Autoprotolysis of Water

☞ Pure water has an equilibrium with H_3O^+ and OH^- called **autoprotolysis** or **autodissociation**.

H_2O	+	H_2O	$\rightleftharpoons$	H_3O^+	+	OH^-
$base_1$		$acid_2$		$acid_1$		$base_2$

☞ For water at 25 °C

$$K_w = [H_3O^+][OH^-] = 1.0 \text{ x } 10^{-14} \text{ M}^2$$

☞ K_w, the **ion product** or **dissociation constant** of water, is obeyed for all aqueous solutions, except at extremely high concentration.

Neutral, Acidic, Basic

☞ For **neutral water**,

$$[H_3O^+] = [OH^-] = 1.0 \times 10^{-7} \text{ M}$$

☞ For an **acidic solution**,

$$[H_3O^+] > 10^{-7} \text{ M and } [OH^-] < 10^{-7} \text{ M}$$

☞ For a **basic solution**,

$$[H_3O^+] < 10^{-7} \text{ M and } [OH^-] > 10^{-7}$$

pH and pOH

✓ The letter "p" in front of a quantity means "the negative logarithm of" the quantity.

☞ pH and pOH are defined as

$$pH = -\log [H_3O^+] \qquad pOH = -\log [OH^-]$$

- The relationship between pH and pOH is derived from K_w:

$$K_w = [H_3O^+][OH^-] = 1.0 \text{ x } 10^{-14}$$

$$\log K_w = \log[H_3O^+][OH^-] = -14.00$$

$$-\log K_w = pK_w = -\log[H_3O^+] - \log[OH^-] = 14.00$$

$$pK_w = pH + pOH = 14.00$$

Neutral, Acidic, Basic

☞ For **neutral water**,

$$pH = pOH = 7$$

☞ For an **acidic solution**,

$$pH < 7 \text{ and } pOH > 7$$

☞ For a **basic solution**,

$$pH > 7 \text{ and } pOH < 7$$

☞ For all solutions

$$pH + pOH = 14.00$$

Simultaneous Equilibria
Solution of a Strong Acid in Water -– 5.0×10^{-2} M HCl

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$
$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$

	HCl	H_3O^+	Cl^-	OH^-
Add	5.0×10^{-2}	10^{-7}	0	10^{-7}
Get	0	$\sim 5.0 \times 10^{-2}$	5.0×10^{-2}	$<10^{-7}$

☞ Charge Balance Expression - expresses the total concentration of one ion in terms of equivalent concentrations of ions of the opposite charge.

$$[H_3O^+] = [H_3O^+]_{acid} + [H_3O^+]_{water}$$

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

☞ Mass Balance Expression - accounts for the distribution of the analytical concentration (what was added) in terms of concentrations of species formed through dissociation (what you get) in solution.

$$C = [H_3O^+]_{acid} = [Cl^-] = 5.0 \times 10^{-2} \text{ M}$$

Solution of a Strong Acid in Water — 5.0 x 10^{-2} M HCl
Simplifying Assumptions

☞ Substituting the mass balance result into the previous charge balance expression gives

$$[H_3O^+] = 5.0 \times 10^{-2} + [OH^-]$$

☞ In pure water $[OH^-] = 1.0 \times 10^{-7}$ M, which is negligible by comparison to 5.0×10^{-2} M. Moreover, this is an acidic solution, so by LeChatelier's principal we expect that $[OH^-] << 1.0 \times 10^{-7}$ M. Therefore, we can ignore $[OH^-]$ in our charge balance expression and write

$$[H_3O^+] \approx 5.0 \times 10^{-2} \text{ M}$$

From this we calculate

$$pH = -\log(5.0 \times 10^{-2}) = 1.30$$

☞ Only the HCl was a major source of H_3O^+ in this solution.

☞ To find the concentration of hydroxide ion in the solution, we use $K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$:

$$[OH^-] = K_w/[H_3O^+] = 1.0 \times 10^{-14}/5.0 \times 10^{-2}$$
$$= 2.0 \times 10^{-13} \text{ M} = [H_3O^+]_{water}$$

Strong Acid in Water

$$HA + H_2O \rightarrow H_3O^+ + A^-$$

For solutions of a **strong acid** in water at moderate concentrations ($C_{HA} > 10^{-5}$ M), assume virtually all H_3O^+ comes from the acid. Thus,

$$[H_3O^+] = C_{HA}$$

$$pH = -\log C_{HA}$$

$$pOH = 14.00 - pH$$

Strong Base in Water

$$M(OH)_n(aq) \rightarrow M^{n+}(aq) + nOH^-(aq)$$

For solutions of a **strong base** in water at moderate concentrations ($C_B > 10^{-5}$ M), assume virtually all OH^- comes from the base. Thus,

$$[OH^-] = nC_B$$

$$pOH = -\log nC_B$$

$$pH = 14.00 - pOH$$

Extreme Dilution

☞ Any acid or base at extreme dilution ($<10^{-7}$ M) makes no significant contribution to the total $[H_3O^+]$ or $[OH^-]$ concentration in the solution.

☞ Thus, water is the principal source of both ions:

$$[H_3O^+] = [OH^-] = 1.0 \times 10^{-7} \text{ M}$$

$$pH = pOH = 7.00$$