# ACIDS AND BASES_____ H Ch 9, 8-4; Z Ch 7.8

What is the pH of a $1.0 \times 10^{-8}$ M solution of HBr?

It cannot be pH 8.00. It should be an acidic solution with a pH lower than 7.00!

There are two reactions that are important.

$HBr(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Br^-(aq)$

$2\ H_2O(l) \iff H_3O^+(aq) + OH^-(aq)$

## H 8-4 Systematic Treatment of Equilibrium

General approach includes

1. write down the pertinent chemical reactions and their equilibrium expressions
2. write down all species present in solution according to #1
3. set up the charge balance equation (the solution must be electrically neutral so the number of positive charges = the number of negative charges)
4. apply the material balance equation (conservation of matter) – may be more than one
5. are there enough equations to solve for the unknowns?

Charge Balance – solution must be electrically neutral

**EX 1.** Write the charge balance for a solution containing only the following ions:

$H^+$, $OH^-$, $Na^+$, $Ba^{2+}$, $PO_4^{3-}$, $Ag^+$, $SO_4^{2-}$

**EX 2.** Write the charge balance for a solution containing $(NH_4)_3PO_4$. Be sure to consider all possible equilibrium reactions.

Formality (F) and Molarity (M)

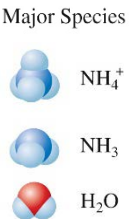
same for a species that does not dissociate into ions (or react with water to produce ions) such as glucose

molarity is the concentration of the actual species in solution such as 1 M $Cl^-$

formality is the concentration originally placed in water – acetic acid ($CH_3COOH$) is a weak acid and reacts with water to produce a small amount of $CH_3COO^-$. So a 1.0 F solution of acetic acid means that 1.0 = [$CH_3COOH$] + [$CH_3COO^-$]

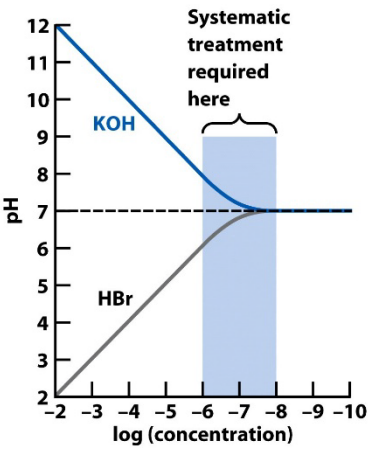
Mass Balance (material balance) – conservation of matter; the quantity of all species in a solution containing a particular atom (or group of atoms) must equal the amount of that atom (or group) delivered to the solution.

**EX 3.** What is the mass balance equation for a solution prepared by adding 0.100 moles of ammonia to 1.000 L of water




## H 9-1 Strong Acids and Bases (Systematic Approach)

**EX 4.** What is the pH of a $1.0 \times 10^{-8}$ M solution of HBr?

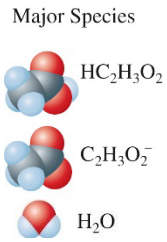



A systematic treatment is only needed in a small range of acid and base concentrations. Outside this range [$H^+$] from $K_w$ is either too small (> $10^{-6}$) or the solution cannot practically be prepared (< $10^{-8}$).

## H 9-2 – 9-3 Weak Acid Equilibria (Systematic Approach): $K = x^2 / (F - x)$

**EX 5.** Set up the systematic equations for a 0.0100 M solution of $CH_3COOH$.

1) reactions
2) species
3) charge balance
4) material balance




Set up an ICE table corresponding to EX 5 and correlate the approximations.

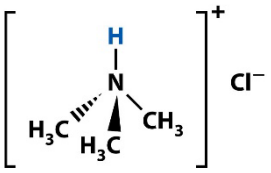
$$HA(aq) + H_2O(l) \;<=>\; H_3O^+(aq) + A^-(aq)$$

**I**nitial

**C**hange

**E**quilibrium

**EX 6.** What is the pH of 0.050 M weak acid whose $K_a = 1.59 \times 10^{-10}$?

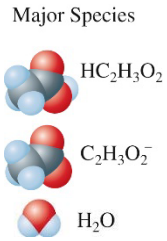


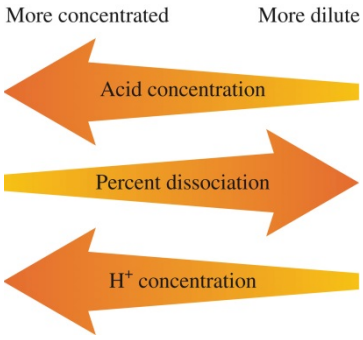

**Approximations in Equilibrium Calculations** (H p 195, Z p. 207)

1% rule: $[HA]_0 - x \approx [HA]_0$ if $x \leq 1\%\ [HA]_0$ (Zumdahl uses a more liberal 5% rule)

## Dilution of Weak Acid

**EX 7.** $K_a = 1.76 \times 10^{-5}$ for acetic acid, $CH_3COOH$. Determine $[H_3O^+]$, pH, and % ionization for 0.010 M and 0.0010 M acetic acid.



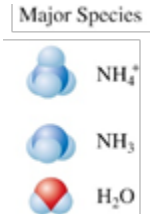

effect on equilibrium  effect on $[H_3O^+]$  effect on pH  effect on ionization

## H 9-4 Calculating the pH of Weak Base Solutions, $K_b = x^2 / (F - x)$

**EX 10.** $K_b = 1.8 \times 10^{-5}$ for $NH_3$. What is the pH of a 0.25 M solution of ammonia in water?

$$NH_3(aq) + H_2O(l) \iff OH^-(aq) + NH_4^+(aq)$$

Ammonia




## Z 7.8 Acid-Base Properties of Salt and Metal Ion Solutions

Salt – any ionic compound than does not contain $OH^-$ as the anion. The cations (anions) of salts can have acidic (basic) properties if they are the conjugate acid (base) of a weak base (acid).

| cation* | anion** | example | pH of solution |
|---|---|---|---|
| from strong base | from strong acid (conjugate base of) | $MgI_2$, $KClO_4$ | neutral |
| from strong base | from weak acid (conjugate base of) | KF, AgCN | basic |
| from weak base (conjugate acid of) | from strong acid (conjugate base of) | $NH_4Br$ | acidic |
| from weak base (conjugate acid of) | from weak acid (conjugate base of) | $NH_4NO_2$ | acidic if $K_a > K_b$<br>basic if $K_b > K_a$<br>neutral if $K_a = K_b$ |
| highly charged metal ion (hydrated in water) | from strong acid (conjugate base of) | $Al(NO_3)_3$, $Cr(H_2O)_6^{3+}$ | acidic |

*cation from strong base (Group I and II hydroxides, excluding Be) and silver:

$Li^+$, $Na^+$, $K^+$, $Rb^+$, $Cs^+$
$Mg^{2+}$, $Ca^{2+}$, $Sr^{2+}$, $Ba^{2+}$
$Ag^+$

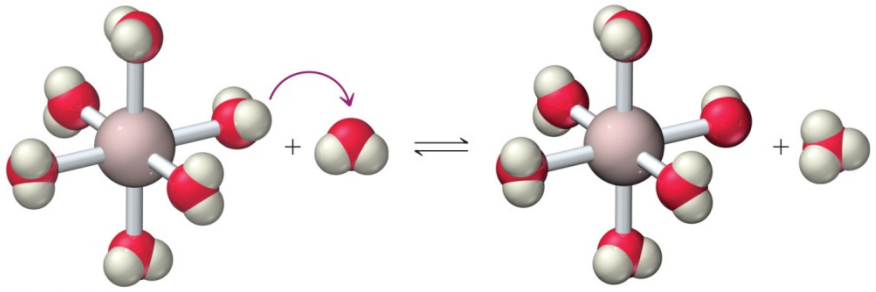
**anion from strong acid: conjugate base of six of the seven common strong acids

$C\lambda^-$, $Br^-$, $I^-$
$ClO_4^-$, $ClO_3^-$, $NO_3^-$ (**not** $HSO_4^-$ - conjugate base of a strong acid so it is an ineffective base, but has a proton so it is acidic)

metal ions in solution

Due to ion-dipole forces highly charged metal cations ($Al^{3+}$, $Cr^{3+}$, $Fe^{3+}$, etc) dissolve in water forming hydrated species. The electronegative O atom of water is closest to the positively charged metal. The high charge polarizes the O – H bonds of water, weakening them, and making them more acidic.

$$Al(H_2O)_6^{3+}(aq) + H_2O(aq) \rightleftharpoons Al(H_2O)_5(OH)^{2+}(aq) + H_3O^+(aq)$$



## Summary of Equilibria Involving Weak Acids and Bases

determined by properties of the solvent, generally water

**autoionization of water** – water ionization constant, $K_w$

$2\ H_2O(l) \iff H_3O^+(aq) + OH^-(aq)$ $\qquad$ $K_w = [H_3O^+][OH^-] = 1.01 \times 10^{-14}$ (at 25°C)

**pH scale**

$pH = -\log_{10}[H_3O^+] \Rightarrow [H_3O^+] = 10^{-pH}$ $\qquad$ $pOH = -\log_{10}[OH^-] \Rightarrow [OH^-] = 10^{-pOH}$

$$pK_w = -\log_{10}K_w \Rightarrow pK_w = pH + pOH = 14 \text{ (at 25°C)}$$

**acid (HA) dissociation**

$HA(aq) + H_2O(l) \iff H_3O^+(aq) + A^-(aq)$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{x^2}{F-x} \quad \text{or} \quad pK_a = -\log_{10}K_a$$

if HA not too dilute or too weak

**base (B:) ionization**

$B{:}(aq) + H_2O(l) \iff OH^-(aq) + BH^+(aq)$

$$K_b = \frac{[OH^-][BH^+]}{[B{:}]} = \frac{x^2}{F-x} \quad \text{or} \quad pK_b = -\log_{10}K_b$$

if B: not too dilute or too weak

**conjugate acid/base pair**

$$K_a \times K_b = K_w \quad \text{or} \quad pK_w = pK_a + pK_b$$

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boxed entries => definitions which are independent of temperature
of course, rigorously, the equilibrium constants should be given in terms of activities