Isoelectric point (IEP)

e.g. pH of milk 6.6 (casein IEP=4.6)

- It is pH at which zwitterion concentration at maximum
- It has been used for determination of protein and amino acids.
- The molecules have ------------- solubility at IEP.
- The net charge of a molecule at its IEP is -----------.
- Charge of a molecule at pH above its IEP is ----------- and below is -----------.

Solutions containing Strong acids

Strong acid concentration of H is equal to initial concentration of acid.

Solutions containing Only a Weak Acid

$$[H_3O^+] = \sqrt{K_a C_a}$$

EXAMPLE 7–12

Calculate pH

Calculate the pH of a 0.01 M solution of salicylic acid, which has a $K_a = 1.06 \times 10^{-3}$ at 25°C.

(*a*) Using equation (7–102), we find

$$[H_3O^+] = \sqrt{(1.06 \times 10^{-3}) \times (1.0 \times 10^{-2})}$$
$$= 3.26 \times 10^{-3}\ M$$

pH=2.48

EXAMPLE 7–13

Calculate pH

Calculate the pH of a 1-g/100 mL solution of ephedrine sulfate. The molecular weight of the salt is 428.5, and K_b for ephedrine base is 2.3×10^{-5}.

(*a*) The ephedrine sulfate, $(BH^+)_2SO_4$, dissociates completely into two BH^+ cations and one SO_4^{2-} anion. Thus, the concentration of the weak acid (ephedrine cation) is twice the concentration, C_s, of the salt added.

$$C_a = \boxed{2C_s} = \frac{2 \times 10\ \text{g/liter}}{428.5\ \text{g/mole}} = 4.67 \times 10^{-2}\ \text{M}$$

(*b*)
$$K_a = \frac{1.00 \times 10^{-14}}{2.3 \times 10^{-5}} = 4.35 \times 10^{-10}$$

(*c*)
$$[H_3O^+] = \sqrt{(4.35 \times 10^{-10}) \times (4.67 \times 10^{-2})} = 4.51 \times 10^{-6}\ \text{M}$$

All assumptions are valid. We have

$$\text{pH} = -\log(4.51 \times 10^{-6}) = 5.35$$

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Solutions Containing Only a Weak Base

$$[H_3O^+] = \sqrt{\frac{K_a K_w}{C_b}}$$

$$[OH] = \sqrt{K_b C_b}$$

EXAMPLE 7–14

Calculate pH

What is the pH of a 0.0033 M solution of cocaine base, which has a basicity constant of 2.6×10^{-6}? We have

$$[OH^-] = \sqrt{(2.6 \times 10^{-6}) \times (3.3 \times 10^{-3})} = 9.26 \times 10^{-5}\ \text{M}$$

All assumptions are valid. Thus,

$$\text{pOH} = -\log(9.26 \times 10^{-5}) = 4.03$$
$$\text{pH} = 14.00 - 4.03 = 9.97$$

Solutions Containing a Single Conjugate Acid–Base Pair

$$\boxed{[H_3O^+] = \frac{K_a C_a}{C_b}}$$

EXAMPLE 7–16

Calculate pH

What is the pH of a solution containing acetic acid 0.3 M and sodium acetate 0.05 M? We write

$$[H_3O^+] = \frac{(1.75 \times 10^{-5}) \times (0.3)}{5.0 \times 10^{-2}}$$
$$= 1.05 \times 10^{-4}\ \text{M}$$

All assumptions are valid. Thus,

$$\text{pH} = -\log(1.05 \times 10^{-4}) = 3.98$$

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EXAMPLE 7–17

Calculate pH

What is the pH of a solution containing ephedrine 0.1 M and ephedrine hydrochloride 0.01 M? Ephedrine has a basicity constant of 2.3×10^{-5}; thus, the acidity constant for its conjugate acid is 4.35×10^{-10}.

$$[H_3O^+] = \frac{(4.35 \times 10^{-10}) \times (1.0 \times 10^{-2})}{1.0 \times 10^{-1}}$$
$$= 4.35 \times 10^{-11}\ \text{M}$$

All assumptions are valid. Thus,

$$\text{pH} = -\log(4.35 \times 10^{-11}) = 10.36$$

Solutions Containing Two Weak Acids

$$\boxed{[H_3O^+] = \sqrt{K_1 C_{a1} + K_2 C_{a2}}}$$

EXAMPLE 7–21

Calculate pH

What is the pH of a solution containing acetic acid, 0.01 mole/liter, and formic acid, 0.001 mole/liter? We have

$$[H_3O^+] = \sqrt{(1.75 \times 10^{-5})(1.0 \times 10^{-2}) + (1.77 \times 10^{-4})(1.0 \times 10^{-3})}$$
$$= 5.93 \times 10^{-4} \text{ M}$$
$$\text{pH} = -\log(5.93 \times 10^{-4}) = 3.23$$

Solutions Containing a Salt of a Weak Acid and a Weak Base

$$\boxed{[H_3O^+] = \sqrt{K_1 K_2}}$$

$$\underset{\text{Acid}_1}{NH_4^+} + \underset{\text{Base}_2}{AC^-} \rightleftharpoons \underset{\text{Acid}_2}{HAc} + \underset{\text{Base}_1}{NH_3}$$

EXAMPLE 7–22

Calculate pH

Calculate the pH of a 0.01 M solution of ammonium acetate. The acidity constant for acetic acid is $K_2 = K_a = 1.75 \times 10^{-5}$, and the basicity constant for ammonia is $K_b = 1.74 \times 10^{-5}$.

(*a*) K_1 can be found by dividing K_b for ammonia into K_w:

$$K_1 = \frac{1.00 \times 10^{-14}}{1.74 \times 10^{-5}} = 5.75 \times 10^{-10}$$

$$[H_3O^+] = \sqrt{(5.75 \times 10^{-10}) \times (1.75 \times 10^{-5})}$$
$$= 1.00 \times 10^{-7} \text{ M}$$

Note that all of the assumptions are valid. We have

$$\text{pH} = -\log(1.00 \times 10^{-7}) = 7.00$$

Solutions Containing a Weak Acid and a Weak Base

$$\underset{\text{Acid}_1}{HC_6H_5O_7^{2-}} + \underset{\text{Base}_2}{H_2PO_4^-} \rightleftharpoons \underset{\text{Acid}_2}{H_3PO_4} + \underset{\text{Base}_1}{C_6H_5O_7^{3-}}$$

$$\boxed{[H_3O^+] = \sqrt{K_1 K_2}}$$

EXAMPLE 7-24

Calculate pH

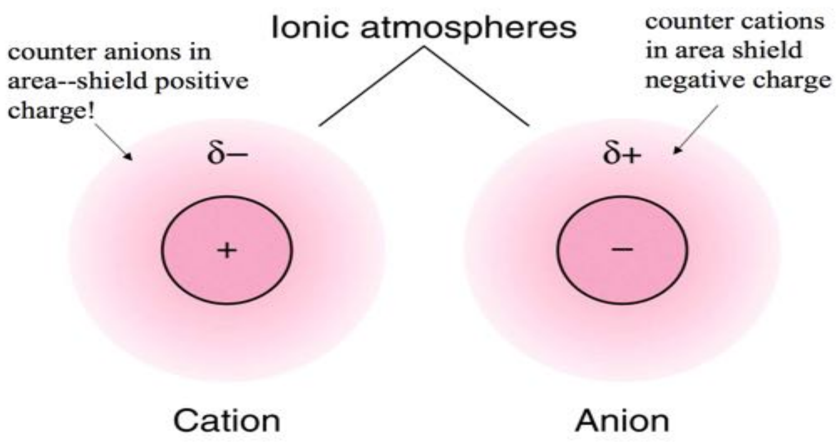
What is the pH of a solution containing NaH_2PO_4 and disodium citrate (disodium hydrogen citrate) $Na_2HC_6H_5O_7$, both in a concentration of 0.01 M? The third acidity constant for $HC_6H_5O_7^{2-}$ is 4.0×10^{-7}, whereas the first acidity constant for phosphoric acid is 7.5×10^{-3}. We have

$$[H_3O^+] = \sqrt{(4.0 \times 10^{-7}) \times (7.5 \times 10^{-3})}$$
$$= 5.48 \times 10^{-5}\ M$$

All assumptions are valid. We find

$$pH = -\log(5.48 \times 10^{-5}) = 4.26$$

Ionic strength



Effect of Ionic Strength on Acidity Constants

$$HB + H_2O \rightleftharpoons H_3O^+ + B$$

$$K = \frac{\alpha_{H_3O} + \alpha_B}{\alpha_{HB}} = \frac{[H_3O^+][B]}{[HB]} \cdot \frac{\gamma H_3O^+ \gamma_B}{\gamma_{HB}}$$

For monotropic molecule

$$\boxed{pK' = pK + \frac{0.51(2Z - 1)\sqrt{\mu}}{1 + \sqrt{\mu}}}$$

For zwitterion molecule

$$\boxed{pK_1' = pK_1 + \frac{0.51\sqrt{\mu}}{1 + \sqrt{\mu}} - K_r\mu}$$

$$\boxed{pK_2' = pK_2 - \frac{0.51\sqrt{\mu}}{1 + \sqrt{\mu}} + K_r\mu}$$

K_r=Salting in constant=0.32 for amino acid in water

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EXAMPLE 7-27

Calculate pH

Calculate the pH of a 0.1 M solution of acetic acid to which enough KCl had been added to give an ionic strength of 0.1 M at 25°C. The pK_a for acetic acid is 4.76.

(*a*)
$$pK_a' = 4.76 - \frac{0.51\sqrt{0.10}}{1 + \sqrt{0.10}}$$
$$= 4.76 - 0.12 = 4.64$$

(*b*) Taking logarithms of equation (7-99) gives

$$pH = \frac{1}{2}(pK_a' - \log C_a)$$

in which we now write pK_a as pK'_a:

$$pH = \frac{1}{2}(4.64 + 2.00) = 3.32$$

EXAMPLE 7-28

Calculate pH

Calculate the pH of a 10^{-3} M solution of glycine at an ionic strength of 0.10 at 25°C. The pK_a values for glycine are pK_1 = 2.35 and pK_2 = 9.78.

(*a*)
$$pK_1' = 2.35 + \frac{0.51\sqrt{0.10}}{1+\sqrt{0.10}} - 0.32(0.10)$$
$$= 2.35 + 0.12 - 0.03 = 2.44$$

(*b*)
$$pK_2' = 9.78 - \frac{0.51\sqrt{0.10}}{1+\sqrt{0.10}} + 0.32(0.10)$$
$$= 9.78 - 0.12 + 0.03 = 9.69$$

(*c*) Taking logarithms of equation (7–118) gives
$$pH = \frac{1}{2}(pK_1 + pK_2)$$
$$= \frac{1}{2}(2.44 + 9.69) = 6.07$$

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Thanks for your attention