Chemistry 6A F2007

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THE AUTO-IONIZATION OF WATER

A sample of absolutely pure water does not contain only H_2O molecules. In addition, small but equal amounts of H_3O^+ and OH^- ions are also present.

The reason for this is that in one liter of pure water 1.0×10^{-7} moles of water molecules behave as Brønsted acids and donate protons to another 1.0×10^{-7} moles of water molecules, which act as Brønsted bases. The reaction is:

$$H_2O(l) + H_2O(l) \rightleftarrows H_3O^+(aq) + OH^-(aq)$$

As a result, absolutely pure water contains 1.0×10^{-7} mol/L of both H_3O^+ and OH^-.

The term ***neutral*** is used to describe any water solution in which the concentrations of H_3O^+ and OH^- are equal.

Thus, pure water is neutral because each of the ions is present at a concentration of 1.0×10^{-7} M.

THE ION PRODUCT OF WATER

The reaction given earlier for the formation of H_3O^+ and OH^- in pure water is called the auto-ionization of water. The reversible nature of the reaction (indicated by the double arrow) means that an equilibrium is established and an equilibrium expression can be written for the reaction. The equilibrium expression is:

$$2H_2O \rightleftarrows H_3O^+ + OH^-$$

$$K = \frac{[H_3O^+]\times[OH^-]}{[H_2O]^2}$$

This expression contains the square of the molar concentration of water in the denominator. However, only a tiny amount of water reacts to establish the equilibrium, so the concentration of water remains essentially constant.

The equilibrium expression can be rearranged to give:

$$K[H_2O]^2 = [H_3O^+][OH^-]$$

Because the concentration of water is essentially constant, the product of K multiplied by the square of the water concentration is equal to another constant designated as Kw, and called **the ion product of water**. The equation then becomes:

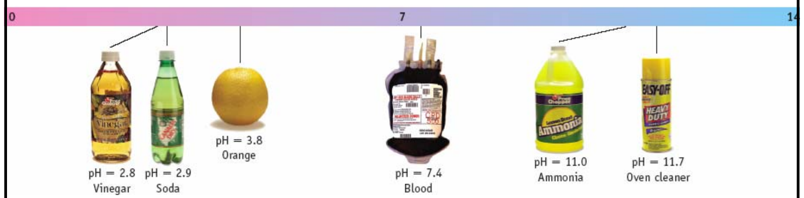
$$K_w = [H_3O^+][OH^-]$$

Because the molar concentration of both H_3O^+ and OH^- in pure water is 1.0×10^{-7}, the numerical value for Kw can be calculated:

$$K_w = [H_3O^+][OH^-] = (1.0\times10^{-7})^2 = 1.0\times10^{-14}$$

The pH Scale: 0 to 14

The pH of a solution provides a way to express the ***acidity***, or the concentration of H^+ in solution:



low pH = high [H^+]
acidic solution

high pH = low [H^+]
basic solution

a pH of 7 indicates that the solution is ***neutral***

The pH Scale:

What we call *pH* is actually a mathematical function, "*p*"

p is a shorthand notation for " $-\log_{10}$" *(the negative logarithm, based 10)*

Quick Review of logs…

$\log x = n$ where $x = 10^n$

$\log 1000 = \log(10^3) = 3$

$\log 10 = \log(10^1) = 1$

$\log 0.001 = \log(10^{-3}) = -3$

Example: A student is given a solution that is labeled pH = 4.72, what is the molarity of H^+ in this solution?

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

plugging in $10^{-4.72}$ into you calculators yields: 1.90546×10^{-5}

but wait… how many sig. figs. are allowed?

$$10^{-4.72} = 10^{(0.28-5)} = 10^{0.28} \times 10^{-5}$$

$10^{0.28} = 1.9$ *2 sig. figs.!*

therefore the concentration should be reported as: 1.9×10^{-5} M [H^+]

Calculate the pH of a 0.0045 nitric acid solution.

$$pH = -\log[H_3O^+]$$

$$0.0045 = 4.5\times10^{-3}$$

$$-\log(4.5\times10^{-3}) = -\log(4.5) + \{-\log(10^{-3})\}$$

$$= -0.65 + 3$$

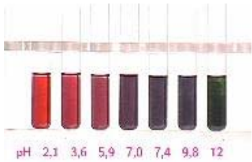
$$= 2.35$$

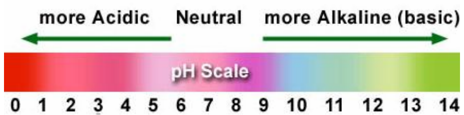
notice that you get 2 sig figs behind the decimal!

pH Indicators:

And some indicators can be found at the grocery store!

When diced into little pieces and extracted with hot water, ***Red Cabbage*** juice is a universal pH indicator!





the color changes from reds to greens across the pH range!

Warning! Red cabbage juice is pretty stinky…

Calculate the pH of a 0.025M NaOH solution:

(1) You know that the solution will have a pH > 7 due to the presence of base (OH^-)

(2) To find pH one needs $[H_3O^+]$

(3) Recall that H_3O^+ and OH^- are related by K_W $\quad \mathbf{K_w = [H_3O^+][OH^-]} = 1.00 \times 10^{-14}$

(4) Since NaOH is a strong base, [NaOH] = $[OH^-]$

(5) Substituting and solving: $\quad [H_3O^+] = \dfrac{K_W}{[OH^-]}$

$$[H_3O^+] = \frac{1.00 \times 10^{-14}}{0.025} = 4.0 \times 10^{-13}\ \text{M}$$

$$\text{pH} = -\log[4.0 \times 10^{-13}] = 12.40$$

2 sig figs behind the decimal

pH and pOH

$$\text{-log}\{[H_3O^+][OH^-] = 1.00 \times 10^{-14}\}$$

$$\text{-log}[H_3O^+] + (\text{-log}[OH^-]) = 14.00$$

$$\text{pH} + \text{pOH} = 14.00$$

So knowing pH you can find pOH and $[OH^-]$ and *vice versa*!

THE STRENGTH OF ACIDS AND BASES

- The strength of an acid or base is determined by the extent to which the acid or base dissociates to form ions.
- A strong acid or base dissociates 100%, while a weak or moderately weak one dissociates less than 100%.

Weak acids form equilibrium mixtures in aqueous solutions:

weak acid

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

conjugate base of the weak acid

The relative strength of a weak acid is measured by its equilibrium constant, K_a.

MONOPROTIC, DIPROTIC AND TRIPROTIC ACIDS

Monoprotic acids give up only one proton per molecule when dissolved in water.

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

Diprotic acids give up a maximum of two protons per molecule when dissolved in water.

$$H_2A(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + HA^-(aq)$$

$$HA^-(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + A^{2-}(aq)$$

Triprotic acids give up a maximum of three protons per molecule when dissolved in water.

$$H_3A(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + H_2A^-(aq)$$

$$H_2A^-(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + HA^{2-}(aq)$$

$$HA^{2-}(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + A^{3-}(aq)$$

ACID DISSOCIATION CONSTANTS

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

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

Since the concentration of water remains essentially constant, it becomes part of the equilibrium constant itself.

K becomes K_a, the acid dissociation constant.

WEAK BASE DISSOCIATION CONSTANTS

$$B(aq) + H_2O(l) \rightleftarrows HB^+(aq) + OH^-(aq)$$

$$K_b = \frac{[HB^+]\ [OH^-]}{[B]}$$

Since the concentration of water remains essentially constant, it becomes part of the equilibrium constant itself.

K becomes K_b, the base dissociation constant.