

Acid/Base Chemistry

Introduction

Pure water contains hydrogen ion and hydroxyl ion in equal concentration at a level of 10^{-7} M. Addition of acidic compounds to water causes an increase in the hydrogen ion concentration and a decrease in the concentration of the hydroxyl ion. On the other hand, the addition of basic compounds to water increases the concentration of hydroxyl ion and decreases the hydrogen ion concentration. Even though the concentrations of the hydrogen ion and hydroxyl ion in pure water change on the addition of acids and bases, the product of these concentrations remain constant.

$$[H^+][OH^-] = 1 \times 10^{-14} = K_w$$

For dilute acid-base solutions (dilute is defined as 1 M or less), the hydrogen concentration can have values that run from one to 1×10^{-14} M. Because the range of concentration values for hydrogen ion is so large, it is convenient to define a function that expresses the hydrogen ion concentration in terms of a power of ten. This function is called pH, and it is defined as the negative value of the logarithm (base 10) of the molarity of the hydrogen ion.

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

Example Calculation #1

Calculate the concentration of hydroxyl ion and the pH in an aqueous solution that has a hydrogen concentration of 0.002 M.

Note that $[H^+] = 0.002 > 10^{-7}$ therefore, the solution is acidic

Remember that $[H^+][OH^-] = 1 \times 10^{-14}$

$$\begin{aligned} \text{Therefore } [OH^-] &= \frac{1 \times 10^{-14}}{[H^+]} &&= \frac{1 \times 10^{-14}}{0.002} \\ &&&= 5 \times 10^{-12} \text{ M} \end{aligned}$$

Note that the $[OH^-]$ is not zero in this acid solution; however, it is very small.

$$\text{Finally } \text{pH} = -\log [H^+] = -\log (0.002) = -(-2.7) = 2.7$$

Note that $\text{pH} = 2.7 < 7.0$

Example Calculation #2

Calculate the hydroxyl ion concentration, pOH, and hydrogen ion concentration of a solution that has a pH of 2.34.

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

$$-\log [\text{H}^+] = 2.34$$

$$\log [\text{H}^+] = -2.34$$

$$[\text{H}^+] = \text{INV log } (-2.34)$$

$$[\text{H}^+] = 4.57 \times 10^{-3}$$

In pure water where the concentrations of hydrogen ion and hydroxyl ion are 10^{-7} M and the pH is 7, the system is said to be neutral. In acidic solutions the concentration of hydrogen ion is greater than 10^{-7} M, and the pH is lower than 7. Finally, in basic solutions the hydrogen ion concentration is less than 10^{-7} M, and the pH is greater than 7.

In summary

$[\text{H}^+] > 10^{-7}$ M, $[\text{OH}^-] < 10^{-7}$ M, pH < 7, acidic solution

$[\text{H}^+] = 10^{-7}$ M, $[\text{OH}^-] = 10^{-7}$ M, pH = 7, neutral solution

$[\text{H}^+] < 10^{-7}$ M, $[\text{OH}^-] > 10^{-7}$ M, pH > 7, basic solution

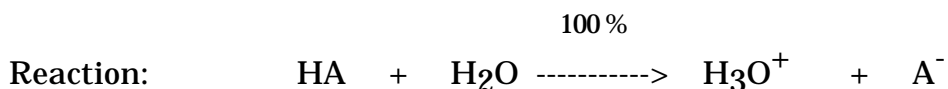
There are really three aspects of acid/base chemistry problem solving (recognition, calculation, and writing of the reactions). The first is the recognition of the type of acid/base system (strong acid, strong base, weak acid, weak base, buffer, and polyprotic acid) so that the proper calculation method can be applied. The second issue is learning the methods to find the pH, $[\text{H}^+]$, etc. for a given acid/base system (strong acid, strong base, weak acid, weak base, buffer, and polyprotic acid). Finally, both of these first two issues require the ability to write a chemical reaction for the acid/base character of the solution.

Strong Acid Systems

Recognition:

Five Strong Acids for this course

1. HCl - hydrochloric acid, 2. HBr - hydrobromic acid, 3. HI - hydroiodic acid, 4. HNO₃ - nitric acid, 5. HClO₄ - perchloric acid



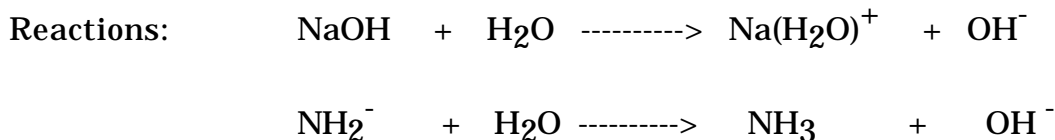
Method: $[\text{H}^+] = [\text{strong acid}]_{\text{initial}}$

Strong Base Systems

Recognition:

Typically Two Commonly used Strong Bases NaOH and KOH

Other less Typically used Strong Bases NaNH₂, NaOCH₃



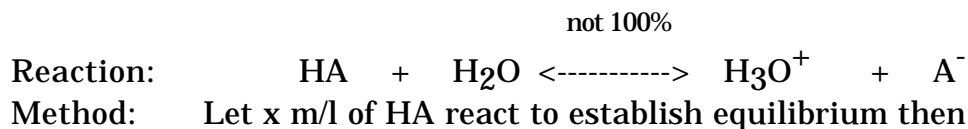
Method: $[\text{OH}^-] = [\text{strong base}]_{\text{initial}}$

Weak Acid Systems

Recognition:

Not one of the five strong acids (this could, of course, get you into trouble -- but not in this class). The best way to determine the strength of an acid is to look up the value of K_a, and if the K_a is small, the acid is weak. A few examples of weak acids.

HC₂H₃O₂ (acetic acid), HNO₂ (nitrous), HF (hydrofluoric), HCN (hydrocyanic), HOCl (hypochlorous),



$$[\text{HA}] = \text{initial conc.} - x$$

$$[\text{H}^+] = x \quad \text{and} \quad [\text{A}^-] = x \quad \text{and}$$

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{x \cdot x}{\text{initial conc.} - x}$$

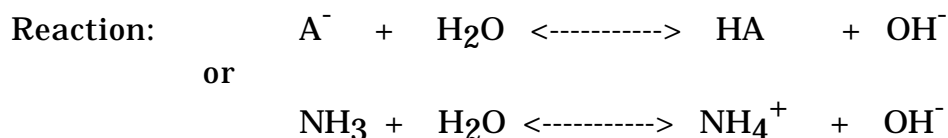
If K_a is small then $x \ll \text{initial conc.}$ and
 $\text{initial conc.} - x = \text{initial conc.}$

$$\text{so } K_a = \frac{x \cdot x}{\text{initial conc.}} \quad \text{or} \quad [\text{H}^+] = x = \sqrt{K_a (\text{initial conc.})}$$

Weak Bases

Recognition: Weak bases will be the anions of weak acids. The weaker the acid the stronger the base.

Some typical weak bases. F^- , fluoride; CN^- , cyanide; $\text{C}_2\text{H}_3\text{O}_2^-$, acetate; NO_2^- nitrite; and NH_3 , ammonia. Note that NH_3 is an exception and not an anion.



Method: Let x m/l of A^- react to establish equilibrium then

$$[\text{A}^-] = \text{initial conc.} - x$$

$$[\text{OH}^-] = x \quad \text{and} \quad [\text{HA}] = x \quad \text{and}$$

$$K_b = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} = \frac{x \cdot x}{\text{initial conc.} - x}$$

If K_b is small then $x \ll \text{initial conc.}$ and
 $\text{initial conc.} - x = \text{initial conc.}$

$$\text{so } K_b = \frac{x \cdot x}{\text{initial conc.}} \quad \text{or } [\text{OH}^-] = x = \sqrt{K_b (\text{initial conc.})}$$

Point Perhaps a point should be made at this point. Often books list only Ka's and not Kb's. One needs to know, therefore, that

$$K_a^{\text{HA}} \times K_b^{\text{A}^-} = 1 \times 10^{-14}$$

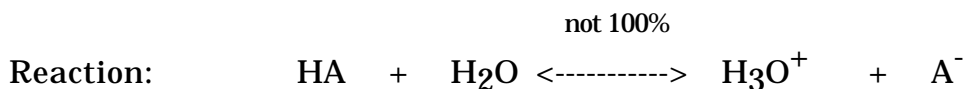
and that if one knows Ka one can calculate Kb

Buffer System

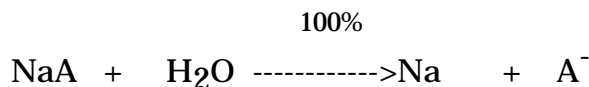
Recognition:

Mixture of weak acid and salt of the anion

Some Examples: HoAc and NaOAc, HNO₂ and NaNO₂, HCN and NaCN, H₂CO₃ and NaHCO₃



and



Method: Let x m/l of HA react to establish equilibrium then

$$[\text{HA}] = \text{initial conc. of HA} - x$$

$$[\text{H}^+] = x \quad \text{and} \quad [\text{A}^-] = x + \text{initial conc. of NaA}$$

and

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{x(x + \text{initial conc. of NaA})}{\text{initial conc. of HA} - x}$$

If Ka is small then $x \ll \text{initial conc. of both HA and NaA}$
and $\text{initial conc.} - x = \text{initial conc.}$

$$\text{so } K_a = \frac{x (\text{initial conc. of NaA})}{\text{initial conc. of HA}}$$

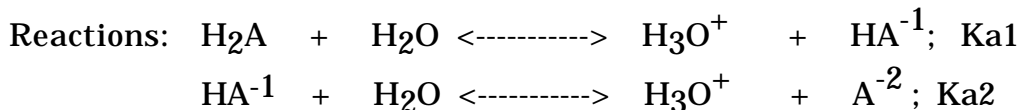
$$\text{so so so } \xrightarrow{\text{---}} x = [\text{H}^+] = K_a \frac{\text{initial conc. of HA}}{\text{initial conc. of NaA}}$$

Polyprotic Acid

Recognition:

Acid of the form H_xA where $x > 1$

Some Examples: H_2CO_3 (carbonic), $H_2C_2O_4$ (oxalic acid), H_3PO_4 (Phosphoric acid), and H_2S (hydrogen sulfide)



$$K_{a1} = \frac{[H^+][HA^{-1}]}{[H_2A]} \quad \text{and} \quad K_{a2} = \frac{[H^+][A^{-2}]}{[HA^{-1}]}$$

Typically $K_{a1} \gg K_{a2}$ and are found in Books

Method: Let x m/l of H_2A react to establish equilibrium via reaction 1

and

Let y m/l of HA^{-1} react to establish equilibrium via reaction 2

$$[H_2A] = \text{initial conc. of } H_2A - x$$

$$[HA^{-1}] = x - y$$

$$[H^+] = x + y \quad \text{and} \quad [A^{-2}] = y$$

so
$$K_{a1} = \frac{[H^+][HA^{-1}]}{[H_2A]} = \frac{(x+y)(x-y)}{\text{initial conc. of } H_2A - x}$$

so again
$$K_{a2} = \frac{[H^+][A^{-2}]}{[HA^{-1}]} = \frac{(x+y)y}{x-y}$$

Two equations and two unknowns; however,

If K_a is small then $x \ll \text{initial conc. of } H_2A$ and $y \ll x$
 then

$$K_{a1} = \frac{(x)(x)}{\text{initial conc. of H}_2\text{A}} \quad \text{and one can solve for } x$$

$$K_{a2} = y$$

finally $[\text{H}_2\text{A}] = \text{initial conc. of H}_2\text{A}$

$$[\text{HA}^{-1}] = x$$

$$[\text{H}^+] = x \quad \text{and} \quad [\text{A}^{-2}] = y$$