Chapter 15

ACID-BASE EQUILIBRIA

(Cont.)

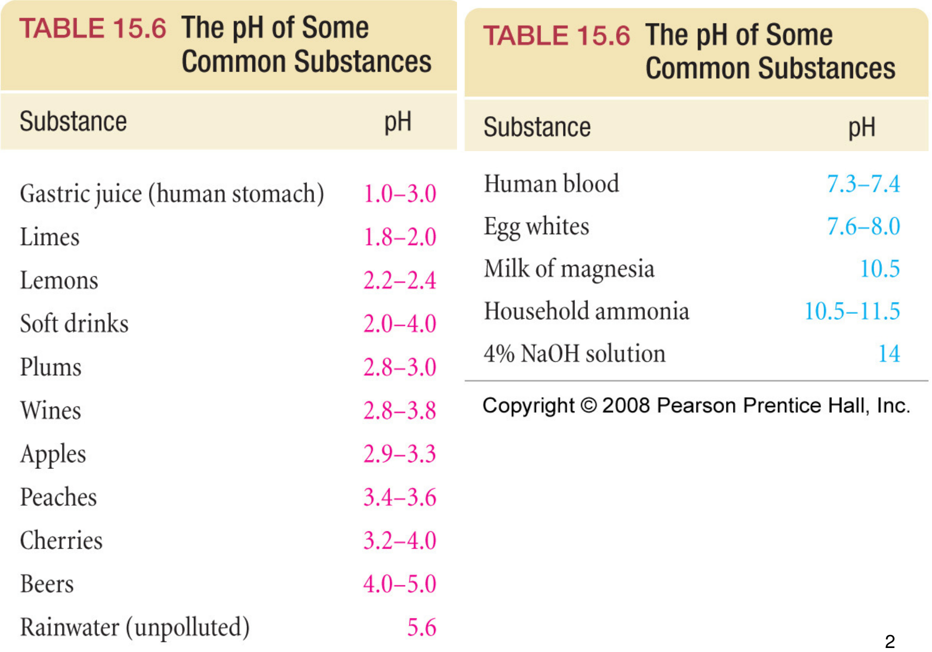


TABLE 15.6 The pH of Some Common Substances

Substance	pH
Gastric juice (human stomach)	1.0–3.0
Limes	1.8–2.0
Lemons	2.2–2.4
Soft drinks	2.0–4.0
Plums	2.8–3.0
Wines	2.8–3.8
Apples	2.9–3.3
Peaches	3.4–3.6
Cherries	3.2–4.0
Beers	4.0–5.0
Rainwater (unpolluted)	5.6
Human blood	7.3–7.4
Egg whites	7.6–8.0
Milk of magnesia	10.5
Household ammonia	10.5–11.5
4% NaOH solution	14

Summary: pH calculations of strong acids and strong bases

1. At relatively **high [S.A]** or **high [S.B.]**, i.e. ≥ 10^{-6} M, *pH is calculated from [S.A.] or [S.B.]*
2. In **very dilute [S.A] or [S.B.]**, i.e. ≤ 10^{-8} M, dissociation of water is more important, so the **pH is 7**.

Question: How do we know if a given acid is strong or weak?

Know the following by heart: *You have to be able to name them too.*

There are only **six (6) strong acids** to remember:
HCl, HBr, HI, H_2SO_4, HNO_3, $HClO_4$

Perchloric acid

There are only **six (6) strong bases** to remember:
LiOH, NaOH, KOH, $Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$

Determining the pH of solutions

Solutions of **weak acids (W.A.)**

- Ionization is incomplete; Equilibrium is set up

Ionization (dissociation) equation:

$$HA_{(aq)} + H_2O_{(l)} \overset{K_a}{\rightleftarrows} H_3O^+_{(aq)} + A^-_{(aq)}$$

Or simply: $$HA_{(aq)} \overset{K_a}{\rightleftarrows} H^+_{(aq)} + A^-_{(aq)}$$

where K_a is the acid ionization (or dissociation) constant

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

- The ***K_a* for W.A. is < 1.**

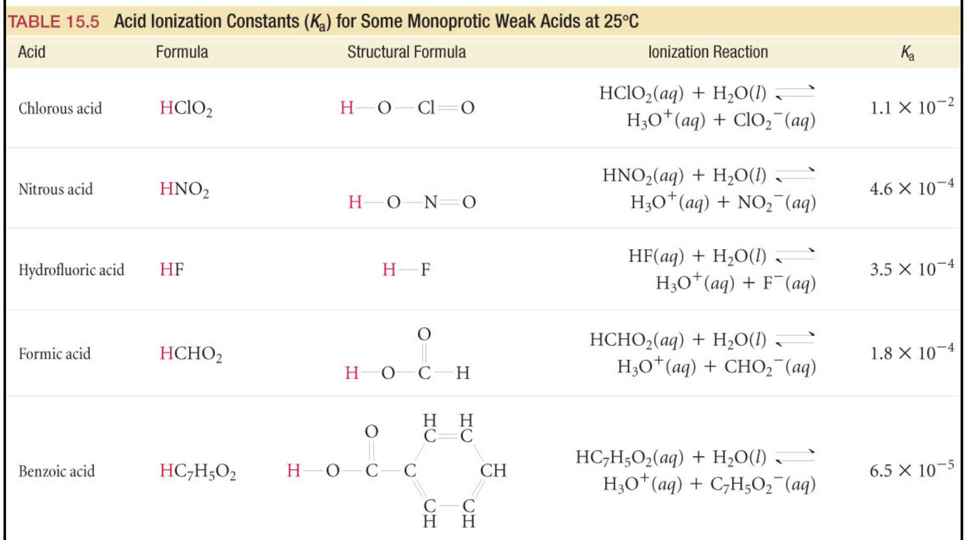


TABLE 15.5 Acid Ionization Constants (K_a) for Some Monoprotic Weak Acids at 25°C

Acid	Formula	Structural Formula	Ionization Reaction	K_a
Chlorous acid	$HClO_2$	$H-O-Cl=O$	$HClO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + ClO_2^-(aq)$	1.1×10^{-2}
Nitrous acid	HNO_2	$H-O-N=O$	$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)$	4.6×10^{-4}
Hydrofluoric acid	HF	$H-F$	$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$	3.5×10^{-4}
Formic acid	$HCHO_2$	$H-O-\overset{\overset{O}{\Vert}}{C}-H$	$HCHO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CHO_2^-(aq)$	1.8×10^{-4}
Benzoic acid	$HC_7H_5O_2$		$HC_7H_5O_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_7H_5O_2^-(aq)$	6.5×10^{-5}

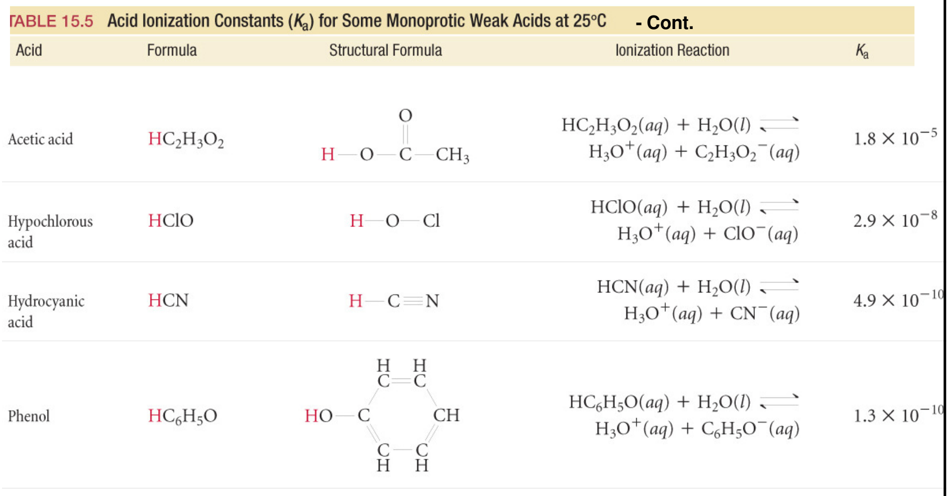


TABLE 15.5 Acid Ionization Constants (K_a) for Some Monoprotic Weak Acids at 25°C **- Cont.**

Acid	Formula	Structural Formula	Ionization Reaction	K_a
Acetic acid	$HC_2H_3O_2$	$H-O-\overset{O}{\overset{\Vert}{C}}-CH_3$	$HC_2H_3O_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_2H_3O_2^-(aq)$	1.8×10^{-5}
Hypochlorous acid	$HClO$	$H-O-Cl$	$HClO(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + ClO^-(aq)$	2.9×10^{-8}
Hydrocyanic acid	HCN	$H-C\equiv N$	$HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$	4.9×10^{-10}
Phenol	HC_6H_5O		$HC_6H_5O(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_6H_5O^-(aq)$	1.3×10^{-10}

Determining the pH of Weak Acids

Example: What is the H_3O^+ concentration and pH of a 0.10 M solution of hypochlorous acid, HOCl, $K_a = 3.5 \times 10^{-8}$?

❖ Note that the K_a is a small number (i.e. HOCl is a weak acid. Start with the equilibrium equation:

$$HOCl + H_2O \overset{K_a}{\rightleftharpoons} H_3O^+ + OCl^-$$

$$\text{or} \quad HOCl_{(aq)} \Leftrightarrow H^+_{(aq)} + OCl^-_{(aq)}$$

❖ HOCl is W.A.; only a fraction of 0.10 M HOCl will dissociate, i.e. we can set up our ICE table as:

	$HOCl$ + $H_2O_{(l)}$	$\rightleftharpoons$	H_3O^+ +	OCl^-
I:	0.10		0	0
C:	$-x$		$+x$	$+x$
E:	$(0.10 - x)$		x	x

- The K_a expression is:

$$K_a = \frac{[OCl^-][H_3O^+]}{[HOCl]} = \frac{(x)(x)}{(0.10 - x)}$$

$$3.5 \times 10^{-8} = \frac{x^2}{(0.10 - x)}$$

Assuming x << 0.10 (since K_a is very small) and solving for x, we get:

$$x = 5.9_2 \times 10^{-5}\ M = [H_3O^+] = [OCl^-]$$

Check: Since $5.9 \times 10^{-5} << 0.10$ our assumption is valid. We calculate pH as:

pH = - log ($5.9_2 \times 10^{-5}$) = **4.23**

Weak Acid Equilibria – *Cont.*

Exercise: Calculate the pH of a 1.50×10^{-2} M formic acid, HCO_2H. ($pK_a = 3.745$).

Answer: pH = 2.808

HINT: You must first determine K_a from pK_a. *How?*

Determining K_a from Measured pH

Example: A student measured the pH of a 0.10 M solution of formic acid, HCOOH, to be 2.38 at 25 ^{0}C. Calculate K_a for formic acid at 25 ^{0}C.

Answer: $K_a = 1.8 \times 10^{-4}$

Percent Ionization of a Weak Acid

The ***percent ionization*** of a weak acid HA refers to the percentage of HA in ionized form, H^+ (and A^-)

$$\% \text{ ionization} = \frac{[H_3O^+]_{eq}}{[HA]_{initial}} \times 100$$

Example: What is percent of HOCl in ionized form in the previous example? {Recall that $[H^+] = 5.92 \times 10^{-5}$ M and initial [HOCl] = 0.10 M}

Answer: **0.059 % ionized**

Weak Base Equilibria: *Hydrolysis*

- Recall that B-L bases are H^+ acceptor.
- In aqueous solutions, a weak base "grabs" a H^+ from water, forming its conjugate acid and OH^-. This reaction is called ***hydrolysis***.

For a monobasic species, B, the *hydrolysis equation* is:

$$\mathbf{B + H_2O \overset{K_b}{\rightleftharpoons} BH^+ + OH^-}$$

Weak base
(H^+ acceptor)

Conj. acid

***Hydroxide* ion**

The equilibrium constant expression for this reaction is:

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

Hydrolysis – Cont.

Exercise: Write the hydrolysis reaction of each of the following bases:

- Carbonate, CO_3^{2-}
- Bicarbonate, HCO_3^-
- Sulfate, SO_4^{2-}
- Phosphate, PO_4^{3-}

$$CO_3^{2-} + H_2O \overset{K_b}{\rightleftharpoons} HCO_3^- + OH^-$$

$$HCO_3^- + H_2O \overset{K_b}{\rightleftharpoons} H_2CO_3 + OH^-$$

$$SO_4^{2-} + H_2O \overset{K_b}{\rightleftharpoons} HSO_4^- + OH^-$$

$$PO_4^{3-} + H_2O \overset{K_b}{\rightleftharpoons} HPO_4^{2-} + OH^-$$

Note: Add a **+1** charge to the base to determine charge of conjugate acid

Determining pH of Solutions of Weak Bases

Ammonia is the most commonly used weak base. The hydrolysis of ammonia is written as:

$$\mathbf{NH_3 + H_2O \overset{K_b}{\rightleftarrows} NH_4^+ + OH^-}$$

Weak base

The K_b expression for NH_3 can be written as:

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

Exercise: Calculate the concentration of OH^- in a 0.15 M solution of NH_3. K_b for NH_3 is 1.8×10^{-5} at 25 ^{0}C. What is the pH of this solution?

$$NH_3 + H_2O \overset{K_b}{\rightleftarrows} NH_4^+ + OH^-$$

WB

	NH_3	NH_4^+	OH^-
I:	0.15	0	0
C:	$-y$	$+y$	$+y$
E:	$(0.15 - y)$	y	y

K_b and pH can be expressed as:

$$\boxed{K_b = \frac{y^2}{(M_B - y)}}$$

and $pH = 14.00 - pOH$

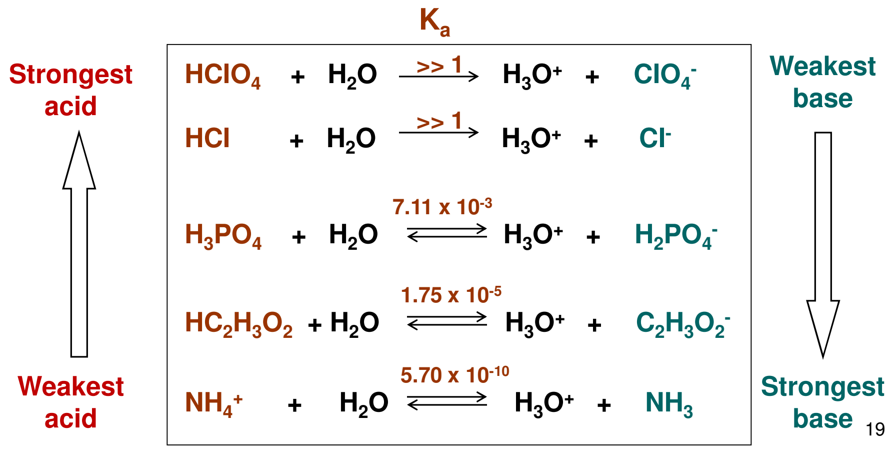
$= 14.00 - (-\log [OH^-])$

or $\boxed{pH = 14.00 - \log (y)}$

Relationship Between K_a and K_b

Recall: *Conjugate species* = related by one H (as H^+)

- The ***stronger the acid*** the ***weaker its conj. base***
- Similarly, the stronger the base the weaker its conj. acid



$HClO_4 + H_2O \xrightarrow{>> 1} H_3O^+ + ClO_4^-$

$HCl + H_2O \xrightarrow{>> 1} H_3O^+ + Cl^-$

$H_3PO_4 + H_2O \overset{7.11 \times 10^{-3}}{\rightleftharpoons} H_3O^+ + H_2PO_4^-$

$HC_2H_3O_2 + H_2O \overset{1.75 \times 10^{-5}}{\rightleftharpoons} H_3O^+ + C_2H_3O_2^-$

$NH_4^+ + H_2O \overset{5.70 \times 10^{-10}}{\rightleftharpoons} H_3O^+ + NH_3$

Relationship Between K_a and K_b

- The K_a of an acid is also related to the K_b of its conj. base, i.e.

For ***conjugate acid-base pairs***:

$K_a \times K_b = K_w$ $\qquad$ $pK_a + pK_b = 14.00$

Exercises:

(1) Calculate the K_b for CO_3^{2-} if K_a for HCO_3^- is 5.6×10^{-11}.

(2) Hydrofluoric acid, HF, has a pK_a of 3.17. Calculate K_b for fluoride ion, F^-.

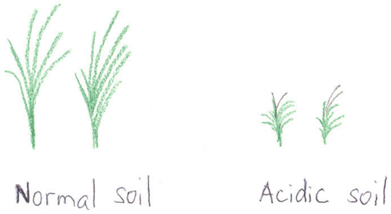
Answers: (1) $K_b = 1.8 \times 10^{-4}$; (2) $K_b = 1.5 \times 10^{-11}$

Importance of pH Control

What if pH is not controlled?

- Hyperacidic stomach

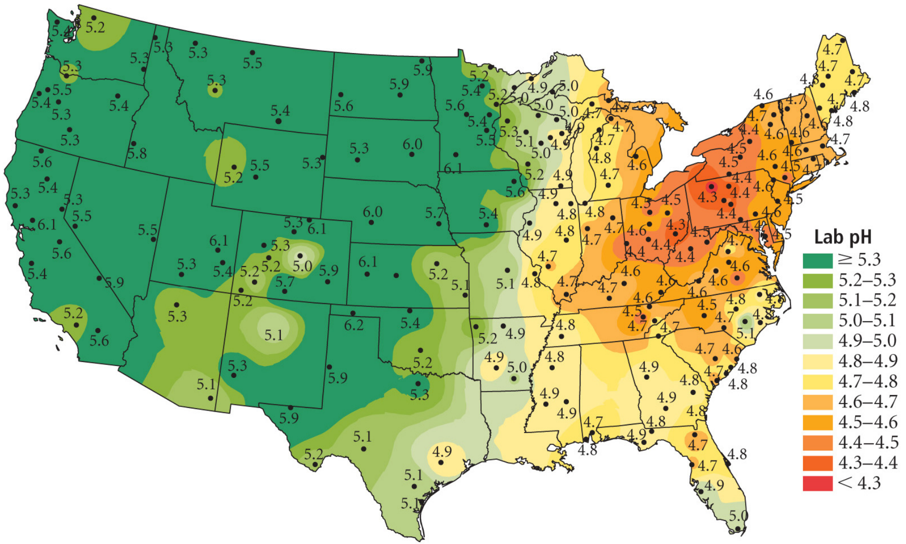
- Highly acidic soil => low crop yield



- Air pollutants => acid rain
  - Acidic lakes/rivers => fish kills; erosion of statues; vegetation dies

There must be a way to control pH

Acid rain: a significant problem in the Northeastern U.S.



Damages Caused by Acid Rain

Damage to aquatic life

http://www.sciencemaster.com/jump/earth/acid_rain.php

In some sensitive lakes and streams, ***acidification has completely eradicated fish species***, such as the **brook trout**, leaving these bodies of water barren. In fact, hundreds of the lakes in the **Adirondacks** surveyed in the NSWS have acidity levels indicative of chemical conditions unsuitable for the survival of sensitive fish species.

Damage to vegetation and outdoor artwork (limestone)

(a) (b)

Ways of Controlling pH

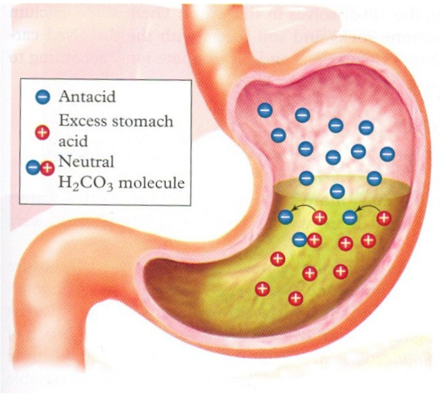
1) Through ***neutralization*** reactions = acid-base reactions

Ex. **HCl** + **antacid** (a carbonate) => **salt** + H_2O

Excess stomach acid

A base

Always produced in neutralization



Source: C. Baird and W. Gloffke, “Chemistry In Your Life.” New York: Freeman, 2003. (p. 427)

Writing Neutralization Reactions

1) The metal from the base is always *written* (or *named*) *first*.

2) The metal from the base ***replaces*** the hydrogen of the acid.

$HCl + NaOH \longrightarrow \underset{\text{salt}}{\underline{NaCl}} + \underline{HOH}$ (or H_2O)

$HNO_3 + KOH \longrightarrow \underset{\text{salt}}{\underline{KNO_3}} + \underline{H_2O}$

$HCN + NaOH \longrightarrow \underset{\text{salt}}{\underline{NaCN}} + \underline{H_2O}$

Ways of Controlling pH (Cont.)

2) Through the action of ***buffers***

- Substances that resist drastic changes in pH. HOW?
- They consist of a mixture of a ***weak acid*** and its conjugate ***base*** (i.e. an acid-base pair).

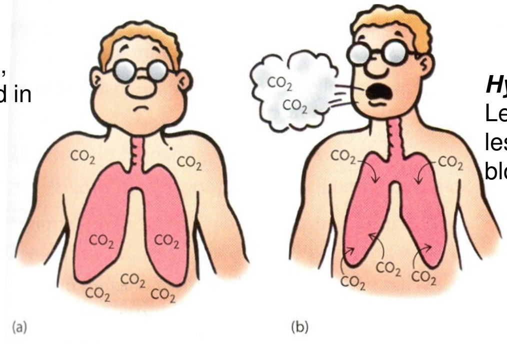
Ex. The pH of blood is maintained by a biological buffer, a mixture of ***carbonic acid*** and ***bicarbonate ions***.

acid component

base component

Ways of Controlling pH: *Action of Buffers* (Cont.)

Hypoventillation:
More CO_2 in lungs,
more carbonic acid in
blood = acidosis



Hyperventillation:
Less CO_2 in lungs,
less carbonic acid in
blood = alkalosis

- During alkalosis (blood pH rises) the <u>acid component</u> (H_2CO_3) of our *biological buffer* neutralizes the excess base and restores the pH to around 7.4, the normal pH of blood.

- During **acidosis** (blood pH drops), the <u>base component</u> (HCO_3^-) neutralizes the excess acid and restores the pH to around 7.4.

Acid-Base Properties of Salts

Acid-Base Properties of Salts

Recall: Acids and bases can be electrically neutral (ex. HCl, NH_3) or charged (ex. NH_4^+, CO_3^{2-})

- *Implication*: **Salts**, ionic compounds formed from neutralization reactions, can be acidic, basic or neutral solutions.
    - The anion or the cation of a salt, or both, can react with water (= ***hydrolysis*** reaction)
    - The pH of salt solution depends on the strengths of the original acids and bases

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Salts – *Cont.*

Q. What is the pH of an aqueous solution of a salt?

- The pH of the salt depends on the strengths of the original acids and bases

Acid	**Base**	**Salt pH**	**Example of salt**
Strong	Strong	7 (Neutral)	NaCl, KNO_3, $CaBr_2$
Weak	Strong	> 7 (Basic)	Na_2CO_3, K_3PO_4
Strong	Weak	< 7 (Acidic)	NH_4Cl, CH_3NH_3Br
Weak	Weak	Depends on which is stronger	NH_4ClO, $(NH_4)_2CO_3$

Salts – *Cont.*

Predicting whether a **salt solution** will be acidic, basic or neutral:

1. Break the salt down into its cation and anion.

2. Identify (+) and (-) ions as either:

   - Spectator ion* (SI)
   - Weak acid (WA)
   - Weak base (WB)

A **spectator ion**, SI, does not react with water (i.e. it does not hydrolyze) and does not change the pH of water because it is neither acidic nor basic.

3. Add the two effects to decide on effect on solution pH

Exercise: Show that Na_2CO_3 hydrolyzes in water to form a basic solution.

Work:

(1) Ionize **Na_2CO_3** → **2 Na^+**, **CO_3^{-2}**

(2) ID ions as SI, WA or WB

Na_2CO_3 → **Na^+** = **SI** } Comes from **SB NaOH; *no reaction* with water!**

Na_2CO_3 → **CO_3^{-2}** = **WB** (There's no acidic H!) → Will **hydrolyze** to form **OH^-**

Hydrolysis of CO_3^{-2}:

$$\underbrace{CO_3^{-2}}_{\text{Base}} + H_2O \rightleftharpoons HCO_3^- + \underbrace{OH^-}_{\text{Basic!}}$$

(will grab H+ from water)

Exercise: Show that ammonium chloride hydrolyzes in water to form an acidic solution.

Work:

$NH_4Cl \nearrow NH_4^+$ = **WA**

$NH_4Cl \searrow Cl^-$ → **SI** – comes from a strong acid, HCl

Hydrolysis of NH_4^+:

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + \underbrace{H_3O^+}_{\text{Acidic!}}$$

Exercise: 1) Predict whether each of the following salts will be acidic, basic or neutral in water. Show your work, including applicable hydrolysis equations.

$SrCl_2$

$NaCHO_2$

$AlBr_3$

NH_4NO_3

Exercise 2) Calculate the pH of each of the following aqueous solutions: (a) 0.100 M $NaCHO_2$, (b) 0.100 M $AlBr_3$ and (c) 0.100 M NH_4NO_3

WORK:

(a) pH of 0.100 M $\underbrace{CHO_2^-}_{\text{W.B.}}$ (Na^+ is S.I.)

W.B. = will hydrolyze to form OH-

$$CHO_{2\,(aq)}^- + H_2O_{(l)} \Leftrightarrow HCHO_{2\,(aq)} + \mathbf{OH^-}_{(aq)}$$

I	0.100		0	0
C	- *x*		+ *x*	+ *x*
E	(0.100 – *x*)		*x*	*x*

Next we ***need*** $\mathbf{K_b}$ => use K_a ($HCHO_2$) and K_w

Table: K_a ($HCHO_2$) = 1.80×10^{-4}

WORK – Cont.

(a) pH of 0.100 M CHO_2^-

$$\text{Table: } K_b\,(CHO_2^-) = \frac{1.00 \times 10^{-14}}{1.80 \times 10^{-4}} = 5.56 \times 10^{-11}$$

Hydrolysis: $CHO_{2\,(aq)}^- + H_2O_{(l)} \Leftrightarrow HCHO_{2\,(aq)} + \mathbf{OH^-}_{(aq)}$

$$K_b = 5.56 \times 10^{-11} = \frac{x^2}{(0.100 - x)} \quad \text{Assume } x << 0.100$$

$x = 2.36 \times 10^{-6}$ M = $[OH^-]$

pOH = 5.63; **pH = 8.37**

WORK:
(b) pH of 0.100 M $AlBr_3$ (Br^- is S.I. – comes from HBr, SA)

Al^{3+} is a WA which exists as **$Al(H_2O)_6^{3+}$** in water (See K_a table)
K_a for $Al(H_2O)_6^{3+} = 1.4 \times 10^{-5}$

Dissociation: $Al(H_2O)_6^{3+}{}_{(aq)} + H_2O_{(l)} \Leftrightarrow Al(H_2O)_5(OH)^{3+}{}_{(aq)} + \mathbf{H_3O^+}{}_{(aq)}$

I	0.100		0	0
C	- *x*		+ *x*	+ *x*
E	(0.100 – *x*)		*x*	*x*

$$K_a = 1.4 \times 10^{-5} = \frac{x^2}{(0.100 - x)}$$ Assume x << 0.100

$x = 1.18 \times 10^{-3}$ M = $[H_3O^+]$

pH = 2.93

WORK:
(c) pH of 0.100 M NH_4NO_3 (NO_3^- is S.I. – comes from HNO_3, SA)

NH_4^+ is a WA (CA of WB NH_3; From K_a and K_b table,
K_b of $NH_3 = 1.76 \times 10^{-5}$)

$$K_{a\,(NH_4^+)} = \frac{1.00 \times 10^{-14}}{1.76 \times 10^{-5}} = 5.68 \times 10^{-10}$$

Ionization: $NH_4^+{}_{(aq)} + H_2O_{(l)} \Leftrightarrow NH_{3\,(aq)} + \mathbf{H_3O^+}{}_{(aq)}$

I	0.100		0	0
C	- *x*		+ *x*	+ *x*
E	(0.100 – *x*)		*x*	*x*

$$K_a = 5.68 \times 10^{-10} = \frac{x^2}{(0.100 - x)}$$ Assume x << 0.100

$x = 7.54 \times 10^{-6}$ M = $[H_3O^+]$

pH = 5.12

Diprotic Acids and Bases

General formulas:

- **H_2A** = fully acidic form
- **HA^-** = intermediate form; amphoteric
- **A^{2-}** = fully basic or fully deprotonated form

Equilibria involved: Diprotic Acids and Bases

Diprotic Acid, H_2A

First dissociation: $$H_2A + H_2O \xrightleftharpoons{K_{a1}} HA^- + H_3O^+$$

Second dissociation: $$HA^- + H_2O \xrightleftharpoons{K_{a2}} A^{-2} + H_3O^+$$

Dibasic species, A^{2-}

First hydrolysis: $$A^{2-} + H_2O \xrightleftharpoons{K_{b1}} HA^- + OH^-$$

Second hydrolysis: $$HA^- + H_2O \xrightleftharpoons{K_{b2}} H_2A + OH^-$$

Q. How do we calculate K_{b1} and K_{b2} from K_a values?

Note that H_2A and HA^- species in the K_{a1} expression both appear in the K_{b2} expression. Similarly, the conjugates HA^- and A^{2-} in the K_{a2} expression both appear in the K_{b1} expression.

Thus,

$$K_{a1} \cdot K_{b2} = K_w$$

$$K_{a2} \cdot K_{b1} = K_w$$

Proof:

$$\cancel{H_2A} + H_2O \xrightleftharpoons{K_{a1}} \cancel{HA^-} + H_3O^+$$

$$+ \quad \cancel{HA^-} + H_2O \xrightleftharpoons{K_{b2}} \cancel{H_2A} + OH^-$$

$$2H_2O \xrightleftharpoons{K_w} H_3O^+ + OH^- \qquad K_w = K_{a1} \times K_{b2}$$

Harris, *Quantitative Chemical Analysis*, 8e

pH Calculation: Diprotic Acids and Bases

1. The fully acidic form, H_2A

Approximation: In a solution of H_2A (Ex. 0.050 M H_2SO_3), the 2nd dissociation is usually negligible that *H_2A behaves* as a *monoprotic acid*. Also, $[A^{2-}] \approx 0$ M.

Calculation of pH and [species]

$$H_2A + H_2O \xrightleftharpoons{K_{a1}} HA^- + H_3O^+$$

Equil: F-*x* *x* *x*

$$K_{a1} = \frac{x^2}{F - x}$$

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pH Calculation: Fully acidic form (H_2A) – *Cont.*

Problem 1: Find the pH of a 0.050 M H_2SO_3 solution.
$K_{a1} = 1.23 \times 10^{-2}$; $K_{a2} = 6.6 \times 10^{-8}$

$$H_2SO_3 + H_2O \xrightleftharpoons{K_{a1}} HSO_3^- + H_3O^+$$

Equil: 0.050-*x* *x* *x*

$$K_{a1} = 1.23 \times 10^{-2} = \frac{x^2}{(0.050 - x)}$$

x cannot be ignored since K_{a1} isn't too small

$$x^2 + 1.23 \times 10^{-2} x - 6.15 \times 10^{-4}$$

Solve for x using quadratic equation

$$x = 1.94 \times 10^{-2} M = [H_3O^+] = [HSO_3^-]$$

$$pH = 1.71$$

***pH Calculations*: Diprotic systems** – *Cont.*

2. The fully basic form, A^{2-}

Approximation: In a solution of A^{2-} (Ex. 0.050 M Na_2SO_3), the 2nd hydrolysis is usually negligible that *A^{2-} behaves* as a *monobasic species.* Also, $[H_2A] \approx 0$ M.

Calculation of pH and [species]

$$A^{2-} + H_2O \underset{}{\overset{K_{b1}}{\rightleftharpoons}} HA^{-} + OH^{-}$$

Equil: F-*y* *y* *y*

$$K_{b1} = \frac{y^2}{F - y}$$

pOH = -log (*y*)
pH = 14 - pOH

Recall: $K_{b1} = K_w/K_{a2}$

Problem 2: Find the pH of 0.050 N Na_2SO_3 solution:

$K_{a1} = 1.23 \times 10^{-2}$;
$K_{a2} = 6.6 \times 10^{-8}$

***Answer:* pH = 9.94; $[OH^-] = 8.7 \times 10^{-5}$ M**

***pH Calculations*: Diprotic systems** – *Cont.*

3. The intermediate (amphoteric) form, HA^-

- HA^- can act as an acid or a base

  Q. What is the predominant species in a solution of HA^-?

Compare K_{a2} and K_{b2} equilibria:

Dissociation: $HA^- + H_2O \underset{\longleftarrow}{\xrightarrow{K_{a2}}} A^{2-} + H_3O^+$

Hydrolysis: $HA^- + H_2O \underset{\longleftarrow}{\xrightarrow{K_{b2}}} H_2A + OH^-$

- HA^- will dissociate/hydrolyze to form A^{2-} and H_2A

No pH calculation involving HA^-

The intermediate form, HA^- *(Cont.)*

Calculation of pH and [species]

$$[\mathrm{H}^+] \approx \sqrt{\frac{K_1K_2\mathrm{F} + K_1K_\mathrm{w}}{K_1 + \mathrm{F}}}$$

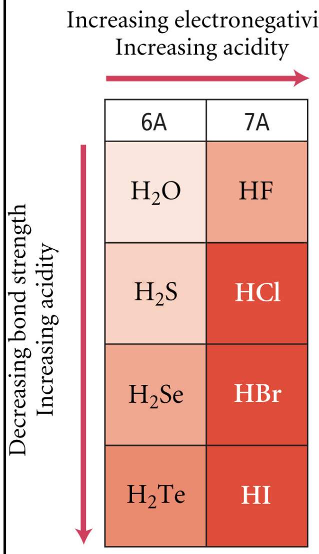
Where
$K_1 = K_{a1}$
$K_2 = K_{a2}$
$F = F_{HA-}$

pH = -log $[H^+]$

Quick check: pH = ½ (pK_1 + pK_2)

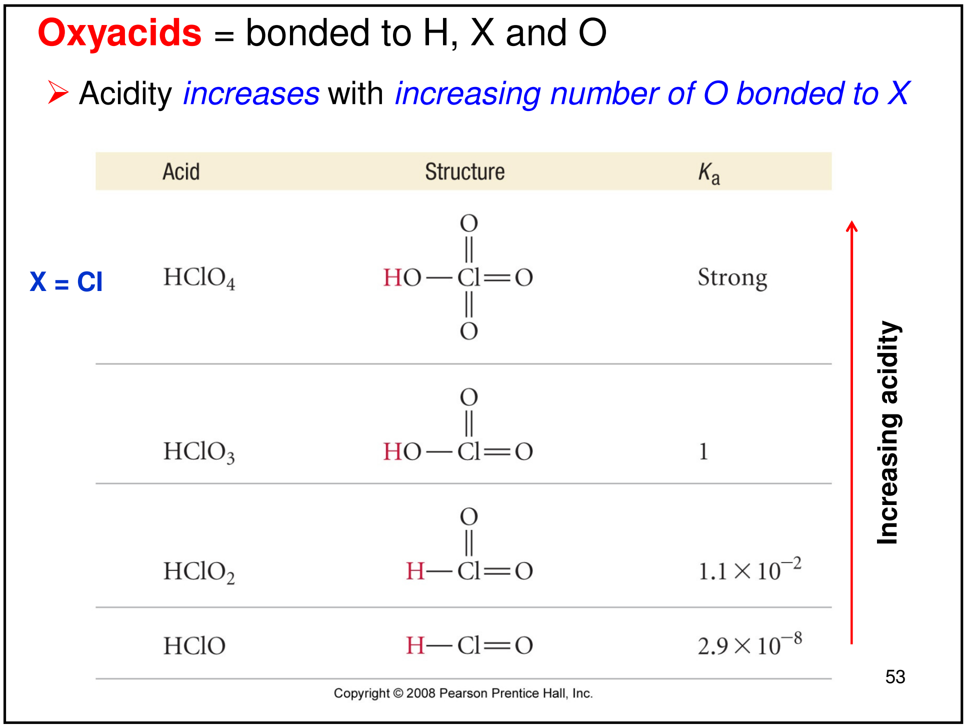
- Solve for $[H_2A]$ and $[A^{2-}]$ using $[H^+]$ above and K_1 & K_2 equilibria

Trends in Acidity



6A	7A
H_2O	HF
H_2S	HCl
H_2Se	HBr
H_2Te	HI

1. Effect of **bond strength** on binary acids, HX
   - Acidity *increases* with *decreasing bond strength* (top to bottom within a group)
   - Easier to pull out H as H^+
2. Effect of **electronegativity** of X in binary acids, HX
   - Acidity *increases* with *increasing electronegativity* (left to right across the table)
   - H-X bond becomes more polar; easier to pull out H^+



Oxyacids = bonded to H, X and O

- Acidity *increases* with *increasing number of O bonded to X*

X = Cl

Acid	Structure	K_a
$HClO_4$	$\mathrm{HO{-}\underset{\underset{\displaystyle O}{\Vert}}{\overset{\overset{\displaystyle O}{\Vert}}{Cl}}{=}O}$	Strong
$HClO_3$	$\mathrm{HO{-}\overset{\overset{\displaystyle O}{\Vert}}{Cl}{=}O}$	1
$HClO_2$	$\mathrm{H{-}\overset{\overset{\displaystyle O}{\Vert}}{Cl}{=}O}$	1.1×10^{-2}
HClO	$\mathrm{H{-}Cl{=}O}$	2.9×10^{-8}

Increasing acidity