlorite is basic since OCl^- is the conjugate base of a weak acid.
b) $K_b = K_w/K_a(HOCl) = 1.0 \times 10^{-14}/2.8 \times 10^{-8} = 3.6 \times 10^{-7}$
c) First, we must convert the 5% (wt/wt) concentration into one we can use in chemical calculations, molarity (or more precisely activities).
For a 5% soln there is 5 g NaOCl per 100 g of solution. Assuming the density of the solution is close to 1000 g/L, we have;

$$\frac{5\text{ g NaOCl}}{100\text{ g soln}} \text{ x } \frac{1\text{ mol NaOCl}}{74.45\text{ g NaOCl}} \text{ x } \frac{1000\text{ g}}{1\text{ L}} = 0.67\text{ M}$$

The potentially relevant equilibria are:

$OCl^- + H_2O$ ==== $HOCl + OH^-$

$Na^+ + H_2O \leftarrow NaOH + H^+$

$2\ H_2O$ ==== $H_3O^+ + OH^-$ $K_w = 1.0 \times 10^{-14}$

Using the first and last of these, we can set up an equilibrium table as follows.

	OCl^- + H_2O ====	$HOCl$ +	OH^-	$K_b = 3.6 \times 10^{-7}$
I	0.67 M	0	10^{-7}	
C	$-x$	x	x	
E	$0.67 - x$	x	$10^{-7} + x$	

$K_b = [HOCl]\,[OH^-]/[OCl^-] = (x)\,(10^{-7} + x)/(0.67-x) = 3.6 \times 10^{-7}$
Expand and solve using quadratic formula
OR ASSUME THAT IF $x >> 10^{-7}$ and $x << 0.67$,
Then the above expression simplifies to
$x^2/0.67 = 3.6 \times 10^{-7}$
so, $x = 4.9 \times 10^{-4}$ and *assumptions check*

Therefore, $[OH^-] = 4.9 \times 10^{-4}$ M and pOH = 3.31
Therefore, pH = 14 – pOH = 10.7