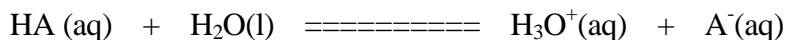


## Review of Simple Acid/Base Properties

Where HA is used to represent any generic Bronsted acid:



$$K_a = \{[\text{H}_3\text{O}^+][\text{A}^-]/[\text{HA}]\}$$

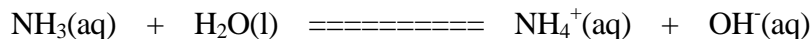
**STRONG ACIDS** completely dissociate and therefore have very large values of  $K_a$ . Examples include HCl, HNO<sub>3</sub>, HClO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub>. The conjugate base of strong acids are very weak bases. Therefore, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> 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<sub>2</sub>, HOCl and H<sub>2</sub>S. The conjugate bases of weak acids are relatively strong bases. Therefore, F<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, OCl<sup>-</sup> and S<sup>2-</sup> are examples of basic anions.

**STRONG BASES** are quantitatively converted into hydroxide ion in aqueous solution.

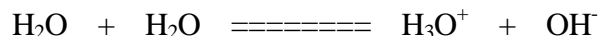
NaOH, KOH, Ca(OH)<sub>2</sub> and Mg(OH)<sub>2</sub> are examples of strong bases, although the latter two have limited solubility in water.

**WEAK BASES** partially react with water to produce hydroxide ions.



$$K_b = \{[\text{NH}_4^+][\text{OH}^-]/[\text{NH}_3]\}$$

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.



$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] \quad K_w = 1.0 \times 10^{-14} \text{ at } 25^\circ\text{C}$$

In general:  $K_b(\text{base}) = K_w/K_a(\text{conjugate acid})$  and  $K_a(\text{acid}) = K_w/ K_b(\text{conjugate base})$

Thus,  $K_a(\text{NH}_4^+) = K_w/K_b(\text{NH}_3)$

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

In general:  $\text{pH} + \text{pOH} = \text{p}K_w$

In pure water at 25°C;  $\text{pH} = \text{pOH} = 7.0$

## Rules for Predicting the pH of Aqueous Solutions

In general: Aqueous solutions of covalent oxides are acidic (i.e., CO<sub>2</sub>, SO<sub>2</sub>, SO<sub>3</sub> and NO<sub>2</sub>)  
Note: rainwater is naturally acidic (pH ~ 5.8 - 6.2) due to the presence of atmospheric CO<sub>2</sub>

Aqueous solutions of ionic oxides are basic (i.e., CaO, MgO and K<sub>2</sub>O)

Neutral ions: All Group 1A and 2A cations (e.g., Na<sup>+</sup>, Ca<sup>2+</sup> etc)  
Anions which are conjugates of strong acids (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> etc)

Acids: Uncharged strong or weak acids (e.g., HCl, H<sub>2</sub>CO<sub>3</sub> etc.)  
Metal cations other than those of Groups 1A and 2A  
Cationic conjugates of nitrogen bases (e.g., NH<sub>4</sub><sup>+</sup>, C<sub>5</sub>H<sub>5</sub>NH<sup>+</sup> etc)  
The two anions HSO<sub>4</sub><sup>-</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup>

Bases: All anions not listed above  
Uncharged nitrogen bases, such as NH<sub>3</sub>, C<sub>5</sub>H<sub>5</sub>N etc

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*Sample Exercises:*

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

- CuCl<sub>2</sub>
- Na<sub>3</sub>PO<sub>4</sub>
- NH<sub>4</sub>Br
- MgS

2. Calculate the concentration of ammonium chloride in a solution whose pH is measured as 5.13, given that the K<sub>a</sub> for the ammonium ion is 5.6 x 10<sup>-10</sup> M.

3. Calculate the value of K<sub>b</sub> for cyanide ion, given that a 1.6 x 10<sup>-2</sup> M solution of potassium cyanide has a pH of 10.76. (Compare your answer with that obtained using the K<sub>a</sub> for HCN).

4. Commercial bleach is a 5% (wt/wt) solution of sodium hypochlorite. The value of K<sub>a</sub> for hypochlorous acid (HOCl) is 2.8 x 10<sup>-8</sup>.

- Do you expect bleach to be acidic or basic?
- Calculate the K<sub>b</sub> of hypochlorite ion.
- Calculate the pH of a 5% bleach solution.

### Solutions:

1. Using the rules for predicting the pH of aqueous solutions.

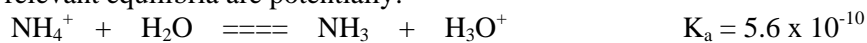
a) acidic ( $\text{Cu}^{2+}$  metal cations other than alkali and alkali earth metals are slightly acidic,  $\text{Cl}^-$  is neutral)

b) basic ( $\text{Na}^+$  is an alkali metal, therefore neutral and  $\text{PO}_4^{3-}$  is the conjugate base of  $\text{HPO}_4^{2-}$ , which is a weak acid. Therefore the solution is basic)

c) acidic (ammonium ion is acidic, chloride is neutral)

d) basic ( $\text{Mg}^{2+}$  is an alkali earth metal, therefore neutral and  $\text{S}^{2-}$  is the conjugate base of a weak acid  $\text{HS}^-$ . Therefore the solution is basic)

2. The relevant equilibria are potentially:



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

Where  $x = 7.31 \times 10^{-6}$ , since  $\text{pH} = 5.13$ , the  $[\text{H}^+] = 10^{-5.13} = 7.41 \times 10^{-6} \text{ M}$

	$\text{NH}_4^+$	+	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{NH}_3$	+	$\text{H}_3\text{O}^+$	$K_a$
I	$i$				0		$10^{-7}$	
C	$-x$				$x$		$x$	
E	$i - x$				$x$		$x + 10^{-7}$	
	$i - 7.31 \times 10^{-6}$				$7.31 \times 10^{-6}$		$7.41 \times 10^{-6}$	

Using the expression for  $K_a(\text{NH}_4^+)$

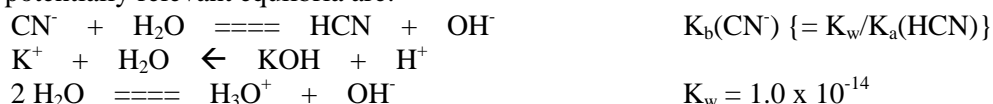
$$K_a = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} = 5.6 \times 10^{-10}$$

$$\text{So, } (7.41 \times 10^{-6})(7.31 \times 10^{-6}) / (i - 7.31 \times 10^{-6}) = 5.6 \times 10^{-10}$$

Solving for  $i$  yields,  $i = 0.0097 \text{ M}$

(this is the initial concentration of  $\text{NH}_4^+$ , which corresponds to the number of moles of  $\text{NH}_4\text{Cl}$  dissolved per liter. In grams, this is 0.52 g/L)

3. The potentially relevant equilibria are:



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  $\text{pH} = 10.76$ , the  $\text{pOH} = 3.24$  and  $[\text{OH}^-] = 10^{-3.24} = 5.75 \times 10^{-4}$  M,

	$\text{CN}^-$	+	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{HCN}$	+	$\text{OH}^-$	$K_b$
I	$1.6 \times 10^{-2}$ M				0		$10^{-7}$	
C	$-x$				$x$		$x$	
	$-5.75 \times 10^{-4}$ M				$5.75 \times 10^{-4}$		$5.75 \times 10^{-4}$	
E	$1.6 \times 10^{-2} - 5.75 \times 10^{-4}$				$5.75 \times 10^{-4}$		$10^{-7} + 5.75 \times 10^{-4}$	
	$1.54 \times 10^{-2}$ M				$5.75 \times 10^{-4}$		$\sim 5.75 \times 10^{-4}$	

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

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

4. a) Sodium hypochlorite is basic since  $\text{OCl}^-$  is the conjugate base of a weak acid.

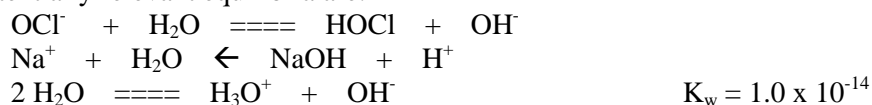
b)  $K_b = K_w/K_a(\text{HOCl}) = 1.0 \times 10^{-14} / 2.8 \times 10^{-8} = 3.6 \times 10^{-7}$

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;

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

The potentially relevant equilibria are:



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

	$\text{OCl}^-$	+	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{HOCl}$	+	$\text{OH}^-$	$K_b = 3.6 \times 10^{-7}$
I	0.67 M				0		$10^{-7}$	
C	$-x$				$x$		$x$	
E	$0.67 - x$				$x$		$10^{-7} + x$	

$$K_b = [\text{HOCl}] [\text{OH}^-] / [\text{OCl}^-] = (x) (10^{-7} + x) / (0.67 - x) = 3.6 \times 10^{-7}$$

Expand and solve using quadratic formula

OR ASSUME THAT IF  $x \gg 10^{-7}$  and  $x \ll 0.67$ ,

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,  $[\text{OH}^-] = 4.9 \times 10^{-4}$  M and  $\text{pOH} = 3.31$

Therefore,  $\text{pH} = 14 - \text{pOH} = 10.7$