14.7.1: Foods- From Cleaning and Disinfection to Microbial Nutrition and Protein Modification

How are conjugate acid-base pairs related to microorganisms, imitation fish products, and bread baking?

Pseudomonas aeruginosa	Surimi	Error creating thumbnail: /home/luis_acs/mediawiki/htdocs/bin/ulimit4. h: line 4: /usr/bin/convert: No such file or directory Yeast leavened bread

One of the more useful aspects of the Brönsted-Lowry definition of acids and bases in helping us deal with the pH of solutions is the concept of the conjugate acid-base pair. The strength of an acid and its conjugate base are inversely related. The stronger one is, the weaker the other will be. The acids presented in Weak acids in foods - pH and beyond generate relatively strong bases with respect to the strength of their conjugate acid. The function of these acids and bases in foods and other biological systems largely depends on the pH of the medium. Another important conjugate acid-base pair related to foods is hypochlorous acid and hypochlorite (HClO/ClO⁻). Yes, even though this pair does not occur naturally in foods, it is of great importance in food processing. NaOCl is an ideal disinfectant and possesses excellent cleaning action making it the most widely used disinfectant for processing equipment, finished products, ingredients, and worker's hands in the food industry . **A dynamic pair: HClO/ClO⁻**

Sodium hypochlorite solutions are obtained by the absorption of gaseous chlorine in a sodium hydroxide solution,

$Cl_2 + 2NaOH \rightleftharpoons NaOCL + NaCl + H_2O$ The effectiveness of the cleaning and disinfecting activity of sodium hypochlorite depends not only on its concentration but also on the the pH of the solution.[1] In solution, the hipochlorite ion will form hypochlorous acid and hydroxide ions $ClO^- + H_2O \rightleftharpoons HOCL + OH^-$ generating basic solutions. As the pH of a sodium hypochlorite solution decreases, between 4 and 6, HOCl becomes the predominant species. At lower pH, around 4, HOCl will be converted to chlorine gas (Cl₂). $HOCL + H^+ + Cl^- \rightleftharpoons Cl_2 + H_2O$ Thus, depending on the pH, chlorine can exists in three different forms in aqueous solutions: Cl₂, HOCl, and ClO⁻. Chlorine gas is extremely toxic, reason why it is so important not to mix sodium hypochlorite solutions with acidic cleaning products. Commercial sodium hypochlorite solutions can be found in different concentrations ranging from 5 to 40% to which sodium chloride and alkali (usually NaOH), are added in order to ensure a solution with basic pH and reduce the corrosive effect of ClO⁻. Commercial solutions between 5-15% NaClO contain 0.25 - 0.35% free alkali and 0.5 - 1.5% NaCl.[2]

What is the relationship between conjugate acid-base pairs? How can we calculate the pH of their solutions? The relationship between the strength of an acid and its conjugate base can be expressed quantitatively in terms of a very simple mathematical equation involving the appropriate acid and base constants. Suppose that we have a weak acid HA whose conjugate base is A⁻. If either or both of these species are dissolved in H₂O, the following equilibria will occur simultaneously. $HA + H_2O \rightleftharpoons H_3O^+ + A^-$ in which HA acts as acid and $A^- + H_2O \rightleftharpoons HA + OH^-$ in which A⁻ acts as base To the first of these equilibria we can apply the equilibrium constant K_a(HA): $K_a(HA) = \frac{[H_3O^+][A^-]}{[HA]}$ while to the second we can apply the equilibrium constant K_b(A⁻): $K_b(A^-) = \frac{[HA][OH^-]}{[A^-]}$

Multiplying these two constants together, we obtain a simple relationship between them.

$$K_a(HA) \times K_b(A^-) = \frac{[H_3O^+][A^-]}{[HA]} \times \frac{[HA][OH^-]}{[A^-]} \tag{14.7.1.1}$$

$$\tag{14.7.1.2}$$

$$= [H_3O^+][OH^-] \tag{14.7.1.3}$$

$K_a(HA) \times K_b(A^-) = K_w$ (1)

If we divide both sides of this equation by the units and take negative logarithms of both sides, we obtain

$$pK_a = -\log\frac{K_a(HA)}{mol\,dm^{-3}} - \log\frac{K_b(A^-)}{mol\,dm^{-3}} \tag{14.7.1.4}$$

$$\tag{14.7.1.5}$$

$$= -\log\frac{10^{-14}\,mol^2\,dm^{-6}}{mol^2\,dm^{-6}} \tag{14.7.1.6}$$

$pK_a(HA) + pK_b(A^-) = pK_w$ (2) Thus the product of the acid constant for a weak acid and the base constant for the conjugate base must be K_w, and the sum of pK_a and pK_b for a conjugate acid-base pair is 14.

Equation (1) or (2) enables us to calculate the base constant of a conjugate base from the acid constant of the acid, and vice versa. Given the acid constant for a weak acid like HOCl, for instance, we are able to calculate not only the pH of HOCl solutions but also the pH of solutions of salts like NaOCl or KOCl which are, in effect, solutions of the conjugate base of HOCl, namely, the hypochlorite ion, OCl⁻.

EXAMPLE 1 Find the pH of (a) 35% (m/v%) HOCl (hypochlorous acid) and (b) 35% (m/v%) commercial solution of NaOCl (sodium hypochlorite) from the value for K_a given in the table of K_a values.

Solution

a) For 35% (m/v%) HOCl, the solution contains 35 g of hypochlorous acid in 100 mL of solution and

$$n_{HOCl} = \frac{35.0 \text{ gHOCl}}{52.46 \text{ g mol}^{-1}} \tag{14.7.1.7}$$

$$= 6.67 \times 10^{-1} \text{mol HOCl} \tag{14.7.1.8}$$

and its concentration is then

$$[HOCl] = \frac{n_{HOCl}}{V_{solution}} = \frac{6.67 \times 10^{-1} \text{ mol}}{1.0 \times 10^{-1} \text{ dm}^3} \tag{14.7.1.9}$$

$$= 6.67 \text{ mol dm}^{-3} \tag{14.7.1.10}$$

The concentration of hydronium-ions generated from the acid can be calculated using the following equation, discussed in the pH of Solutions of Weak Acids,

$$[H_3O^+] \approx \sqrt{K_a c_a} \tag{14.7.1.11}$$

$$\approx \sqrt{3.9 \times 10^{-8} \text{ mol dm}^{-3} \times 6.67 \text{ mol dm}^{-3}} \tag{14.7.1.12}$$

$$\approx 5.10 \times 10^{-4} \text{ mol dm}^{-3} \tag{14.7.1.13}$$

Checking the accuracy of the approximation we find

$$\frac{[H_3O^+]}{c_a} = \frac{5.10 \times 10^{-4}}{6.67} \tag{14.7.1.14}$$

$$= 7.6 \times 10^{-5}, \text{ } that \text{ } is, \text{ } 0.0076 \text{ percent} \tag{14.7.1.15}$$

so that, the approximation is valid and the pH of the solution is

$$pH = -\log\left(5.10 \times 10^{-4}\right) \tag{14.7.1.16}$$

$$= 3.29 \tag{14.7.1.17}$$

The relatively high concentration of the acid accounts for a weakly acidic solution in spite that the K_a for hypochlorous acid has an order of magnitude of 10⁻⁸.

b) To calculate de pH for a 35% (m/v%) commercial solution of NaOCl, we need to calculate the number of moles that correspond to 35 g NaOCl in 100 mL of solution

$$n_{NaOCl} = \frac{35.0 \text{ g NaOCl}}{74.44 \text{ g mol}^{-1}} \tag{14.7.1.18}$$

$$= 4.7 \times 10^{-1} \text{mol NaOCl} \tag{14.7.1.19}$$

and its concentration is then

$$[NaOCl] = \frac{n_{NaOCl}}{V_{solution}} = \frac{4.7 \times 10^{-1} \text{ mol}}{1.0 \times 10^{-1} \text{ dm}^3} \tag{14.7.1.20}$$

$$= 4.7 \text{ mol dm}^{-3} \tag{14.7.1.21}$$

Since 1 mol of NaOCL dissociates in 1 mol of Na⁺ and 1 mol OCl⁻, this solution contains 4.7 mol dm⁻³ OCl⁻ ions. Now, we must calculate K_b:

$$K_b(OCl^-) = \frac{K_w}{K_a(HOCl)} \tag{14.7.1.22}$$

$$= \frac{1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}}{3.9 \times 10^{-8} \text{ mol dm}^{-3}} \tag{14.7.1.23}$$

$$= 2.56 \times 10^{-7} \text{ mol dm}^{-3} \tag{14.7.1.24}$$

Thus

$$[\text{OH}^-] \approx \sqrt{K_b c_b} \tag{14.7.1.25}$$

$$\approx \sqrt{2.56 \times 10^{-7}\ \text{mol dm}^{-3} \times 4.7\ \text{mol dm}^{-3}} \tag{14.7.1.26}$$

$$\approx 1.1 \times 10^{-3}\ \text{mol dm}^{-3} \tag{14.7.1.27}$$

Checking the accuracy of the approximation we find

$$\frac{[\text{OH}^-]}{c_b} = \frac{1.1 \times 10^{-3}}{4.7} \tag{14.7.1.28}$$

$$= 2.3 \times 10^{-4},\ that\,is,\ 0.023\ \text{percent} \tag{14.7.1.29}$$

The pOH of this solution is then

$$\text{pOH} = -\log\left(1.1 \times 10^{-3}\right) \tag{14.7.1.30}$$

$$= 2.96 \tag{14.7.1.31}$$

and the pH

$$\text{pH} = 14 - \text{pOH} \tag{14.7.1.32}$$

$$= 14 - 2.96 \tag{14.7.1.33}$$

$$= 11.04 \tag{14.7.1.34}$$

Again, the concentration of the base , OCl^-, accounts for a pH around 11.0 in this solution. **What makes HClO/ClO⁻ disinfecting agents?**

size=175</chemeddl-jmol2>
Hypochlorous acid

HOCl and ClO⁻ are both strong oxidizing agents and react with a wide variety of biological molecules including proteins, amino acids, lipids, and DNA. Such reactivity...

How does ClO⁻ clean a surface?

A detergent functions by minimizing the magnitude of attractive forces between soil and the solid surface by adsorption of detergent components both on soil and on the solid surface. Breaking the organic soil...

Factors affecting the effectiveness of NaClO solutions

The most relevant factors affecting the effectiveness of cleaning and disinfecting products...

Environmental and health risks

Chlorine based disinfectants can react with organic matter in water and form by-products like...

alt	**Task:** Look for actual numbers of volumes of NaClO used in the industrySverazo 00:49, 3 December 2009 (UTC) (**Sofia Erazo**)

Conjugate acid-base pairs and microbial nutrition

Ammonium salts such as chloride and sulfate are employed in media growth for microorganisms as a source of nitrogen. Ammonium chloride is called "yeast food" in diverse fermentation processes including bread baking (*S. cerevisiae*) and production of citric acid (*Y. lipolytica*).
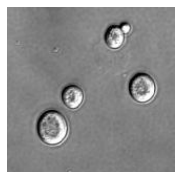
Sacharomyces cerevisiae cells under differential interference microscopy	Wet yeast	Error creating thumbnail: /home/luis_acs/mediawiki/htdocs/bin/ulimit4.h: line 4: /usr/bin/convert: No such file or directory Yeast leavened bread

EXAMPLE 2 Find the pH of 0.05 M NH$_4$Cl (ammonium chloride), using the value $K_b(\text{NH}_3) = 1.8 \times 10^{-5}\ \text{mol dm}^{-3}$.

Solution We regard this solution as a solution of the weak acid NH_4^+ and start by finding K_a for this species:

$$K_a(\text{NH}_4^+) = \frac{K_w}{K_b(\text{NH}_3)} = \frac{1.00 \times 10^{-14}\ \text{mol}^2\ \text{dm}^{-6}}{1.8 \times 10^{-5}\ \text{mol dm}^{-3}} \tag{14.7.1.35}$$

$$= 5.56 \times 10^{-10}\ \text{mol dm}^{-3} \tag{14.7.1.36}$$

We can now evaluate the hydronium-ion concentration with the usual approximation:

$$\left[\text{H}_3\text{O}^+\right] = \sqrt{K_a c_a} \tag{14.7.1.37}$$

$$= \sqrt{5.56 \times 10^{-10}\ \text{mol dm}^{-3} \times 0.05\ \text{mol dm}^{-3}} \tag{14.7.1.38}$$

$$= 5.27 \times 10^{-6}\ \text{mol dm}^{-3} \tag{14.7.1.39}$$

hence, $\text{pH} = \log\left(5.27 \times 10^{-6}\right) = 5.28$ *Note*: The ammonium ion is a very weak acid (as seen in the Tables of Ka and and Kb values). A solution of NH_4^+ ions will thus not produce a very acidic solution. A pH of 5 is about the same pH as that of black coffee, not very acidic. Before the Brönsted-Lowry definition of acids and bases and the idea of conjugate acid-base pairs became generally accepted, the interpretation of acid-base behavior revolved very much around the equation $\text{Acid} + \text{Base} \rightarrow \text{Salt} + \text{Water}$ In consequence the idea prevailed that when an acid reacted with a base, the resultant salt should be neither acidic or basic, but neutral. In order to explain why a solution of sodium acetate was basic or a solution of ammonium chloride was acidic, a special term called **hydrolysis** had to be invoked. Thus, for instance, sodium acetate was said to be hydrolyzed because the acetate ion reacted with water according to the reaction $\text{CH}_3\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{OH}^-$ From the Brönsted-Lowry point of view there is, of course, nothing special about such a hydrolysis. It is a regular proton transfer. Nevertheless you should be aware of the existence of the term hydrolysis since it is still often used in this context.

Because the Brönsted-Lowry definition is so successful at explaining why some salt solutions are acidic and some basic, one must beware of making the mistake of assuming that no salt solutions are neutral. Many are. A good example is 0.10 M NaNO_3. This solution is neutral because neither the Na^+ ion nor the NO_3^- ion shows any appreciable acidic or basic properties. Since NO_3^- is the conjugate base of HNO_3 we might expect it to produce a basic solution, but NO_3^- is such a weak base that it is almost impossible to detect such an effect. Just how weak a base NO_3^- is can be demonstrated using the value of K_a (HNO_3) = 20 mol dm^{-3} obtained from the Tables of Ka and and Kb values.

$$K_b(\text{NO}_3^-) = \frac{K_w}{K_a(\text{HNO}_3)} \tag{14.7.1.40}$$

$$= \frac{1.00 \times 10^{-14}\ \text{mol}^2\ \text{dm}^{-6}}{20\ \text{mol dm}^{-3}} \tag{14.7.1.41}$$

$$= 5.0 \times 10^{-16}\ \text{mol dm}^{-3} \tag{14.7.1.42}$$

If we now apply the conventional formula from equation 4 from the section on the pH of weak base solutions to calculate [OH$^-$] in 0.10 M NaNO_3, we obtain

$$\left[\text{OH}^-\right] = \sqrt{K_b c_b} \tag{14.7.1.43}$$

$$= \sqrt{5.0 \times 10^{-16} \times 1.0 \times 10^{-1}\ \text{mol dm}^{-3}} \tag{14.7.1.44}$$

$$= 7.1 \times 10^{-9}\ \text{mol dm}^{-3} \tag{14.7.1.45}$$

But this is less than one-tenth the concentration of OH$^-$ ion which would have been present in pure H_2O, with no added NaNO_3. Essentially all the OH$^-$ ions are produced by H_2O, and the pH turns out to be only slightly above 7.00. (Note also that the derivation of equation 4 from the pH of weak base solutions section assumed that the [OH$^-$] produced by H_2O was negligible. To get an accurate result in this case requires a completely different equation.)

In general, all salts that combine group I and group II cations with anions (conjugate bases) derived from of strong acids yield neutral solutions when dissolved in water. Examples are CaI_2, LiNO_3, KCl, and $\text{Mg(ClO}_4)_2$.

There is only one exception to this rule. The hydrated beryllium ion, $\text{Be(H}_2\text{O)}_4^{2+}$, is a weak acid ($K_a = 3.2 \times 10^{-7}$ mol dm^{-3}) so that solutions of beryllium salts are acidic.

EXAMPLE 3 The following are salts used in food processing, classify them as acidic, basic, or neutral: (a) 1 M Potassium bromate; (b) 1 M trisodium citrate; (c)1 M trisodium phosphate; (d) 1 M Sodium aluminum sulfate; (e) 1 M potassium hydrogen sulfate; (f) 1 M ammonium chloride.

Solution

Salt	Cation	Anion	Overall	Used in[1] [2]

KBrO$_3$	Neutral	Neutral	Neutral	Flour conditioning: Oxidation of wheat glutathione into its disulfide.
Na$_3$C$_6$H$_5$O$_7$	Neutral	Basic	Basic	Condensed milk for pH adjustment and binding of calcium to avoid aggregation of casein.
Na$_3$PO$_4$	Neutral	Basic	Basic	Emulsifier, protein modifier, buffering agent in confectionery,cereals, and processed cheese.
NaAl(SO$_4$)$_2$	Neutral, Acidic	Neutral	Acidic	Because of its slow reaction rate, it is used in combination with other leavening acids to provide tunneling or blistering effects in baked products.
KH$_2$PO$_4$	Neutral	Acidic	Acidic	Buffering agent, mineral supplement.
NH$_4$Cl	Acidic	Neutral	Acidic	Yeast fermentation processes as a source of nitrogen for yeast metabolism.

The table lists the acid-base properties of some of the more frequently encountered ions and provides a quick reference for deciding whether a given salt will be acidic, basic, or neutral in solution. Note that the table tells us nothing about the strength of any acid or base. If we need to know more about the pH, other than whether it is above, below, or equal to 7, we need information about the actual value of the acid or base constant. The table also lists the SO$_4^{2-}$ion as neutral, though classifying it as very feebly basic would be more accurate. **The Acid-Base Properties of Some Common Ions**

Cations	**Anions**	**Anion**
Acidic	Cr^{3+}, Fe^{3+}, Al^{3+} Hg^{2+}, Be^{2+} NH$_4^+$, H$_3$O$^+$	HSO$_4^-$
Neutral	Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} Li$^+$, Na$^+$, K$^+$ Ag$^+$	NO$_3^-$, ClO$_4^-$ Cl$^-$, Br$^-$, I$^-$ SO$_4^{2-}$ (very weakly basic)
Basic	None	PO$_4^{3-}$, CO$_3^{2-}$, SO$_3^{2-}$ F$^-$, CN$^-$, OH$^-$, S^{2-} CH$_3$COO$^-$, HCO$_3^-$

EXAMPLE 4 Without actually doing any calculations, match the following solutions and pH values, using the Tables of Ka and and Kb values, and the table on this page.
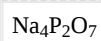
Aqueous Solution 1 M	pH ?
NH$_4$NO$_3$	8.0
Na$_4$P$_2$O$_7$	11.7
NaNO$_3$	9.4

MgSO$_4$	7.0
(CH$_3$COO)$_2$Ca (calcium acetate)	1.0
KHSO$_4$	4.6

Solution The pH of 7.0 is easiest to pick. Only one of the salt solutions given has both a neutral anion and a neutral cation. This is NaNO$_3$. In the case of MgSO$_4$ the Mg^{2+} ion is neutral but the SO$_4^{2-}$ ion is very feebly basic; this would agree with a pH of 8.0, only slightly basic. The SO$_4^{2-}$ ion is such a feeble base because its conjugate acid, HSO$_4^-$, is quite a strong acid, certainly the most acidic of all the ions featured. Accordingly we expect 1 M KHSO$_4$ to correspond to the lowest pH, namely, 1.0. The only other acidic solution is 4.6, and this must correspond to 1 M NH$_4$NO$_3$ since NH$_4^+$ is the only other acidic ion present. Among basic ions the pyrophosphate ion,P$_2$O$_7$, is the strongest. The most basic pH, 11.7, thus corresponds to 1 M Na$_4$P$_2$O$_7$. Only one solution is left: 1 M (CH$_3$COO)$_2$Ca. This should be feebly basic and so matches the remaining pH of 9.4 rather well.

Aqueous Solution
1 M

Application pH in food [3] [4]

NH_4NO_3	Fertilizer and fermentation processes.
$Na_4P_2O_7$	Used in milk based bev...

ent, coagulant, pH adjustment. [3]

NaNO$_3$

Preserved color of neat a t a

7 0 0

nd antimicrobial activity against *C. botulinum* (*it s activiyi*

MgSO₄

80

	otein production of tofu.
(CH₃COO)₂Ca (calcium acetate)	Chelating agent for stabilization

	...on of color, aroma, and texture.
$KHSO_4$	Antimicrobial. 1.0 and acidulant.

References

1. Food Chemistry 3rd Ed. 2004 Belitz, et al.
2. Food Additives, 2nd ed. 2002, Branen, A., Davidson, M.P., Salminen, S. and Thorngate III, J.H.
3. Humphreys, J.L., Carlson, M.S., Lorenzen, C.L. 2009. Dietary supplementation of magnesium sulfate and sodium bicarbonate and its effect on pork quality during environmental stress. Livestock Sci. 125:1:15-21

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