

## PREDICTING THE pH OF AQUEOUS SOLUTIONS OF SALTS

Chemistry BC2001x

When a salt dissolves, cations and anions are introduced into solution. To determine whether the resulting solution is acidic, basic, or neutral, consider each ion: ask whether it can undergo a hydrolysis reaction (a reaction with water) that will alter the balance of  $H^+$  and  $OH^-$  in solution.

### CATIONS

**Metal ions are generally neutral (neither acidic nor basic).** While some highly charged metal ions can associate with hydroxide, making the solution slightly acidic (Chang 5th Ed, p. 560-561), this effect is weak and may generally be ignored.

**Some cations are acidic:** they have a labile proton. Primary among these is ammonium,  $NH_4^+$ .

### ANIONS

**Many anions are basic:** they may combine with  $H^+$  from water to form the conjugate acid, leaving  $OH^-$  in solution:



This reaction will proceed to some extent *unless* the conjugate acid is strong. Thus anions  $NO_3^-$ ,  $Cl^-$ ,  $Br^-$ ,  $I^-$ , and  $ClO_4^-$  are not basic; all others have basic properties:  $NO_2^-$ ,  $CH_3COO^-$ ,  $SO_4^{2-}$ .

**Some anions are also potentially acidic:** they have a labile proton. These include diprotic acids that have lost one proton and triprotic acids that have lost one or two. **The anion  $HX^-$**  (the monobasic form of the diprotic acid  $H_2X$ ) is an ampholyte: it is potentially both acidic and basic. Which dominates? Compare its acidity and basicity. Both reactions proceed to a small extent:



*Therefore* If  $K_{a2}(H_2X) > K_w / K_{a1}(H_2X)$ , the ion is acidic. Multiply through by  $K_{a1}$

*or* If  $K_{a1}(H_2X) K_{a2}(H_2X) > K_w$  the ion is acidic. Taking  $-\log_{10}$  or both sides gives

*or* If  $\frac{1}{2}(pK_1 + pK_2) < 7$ , the ion is acidic.

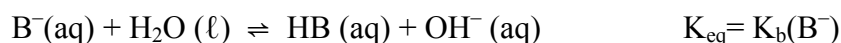
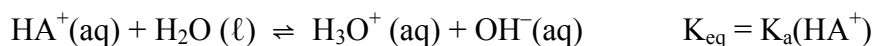
$HCO_3^-$  is basic:  $\frac{1}{2}(pK_1 + pK_2) = \frac{1}{2}(6.36 + 10.32) = 8.34$

$HSO_3^-$  is acidic:  $\frac{1}{2}(pK_1 + pK_2) = \frac{1}{2}(1.92 + 7.21) = 4.56$

Since  $H_2SO_4$  is a strong acid,  $HSO_4^-$  is acidic; no need to consider  $K_a$ 's.

Then look at the combined effect in the **SALT**

- 1) Salts with **neutral cations** and **neutral anions** are **neutral**. ( $NaCl$ ,  $CaCl_2$ ,  $KNO_3$ ,  $LiClO_4$ ).
- 2) Salts with **acidic cations** and **neutral anions** are **acidic**.  
( $NH_4Cl$ ;  $NH_4NO_3$ ;  $CH_3NH_3Br$ ;  $C_5H_5NHClO_4$ ;  $C_6H_5NH_3Cl$ ;  $NH_4HSO_4$ )
- 3) Salts with **neutral cations** and **basic anions** are **basic**  
( $KCN$ ;  $NaCH_3COO$ ;  $K_2S$ ;  $Na_2CO_3$ ;  $Ba(NO_2)_2$ ;  $Na_3PO_4$ ; also  $NaHCO_3$ ,  $KHS$ )
- 4) Salts with **neutral cations** and **acidic anions** are **acidic**.  
( $NaHSO_4$ ,  $KHSO_3$ ,  $NaHC_2O_4$ ).
- 5) Salts with **acidic cations** and **basic anions** may be acidic *or* basic, depending on the  $K$ 's:  
Compare the two hydrolysis reactions, with cation  $HA^+$  and anion  $B^-$ :



If  $K_a(\text{cation}) > K_b(\text{anion})$  the salt is acidic [example:  $HONH_3CH_3COO$ ],

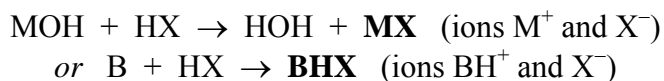
if  $K_a(\text{cation}) < K_b(\text{anion})$  the salt is basic [example:  $NH_4CN$ ],

if  $K_a(\text{cation}) = K_b(\text{anion})$  the salt is neutral [example:  $NH_4CH_3COO$ ]

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**Alternate method:** One may view any salt as the product of a reaction of a base with an acid



Generalizations about the acidity of the salt are then based on the properties of the parent acid and base. Observe how these statements relate to those on the previous page.

1. Salts formed from strong acids and strong bases are **neutral**.

(Aqueous solutions of neutral salts have  $\text{pH} = 7.00$  at  $25^\circ\text{C}$ ).

Examples:  $\text{NaCl}$ ;  $\text{KNO}_3$ ;  $\text{LiClO}_4$ ;  $\text{CaBr}_2$ ;  $\text{Ba}(\text{NO}_3)_2$ .

[Note: this rule is guaranteed to hold only for monoprotic strong acids, not  $\text{H}_2\text{SO}_4$ .]

2. Salts formed from strong acids and weak bases are **acidic**.

(Aqueous solutions of acidic salts have  $\text{pH} < 7.00$  at  $25^\circ\text{C}$ ).

Examples:  $\text{NH}_4\text{Cl}$ ;  $\text{NH}_4\text{NO}_3$ ;  $\text{CH}_3\text{NH}_3\text{Br}$ ;  $\text{C}_5\text{H}_5\text{NHClO}_4$ ;  $\text{C}_6\text{H}_5\text{NH}_3\text{Cl}$ ;  $\text{NH}_4\text{HSO}_4$ .

[If the strong acid is diprotic, that is,  $\text{H}_2\text{SO}_4$ , this rule is guaranteed to hold only if the strong acid has transferred just one proton to the weak base, that is, if the anion in the salt is  $\text{HSO}_4^-$ .]

3. Salts formed from strong bases and weak acids are **basic**.

(Aqueous solutions of basic salts have  $\text{pH} > 7.00$  at  $25^\circ\text{C}$ ).

Examples:  $\text{KCN}$ ;  $\text{NaCH}_3\text{COO}$ ;  $\text{K}_2\text{S}$ ;  $\text{Na}_2\text{CO}_3$ ;  $\text{Ba}(\text{NO}_2)_2$ ;  $\text{Na}_2\text{SO}_3$ ;  $\text{Na}_3\text{PO}_4$ .

[If the weak acid is polyprotic, this rule always holds if the weak acid has lost all its protons to the strong base. This rule may not hold for salts containing partially protonated anions  $\text{HX}^{n-}$ .]

4. (a) A salt formed from a weak acid and a weak base is **acidic** if  $K_a > K_b$ .

Example: hydroxylammonium acetate ( $\text{HONH}_3\text{CH}_3\text{COO}$ ) is acidic, because  $K_a(\text{HONH}_3^+) > K_b(\text{CH}_3\text{COO}^-)$  or  $K_a(\text{CH}_3\text{COOH}) > K_b(\text{HONH}_2)$ .

- (b) A salt formed from a weak acid and a weak base is **basic** if  $K_b > K_a$ .

Example: ammonium cyanide ( $\text{NH}_4\text{CN}$ ) is basic, because  $K_b(\text{CN}^-) > K_a(\text{NH}_4^+)$  or  $K_b(\text{NH}_3) > K_a(\text{HCN})$ .

- (c) A salt formed from a weak acid and a weak base is **neutral** if  $K_a = K_b$ .

Example: ammonium acetate ( $\text{NH}_4\text{CH}_3\text{COO}$ ) is neutral, because  $K_a(\text{NH}_4^+) = K_b(\text{CH}_3\text{COO}^-)$  or  $K_b(\text{NH}_3) = K_a(\text{CH}_3\text{COOH})$ .

5. A salt formed from a strong base and a polyprotic weak acid which has not transferred all its protons to the strong base contains an **ampholyte** anion, which is *both* an acid and a base.

Such an ampholyte salt will be

(a) acidic if  $K_a(\text{anion}) > K_b(\text{anion})$ , or equivalently for a diprotic acid,  $K_1 K_2 > K_w$ .

(b) basic if  $K_b(\text{anion}) > K_a(\text{anion})$ , or equivalently for a diprotic acid,  $K_1 K_2 < K_w$ .

(c) neutral if  $K_a(\text{anion}) = K_b(\text{anion})$ , or equivalently for a diprotic acid,  $K_1 K_2 = K_w$ .

Example:  $\text{NaHOCCOO}$  is acidic, because  $K_a(\text{HOCCOO}^-) > K_b(\text{HOCCOO}^-)$ .

Example:  $\text{NaHCO}_3$  is basic, because  $K_b(\text{HCO}_3^-) > K_a(\text{HCO}_3^-)$ ;  $K_1 K_2 = 2 \times 10^{-17} < 10^{-14}$ .

The approximate pH of a solution of a salt containing an ampholyte anion is  $\frac{1}{2}(\text{p}K_1 + \text{p}K_2)$ , where  $K_1$  and  $K_2$  are the successive acidity constants of the acid conjugate to the ampholyte.

Example: the pH of a solution of sodium bicarbonate ( $\text{NaHCO}_3$ ) is  $\frac{1}{2}(6.36 + 10.32) = 8.34$ .