

Chapter 6



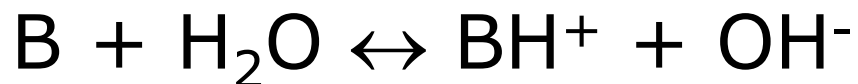
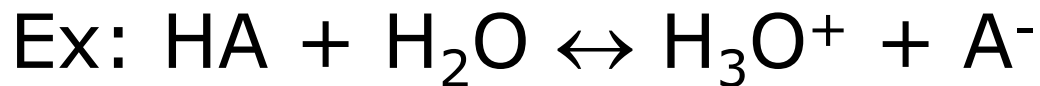
Acid-Base Equilibria

6.1 Acid- Base Theorise

□ Arrhenius theory: is applicable only to water

acid: any substance that ionizes in water to given hydrogen ions.

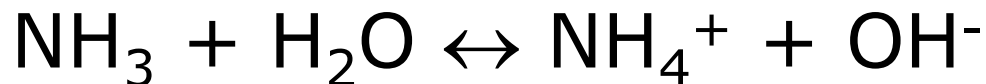
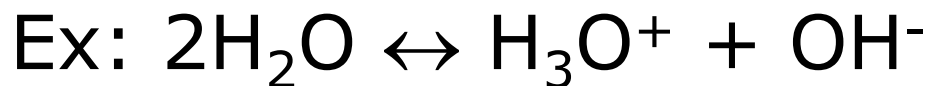
base: ionizes in water to given hydroxyl ions.



□ Franklin theory: theory of solvent systems

acid: a solute that yields the cation of the solvent.

base: a solute that yields the anion of the solvent.



- Brønsted-Lowry theory: is applicable to acid-base reactions in nonionizable solvent.

Ex: benzene

acid: any substance that can donate a proton.

base: any substance that can accept a proton.

conjugate acid-base pair:



leveling effect:

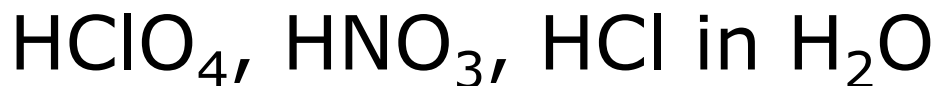


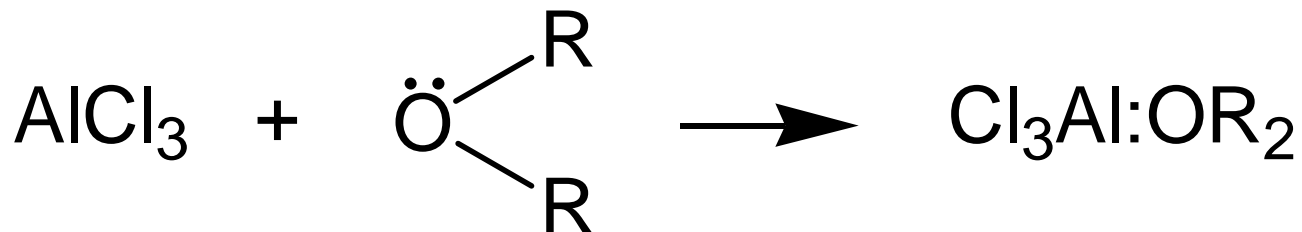
Table 6.1

□ Lewis theory:

acid: a substance that can accept an electron pair.

base: a substance that can donate an electron pair.

Ex:



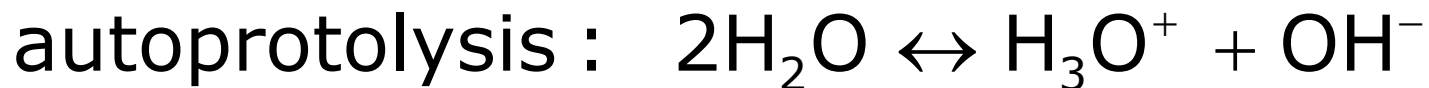
6.2 Acid-Base Equilibria in Water

Table 6.2



$$K_a^\circ = \frac{a_{\text{H}_3\text{O}^+} \cdot a_{\text{OAc}^-}}{a_{\text{HOAc}} \cdot a_{\text{H}_2\text{O}}} \Rightarrow \frac{a_{\text{H}_3\text{O}^+} \cdot a_{\text{OAc}^-}}{a_{\text{HOAc}}}$$

$$K_w^\circ = a_{\text{H}_3\text{O}^+} \cdot a_{\text{OH}^-}$$



6.3 The pH Scale

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

$$\text{pK}_w = \text{pH} + \text{pOH} \text{ at } 25^\circ\text{C}, \text{pK}_w = 14.00$$

$$\text{neutral sol'n} \Rightarrow [\text{H}^+] = [\text{OH}^-]$$

$$\text{acidic sol'n} \Rightarrow [\text{H}^+] > [\text{OH}^-]$$

$$\text{basic sol'n} \Rightarrow [\text{H}^+] < [\text{OH}^-]$$

Ex: 6.6

6.4 Blood pH

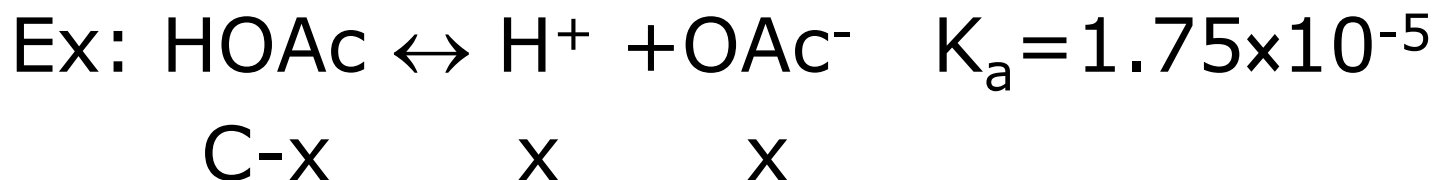
The pH of blood at 37 °C is 7.35 to 7.45

At 37 °C, $K_w = 2.5 \times 10^{-14}$; $pK_w = 13.60$

a neutral sol'n: $pH = 6.80 \approx 1.6 \times 10^{-7} M$

The hydrochloric acid concentration in the stomach \Rightarrow 0.1 to 0.02M

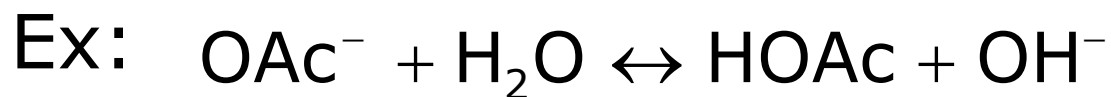
6.5 Weak Acids and Bases



$$\text{C-x} \approx \text{C}, \quad \text{if } C_{\text{HA}} > 100K_a$$

We neglected the $[\text{H}^+]$ from the ionization of water except for very dilute ($< 10^{-6}\text{M}$) or very weak ($K_a < 10^{-12}$) acids.

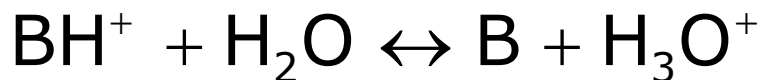
6.6 Salts of Weak Acids and Bases



$$K_b = \frac{[\text{HOAc}][\text{OH}^-]}{[\text{OAc}^-]} = \frac{K_w}{K_a}$$

$$C - x \approx C, \quad \text{if } C^{A^-} > 100K_b$$

$$[\text{OH}^-] = \sqrt{\frac{K_w}{K_a} \cdot C_{A^-}} = \sqrt{K_b \cdot C_{A^-}}$$

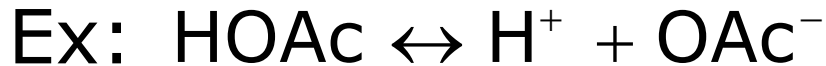


$$[\text{H}^+] = \sqrt{\frac{K_w}{K_b} \cdot C_{\text{BH}^+}} = \sqrt{K_a \cdot C_{\text{BH}^+}}, \quad \text{if } C_{\text{BH}^+} > 100K_a$$

6.7 Buffers

□ Buffer:

a solution that resists change in pH when a small amount of an acid or base is added or when the solution is diluted.



$$[\text{H}^+] = K_a \frac{[\text{HOAc}]}{[\text{OAc}^-]}$$

$$-\log[\text{H}^+] = -\log K_a - \log \frac{[\text{HOAc}]}{[\text{OAc}^-]}$$

$$\text{pH} = \text{p}K_a - \log \frac{[\text{HOAc}]}{[\text{OAc}^-]} \Rightarrow \text{pH} = \text{p}K_a + \log \frac{[\text{OAc}^-]}{[\text{HOAc}]}$$

Henderson – Hasselbalch equation :

$$\text{pH} = \text{p}K_a + \log \frac{[\text{proton acceptor}]}{[\text{proton donor}]}$$

Buffer capacity (buffer intensity, buffer index):

$$\beta = \frac{d C_{\text{BOH}}}{d \text{pH}} = - \frac{d C_{\text{HA}}}{d \text{pH}}$$

The higher the concentration of [HA] and [A⁻], the more acid or base the solution can tolerate.

The larger the buffer capacity is, the more resistant the solution is to pH change.

If buffer solution $> 0.001\text{M}$

$$\Rightarrow \beta = 2.303 \frac{C_{\text{HA}} C_{\text{A}^-}}{C_{\text{H}^+} A + C_{\text{A}^-}}$$

Ex: $[\text{HA}] = 0.10\text{M}$; $[\text{A}^-] = 0.10\text{M}$

$\Rightarrow = 0.050\text{M}$ per pH

when adding 0.0050M $[\text{NaOH}]$

$\Rightarrow \text{pH} = 0.10$

The buffer capacity is maximum when the ratio is unity

$$\Rightarrow \text{pH} = \text{pK}_a$$

In general:

the buffering capacity is satisfactory over a pH range of $\text{pK}_a \pm 1$

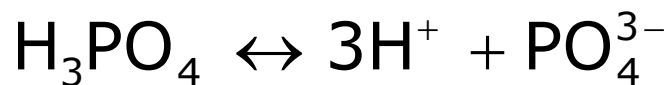
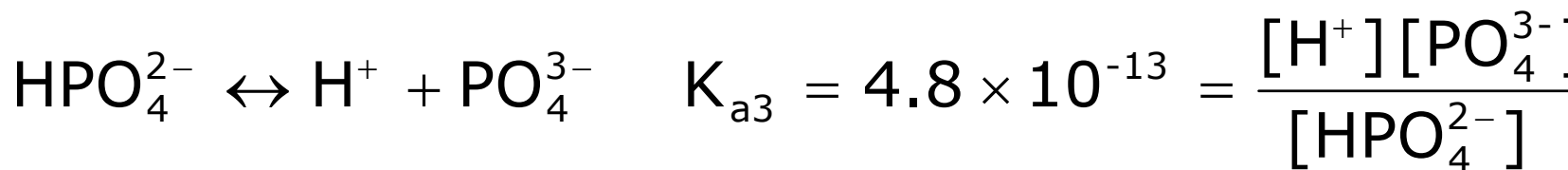
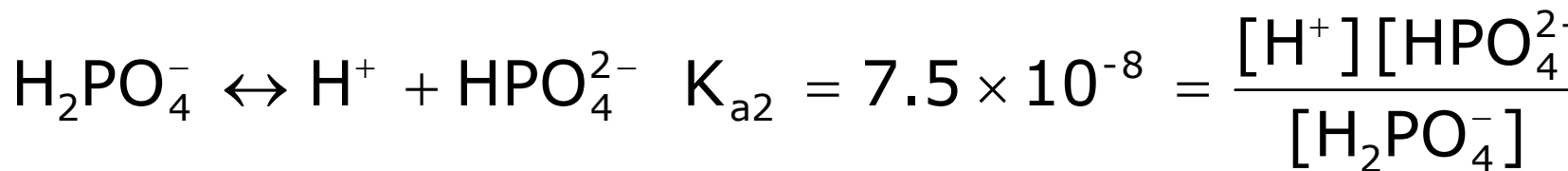
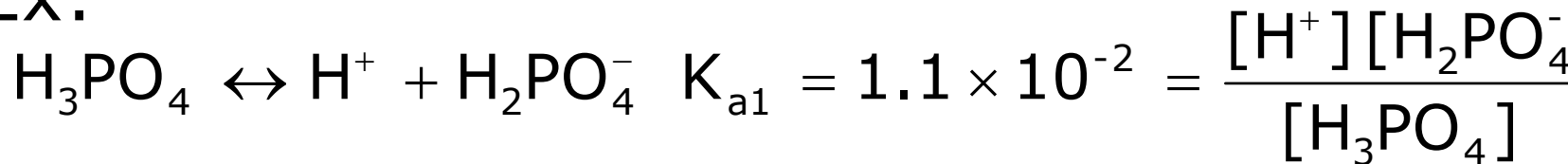
For mixtures of a weak base and its salt.

$$\begin{aligned} \text{pOH} &= \text{p}K_b + \log \frac{[\text{BH}^+]}{[\text{B}]} \\ &= \text{p}K_b + \log \frac{[\text{proton donor}]}{[\text{proton acceptor}]} \end{aligned}$$

The buffering capacity is maximum at a pH equal to $\text{p}K_a$ or $\text{pOH} = \text{p}K_b$

6.8 Polyprotic Acid and Their Salts

Ex:



$$K_a = K_{a1}K_{a2}K_{a3} = 4.0 \times 10^{-22} = \frac{[\text{H}^+]^3[\text{PO}_4^{3-}]}{[\text{H}_3\text{PO}_4]}$$

$$\text{p}K_{a1} = 1.96; \quad \text{p}K_{a2} = 7.12; \quad \text{p}K_{a3} = 12.32$$

If the difference between successive ionization constants is at least 10^4 , each proton can be differentiated in a titration.

If an ionization constant is too small for a pH break to be exhibited in the titration curve.

- Fractions of dissociating species at a given pH: values



$$a_0 = \frac{[\text{H}_3\text{PO}_4]}{\text{CH}_3\text{PO}_4}; a_1 = \frac{[\text{H}_2\text{PO}_4^-]}{\text{CH}_3\text{PO}_4};$$

$$a_2 = \frac{[\text{HPO}_4^{2-}]}{\text{CH}_3\text{PO}_4}; a_3 = \frac{[\text{PO}_4^{3-}]}{\text{CH}_3\text{PO}_4}$$

$$a_0 + a_1 + a_2 + a_3 = 1$$

6.8-4

$$[\text{PO}_4^{3-}] = \frac{K_{a3}[\text{HPO}_4^{2-}]}{[\text{H}^+]} \quad ; \quad [\text{HPO}_4^{2-}] = \frac{K_{a2}[\text{H}_2\text{PO}_4^-]}{[\text{H}^+]} \quad ;$$

$$[\text{H}_2\text{PO}_4^-] = \frac{K_{a1}[\text{H}_3\text{PO}_4]}{[\text{H}^+]}$$

$$\Rightarrow [\text{HPO}_4^{2-}] = \frac{K_{a1}K_{a2}[\text{H}_3\text{PO}_4]}{[\text{H}^+]^2} \quad ; \quad [\text{PO}_4^{3-}] = \frac{K_{a1}K_{a2}K_{a3}[\text{H}_3\text{PO}_4]}{[\text{H}^+]^3}$$

$$C_{\text{H}_3\text{PO}_4} = \frac{K_{a1}K_{a2}K_{a3}[\text{H}_3\text{PO}_4]}{[\text{H}^+]^3} + \frac{K_{a1}K_{a2}[\text{H}_3\text{PO}_4]}{[\text{H}^+]^2} + \frac{K_{a1}[\text{H}_3\text{PO}_4]}{[\text{H}^+]} + [\text{H}_3\text{PO}_4]$$

6.8-5

$$\frac{1}{a_0} = \frac{K_{a1}K_{a2}K_{a3}}{[H^+]^3} + \frac{K_{a1}K_{a2}}{[H^+]^2} + \frac{K_{a1}}{[H^+]} + 1$$

$$a_0 = \frac{1}{\left(\frac{K_{a1}K_{a2}K_{a3}}{[H^+]^3}\right) + \left(\frac{K_{a1}K_{a2}}{[H^+]^2}\right) + \left(\frac{K_{a1}}{[H^+]}\right) + 1}$$

$$a_0 = \frac{[H^+]^3}{[H^+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3}}$$

$$a_1 = \frac{K_{a1} [H^+]^2}{[H^+]^3 + K_{a1} [H^+]^2 + K_{a1} K_{a2} [H^+] + K_{a1} K_{a2} K_{a3}}$$
$$a_2 = \frac{K_{a1} K_{a2} [H^+]}{[H^+]^3 + K_{a1} [H^+]^2 + K_{a1} K_{a2} [H^+] + K_{a1} K_{a2} K_{a3}}$$
$$a_3 = \frac{K_{a1} K_{a2} K_{a3}}{[H^+]^3 + K_{a1} [H^+]^2 + K_{a1} K_{a2} [H^+] + K_{a1} K_{a2} K_{a3}}$$

Fig 6.1

□ Salts of polyprotic acids

1. Amphoteric salts, H_2PO_4^-



$$K_{a2} = \frac{[\text{H}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 7.5 \times 10^{-8}$$



$$K_b = \frac{K_w}{K_{a1}} = \frac{[\text{H}_3\text{PO}_4]}{[\text{H}_2\text{PO}_4^-][\text{OH}^-]} = 9.1 \times 10^{-13}$$

6.8-8

$$C_{\text{H}^+} = [\text{H}^+]_{\text{total}} = [\text{H}^+]_{\text{H}_2\text{O}} + [\text{H}^+]_{\text{H}_2\text{PO}_4^-} - [\text{OH}^-]_{\text{H}_2\text{PO}_4^-}$$

$$[\text{H}^+] = [\text{OH}^-] + [\text{HPO}_4^{2-}] - [\text{H}_3\text{PO}_4]$$

$$[\text{H}^+] = \frac{K_w}{[\text{H}^+]} + \frac{K_{a2}[\text{H}_2\text{PO}_4^-]}{[\text{H}^+]} - \frac{[\text{H}_2\text{PO}_4^-][\text{H}^+]}{K_{a1}}$$

$$[\text{H}^+]^2 = \frac{K_w + K_{a2}[\text{H}_2\text{PO}_4^-]}{1 + \frac{[\text{H}_2\text{PO}_4^-]}{K_{a1}}}$$

$$[\text{H}^+] = \sqrt{\frac{K_{a1}K_w + K_{a1}K_{a2}[\text{H}_2\text{PO}_4^-]}{K_{a1} + [\text{H}_2\text{PO}_4^-]}}$$

for the general case HA^- :

$$[\text{H}^+] = \sqrt{\frac{K_{a1}K_w + K_{a1}K_{a2}[\text{HA}^-]}{K_{a1} + [\text{HA}^-]}}$$

If $K_{a1}K_w \ll K_{a1}K_{a2}[\text{HA}^-]$ and $K_{a1} \ll [\text{HA}^-]$

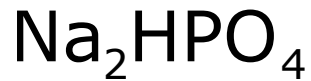
$$\Rightarrow [\text{H}^+] = \sqrt{K_{a1}K_{a2}}$$

Ex:



$$[\text{H}^+] \approx \sqrt{K_{a1}K_{a2}}$$

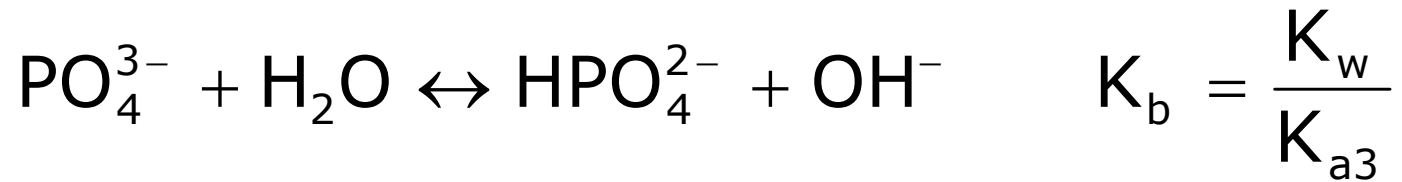
$$= \sqrt{1.1 \times 10^{-2} \times 7.5 \times 10^{-8}} = 2.9 \times 10^{-5} \text{ M}$$



$$[\text{H}^+] \approx \sqrt{K_{a2}K_{a3}}$$

$$= \sqrt{7.5 \times 10^{-8} \times 4.8 \times 10^{-13}} = 1.9 \times 10^{-10} \text{ M}$$

2. Unprotonated salt:



6.9 Physiological Buffers

buffer systems:

hemoglobin / oxyhemoglobin : 62%

$\text{H}_2\text{PO}_4^{2-}$ / HPO_4^{2-} : 22%

plasma protein : 11%

bicarbonate : 5%

for $\text{CO}_2 / \text{HCO}_3^-$

$$\text{pH} = 6.10 + \log \frac{[\text{HCO}_3^-] \approx 26.0 \text{ mmol/L}}{[\text{H}_2\text{CO}_3] \approx 1.3 \text{ mmol/L}}$$

$$\text{pH} = 6.10 + \log \frac{26}{1.3} = 7.40$$

Table 6.3

6.10 Buffers for Biological and Clinical Measurement

- Phosphate buffer:

Table 6.3

limitation:

1. The limited buffering capacity at certain pH values.
2. Phosphat will precipitate or complex many polyvalent cations.

□ Tris buffers:

tris (hydroxymethyl) : $pK_a=8.08$

$[(HOCH_2)_3CNH_2]$ -Tris, or THAM]

advantage:

1. is a primary standard
2. has good stability
3. has a high solubility in physiological fluids

4. is nonhygroscopic and not adsorb CO_2
5. does not precipitate calcium salts
6. does not appear to inhibit many enzyme system
7. is compatible with biological fluids

disadvantage:

its buffering capacity below pH7.5 does begin to diminish

6.11 The Diverse Ion Effect on Acids and Bases: K_a° and K_b°

$$K_a^\circ = \frac{a_{\text{H}^+} \cdot a_{\text{A}^-}}{a_{\text{HA}}} \approx \frac{a_{\text{H}^+} \cdot a_{\text{A}^-}}{[\text{HA}]}$$

$$\Rightarrow K_a^\circ = \frac{[\text{H}^+]f_{\text{H}^+} \cdot [\text{A}^-]f_{\text{A}^-}}{[\text{HA}]} = K_a f_{\text{H}^+} f_{\text{A}^-}$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]} \quad \text{pH} = \text{p}K_a^\circ + \log \frac{a_{\text{A}^-}}{[\text{HA}]}$$

$\mu \uparrow \rightarrow K_a \uparrow \rightarrow f \downarrow \rightarrow \text{p}K_a \downarrow \rightarrow \text{pH} \downarrow$

a buffer solution is dilute, $\mu \downarrow \rightarrow \text{pH} \uparrow$

for $\text{HPO}_4^{2-} / \text{H}_2\text{PO}_4^-$ $\mu \uparrow \rightarrow a_{\text{HPO}_4^{2-}} / a_{\text{H}_2\text{PO}_4^-} \downarrow$

6.12 Logarithmic Concentration Diagrams

Fig 6.2 , Fig 6.3

system point: $\text{pH} = \text{pK}_a$

Fig 6.4