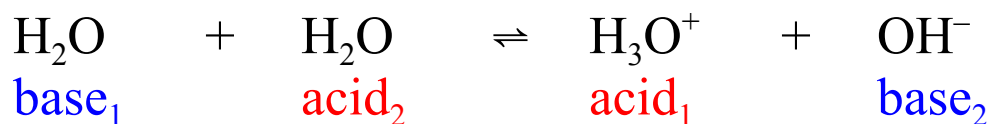


Autoprotolysis of Water

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



- ☞ For water at 25 °C

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ M}^2$$

- ☞ 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,

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$$

☞ For an **acidic solution**,

$$[\text{H}_3\text{O}^+] > 10^{-7} \text{ M and } [\text{OH}^-] < 10^{-7} \text{ M}$$

☞ For a **basic solution**,

$$[\text{H}_3\text{O}^+] < 10^{-7} \text{ M and } [\text{OH}^-] > 10^{-7}$$

pH and pOH

- ✓ The letter “p” in front of a quantity means “the negative logarithm of” the quantity.
- ☞ pH and pOH are defined as

$$\text{pH} = -\log [\text{H}_3\text{O}^+] \quad \text{pOH} = -\log [\text{OH}^-]$$

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

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

$$\log K_w = \log[\text{H}_3\text{O}^+][\text{OH}^-] = -14.00$$

$$-\log K_w = \text{p}K_w = -\log[\text{H}_3\text{O}^+] - \log[\text{OH}^-] = 14.00$$

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

Neutral, Acidic, Basic

☞ For neutral water,

$$\text{pH} = \text{pOH} = 7$$

☞ For an **acidic solution**,

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

☞ For a **basic solution**,

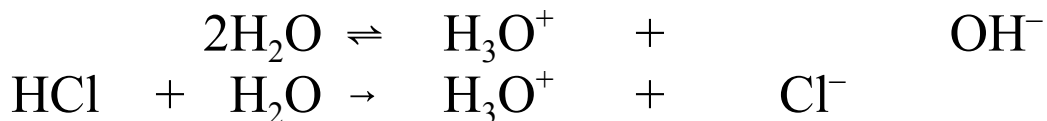
$$\text{pH} > 7 \text{ and } \text{pOH} < 7$$

☞ For all solutions

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

Simultaneous Equilibria

Solution of a Strong Acid in Water — $5.0 \times 10^{-2} \text{ M HCl}$



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.

$$[\text{H}_3\text{O}^+] = [\text{H}_3\text{O}^+]_{\text{acid}} + [\text{H}_3\text{O}^+]_{\text{water}}$$

$$[\text{H}_3\text{O}^+] = [\text{Cl}^-] + [\text{OH}^-]$$

- ☞ 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.

$$C = [\text{H}_3\text{O}^+]_{\text{acid}} = [\text{Cl}^-] = 5.0 \times 10^{-2} \text{ M}$$

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

Simplifying Assumptions

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

$$[\text{H}_3\text{O}^+] = 5.0 \times 10^{-2} + [\text{OH}^-]$$

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

$$[\text{H}_3\text{O}^+] \approx 5.0 \times 10^{-2} \text{ M}$$

From this we calculate

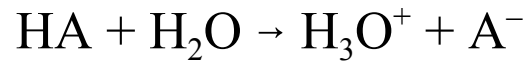
$$\text{pH} = -\log(5.0 \times 10^{-2}) = 1.30$$

- ☞ **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 $K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$:

$$\begin{aligned} [\text{OH}^-] &= K_w / [\text{H}_3\text{O}^+] = 1.0 \times 10^{-14} / 5.0 \times 10^{-2} \\ &= 2.0 \times 10^{-13} \text{ M} = [\text{H}_3\text{O}^+]_{\text{water}} \end{aligned}$$

Strong Acid in Water



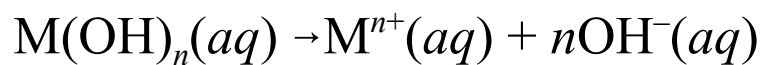
For solutions of a **strong acid** in water at moderate concentrations ($C_{\text{HA}} > 10^{-5} \text{ M}$), assume virtually all H_3O^+ comes from the acid. Thus,

$$[\text{H}_3\text{O}^+] = C_{\text{HA}}$$

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

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

Strong Base in Water



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

Thus,

$$[\text{OH}^-] = nC_B$$

$$\text{pOH} = -\log nC_B$$

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

Extreme Dilution

- ☞ Any acid or base at extreme dilution ($<10^{-7}$ M) makes no significant contribution to the total $[\text{H}_3\text{O}^+]$ or $[\text{OH}^-]$ concentration in the solution.
- ☞ Thus, water is the principal source of both ions:

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$$

$$\text{pH} = \text{pOH} = 7.00$$