Acid-base equilibrium

Acid-Base Equilibrium

https://www.youtube.com/watch?v=rlvEvwViJGk

https://www.youtube.com/watch?v=Xeuyc55LqiY

Acids and Bases

Acid is a substance which can act as a proton (H^+) donor.

$$HCl \rightarrow H^+ + Cl^-$$

Base is a substance which can act as proton (H^+) acceptor or hydroxyl ion (OH^-) donor.

$$NaOH \rightarrow Na^+ + OH^-$$

$$(CH_3)_2NNH_2 + H_2O \rightarrow (CH_3)_2NNH_3^+ + OH^-$$

Ampholyte is a substance that can act both as acid and base.

$HCO_3^- + H^+ \rightarrow H_2CO_3 + H_2O$ and $HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$

Acid-Base equilibrium

$$HCl \leftrightarrow H^+ + Cl^-$$

$$HAc \leftrightarrow H^+ + Cl^-$$

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$$

No reaction has 100% degree.

Everything in the environment is at the equilibrium.

Equilibrium constant

$$\text{Equilibrium constant} = \frac{\text{Rate of direct reaction}}{\text{Rate of reverse reaction}}$$

$$\text{Direct reaction: } K = \frac{[H^+][Ac^-]}{[HCl]}$$

$$\text{Reverse reaction: } K' = \frac{[HAc]}{[H^+][Ac^-]}$$

Ac – Acetate (CH_3COO^-);

In brackets – molar concentrations at equilibrium.

Water concentration is always excluded from calculations if dealing with aqueous solutions. It is because its concentration is much higher than concentration of all other substances.

Basic of thermodynamics

Enthalpy (H) – internal energy of chemical substance

Entropy (S) – measure of “disorder“ of chemical substance

Gibbs Free Energy (G) – is a measure of both enthalpy and entropy

$$\Delta G = \Delta H - T * \Delta S$$

Enthalpy change

Enthalpy change shows the amount of energy being released or adsorbed

$HCl \leftrightarrow H^+ + Cl^- - 74.85$ kJ/mol

$\Delta H = -74.85$ kJ/mol (thermal energy was released)

$NaCl \leftrightarrow Na^+ + Cl^- + 3.87$ kJ/mol

$\Delta H = 3.87$ kJ/mol (thermal energy was adsorbed)

Question:

Should we heat or cool the system to enhance reverse reaction in these systems?

Le Chatelier’s Principle

If a chemical system at equilibrium experiences a change in concentration, temperature, volume, or partial pressure, the equilibrium shifts to counteract the imposed change and a new equilibrium is established

$$HAc \leftrightarrow H^{+} + Cl^{-}$$

Where will equilibrium be shifted is the concentration of [H+] is increased?

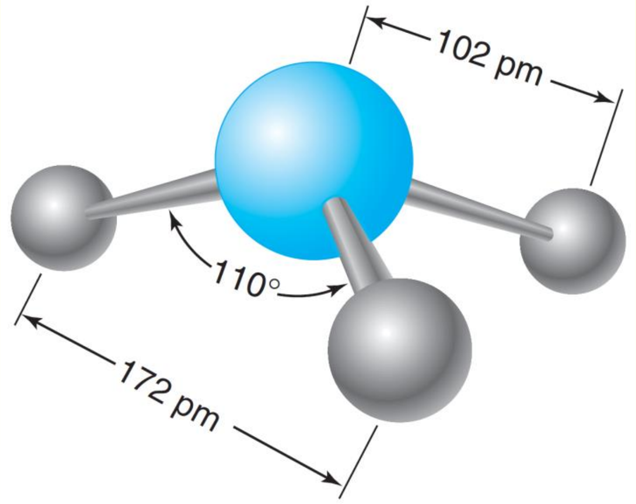
Dissociation of water

Correct form (theory): $2H_2O \leftrightarrow H_3O^+ + OH^-$

Simplified form (for all calculations, etc.): $H_2O \leftrightarrow H^+ + OH^-$

Water autoprotolysis constant $K_w = [OH^-]\,[H^+] = \mathbf{1.01 \times 10^{-14}}$ at 25ºc

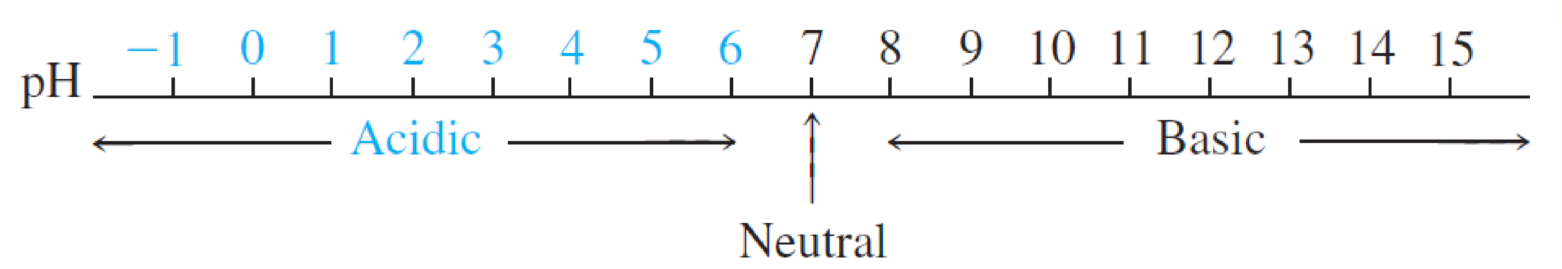
H_3O^+ structure



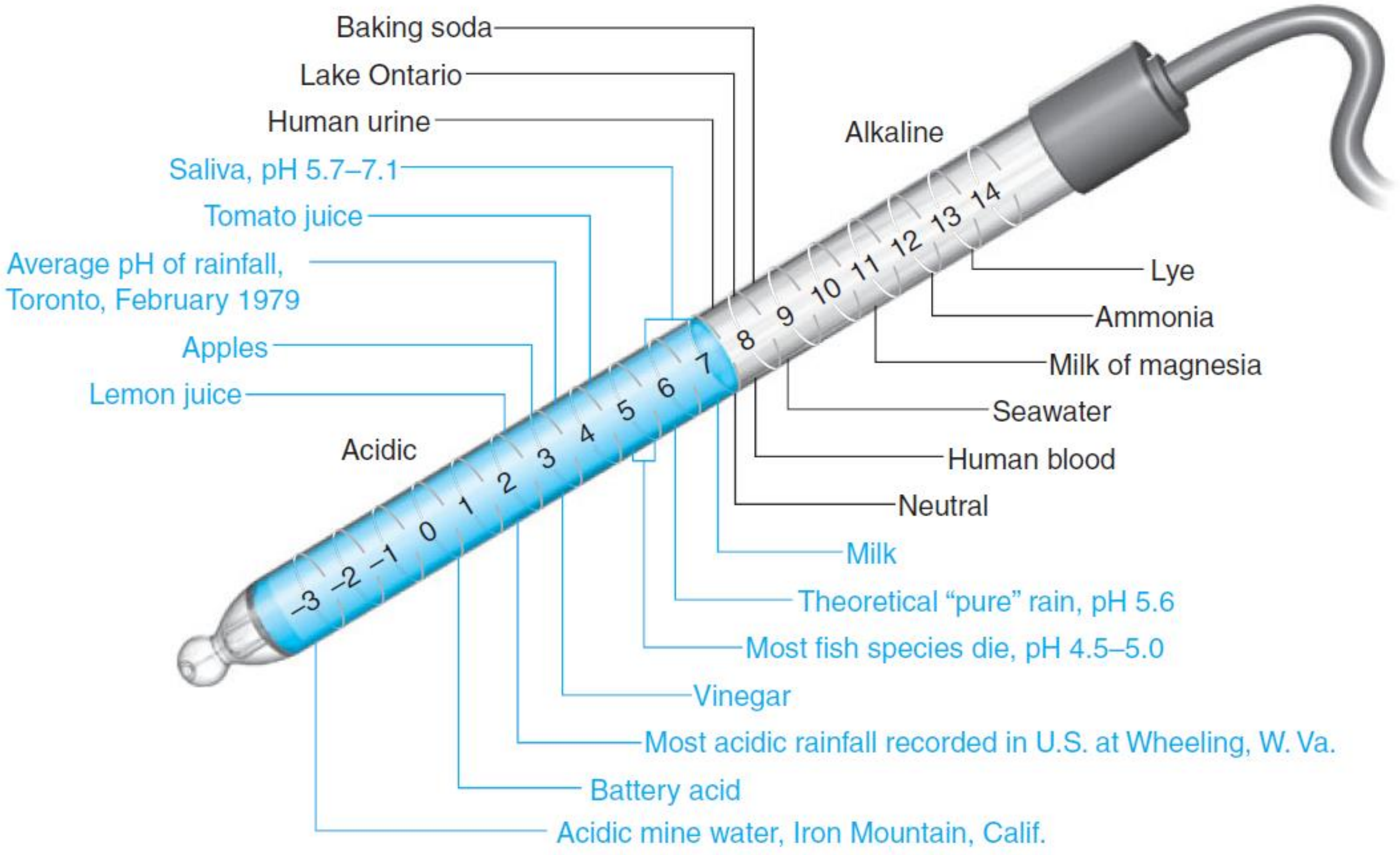
pH

Crucial factor for most environmental and chemical processes.
It shows acidity of sample (solution).

$$pH = -\log[H^+]$$



Acidity of various substances



pOH

$$pOH = 14 - pH$$

Shows the basicity of sample (solution).

Rarely used in calculations.

Strong and weak acids and bases

Strong acids and bases are almost totally dissociated in solution. Examples: hydrochloric, sulphuric, nitric, perchloric acids; lithium, sodium, potassium hydroxides. Dissociation constants are very high for these substances (see handbooks).

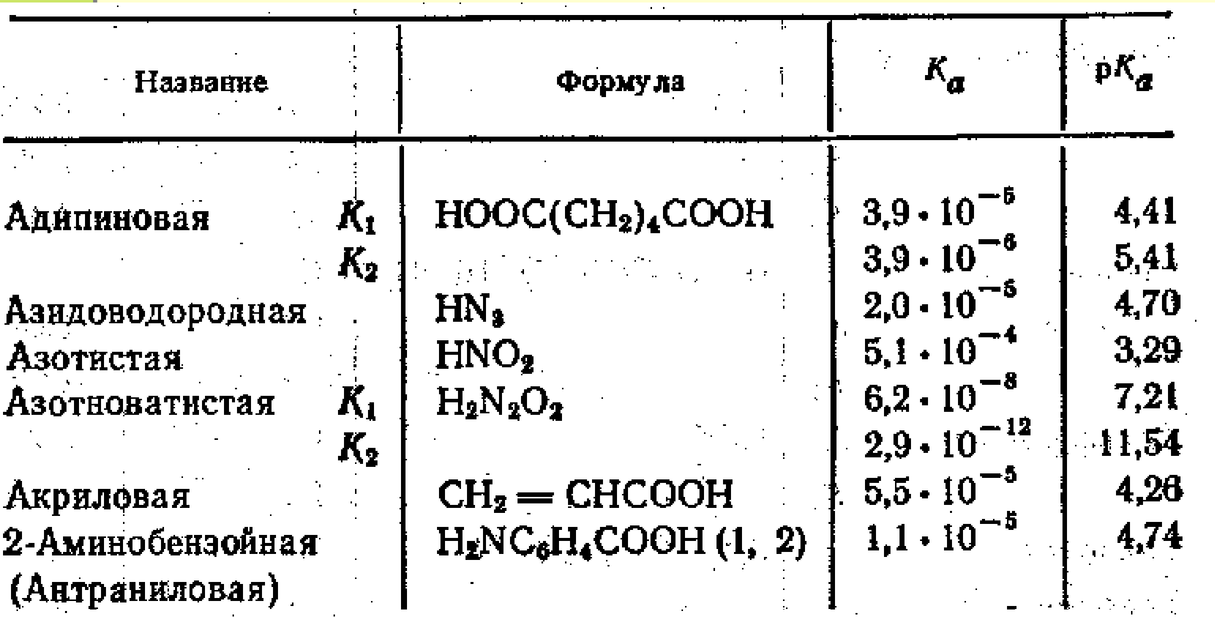
Weak acids and bases are partially dissociated in solutions. Examples: acetic, lemon, formic acids; ammonium hydroxide, amines, hydrazines. Dissociation constants are low for these substances (see handbooks)

Anions formed by dissociation of weak acids are weak bases:

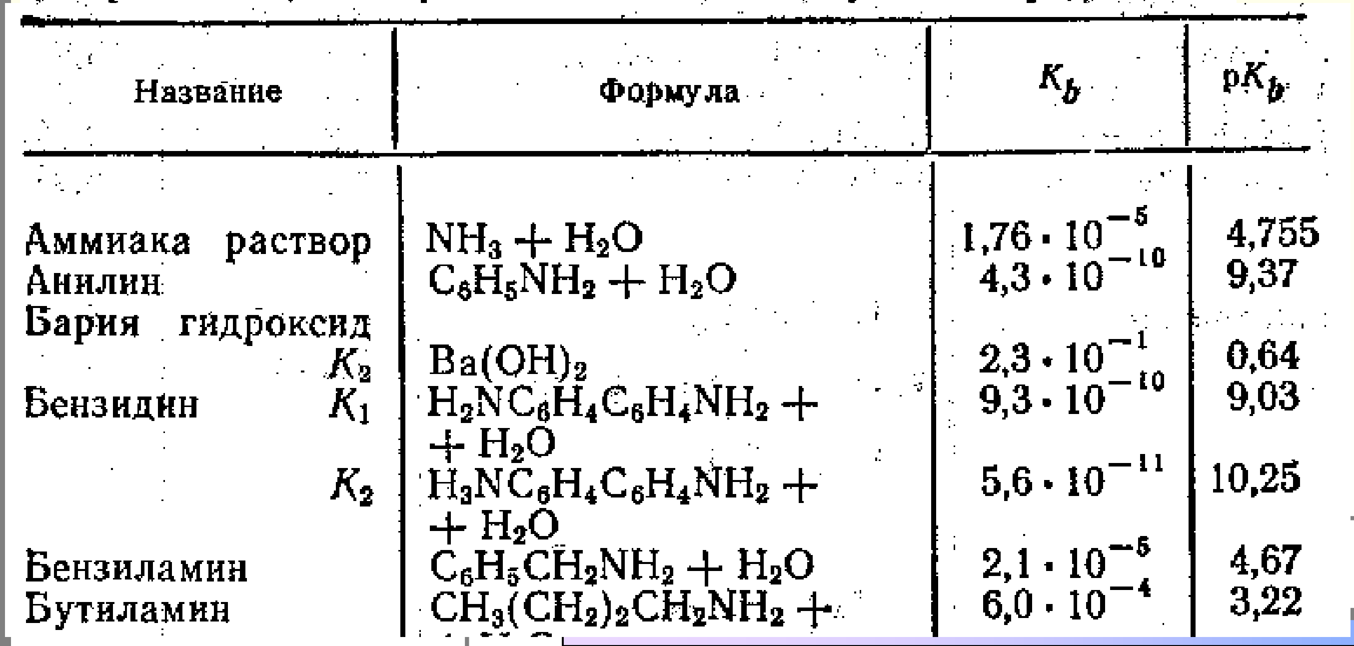
$$Ac^- + H_2O \leftrightarrow HAc + OH^-$$

$$K_a = \frac{[Ac^-]\,[H^+]}{[HAc]}\ ;\ Kb = \frac{[HAc][OH^-]}{[Ac^-]}$$

Acid and base dissociation constants from Lourier handbook



Название		Формула	K_a	pK_a
Адипиновая	K_1	$HOOC(CH_2)_4COOH$	$3{,}9 \cdot 10^{-5}$	4,41
	K_2		$3{,}9 \cdot 10^{-6}$	5,41
Азидоводородная		HN_3	$2{,}0 \cdot 10^{-5}$	4,70
Азотистая		HNO_2	$5{,}1 \cdot 10^{-4}$	3,29
Азотноватистая	K_1	$H_2N_2O_2$	$6{,}2 \cdot 10^{-8}$	7,21
	K_2		$2{,}9 \cdot 10^{-12}$	11,54
Акриловая		$CH_2 = CHCOOH$	$5{,}5 \cdot 10^{-5}$	4,26
2-Аминобензойная (Антраниловая)		$H_2NC_6H_4COOH$ (1, 2)	$1{,}1 \cdot 10^{-5}$	4,74



Название		Формула	K_b	pK_b
Аммиака раствор		$NH_3 + H_2O$	$1{,}76 \cdot 10^{-5}$	4,755
Анилин		$C_6H_5NH_2 + H_2O$	$4{,}3 \cdot 10^{-10}$	9,37
Бария гидроксид	K_2	$Ba(OH)_2$	$2{,}3 \cdot 10^{-1}$	0,64
Бензидин	K_1	$H_2NC_6H_4C_6H_4NH_2 + H_2O$	$9{,}3 \cdot 10^{-10}$	9,03
	K_2	$H_3NC_6H_4C_6H_4NH_2 + H_2O$	$5{,}6 \cdot 10^{-11}$	10,25
Бензиламин		$C_6H_5CH_2NH_2 + H_2O$	$2{,}1 \cdot 10^{-5}$	4,67
Бутиламин		$CH_3(CH_2)_2CH_2NH_2 +$	$6{,}0 \cdot 10^{-4}$	3,22

$$pK_a = -\log K_a$$

$$pK_b = -\log K_b$$

Buffers

A buffered solution resists changes in pH when acids or bases are added or when dilution occurs.

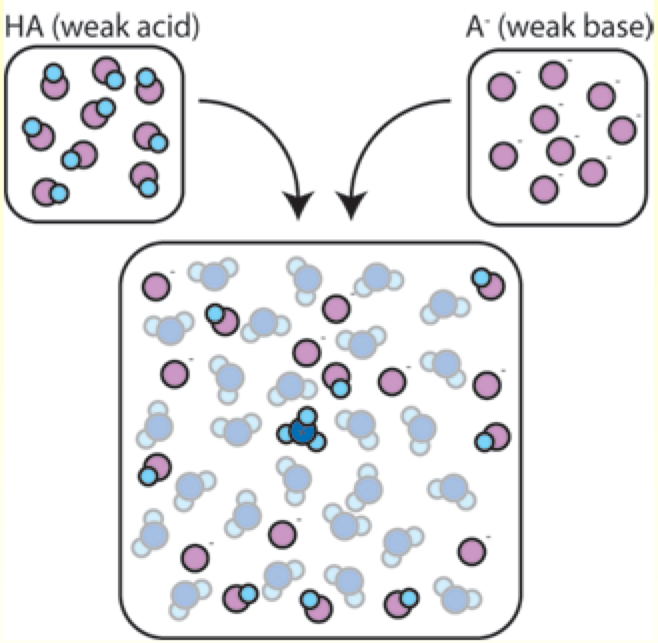
The **buffer** is a mixture of an acid and its conjugate base. There must be comparable amounts of the conjugate acid and base (within a factor of ~10) to exert significant buffering.

Buffer solutions achieve their resistance to pH change because of the presence of an equilibrium between the acid HA and its conjugate base A^-.

$$HA \rightleftharpoons H^+ + A^-$$

Mixing a weak acid with conjugate base

If you mix A moles of a weak acid with B moles of its conjugate base, the moles of acid remain close to A and the moles of base remain close to B. Little reaction occurs to change either concentration.



Mixing a weak acid with conjugate base

To understand why this should be so, look at the K_a and K_b reactions in terms of Le Châtelier's principle. Consider an acid with pK_a 4.00 and its conjugate base with pK_b 10.00. Let's calculate the fraction of acid that dissociates in a 0.10 M solution of HA.

$$\underset{0.10 - x}{\text{HA}} \rightleftharpoons \underset{x}{\text{H}^+} + \underset{x}{\text{A}^-} \qquad \text{p}K_\text{a} = 4.00$$

$$\frac{x^2}{\text{HA}_\text{m} - x} = K_\text{a} \Rightarrow x = 3.1 \times 10^{-3}\,\text{M}$$

Fraction of dissociation *a* = 0.031.

In a solution containing 0.10 mol of A- dissolved in 1.00 L, the extent of reaction of A- with water is even smaller.

$$\underset{0.10 - x}{\text{A}^-} + \text{H}_2\text{O} \rightleftharpoons \underset{x}{\text{HA}} + \underset{x}{\text{OH}^-} \qquad \text{p}K_\text{b} = 10.00$$

$$\frac{x^2}{\text{F} - x} = K_\text{b} \Rightarrow x = 3.2 \times 10^{-6}$$

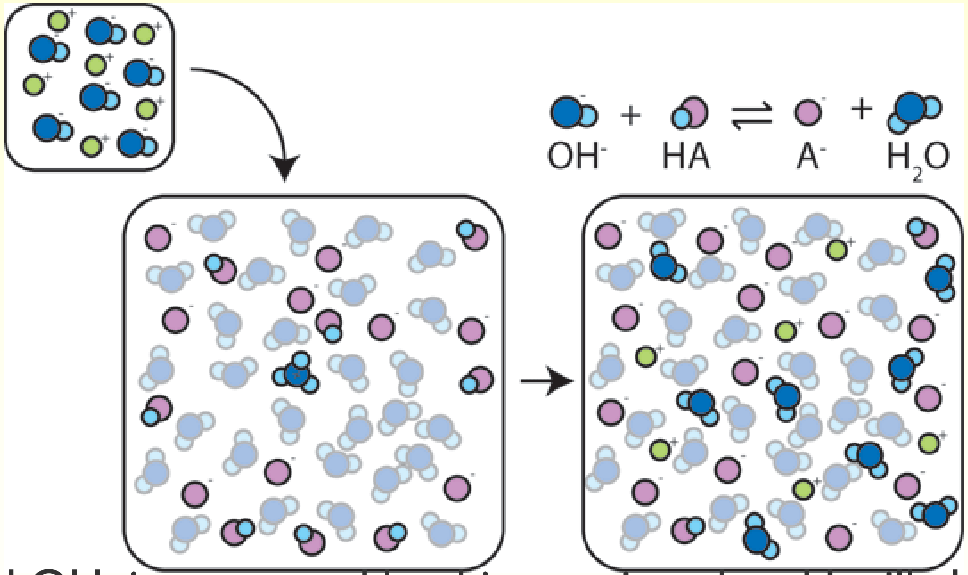
$$\text{Fraction of association} = \alpha = \frac{x}{\text{F}} = 3.2 \times 10^{-5}$$

HA dissociates very little, and adding extra A to the solution makes HA dissociate even less. Similarly, A does not react much with water, and adding extra HA makes A react even less.

Buffer action

If a strong base is added to a buffer, the weak acid will give up its H^+ in order to transform the base (OH^-) into water (H_2O) and the conjugate base:

$$HA + OH^- \rightarrow A^- + H_2O.$$

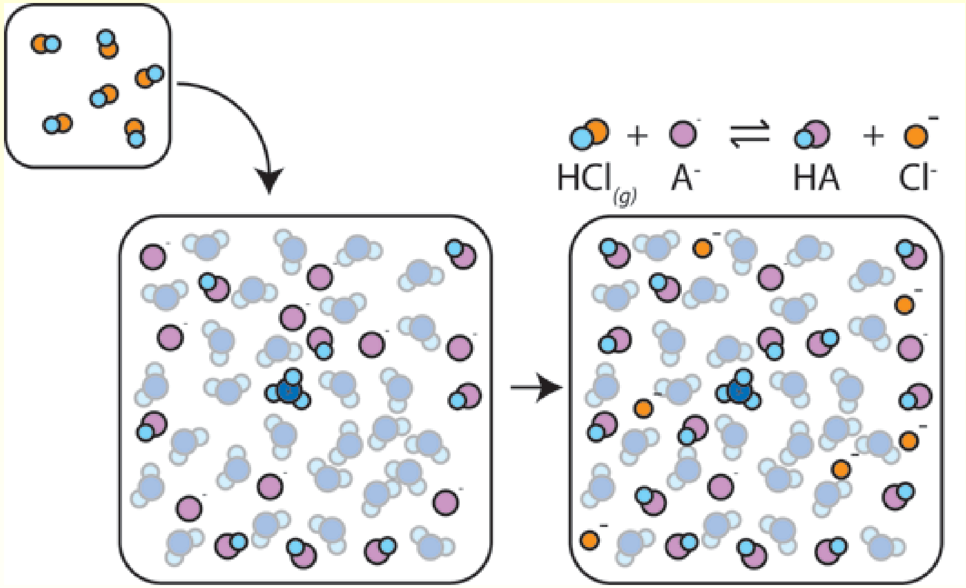


Since the added OH^- is consumed by this reaction, the pH will change only slightly.

Buffer action

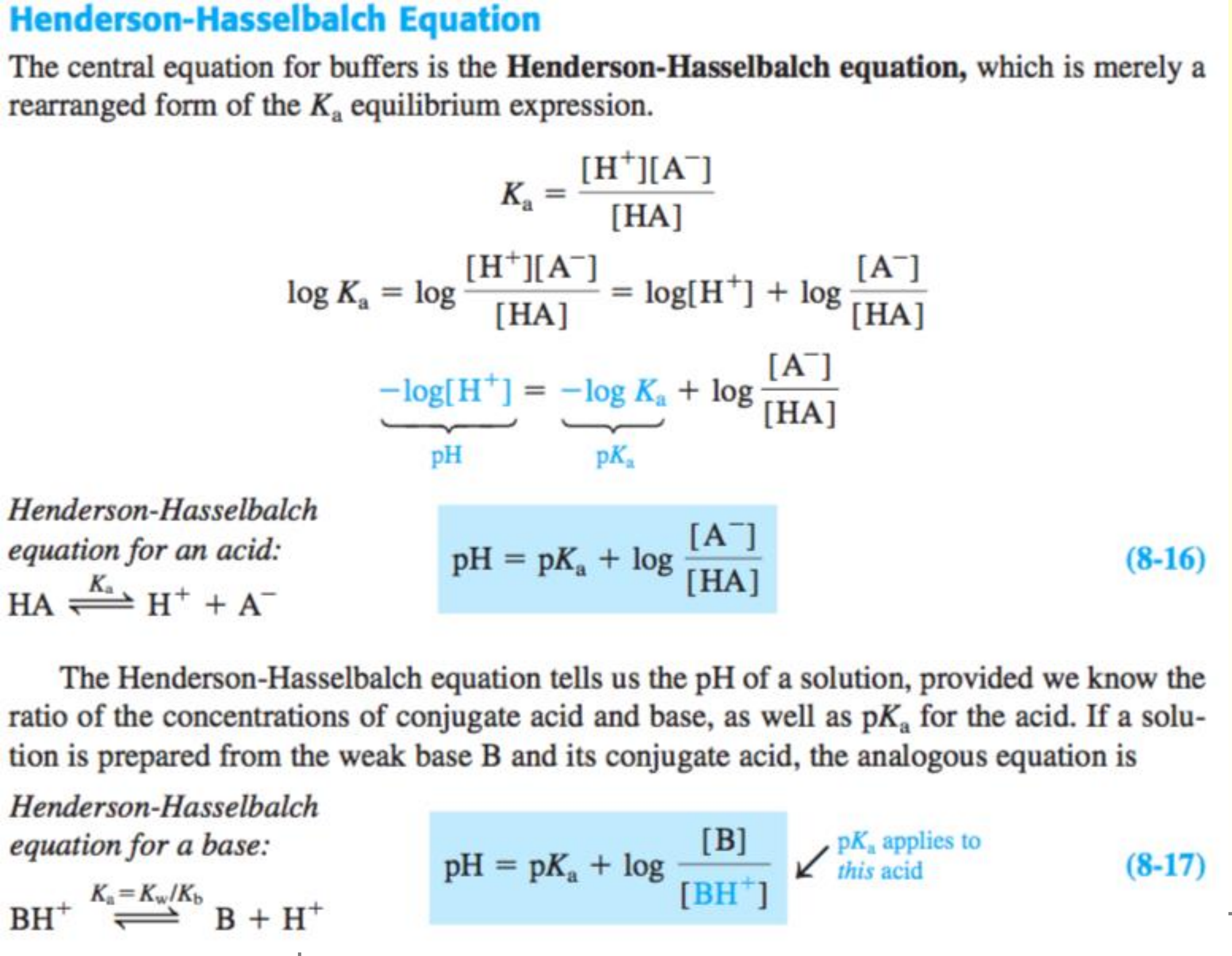
If a strong acid is added to a buffer, the weak base will react with the H^+ from the strong acid to form the weak acid HA:

$$H^+ + A^- \rightarrow HA.$$



The H^+ gets absorbed by the A^- instead of reacting with water to form $H_3O^+(H^+)$, so the pH changes only slightly.

pH of buffer solution



Henderson-Hasselbalch Equation

The central equation for buffers is the **Henderson-Hasselbalch equation,** which is merely a rearranged form of the K_a equilibrium expression.

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$\log K_a = \log \frac{[H^+][A^-]}{[HA]} = \log[H^+] + \log \frac{[A^-]}{[HA]}$$

$$\underbrace{-\log[H^+]}_{pH} = \underbrace{-\log K_a}_{pK_a} + \log \frac{[A^-]}{[HA]}$$

Henderson-Hasselbalch equation for an acid:

$$HA \xrightleftharpoons{K_a} H^+ + A^-$$

$$\boxed{pH = pK_a + \log \frac{[A^-]}{[HA]}} \qquad \textbf{(8-16)}$$

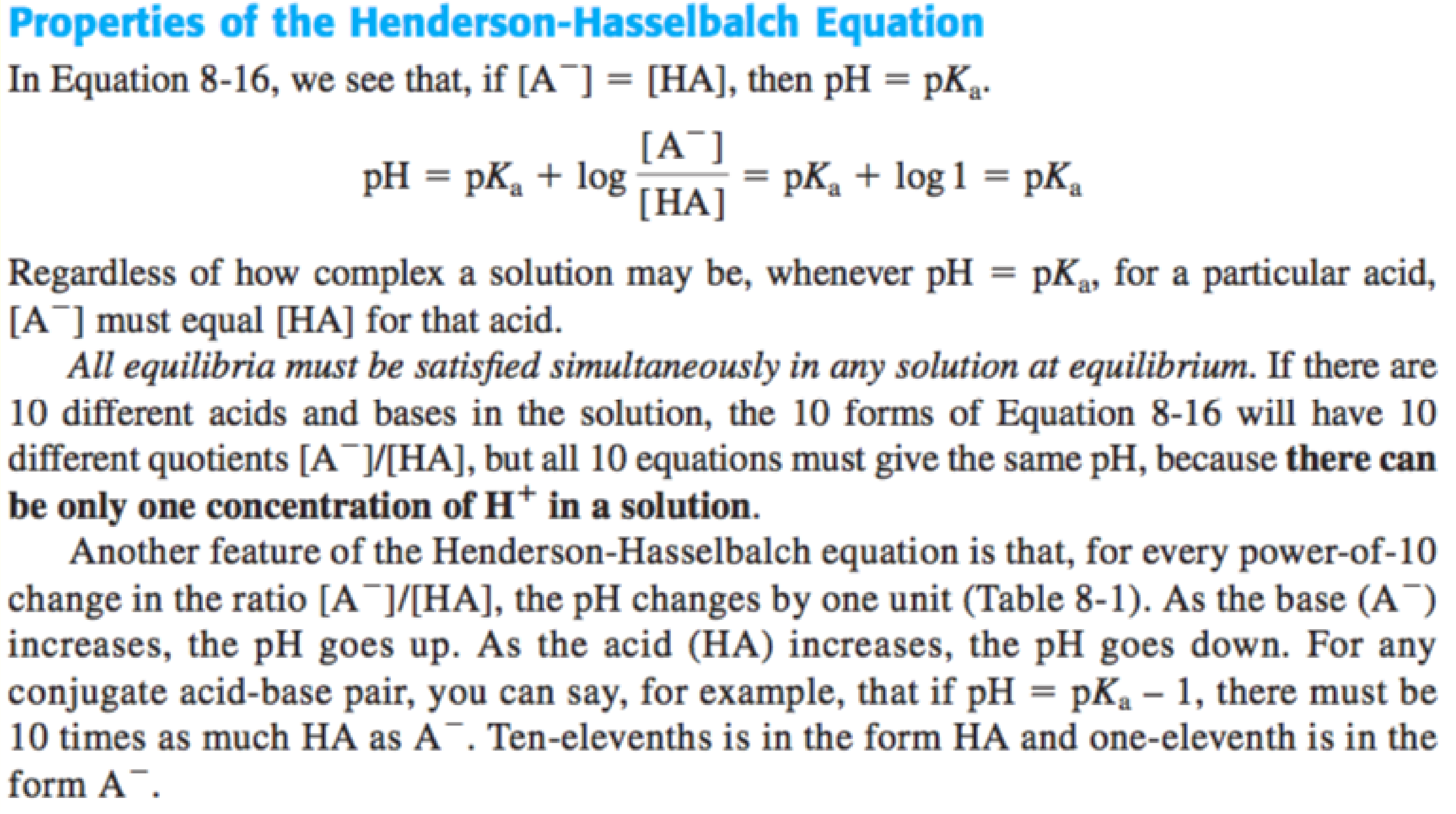
The Henderson-Hasselbalch equation tells us the pH of a solution, provided we know the ratio of the concentrations of conjugate acid and base, as well as pK_a for the acid. If a solution is prepared from the weak base B and its conjugate acid, the analogous equation is

Henderson-Hasselbalch equation for a base:

$$BH^+ \xrightleftharpoons{K_a = K_w/K_b} B + H^+$$

$$\boxed{pH = pK_a + \log \frac{[B]}{[BH^+]}} \swarrow \text{pK_a applies to \textit{this} acid} \qquad \textbf{(8-17)}$$

Acid-Base Equilibrium



Properties of the Henderson-Hasselbalch Equation

In Equation 8-16, we see that, if $[A^-] = [HA]$, then $pH = pK_a$.

$$pH = pK_a + \log\frac{[A^-]}{[HA]} = pK_a + \log 1 = pK_a$$

Regardless of how complex a solution may be, whenever $pH = pK_a$, for a particular acid, $[A^-]$ must equal $[HA]$ for that acid.

All equilibria must be satisfied simultaneously in any solution at equilibrium. If there are 10 different acids and bases in the solution, the 10 forms of Equation 8-16 will have 10 different quotients $[A^-]/[HA]$, but all 10 equations must give the same pH, because **there can be only one concentration of H^+ in a solution.**

Another feature of the Henderson-Hasselbalch equation is that, for every power-of-10 change in the ratio $[A^-]/[HA]$, the pH changes by one unit (Table 8-1). As the base (A^-) increases, the pH goes up. As the acid (HA) increases, the pH goes down. For any conjugate acid-base pair, you can say, for example, that if $pH = pK_a - 1$, there must be 10 times as much HA as A^-. Ten-elevenths is in the form HA and one-eleventh is in the form A^-.