Chemistry 30 Acids & Bases

Properties of Acids (& Bases)

- dissolve in H₂O(I)
- blue litmus \rightarrow red (or red litmus \rightarrow blue)
- taste sour (taste bitter)
- react with Mg, Zn to form H₂(g)
- neutralize bases (neutralize acids)
- conduct

Arrhenius Definition of Acids and Bases

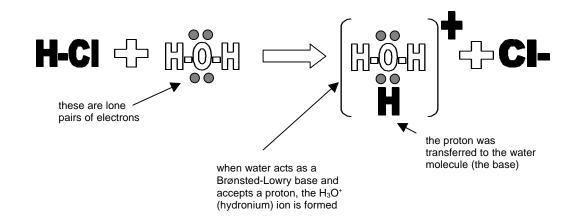
- all acids produce hydrogen ions (H⁺(aq)) when dissolved in water
- all bases produce hydroxide ions (OH (aq)) when dissolved in water
- the properties of acids and bases are due to the H⁺(aq) and OH⁻(aq) produced
- all neutral substances that are neutral are neutral because they don't produce H⁺(aq) when dissolved

| ex: | $HNO_3(aq) \rightarrow H^+(aq) + NO_3^-(aq)$ | - acid |
|------|--|--|
| | $NaOH(aq) \rightarrow Na^{+}(aq) + OH(aq)$ | - base |
| | $LiCl(aq) \rightarrow Li^{+}(aq) + Cl^{-}(aq)$ | - neutral |
| BUT! | $Na_2CO_3(aq) \rightarrow 2Na^+(aq) + CO_3^{2-}(aq)$ | not neutral!!! (basic) |

The Arrhenius definition isn't enough to explain all acidic & basic substances

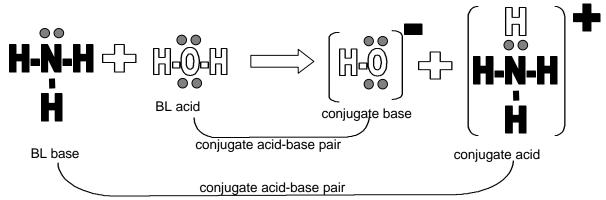
Brønsted-Lowry Acids and Bases

- an acid is a proton donor (i.e. H⁺ donor)
- a base is a proton acceptor (i.e. H⁺ acceptor) must have an lone electron pair to accept the proton
- an acid can only behave like an acid if there's a base present to accept the H⁺ ion (when HCl is dissolved in water, it behaves like an acid, but in a nonpolar solvent, HCl is NOT an acid)
- water can behave as both a proton donor (acid) and a proton acceptor (base) the positive hydrogen ion is attracted to the negative lone pair, and "bonds" to the water molecule instead of the chloride ion, forming the H₃O⁺(aq) (hydronium ion) water is acting as a proton acceptor (base), and HCl(aq) is the proton donor (acid)



ex:

• water can also behave as a proton donor (base), for example with ammonia (NH₃)



- Brønsted-Lowry acids and bases always come in pairs termed conjugate pairs
- when a BL acid (in this case H₂O) donates its proton, it becomes a BL base (OH⁻), the "conjugate base" of water. The pair, H₂O and OH⁻ are called a "conjugate acid-base pair"
- NH₃ behaves as a BL base (accepting a proton), its conjugate acid is NH₄⁺

These reactions are really equilibrium reactions:

| NH ₃ (g) + | H-OH(I) | $\stackrel{\rightarrow}{\rightarrow}$ | NH4 ⁺ (aq) + | OH⁻(aq) |
|-----------------------|---------|---------------------------------------|-------------------------|---------|
| BL-base | BL-acid | | BL-acid | BL-base |

- when a base accepts a proton \rightarrow acid (conjugate acid)
- when an acid donates a proton \rightarrow base (conjugate base)
- conjugate acid-base pair differ only by ONE H⁺ ion
- conjugate base always has a charge -1 compared to its conjugate acid
- \blacklozenge strength of the acid, \blacklozenge strength of the conjugate base

Weak and Strong Acids

• Just like many other reactions, not all acids and bases will completely dissociate – but reach equilibrium instead → Ka (just a special case of Keq for acids, Kb for bases)

| $HCI(aq) + H_2O(I) \rightarrow H_3O^{+}(aq) + CI^{-}(aq)$ | Ka = 1.3 x 10 ⁶ (almost all products) ** strong acid |
|---|--|
| $CH_{3}COOH(aq) + H_{2}O(I) \rightleftharpoons CH_{3}COO-(aq) + H_{3}O^{+}(aq)$ | Ka = 1.8 x 10-5 (very few products) ** weak acid |

- the stronger the acid, the more likely it is to give up a proton (same with bases, the stronger the base, the more likely it is to accept a proton)
- strength has NOTHING to do with the concentration of the acid (or base)

p. 11 in the data booklet -strongest acids are at the top left of the table (↑↑ Ka – 100% ionization) -strongest bases are at the bottom left of the table (↓↓ Ka – means favours the reverse reaction)

 There are only 6 "strong" acids; the "strong" bases are any soluble hydroxides (salts with OH⁻ ions that dissolve in water)

- strong acids and bases ionize 100% (no equilibrium) (ex: HCI(aq) + H₂O(I) \rightarrow H₃O⁺(aq) + CI⁻(aq))
- weak acids and bases ionize < 100% (equilibrium) (ex: HF(aq) + H₂O(I) \Rightarrow H₃O⁺(aq) + F⁻(aq))
- conjugates of the strong acids and bases are SO weak, they will not ionize at all (this is true for all of the 6 strong acids and the soluble hydroxides)
 (ex: Cl⁻(aq) + H₂O(l) ← HCl(aq) + H₂O(l) so no reaction— this reaction will not take place in the forward direction)
- the stronger an acid, the weaker its conjugate base (and vice versa)

Acidity/Basicity of Salts (Salt Hydrolysis)

- a salt is an ionic compound
- whether a salt is acidic, basic or neutral depends on whether the ions that form the salt behave as BL acids, BL bases or neither
- each ion acts independently

 $\begin{array}{ll} \mathsf{NH}_4^+(\mathsf{aq}) + \mathsf{H}_2\mathsf{O}(\mathsf{I}) \rightleftarrows \mathsf{NH}_3(\mathsf{aq}) + \mathsf{H}_3\mathsf{O}^+(\mathsf{aq}) & \mathsf{CO}_3^{\ 2^-}(\mathsf{aq}) + \mathsf{H}_2\mathsf{O}(\mathsf{I}) \rightleftarrows \mathsf{HCO}_3^-(\mathsf{aq}) + \mathsf{OH}^-(\mathsf{aq}) \\ (\mathsf{BL}-\mathsf{A}) & (\mathsf{BL}-\mathsf{B}) & \\ \\ \mathsf{CI}^-(\mathsf{aq}) + \mathsf{H}_2\mathsf{O}(\mathsf{I}) \hookleftarrow \mathsf{no} \ \mathsf{reaction} & \mathsf{Na}^+(\mathsf{aq}) + \mathsf{H}_2\mathsf{O}(\mathsf{I}) \twoheadrightarrow \mathsf{no} \ \mathsf{reaction} \\ (\mathsf{neutral}) & (\mathsf{if} \ \mathsf{an} \ \mathsf{ion} \ \mathsf{isn't} \ \mathsf{on} \ \mathsf{p}.\mathsf{11}, \ \mathsf{assume} \ \mathsf{it} \ \mathsf{is} \ \mathsf{a} \ \mathsf{spectator}) \end{array}$

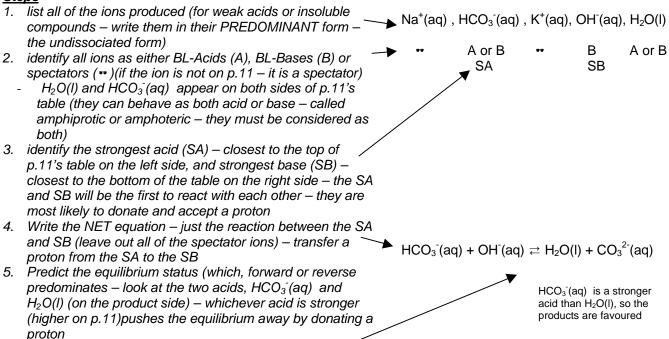
- NH₄Cl(aq) in water, the NH₄⁺(aq) behaves as a BL acid, the Cl⁻(aq) as a BL neutral, so overall, the salt will be an acid
- NaCl(aq) in water, the Na⁺(aq) is neutral, the Cl⁻(aq) is neutral, so the salt is neutral
- (NH₄)₂CO₃(aq) in water, the NH₄⁺(aq) is an acid, the CO₃²⁻(aq) is a base, so the salt will be CLOSE (not precisely) to neutral

Writing Brønsted-Lowry reactions between acids and bases

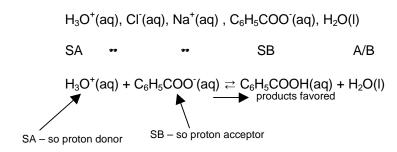
- So far, we've looked only at how acids, bases and salts behave in water
- Brønsted-Lowry theory allows for acid base reactions both with water and in the absence of water
- using Brønsted-Lowry theory, we can write net ionic equations for the reaction taking place and indicate the position of the equilibrium

ex: A solution of KOH(aq) is reacted with a solution of NaHCO₃(aq)

<u>Steps</u>



ex: Predict the reaction between HCI(aq) and NaC₆H₅COO(aq)

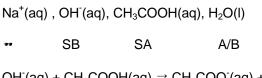


split HCI(aq) into $H_3O^+(aq)$ and CI⁽aq) because HCI(aq) is a strong acid (100% ionization). Split NaC₆H₅COO(aq) because it is soluble (100% dissociation)

CH₃COOH(aq) is NOT split up because it is a weak acid – Ka is very small. so

most of the CH₃COOH(aq) is found undissociated, so it is written as is

ex: NaOH(aq) in CH₃COOH(aq)



 $OH^{-}(aq) + CH_{3}COOH(aq) \rightleftharpoons CH_{3}COO^{-}(aq) + H_{2}O(I)$ products favored

ex: NH₃(aq) in HNO₃(aq)

 $NH_3(g), H_3O^+(aq), NO_3^-(aq), H_2O(I)$

SB SA B A/B

 $NH_3(g) + H_3O^+(aq) \xrightarrow{\simeq} NH_4^+(aq) + H_2O(I)$ products favored

Polyprotic/Polybasic Acids and Bases

- acids (or bases) that can lose (or gain) more than one proton per molecule
- dibasic/diprotic (two protons): H₂CO₃(aq), H₂SO₄(aq), H₂SO₃(aq)
- tribasic/triprotic (three protons): H₃PO₄(aq), H₃BO₃(aq)
- the first proton is the "easiest" to gain (or lose) (Ka or Kb is the largest)
 - others are harder because of the charge (a polyprotic acid that has lost a proton will already have a negative charge and will not lose another proton as easily because of the charge)

** not all molecules that have more than one hydrogen are polyprotic (ex: organic acids)

ex: Write the ionization steps for H₂SO₄(aq)

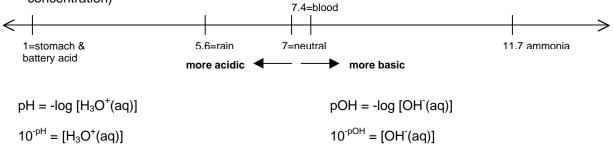
 $H_2SO_4(aq) + H_2O(l) \rightarrow HSO_4(aq) + H_3O^+(aq)$ $HSO_4(aq) + H_2O(l) \Rightarrow SO_4^{-2}(aq) + H_3O^+(aq)$ (this step is one way because H_2SO_4 is strong) (this is equilibrium because HSO_4^- is not strong)

ex: NH2 (aq) is dibasic. Write its ionization steps

 $\begin{array}{l} \mathsf{NH}_2^{\text{-}}(aq) + \mathsf{H}_2\mathsf{O}(\mathsf{I}) \rightleftarrows \mathsf{NH}_3(aq) + \mathsf{OH}^{\text{-}}(aq) \\ \mathsf{NH}_3(aq) + \mathsf{H}_2\mathsf{O}(\mathsf{I}) \rightleftarrows \mathsf{NH}_4^{\text{+}}(aq) + \mathsf{OH}^{\text{-}}(aq) \end{array}$

pH - The scale, what it means, and calculations

- pH = the "power" (exponent) of hydrogen (1909)
- developed to easily compare acidity and basicity
- an difference in pH of one is a difference in concentration of 10 (difference of 3 = 1000x concentration)



pH and pOH are related through the ionization constant of water (more on this later), by:

pH + pOH = 14.00 $[H_3O^+(aq)][OH^-(aq)] = 1.00 \times 10^{-14}$

ex: What is the pH of a solution of HCl(aq) if its concentration is 3.00×10^{-2} mol/L?

Since HCl(aq) is a strong acid: HCl(aq) + H₂O(l) \rightarrow H₃O⁺(aq) + Cl⁻(aq) (this is 100% reaction)

therefore $[H_3O^+(aq)] = [HCI(aq)] = 3.00 \times 10^{-2} \text{ mol/L}$

| <u>SD rules:</u> | |
|--|---|
| in pH only the numbers after the decimal count | |
| (numbers before come from the exponent- if you | 1 |
| remember your log math so don't count) | |

$$pH = -log [H_3O^+(aq)] = -log(3.00 \times 10^{-2}) = 1.523$$

ex: What is the pH of 0.00453 mol/L NaOH(aq)?

Since NaOH(aq) is soluble: NaOH(aq) \rightarrow Na⁺(aq) + OH⁻(aq) (this is 100% reaction) therefore [OH⁻(aq)]=0.00453 mol/L pOH = -log [OH⁻(aq)] = -log(0.00453) = 2.344 pH = 14.00 - 2.344 = 11.656 (keep 3 SD)

ex: Calculate the pH if 4.75 g of NaOH(s) is dissolved in water to make 750 mL of solution

Find [NaOH] first, then [OH⁻(aq)], then from this, pOH and finally pH

$$\frac{4.75g}{40.00g} \times \frac{1}{0.750L} = 0.158 \text{mol}/\text{LNaOH}$$

Since [NaOH(aq)] is soluble, [NaOH(aq)] = [OH (aq)] = 0.158 mol/L

$$pOH = -log [OH^{-}(aq)]$$

= -log (0.158)
= 0.800 (if you rounded in the middle, it would be 0.801)
 $pH = 14.00 - 0.800 = 13.200$

ex: Calculate the mass of HCI(g) required to make 500 mL of a solution with a pOH of 12.00

$$pOH = 12.00$$

pH = 14.00 - 12.00 = 2.00

$$[H_{3}O^{+}(aq)] = 10^{-pH}$$

= 10^{-(2.00)}
= 1.00 x 10⁻² mol/L

$$\frac{1.0x10^{-2}mol}{L} \times \frac{0.500L}{1} \times \frac{36.46g}{1mol} = 0.18g$$

This one is exactly the opposite- from pOH, find pH, then find $[H_3O^+(aq)]$, then [HCI], and finally mass

 $\frac{[H_{3}O^{\dagger}](OH^{-}], \text{ then use}}{[H_{3}O^{\dagger}](OH^{-}] = 1.00 \times 10^{-14} \text{ to}}{(determine [H_{3}O^{+}](don't forget 2OH^{-}per \text{ mol Ba}(OH)_{2}} \times \frac{1}{171.35g} \times \frac{2\text{mol}OH^{-}}{1\text{molBa}(OH)_{2}} \times \frac{1}{0.450L} = 0.0648 \text{mol}/LOH^{-}$ $1.00 \times 10^{-14} = [H_{3}O^{+}][OH^{-}]$ $[H_{3}O^{+}] = \frac{1.00 \times 10^{-14}}{[OH^{-}]}$ $= \frac{1.00 \times 10^{-14}}{0.0648}$ $= 1.54 \times 10^{-13} \text{ mol}/L$

Calculations Involving Weak Acids and Weak Bases

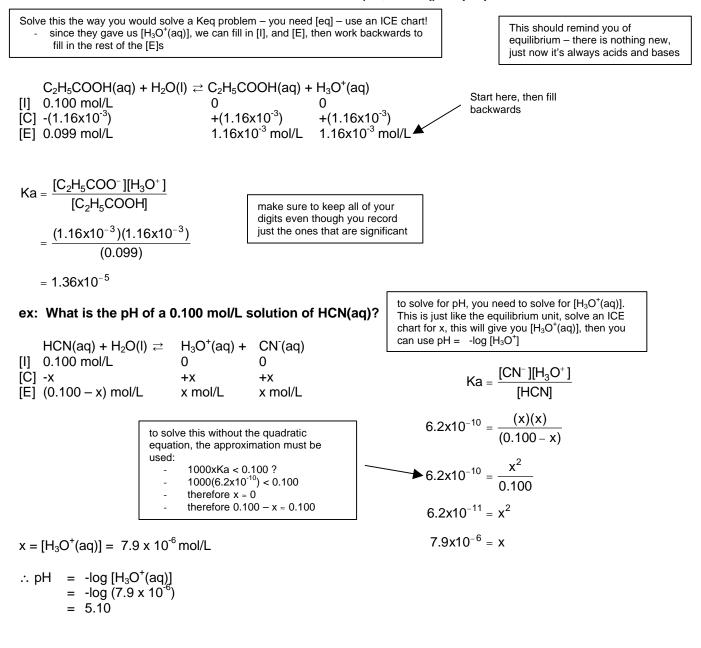
- pH and pOH calculations can be performed for weak acids and bases as well, but must include provisions for the equilibrium that is set up because of the strength of the acid/base

| ex: 0.100 mol/L HCl(aq) | HCl(aq) + H ₂ O(l) → Cl ⁻ (aq) 0.100 mol/L → | + H ₃ O ⁺ (aq) 0.100 mol/L (100% reaction) | |
|--|---|---|--|
| $pH = -log [H_3O^+(aq)]$ = 1.000 | | | |
| 0.100 mol/L CH₃COOH(aq) 0.100 mol/L | CH₃COOH(aq) + H₂O(l) ≓ <0.1 | CH₃COO ⁻ (aq) + H₃O ⁺ (aq) 00 mol/L | |
| pH = -log [H ₃ O ⁺ (aq)] = much more than 1.000 since not all of the acid dissociates | | | |
| ** weak acids will have a higher nH than a strong acid at the same concentration | | | |

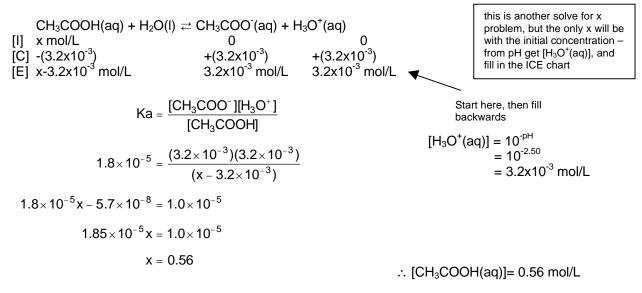
** weak acids will have a higher pH than a strong acid at the same concentration ** \blacklozenge acid strength $\rightarrow \blacklozenge$ Ka $\rightarrow \blacklozenge$ pH

Calculations involving weak acids (or bases) include [H₃O⁺(aq)], [OH⁻(aq)], Ka (or Kb), pH and pOH

ex: In a 0.100 mol/L solution of propanoic acid, the hydronium ion concentration is found to be 1.16x10⁻³ mol/L. Calculate the ionization constant (Ka, or Keq) for propanoic acid.



ex: Determine the initial concentration of an acetic acid solution if its pH is 2.50.



Just another look at $[H_3O^+(aq)]$, $[OH^-(aq)]$

Don't you think it's rather strange that when an acid dissolves in water and donates its proton, it creates OH⁻(aq)?

- (in case you've forgotten): 0.100 mol/L HCl(aq) → 0.100 mol/L H₃O⁺(aq) and since [H₃O⁺(aq)][OH⁻(aq)] = 1.00 x 10⁻¹⁴ then [OH⁻(aq)] = 1.00 x 10⁻¹⁴ / 0.100 = 1.00 x 10⁻¹³ mol/L
- Really, acids don't create OH (aq), they just affect the equilibrium that already exists in the water where they are dissolved :

$$H_2O(I) + H_2O(I) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

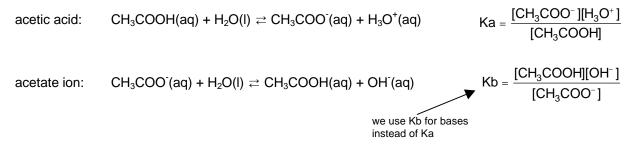
= 1.00 x 10⁻¹⁴ Ka = [H₃O⁺(aq)][OH⁻(aq)]

(at 25°C, in pure water, $[H_3O^+(aq)] = [OH^-(aq)] = \sqrt{1.00 \times 10^{-14}} = 1.00 \times 10^{-7} \text{ mol/L})$

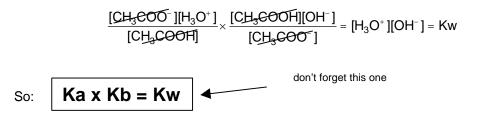
- According to LeChatelier, if $\uparrow H_3O^+(aq)$ (by adding an acid), then the equilibrium will shift \leftarrow , reducing the [OH (aq)] already present to maintain Keq (Ka).
- Since Ka is a constant (1.00 x 10^{-14}) at 25°C, then if one of either H₃O⁺(aq) or OH⁻(aq) is increased, then the other will decrease.
- This equilibrium allows us to perform similar calculations for weak bases that we can for weak acids, even though our Ka table (on p.11) only has Ka values.

The Relationship between Ka and Kb

Looking at the weak acid, $CH_3COOH(aq)$ and its conjugate base, $CH_3COO^{-}(aq)$, we can examine the relationship between Ka and Kb.



Although at first glance, the two don't seem related (*Ka* * 1/Kb), they are related through Kw (the equilibrium constant for water:



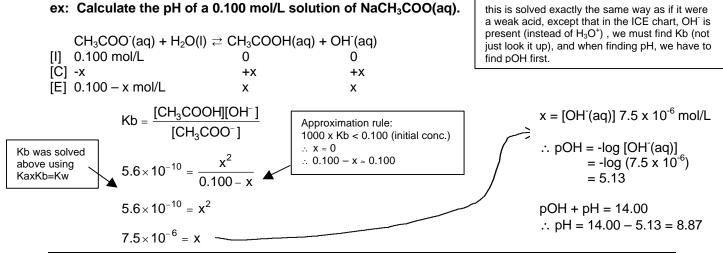
From this relationship, you can calculate Kb (Kb = Kw/Ka), where at 25°C, Kw = 1.00×10^{-14}

ex: Calculate the Kb for NH₃(aq)

From p.11, Ka for NH₄⁺(aq) is 5.8 x 10⁻¹⁰ $Kb = \frac{Kw}{Ka}$ $= \frac{1.00 \times 10^{-14}}{5.8 \times 10^{-10}}$ $= 1.7 \times 10^{-5}$

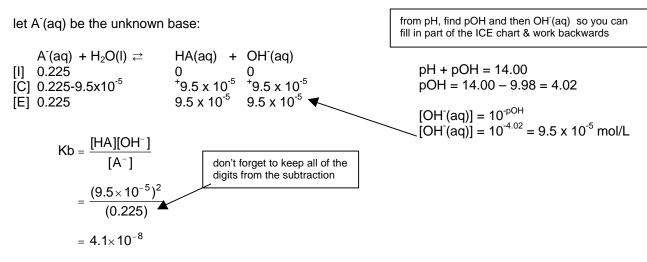
 $Ka \times Kb = Kw$

Once Kb is determined, all of the calculations performed for weak acids can be done for weak bases too.



Chemistry 30 - Unit V Notes

ex: Calculate Kb for an unknown base if a 0.225 mol/L solution has a pH of 9.98.



Buffers

A buffer is a solution that will resist changes in pH when either an acid or a base is added. Buffers are used wherever a specific pH must be maintained – some examples are in the body (the blood buffers), in pools and hot tubs (to allow the chemicals to work properly inhibiting the growth of algae and other organisms) and fish tanks.

There are two basic types of buffers:

Solutions of strong concentrated acids (or strong concentrated bases)

- resist changes in pH when acids are added because they already have such a low pH
- resist changes in pH when (small amounts of) bases are added because they neutralize

Solutions that are able to neutralize both acids or bases

there are two types of this variety of buffer – solutions of amphiprotic (amphoteric) substances (like HCO₃⁻(aq) , or a solution of a weak acid and its conjugate base together (CH₃COOH(aq) and CH₃COO⁻ (aq) often in equal quantities).

These solutions behave as buffers because they are able to remove the excess ions that will lead to a change in pH, $H_3O^+(aq)$ or $OH^-(aq)$.

ex: In a buffer solution of CH₃COOH(aq) and CH₃COO⁻ (aq), HCI(aq) was added. Why is the pH not changed noticeably?

| examine the situation using B-L equations: | CH ₃ COOH(ad | q), CH₃COO ⁻ (ad | q), H₃O⁺(a | q), Cl ⁻ (aq |), H ₂ O(I) |
|--|-------------------------|-----------------------------|------------|-------------------------|------------------------|
| | A | SB | SA | | A/B |
| $CH_3COO^-(aq) + H_3O^+(aq) \rightleftharpoons H_2O(I) + CH_3$ | COOH(aq) | equilibrium | → is favo | ured | |

- since the forward reaction is favoured, most of the reactants (most of the H₃O⁺(aq)) becomes products, and since most of the H₃O⁺(aq) is removed, the pH is not affected greatly.

ex: similarily, when NaOH(aq) is added:

 $\begin{array}{c} \mathsf{CH}_3\mathsf{COOH}(\mathsf{aq}), \, \mathsf{CH}_3\mathsf{COO}(\mathsf{aq}), \, \mathsf{Na}^+(\mathsf{aq}), \, \mathsf{OH}^-(\mathsf{aq}), \, \mathsf{H}_2\mathsf{O}(\mathsf{I}) \\ \mathsf{SA} & \mathsf{B} & \bullet\bullet & \mathsf{SB} & \mathsf{A/B} \end{array}$

 $CH_3COOH(aq) + OH(aq) \rightleftharpoons H_2O(I) CH_3COO(aq)$

equilibrium \rightarrow is favoured

- since the forward reaction is favoured, most of the reactants (most of the OH⁻(aq)) becomes products, and since most of the OH⁻(aq) is removed, the pH is not affected greatly.

Buffers in the Body

The body must maintain a pH of approximately 7.35 to keep enzymes and proteins from denaturing. If proteins and enzymes denature, they cannot function, and the body's cells (and eventually the body) die. The two buffers in the blood are $HCO_3^{-2}(aq)$ and $HPO_4^{-2}(aq)$.

The acid that must be buffered is $H_2CO_3(aq)$, which is produced naturally as $CO_2(g)$ produced by the body's cells during cellular respiration is carried by the blood's plasma to be excreted in the lungs. The level of $CO_2(g)$, and hence $H_2CO_3(aq)$ is constantly changing as we take breaths and exhale. Our body's buffer system must be constantly adjusting to maintain a narrow pH range.

ex: as someone holds their breath (suffocates), what happens to maintain pH in the body?

↑ $CO_2(g) \rightarrow$ ↑ $H_2CO_3(aq) \rightarrow$ ↑ $H_3O^+(aq) \rightarrow$ ↓ pH → protein denaturation → cell death

the increase in $H_3O^+(aq)$ affects the following buffer system:

 $\mathsf{HPO}_4^{2^{-}}(\mathsf{aq}) + \mathsf{H}_3\mathsf{O}^{+}(\mathsf{aq}) \rightleftharpoons \mathsf{H}_2\mathsf{O}(\mathsf{I}) + \mathsf{H}_2\mathsf{PO4}^{-}(\mathsf{aq})$

the equilibrium is shifted \rightarrow due to \Uparrow H₃O⁺(aq) H₃O⁺(aq) is consumed, pH remains steady

ex: if someone hyperventilates, what happens to maintain the pH in their body?

 Ψ CO₂(g) → Ψ H₂CO₃(aq) → Ψ H₃O⁺(aq) → \uparrow pH → protein denaturation → cell death

The decrease in $H_3O^+(aq)$ will cause the opposite shift in the equilibrium system described above.

Calculating the pH of a buffer system

Calculating the pH of a buffer is not unlike the other calculations. The only difference is that they are made with some acid and its conjugate base to start with (both product and reactant are present initially).

ex: (equal amounts of acid and conjugate base) Calculate the resulting pH of a buffer consisting of 0.100 mol/L each of $CH_3COOH(aq)$ and its conjugate base $CH_3COO^{-}(aq)$.

