IONIC EQUILIBRIA

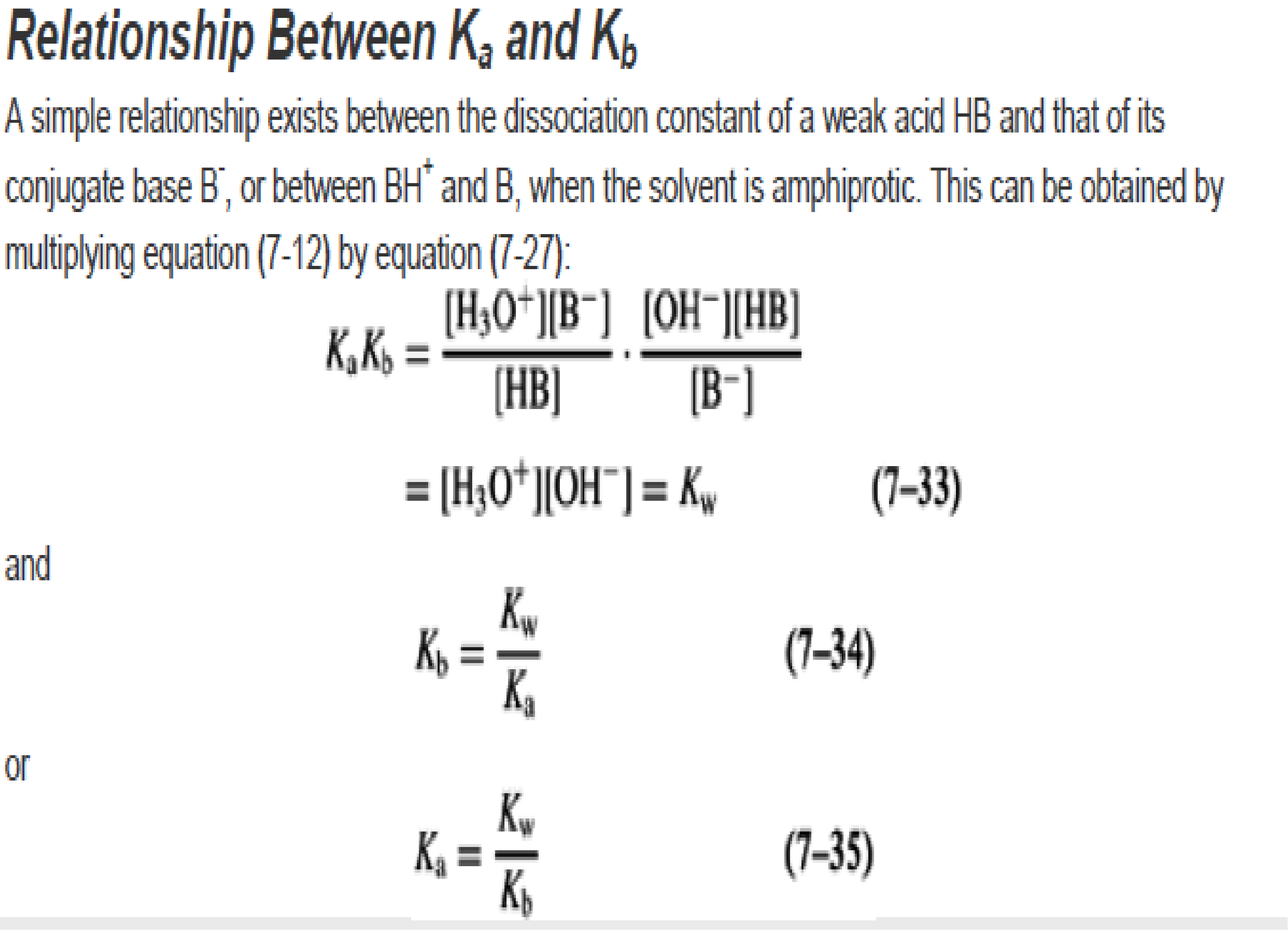
27 December 2022

$$HB + H_2O \rightleftharpoons H_3O^+ + B^- \qquad (7\text{-}11)$$

$$K_a = \frac{[H_3O^+][B^-]}{[HB]} \qquad (7\text{–}12)$$

$$B^- + H_2O \rightleftharpoons OH^- + HB$$

$$K_b = \frac{[OH^-][HB]}{[B^-]} \qquad (7\text{–}27)$$



Relationship Between K_a and K_b

A simple relationship exists between the dissociation constant of a weak acid HB and that of its conjugate base B^-, or between BH^+ and B, when the solvent is amphiprotic. This can be obtained by multiplying equation (7-12) by equation (7-27):

$$K_a K_b = \frac{[H_3O^+][B^-]}{[HB]} \cdot \frac{[OH^-][HB]}{[B^-]}$$

$$= [H_3O^+][OH^-] = K_w \qquad (7\text{–}33)$$

and

$$K_b = \frac{K_w}{K_a} \qquad (7\text{–}34)$$

or

$$K_a = \frac{K_w}{K_b} \qquad (7\text{–}35)$$

$$K_b = \frac{K_w}{K_a} \qquad (7\text{–}34)$$

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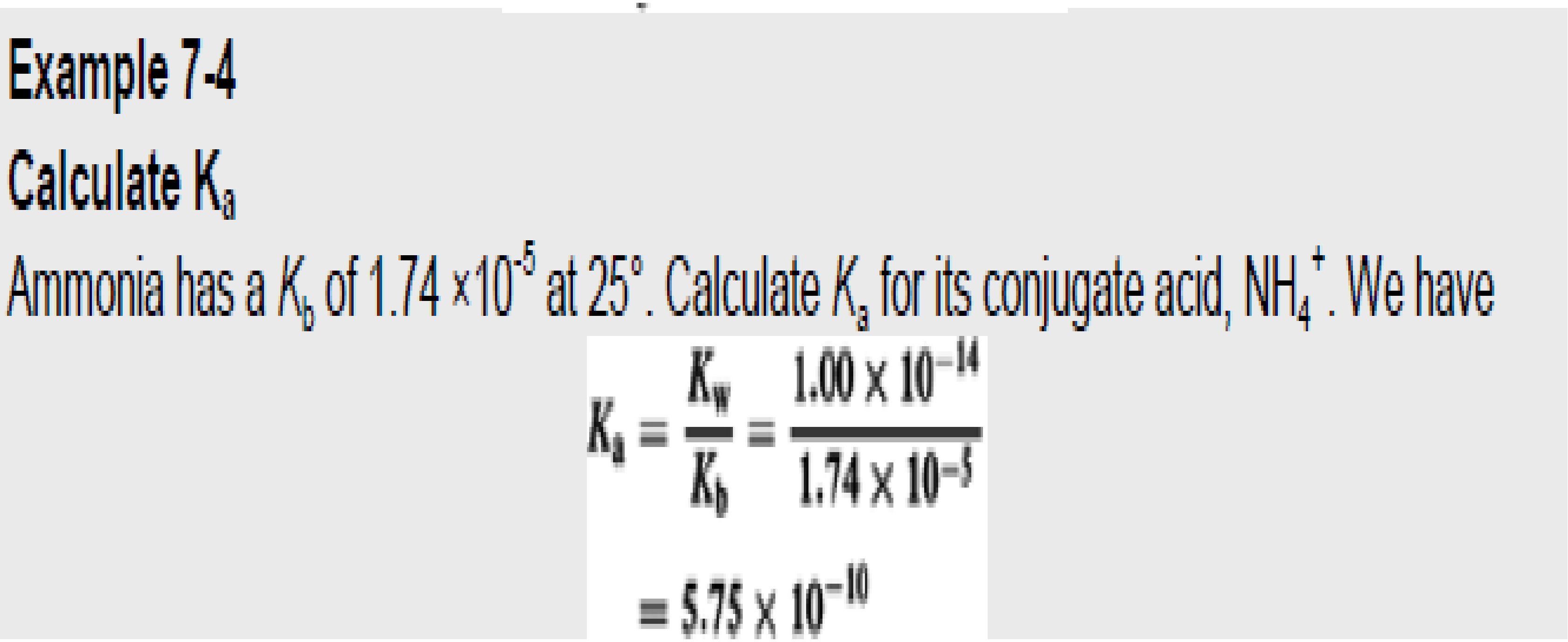


Example 7-4

Calculate K_a

Ammonia has a K_b of 1.74×10^{-5} at 25°. Calculate K_a for its conjugate acid, NH_4^+. We have

$$K_a = \frac{K_w}{K_b} = \frac{1.00 \times 10^{-14}}{1.74 \times 10^{-5}}$$

$$= 5.75 \times 10^{-10}$$

SÖRENSEN'S PH

$$pH = -\log[H_3O^+] \qquad (7\text{–}55)$$

The pH of a solution can be considered in terms of a numeric scale having values from 0 to 14, which expresses in a quantitative way the degree of acidity (7 to 0) and alkalinity (7-14). The value 7 at which the hydrogen and hydroxyl ion concentrations are about equal at room temperature is referred to as the neutral point, or neutrality.

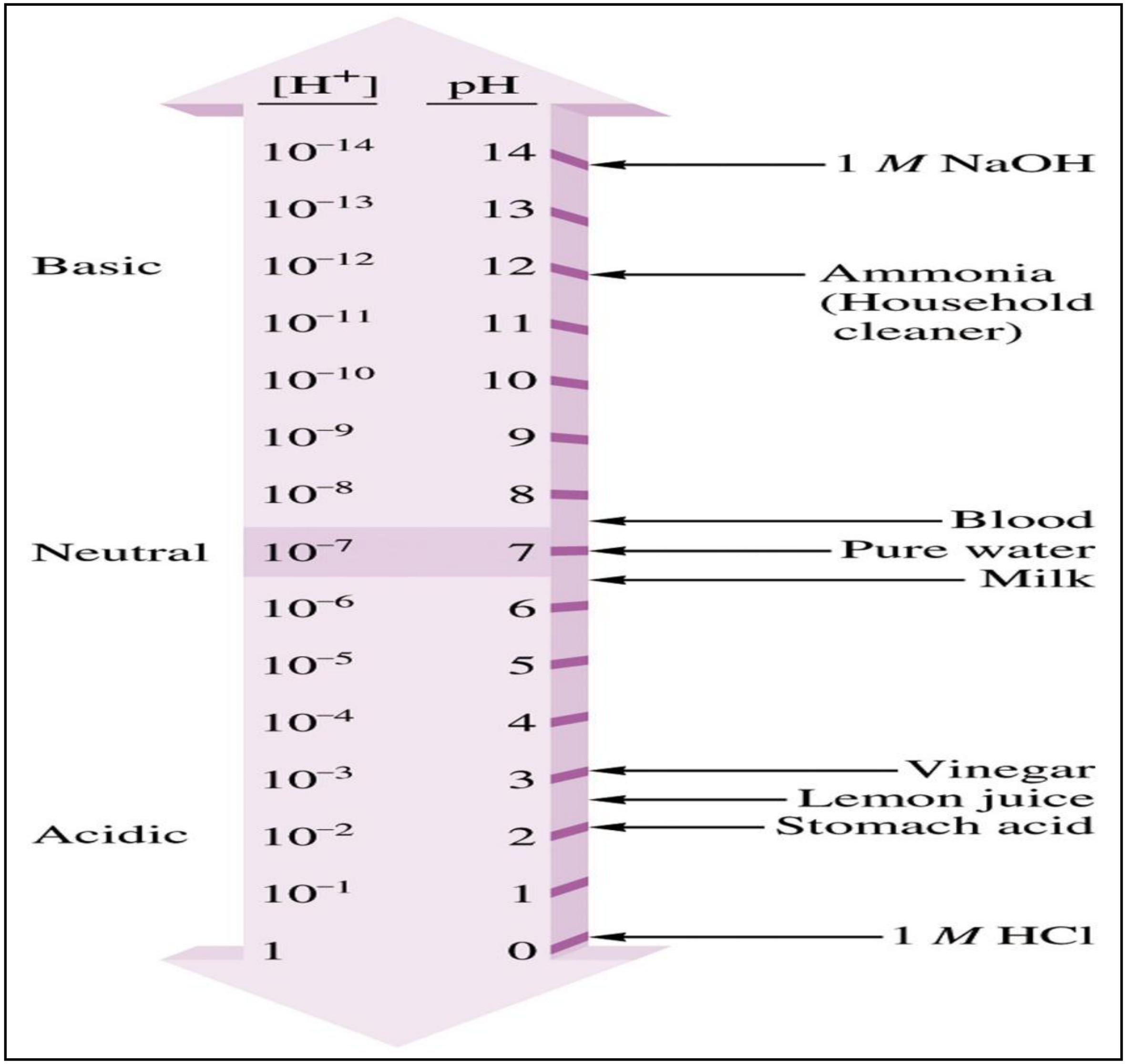
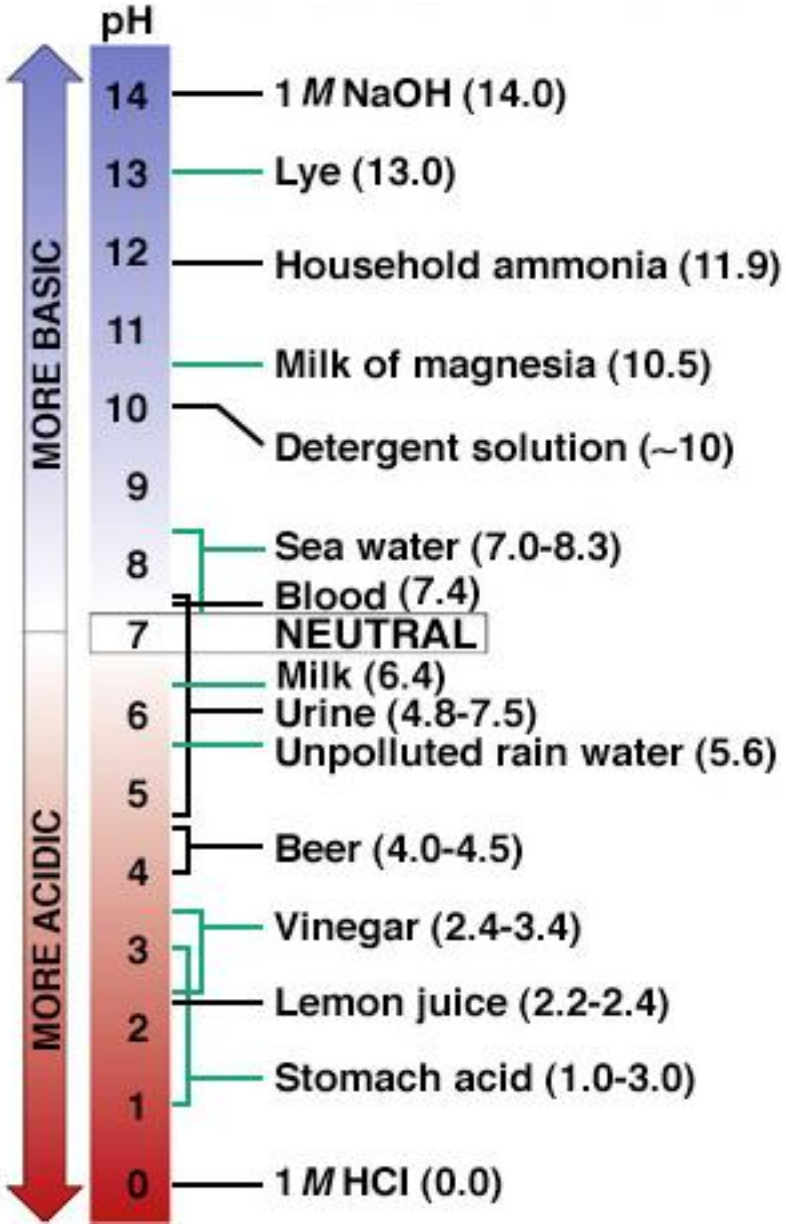
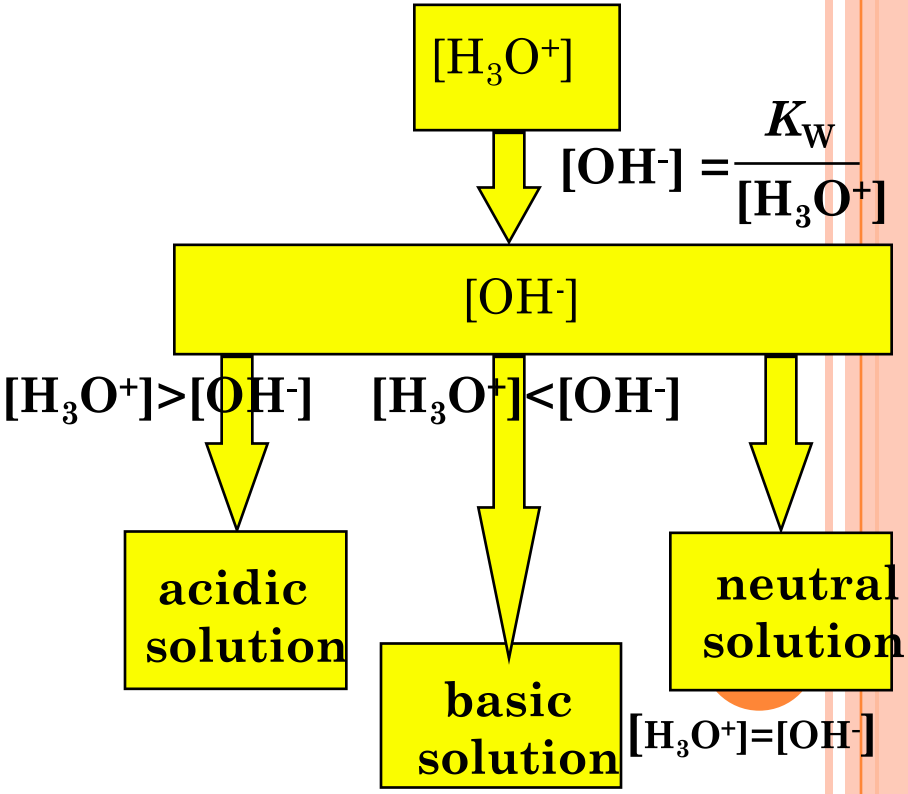


FIGURE 1 : THE PH SCALE AND PH VALUES OF SOME COMMON SUBSTANCES

The pH Values of Some Familiar Aqueous Solutions





$[H_3O^+]$

$$[OH^-] = \frac{K_W}{[H_3O^+]}$$

$[OH^-]$

$[H_3O^+]>[OH^-]$

$[H_3O^+]<[OH^-]$

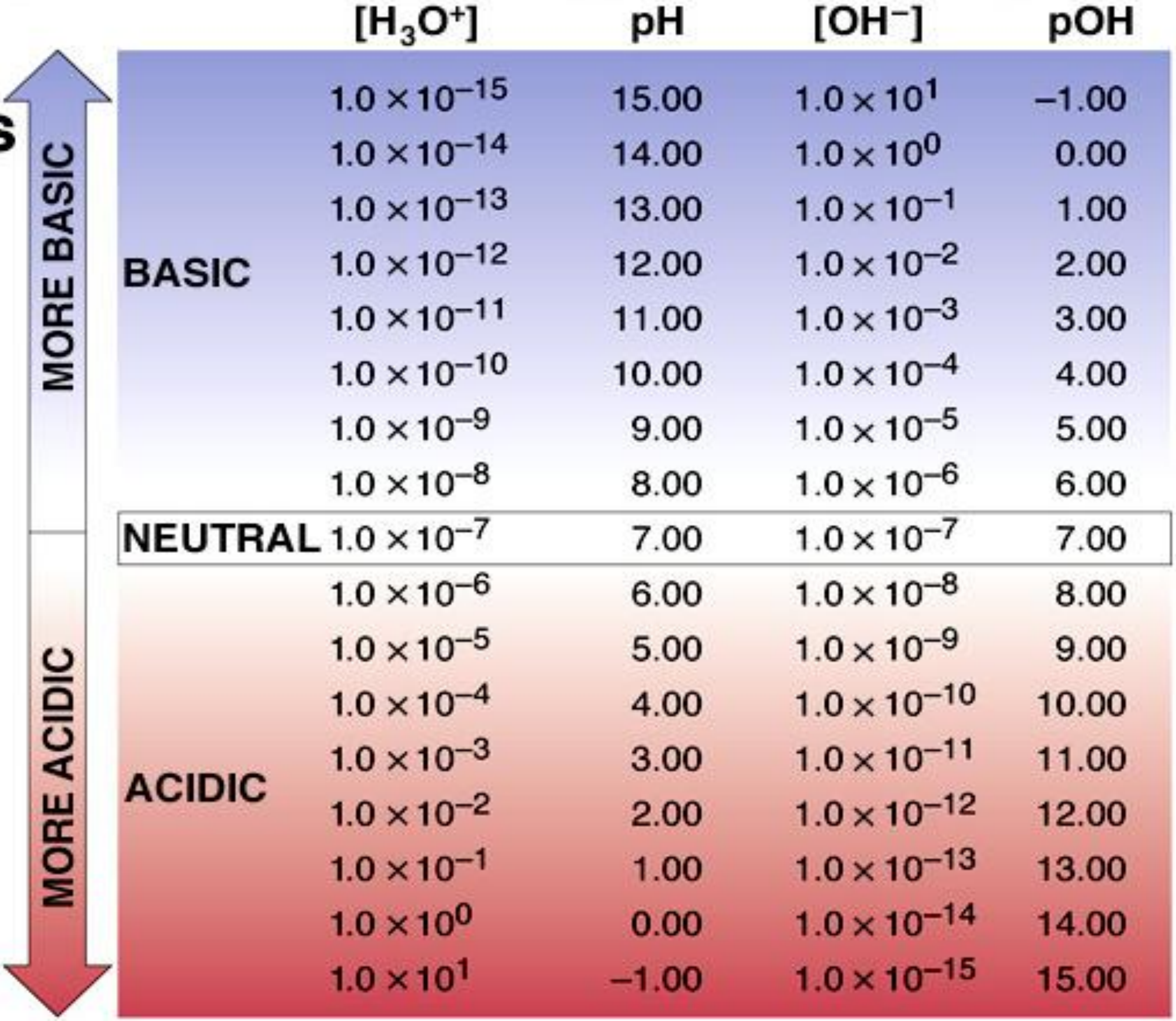
acidic solution

basic solution

neutral solution

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

The Relations Among $[H_3O^+]$, pH, $[OH^-]$, and pOH

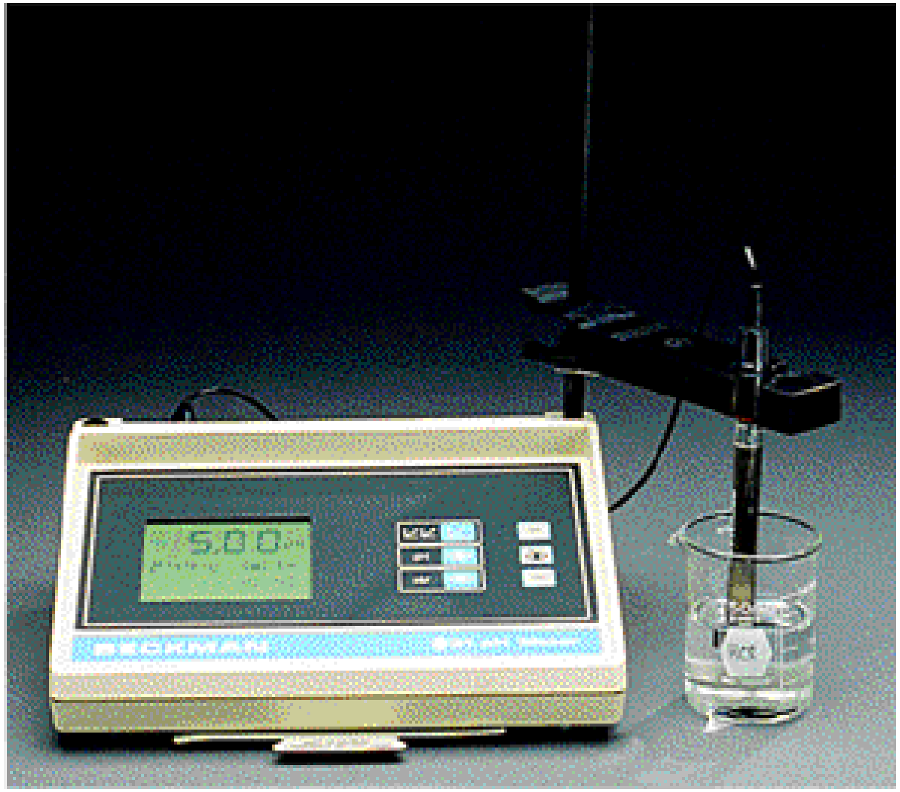


	$[H_3O^+]$	pH	$[OH^-]$	pOH
BASIC	1.0×10^{-15}	15.00	1.0×10^{1}	−1.00
	1.0×10^{-14}	14.00	1.0×10^{0}	0.00
	1.0×10^{-13}	13.00	1.0×10^{-1}	1.00
	1.0×10^{-12}	12.00	1.0×10^{-2}	2.00
	1.0×10^{-11}	11.00	1.0×10^{-3}	3.00
	1.0×10^{-10}	10.00	1.0×10^{-4}	4.00
	1.0×10^{-9}	9.00	1.0×10^{-5}	5.00
	1.0×10^{-8}	8.00	1.0×10^{-6}	6.00
NEUTRAL	1.0×10^{-7}	7.00	1.0×10^{-7}	7.00
ACIDIC	1.0×10^{-6}	6.00	1.0×10^{-8}	8.00
	1.0×10^{-5}	5.00	1.0×10^{-9}	9.00
	1.0×10^{-4}	4.00	1.0×10^{-10}	10.00
	1.0×10^{-3}	3.00	1.0×10^{-11}	11.00
	1.0×10^{-2}	2.00	1.0×10^{-12}	12.00
	1.0×10^{-1}	1.00	1.0×10^{-13}	13.00
	1.0×10^{0}	0.00	1.0×10^{-14}	14.00
	1.0×10^{1}	−1.00	1.0×10^{-15}	15.00

Figure 7.4: (a) Measuring the pH of vinegar. (b) Measuring the pH of aqueous ammonia.

Methods for Measuring the pH of an Aqueous Solution

(a) pH paper



(b) Electrodes of a pH meter

Calculating $[H_3O^+]$, pH, $[OH^-]$, and pOH

Problem: A chemist dilutes concentrated hydrochloric acid to make two solutions: (a) 3.0 *M* and (b) 0.0024 *M*. Calculate the $[H_3O^+]$, pH, $[OH^-]$, and pOH of the two solutions at 25°C.

Plan: We know that hydrochloric acid is a strong acid, so it dissociates completely in water; therefore $[H_3O^+] = [HCl]_{init.}$. We use the $[H_3O^+]$ to calculate the $[OH^-]$ and pH as well as pOH.

Solution:

(a) $[H_3O^+] = \mathbf{3.0}\ \boldsymbol{M}$ pH = $-\log[H_3O^+] = -\log(3.0) =$ ________

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1 \text{ x } 10^{-14}}{3.0} = \underline{\hspace{6em}}\ \boldsymbol{M}$$

$$\text{pOH} = -\log(3.333 \text{ x } 10^{-15}) = 15.000 - 0.477 = \underline{\hspace{4em}}$$

(b) $[H_3O^+] = \mathbf{0.0024}\ \boldsymbol{M}$ pH = $-\log[H_3O^+] = -\log(0.0024) =$ ________

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1 \text{ x } 10^{-14}}{0.0024} = \underline{\hspace{6em}}\ \boldsymbol{M}$$

$$\text{pOH} = -\log(4.167 \text{ x } 10^{-12}) = 12.000 - 0.6198 = \underline{\hspace{4em}}$$

EXAMPLE 7-5

pH Calculation

The hydronium ion concentration of a 0.05 M solution of HCl is 0.05 M. What is the pH of this solution?

$$
\begin{aligned}
\mathrm{pH} &= -\log(5.0 \times 10^{-2}) = -\log 10^{-2} - \log 5.0 \\
&= 2 - 0.70 = 1.30
\end{aligned}
$$

EXAMPLE 7-8

- If the pH of a solution is 4.72, what is the hydronium ion concentration?

$$\mathrm{pH} + \mathrm{pOH} = \mathrm{p}K_w \qquad (7\text{–}58)$$

$$\mathrm{p}K_a + \mathrm{p}K_b = \mathrm{p}K_w \qquad (7\text{–}59)$$