الجامعة المستنصرية

Ionic Equilibria

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COLLEGE OF PHARMACY MUSTANSIRIYAH UNIVERSITY

PHYSICAL PHARMACY

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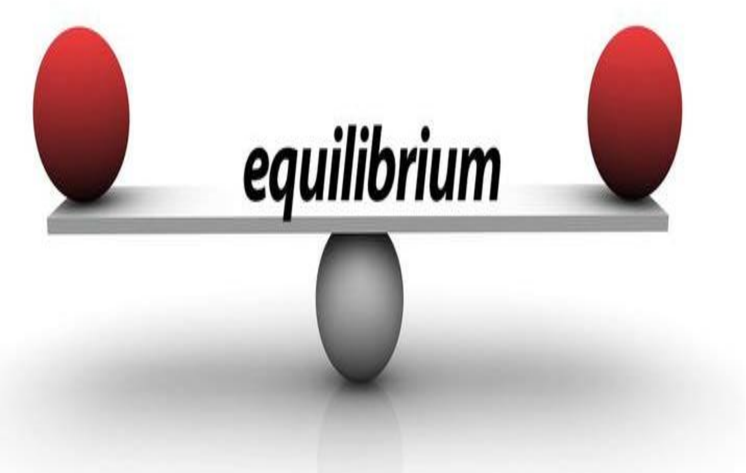


Outline

Definitions:

- Arrhenius, Brønsted–Lowry, Lewis
- Solvent classification
- Acid–base equilibrium, Ka, Kb, Kw
- Dissociation constant - Ka
- Ionization of Weak Bases (Kb)
- Autoionization of Water & Kw
- Relation Between K**a** and K**b**
- SÖRENSEN'S PH
- Proton Balance Equation (PBE)
- Calculation of pH

Arrhenius Definition

Acid: a substance that liberates H^+ upon dissociation.

$$HCl\ (aq) \longrightarrow H^+\ (aq) + Cl^-\ (aq)$$

Base: a substance that supplies OH^- upon dissociation.

$$NaOH\ (aq) \longrightarrow Na^+\ (aq) + OH^-\ (aq)$$

Brønsted–Lowry Definition

Acid: proton (H^+) donor. Any species that donates an H^+ ion. An acid must contain H in its formula; HNO_3 and $H_2PO_4^-$ are two examples, all Arrhenius acids are Brønsted-Lowry acids.

Base: proton (H^+) acceptor. Any species that accepts an H^+ ion. A base must contain lone pair of electrons to bind the H^+ ion; a few examples are NH_3, CO_3^{2-}, F^-, as well as OH^-.

- In an acid-base reaction, the transfer of protons occurs from an acid to a base.
- Conjugate base:

$$\underset{\text{Acid 1}}{CH_3COOH\ (aq)} + \underset{\text{Base 2}}{H_2O\ (l)} \rightleftharpoons \underset{\text{Acid 2}}{H_3O^+\ (aq)} + \overset{\text{Conjugate base}}{\boxed{\underset{\text{Base 1}}{CH_3COO^-\ (aq)}}}$$

- Conjugate acid:

$$\underset{\text{Base 1}}{NH_3\ (aq)} + \underset{\text{Acid 2}}{H_2O\ (l)} \rightleftharpoons \overset{\text{Conjugate acid}}{\boxed{\underset{\text{Acid 1}}{NH_4^+\ (aq)}}} + \underset{\text{Base 2}}{OH^-\ (aq)}$$

- The relative strengths of acids and bases are measured by the tendencies of these substances to give up and take on protons.
- The strength of an acid depends not only on its ability to give up a proton but also on the ability of the solvent to accept the proton from the acid.
- This is called the basic strength of the solvent.

Lewis Electronic Theory

Lewis acid: electron-pair acceptor (e.g.: BF_3, $AlCl_3$ which don't contain H and acts as an acid).

Any substance, such as the H+ ion, that can accept a pair of nonbonding electrons.

Lewis base: electron-pair donor:

Amines (R–NH_2): Nitrogen has a lone pair of electrons.

Ethers (R–O–R): Oxygen atom has two lone pairs.

Carboxylic acid anhydrides (R–CO–O–CO–R): Oxygen atoms have lone pairs that can interact with electron-deficient species.

(They don't contain OH and they act as a base).

Any substance, such as the OH- ion, that can donate a pair of nonbonding electrons.

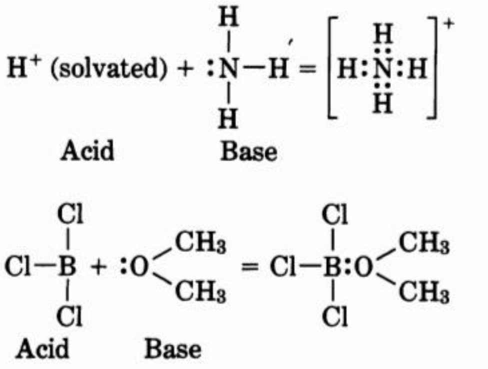
$$AlCl_3 + :Cl^- \rightarrow AlCl_4^-$$

Al has 3 valence electrons, forms 3 bonds with Cl

3 lone pairs (6 electrons)

1 unpaired electron (1 electron available for bonding) because valence is 7

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$



Classification of Solvents

1. A Protophilic (basic solvent): is one that is capable of accepting protons from the solute. Such solvents as acetone, ether, and liquid ammonia.

2. A Protogenic (acidic solvent): is a proton donating compound and is represented by acids such as formic acid, acetic acid, sulfuric acid, liquid HCl, and liquid HF.

3. Amphiprotic solvents: act as both proton acceptors and proton donors, and this includes water and the alcohols.

4. Aprotic solvents: these solvents neither accept nor donate protons. such as the hydrocarbons.

Acid–Base Equilibrium

- Acid–base reactions occur when an acid reacts with a base to form a new acid and a new base.

General form: $\underset{\text{Acid 1}}{HCl} + \underset{\text{Base 2}}{H_2O} \rightleftharpoons \underset{\text{Acid 2}}{H_3O^+} + \underset{\text{Base 1}}{Cl^-}$

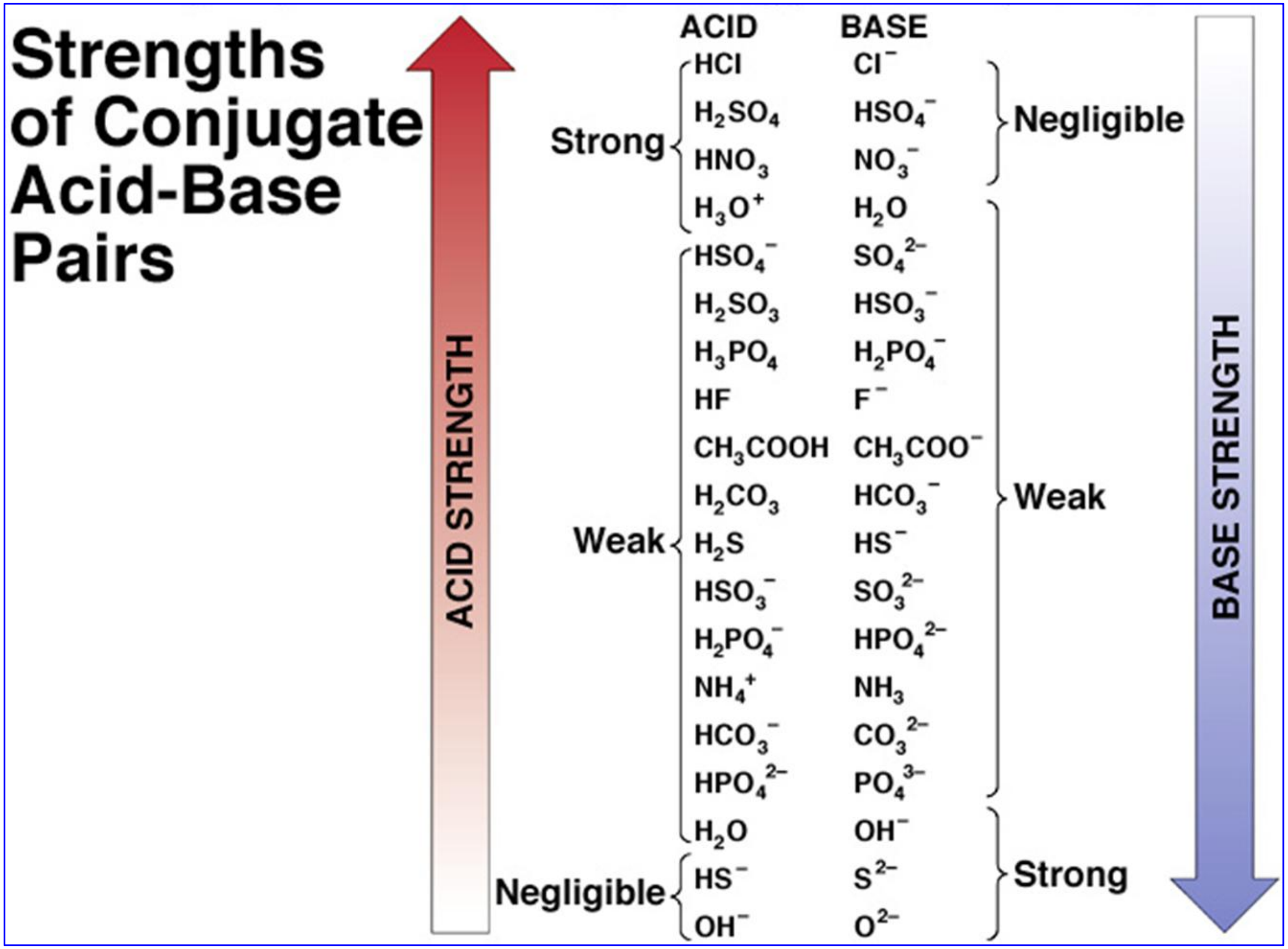
- The arrows pointing in the forward and reverse directions indicate that the reaction is proceeding to the right and left simulataneously.

Acid–Base Equilibrium

According to the concept of equilibrium:

The rate of the forward reaction decreases with time as acetic acid is depleted, whereas the rate of the reverse reaction begins at zero and increases as larger quantities of hydrogen ions and acetate ions are formed. Finally, a balance is attained when the two rates are equal.

Acid–Base Equilibrium



Strengths of Conjugate Acid-Base Pairs

	ACID	BASE	
Strong	HCl	Cl^-	Negligible
	H_2SO_4	HSO_4^-	
	HNO_3	NO_3^-	
	H_3O^+	H_2O	Weak
Weak	HSO_4^-	SO_4^{2-}	
	H_2SO_3	HSO_3^-	
	H_3PO_4	$H_2PO_4^-$	
	HF	F^-	
	CH_3COOH	CH_3COO^-	
	H_2CO_3	HCO_3^-	
	H_2S	HS^-	
	HSO_3^-	SO_3^{2-}	
	$H_2PO_4^-$	HPO_4^{2-}	
	NH_4^+	NH_3	
	HCO_3^-	CO_3^{2-}	
	HPO_4^{2-}	PO_4^{3-}	
	H_2O	OH^-	Strong
Negligible	HS^-	S^{2-}	
	OH^-	O^{2-}	

Dissociation Constant — Ka

Equilibrium constant (Ka) quantifies acid strength (means how much an acid **dissociates (ionizes)** in water**).**

Larger Ka → stronger acid (more ionized) (means that the concentration of **H**$^+$ and **A**$^-$ is high compared to undissociated acid (**HA**)).

Means equilibrium lies far to the **right** → most acid molecules have given up their protons (H^+).

While Small Ka → weak acid (slightly ionized).

In general, the acidity constant for an **uncharged weak acid HB** can be expressed by:

Proton donor

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

Acid 1 Base 2 Acid 2 Base 1

$$Ka = \frac{[H_3O^+][B^-]}{[HB]}$$

Dissociation Constant — Ka

Example 7.1:
In a liter of 0.1 M solution, acetic acid was found by conductivity analysis to dissociate into 1.32 x 10^{-3} g ions ("moles") each of hydrogen and acetate ion at 25°C. What is the acidity or dissociation constant K_a for acetic acid?

$$K_a = \frac{(1.32\ x10^{-3})^2\ \cancel{mole}}{0.1\ \cancel{mole}}$$

$$K_a = \frac{1.74\ x10^{-6}}{1\ x10^{-1}} = 1.74\ x10^{-5}$$

Note:

Molarity (M)= $\frac{\text{moles of solute}}{\text{liters of solution}}$

So if:

$M = 0.1\ M, \qquad V = 1\ L$

Then:

Moles $of\ solute = M \times V$
$= 0.1 \times 1 = 0.1\ mol$

Ionization of Weak Bases (Kb)

- weak bases B, exemplified by NH3, react with water as follows:

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

$$K_b = \frac{[OH^-]\,[BH^+]}{[B]}$$

Example: $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

$$K_b = \frac{[NH_4{}^+][OH^-]}{[NH_3]}$$

Autoionization of Water & Kw

Relation: $K_a \cdot K_b = K_w$ (for conjugate weak acid and weak base pairs)

$$1\ H_2O + 1\ H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$K_C = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

The ion-product for water, Kw:

$K_C \times [H_2O\ ]^2 = K_W = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$ (at 25°C)

For pure water the concentration of hydroxyl and hydronium ions must be equal:

$[H_3O^+] = [OH^-] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7}$ M (at 25°C)

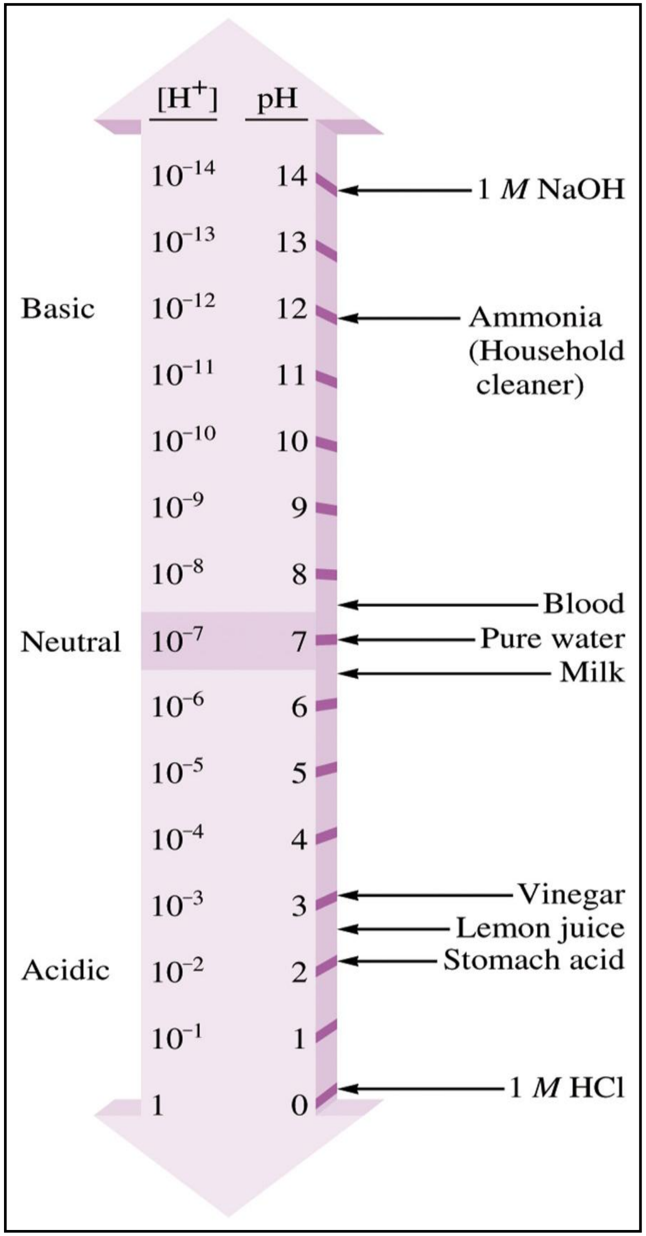
Autoionization of Water & Kw

Example 7.3:

A quantity of HCl (1.5 × 10^{-3}M) is added to water at 25°C to increase the hydrogen ion concentration from 1 × 10^{-7} to 1.5 × 10^{-3} mole/liter. What is the new hydroxyl ion concentration?

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

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{1.5 \times 10^{-3}} = 6.7 \times 10^{-12} \text{ mole/liter}$$



The pH scale and pH values of some common substances

Relation 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.

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

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

$$K_b = \frac{K_w}{K_a}$$

$$K_a = \frac{K_w}{K_b}$$

Relation Between K_a and K_b

Example 7.4:

Calculate K_a

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

$$K_a = \frac{K_w}{K_b} = \frac{1.00\ x\ 10^{-14}}{1.74\ x\ 10^{-5}} = 5.75 \times 10^{-10}$$

SÖRENSEN'S PH

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

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.

$$pH + pOH = pK_w = 14.00 \text{ (at 25 °C)}.$$

$$pK_a + pK_b = pK_w$$

Calculation of pH

Example 7.5:

The hydronium ion concentration of a 0.05 M solution of HCl is 0.05 M. what is the pH of the solution.

$$pH = -\log[H^+] = -\log(5.0 \text{ x } 10^{-2})$$
$$= -\log 10^{-2} - \log 5.0 = 2 – 0.7 = 1.3$$

Proton Balance Equation (PBE)

Stepwise Dissociation of Phosphoric Acid (H_3PO_4)

Phosphoric acid (weak acid), normally only looses 1 proton in solution, but lose all 3 when reacted (strong base with heat).

1. Add water:

$$H_3PO_4\ (aq) + H_2O\ (l) \rightleftharpoons H_2PO_4^-\ (aq) + H_3O^+\ (aq)$$
$$H_2PO_4^-\ (aq) + H_2O\ (l) \rightleftharpoons HPO_4^{-2}\ (aq) + H_3O^+\ (aq)$$
$$HPO_4^{-2}\ (aq) + H_2O\ (l) \rightleftharpoons PO_4^{-3}\ (aq) + H_3O^+\ (aq)$$

2- **Left side $[H_3O^+]$ + Consume proton x No. of proton gained = Right side $[OH^-]$ + Release proton x No. of proton lost**

$3 - PBE$: $[H_3O^+] = [OH^-] + [H_2PO_4^-] + 2[HPO_4^{-2}] + 3[PO_4^{-3}]$

Calculation of pH

Solutions of Strong Acids and Bases

Strong acids and bases are considered to ionize 100% when placed in water.

$$[H_3O^+] \cong C_a$$

C_a : Total acid concentration (1 x 10^{-6} or more)

A similar treatment for a solution of a strong base such as NaOH gives

$$[OH^-] \cong C_b$$

C_b : Total base concentration (1 x 10^{-6} or more)

Calculation of pH

Solutions Containing Only a Weak Acid

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

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 x 10^{-5}

(a) Ephedrine sulfate $(BH^+)_2SO^4$ dissociate 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.

$$C_a = 2C_s = \frac{2 \; x \; 10 \; g/L}{428.5 \; g/mole} = 4.67 \text{ x } 10^{-2} \text{ M}$$

$$\text{Molarity (M)} = \frac{\text{Concentration (g/L)}}{\text{Molecular Weight (g/mol)}}$$

(b) $$K_a = \frac{1 \; x 10^{-14}}{2.3 \; x 10^{-5}} = 4.35 \text{ x } 10^{-10}$$

(C) $$[H_3O^+] = \sqrt{4.35 \text{ x } 10^{-10} \; x \; 4.67 \text{ x } 10^{-2}} = 4.51 \text{ x } 10^{-6} \text{ M}$$

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

Calculation of pH

Solutions Containing Only a Weak Base

$$[\mathrm{OH^-}] = \sqrt{\mathrm{K_b C_b}}$$

Example 7.13:

Calculate pH

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

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

$$\mathrm{pOH} = -\log (9.26 \times 10^{-5}) = 4.03$$

$$\mathrm{pH} = 14 - 4.03 = 9.97$$

Calculation of pH

Solutions Containing a Single Conjugate Acid–Base Pair

In a solution composed of a weak acid and a salt of that acid (e.g., acetic acid and sodium acetate) or a weak base and a salt of that base (e.g., ephedrine and ephedrine hydrochloride.

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

Example 7.16:

Calculate pH

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

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

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

Calculation of pH

Example 7.17:

Calculate pH

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

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

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

Calculation of pH

Solutions Containing Two Weak Acids

$$[H_3O^+] = \sqrt{K_1C_{a1} + K_2C_{a2}}$$

Example 7.16:

Calculate pH

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

$$[H_3O^+] = \sqrt{(1.75 \text{ x } 10^{-5})(1.0 \text{ x } 10^{-2}) + (1.77 \text{ x } 10^{-4})}(1.0 \text{ x } 10^{-3})$$

$$= 5.93 \text{ x } 10^{-4}\ M$$

pH = -log $(5.93 \text{ x } 10^{-4})$ = 3.23


Thank
you