CHEMISTRY 1102 NOTES
ZUMDAHL CHAPTER 14 - ACIDS AND BASES

This and the next chapter are very important especially in biochemical and industrial settings. There are a number of calculation types to be mastered.

1. The Nature of Acids and Bases

Arrhenius Definition - acids are sources of H^+ donors and bases (alkalis) are sources of OH^-.

Brønsted-Lowry Definition - acids are proton donors and bases are proton acceptors.

The example given is an aqueous solution of HCl yielding the *hydronium ion* H_3O^+. The generic equation is:

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

This reaction contains two *conjugate acid-base* pairs, HA/A^- and H_3O^+/H_2O. The reaction can also be viewed as a competition of the two conjugate bases for the H^+. If H_2O is a stronger base than A^-, then the equilibrium will lie to the right:

$$K \; = \; [H_3O^+][A^-]/[H_2O][HA] \qquad K_a \; = \; [H_3O^+][A^-]/[HA]$$

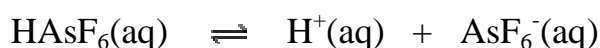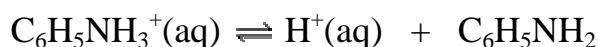Because $[H_2O] \approx 55.6$ and approximately constant for most dilute aqueous solutions.

K_a is called the *acid dissociation constant*. In addition, although we should strictly use H_3O^+ it is used interchangeably with H^+:
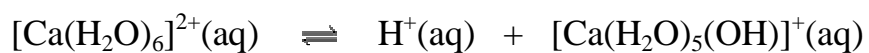
$$HA(aq) \;\; \rightleftharpoons \;\; H^+(aq) \; + \; A^-(aq)$$

$$K_a \; = \; [H_3O^+][A^-]/[HA] \; = \; [H^+][A^-]/[HA]$$

(Equations smust be appropriately balanced all the same!)

Examples of acids:

$HBr(aq) \;\; \rightleftharpoons \;\; H^+(aq) \; + \; Br^-(aq)$

$HC_2H_3O_2(aq) \;\; \rightleftharpoons \;\; H^+(aq) \; + \; C_2H_3O^{2-}(aq)$

$NH_4^+(aq) \;\; \rightleftharpoons \;\; H^+(aq) + NH_3(aq)$

$C_6H_5NH_3^+(aq) \rightleftharpoons H^+(aq) \; + \; C_6H_5NH_2$

$HAsF_6(aq) \;\; \rightleftharpoons \;\; H^+(aq) \; + \; AsF_6^-(aq)$

$$[Ca(H_2O)_6]^{2+}(aq) \rightleftharpoons H^+(aq) + [Ca(H_2O)_5(OH)]^+(aq)$$

The Brønsted-Lowry definition can apply to molecules in the gas phase also, and in cases where the Arrhenius definition does not, for example the reaction of NH_3 with HCl. (There are no OH⁻ groups here at all)

2. Acid Strength

The strength of an acid is defined by the position of equilibrium in its ionization reaction:

TABLE 14.1 Various Ways to Describe Acid Strength

Property	Strong Acid	Weak Acid
K_a value	K_a is large	K_a is small
Position of the dissociation (ionization) equilibrium	Far to the right	Far to the left
Equilibrium concentration of H^+ compared with original concentration of HA	$[H^+] \approx [HA]_0$	$[H^+] \ll [HA]_0$
Strength of conjugate base compared with that of water	A^- much weaker base than H_2O	A^- much stronger base than H_2O

See also Figures 14.1, 14.2 and 14.3

FIGURE 14.1
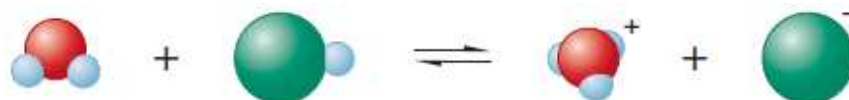The reaction of HCl and H_2O.

FIGURE 14.2
The reaction of an acid HA with water to form H_3O^+ and a conjugate base A^-.

FIGURE 14.3
The reaction of NH_3 with HCl to form NH_4^+ and Cl⁻.

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TABLE 14.2   Values of K_a for Some Common Monoprotic Acids

Formula	Name	Value of K_a*
HSO_4^-	Hydrogen sulfate ion	1.2×10^{-2}
$HClO_2$	Chlorous acid	1.2×10^{-2}
$HC_2H_2ClO_2$	Monochloracetic acid	1.35×10^{-3}
HF	Hydrofluoric acid	7.2×10^{-4}
HNO_2	Nitrous acid	4.0×10^{-4}
$HC_2H_3O_2$	Acetic acid	1.8×10^{-5}
$[Al(H_2O)_6]^{3+}$	Hydrated aluminum(III) ion	1.4×10^{-5}
HOCl	Hypochlorous acid	3.5×10^{-8}
HCN	Hydrocyanic acid	6.2×10^{-10}
NH_4^+	Ammonium ion	5.6×10^{-10}
HOC_6H_5	Phenol	1.6×10^{-10}

Increasing acid strength

*The units of K_a are customarily omitted.

and Table 14.2

The common strong acids are sulphuric acid (H_2SO_4), hydrochloric acid (HCl), nitric acid (HNO_3) and perchloric acid ($HClO_4$). (Hydrogensulphate ion (HSO_4^-) is a weak acid.) Most acids have H attached to an oxgen atom ie they are *oxyacids*. The most well know exceptions are hydrohalic acids but there are others. Organic acids contain the -CO(OH) group - hydrogen bound to carbon is not normally ionizable.
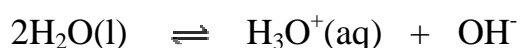
It is not possible to accurately calculate the acid dissociation constants for the strong acids because the (unionized) acid concentrations are so small and difficult to measure accurately. K_a approaches infinity.

Water as an Acid and a Base

Water is *amphoteric*: it can behave either as an acid or a base:

$$H^+(aq) + H_2O(l) \rightleftharpoons H_3O^+$$

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$
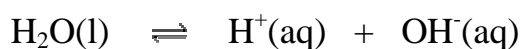
It normally undergoes self- or autoionization:

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

(aq)

Other liquids can do this too: an important one is liquid ammonia. (It is normally a gas).

The equilibrium constant for the self-ionization of water is:

$$K_w = [H_3O^+][OH^-] = [H^+][OH^-] = 1.0 \times 10^{-14} \text{ at 25 °C.}$$

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At 25 ^{o}C, in *neutral* solutions:

$$[H^+] \;=\; [OH^-] \;=\; 1.0 \times 10^{-7}$$

In acid solution, $[H^+] > [OH^-]$ and in basic solution $[H^+] < [OH^-]$

Exercise (14.3):

Calculate $[H^+]$ or $[OH^-]$ as required for each of the following at 25 ^{o}C and say whether the solution is acidic or basic:

a. 1.00×10^{-5} M OH^-

   Answer: $[H^+] \;=\; 1.0 \times 100^{-14}/1.00 \times 10^{-5} \;=\; 1.00 \times 10^{-9}$ M   Solution is *basic*

b. 1.00×10^{-7} OH^-

   Answer: $[H^+] \;=\; 1.00 \times 10^{-14}/1.00 \times 10^{-7} \;=\; 1.00 \times 10^{-7}$ M   Solution is *neutral*

c. 10.0 M H^+

   Answer: $[OH^-] \;=\; 1.00 \times 10^{-14}/10.0 \;=\; 1.00 \times 10^{-15}$ M   Solution is (very!) *acidic*

Exercise (14.4):

At 60 ^{o}C the value of K_w is $1. \times 10^{-13}$;

d. Predict whether the autoionization of water is endo- or exothermic.

   Answer: Use the principle of le Châtelier, which tells us that if a system at equilibrium is heated, it will adjust to consume energy. We note an *increase* in the value of K_w at 60 ^{o}C over the value at 25 ^{o}C. The reaction is shifting towards the right indicating that heat is absorbed as part of this process. Therefore the reaction is *endothermic* in this direction.

e. calculate $[H^+]$ and $[OH^-]$ for a neutral solution.

   Answer: In a neutral solution $[H^+] = [OH^-]$ and since:

   $[H^+][OH^-] \;=\; 10^{-13}\; [H^+]^2 \;=\; [OH^-]^2 \;=\; 10^{-13}$

   Therefore

   $[H^+] \;=\; [OH^-] \;=\; (10^{-13})^{\frac{1}{2}} \;=\; 3 \times 10^{-7}$ M

3. The pH scale

Because the concentration [H+] varies over a very large range (about 15 orders of magnitude) it is convenient to use a log scale to specify acidity. Usually, the concentrations are less than 1 so the logs would tend to be negative numbers. for this reason a new scale is defined:

$$pH = -\log_{10}[H^+] \quad \text{or just} \ -\log[H^+]$$

Note: the logs are expressed to the same number of *decimal places* as the *significant figures* in the actual concentration. Log(231.62) = 2.36478: the original number has 5 significant figures so its log has 5 figures *after the decimal point*

Other log scales are: $pOH = -\log[OH^-]$

$$pK = -\log[K]$$

At 25 $^\circ$C neutral solutions have:

$[H^+] = 10^{-7}$ so pH = 7

$[OH^-] = 10^{-7}$ so pOH = 7

$K_w = 10^{-14}$ so $pK_w = 14$

Since: $[H^+][OH^-] = 10^{-14}$

$$\log([H^+][OH^-]) = \log(10^{-14})$$

$$pH + pOH = pK_w = 14$$

Your scientific calculator should handle the conversions to logs and back from logs (antilog or 10^x) that you will need. Read the manual!

Before tackling acid-base calculations always think carefully about the major species present in the solution.

4. Calculating the pH of Strong Acid Solutions

Example: (14.7a)

Calculate the pH of 0.1 M HNO_3.

Answer:

Nitric acid is a strong acid, therefore the major species in solution are: H^+, NO_3^- and H_2O

We neglect the contribution to $[H^+]$ from the self-ionization of water which will be $< 10^{-7}$

We assume the HNO_3 is completely ionized so:

$[H^+] = 0.1\,M$ and $pH = \log(0.1) = 1.0$

Example: (14.7b)

Calculate the pH of 10^{-15} M HCl

Answer:

HCl is also completely ionized, but its concentration is so small that its effect on the water self-ionization equilibrium will be negligible. The pH will be that of pure water: 7.
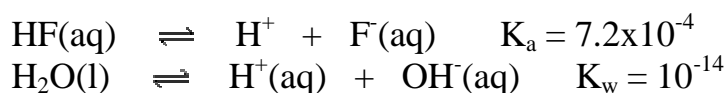
5. **Calculating the pH of Weak Acid Solutions**

   Example:

   Calculate the pH of a 1.00 M solution of HF ($K_a = 7.2 \times 10^{-4}$)

   Answer:

   1. What are the major species in solution? They are HF and H_2O.
   2. Which can furnish $[H^+]$?

      $HF(aq) \rightleftharpoons H^+ + F^-(aq) \qquad K_a = 7.2 \times 10^{-4}$
      $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \qquad K_w = 10^{-14}$

   3. Pick the dominant $[H^+]$ supplier (there will almost always be one!) In this case it is HF.
   4. The starting concentration of HF is 1.00 M

      At equilibrium let the concentrations be:

      $[HF] = (1.0 - A)$
      $[H^+] = A$
      $[F^-] = A$

   5. Set up the calculation:

      $K_a = [H^+][F^-]/[HF] = (A)(A)/(1.00 - A) = 7.2 \times 10^{-4}$

   6. Apply the approximation that $1.00 - A \sim 1.00$ because A will be quite small.

$$7.2 \times 10^{-4} = A^2/1.00 \rightarrow A^2 = 7.2 \times 10^{-4} \rightarrow A = 2.7 \times 10^{-2}$$

7. We are ready to calculate the pH except we should check the validity of the approximation we just made. The back-calculated K_a should not differ from that given by more than about 5%

$$K_a(calcd) = A^2/1.00 - 2.7 \times 10^{-2}) = 7.40 \times 10^{-4}$$

$$(K_a(approx) - K_a)/K_a = 0.027 \text{ or } 2.8\%$$

This OK! (N.B. This method is different to that suggested in the text.)

8. Calculate the pH.

$$pH = \log(2.7 \times 10^{-2}) = 1.57$$

The pH of a Mixture of Weak Acids

Example: (14.9)

Calculate the pH of a mixture containing:

1.00 M HCN ($K_a = 6.2 \times 10^{-10}$)
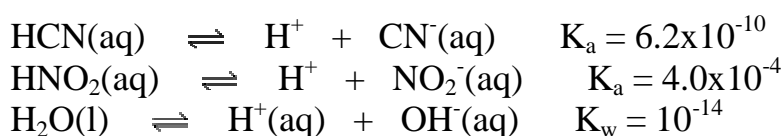5.00 M HNO_2 ($K_a = 4.0 \times 10^{-4}$)

and calculate the CN^- concentration at equilibrium.

Answer:

9. The acids are all weak therefore the major species in solution are:

HCN, HNO_2 and H_2O

10. All three produce H^+:

$$HCN(aq) \rightleftharpoons H^+ + CN^-(aq) \qquad K_a = 6.2 \times 10^{-10}$$
$$HNO_2(aq) \rightleftharpoons H^+ + NO_2^-(aq) \qquad K_a = 4.0 \times 10^{-4}$$
$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \qquad K_w = 10^{-14}$$

11. As often is the case one acid is significantly stronger than the others, in this case the nitrous acid. It will supply the bulk of the H^+.
12. Its starting concentration is 5.00 M

At equilibrium we have:

$$[HNO_2] = 5.00 - A$$
$$[H^+] = A$$
$$[NO_2^-] = A$$

13. Set up the calculation:

$$K_a = 4.0 \times 10^{-4} = [H^+][NO_2^-]/[HNO2] = (A)(A)/5.00-A) \sim A^2/5.00$$

$$A = 4.5 \times 10^{-2} M$$

14. Check the approximation (the book way this time):

$4.5 \times 10^{-2}/5.00 \times 100\% = 0.90\%$ which is fine.

$$pH = \log(4.5 \times 10^{-2}) = 1.35$$

For the CN^- concentration, use:

$$K_a = 6.2 \times 10^{-10} = [H^+][CN^-]/[HCN]$$

Remember, there is only one kind of $[H^+]$ (virtually entirely from the nitrous acid) but the HCN system does not know that, and also remember that very little HCN will dissociate. Therefore:

$$6.2 \times 10^{-10} = (4.5 \times 10^{-2})[CN-]/(1.00)$$

$$[CN^-] = 1.4 \times 10^{-8} M$$

Percent Dissociation

Percent Dissociation = (amount dissociated (M)/initial concentration (M)) x 100%

Example: (14.10a) Calculate the percentage dissociation of 0.1 M acetic acid, $K_a = 1.8 \times 10^{-5}$.

Answer:

The major species in solution are CH_3COOH and H_2O

Acetic acid is much a stronger acid than water, so its contribution to $[H^+]$ dominates:

$$CH_3OOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

$$or \ HOAc(aq) \rightleftharpoons H^+(aq) + OAc^-(aq)$$
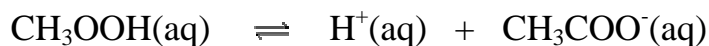
$K_a = 1.8 \times 10\text{-}4 = [H^+][Ac^-]/[HAc]$

The equilibrium concentrations will be:

$[HOAc] = 0.1 - A$
$[H^+] = A$
$[OAc^-] = A$

$1.8 \times 10^{-4} = (A)(A)/)(0.1 - A) \sim A2/0.1$

$[H^+] = A = 1.3 \times 10^{-3} M$

(The approximation is valid - check it!)

The percent dissociation $= 1.3 \times 10^{-3}/0.10 \times 100\% = 1.3\%$

For a 1.0 M solution, $[H^+] = 4.2 \times 1^{-3} M$ and the percent dissociation is 0.42%. Notice that although the solution is nominally more concentrated, and contains a large concentration of $[H^+]$, a smaller percentage of the acetic acid is actually dissociated.

The next problem shows how to get K_a from the percent dissociation:

Example: (14.11)

In a 0.1 M solution of lactic acid ($HC_3H_5O_3$) 3.7% is dissociated. Calculate K_a.

Answer:

15. The major species will be lactic acid and water.
16. The dissociation reaction is:

$HC_3H_5O_3$ (aq) $\rightleftharpoons$ H^+(aq) + $C_3H_5O_3^-$(aq)

for which:

$K_a = [H^+][C_3H_5O_3^-]/[HC_3H_5O_3]$

17. The starting concentration, $[HC_3H_5O_3]_o = 0.10 M$
18. The equilibrium concentrations can be taken as:

$[HC_3H_5O_3] = 0.10 - A$
$[H^+] = A$
$[C_3H_5O_3^-] = A$

19. We calculate A from the known percent dissociation:

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$$3.7/100 \;=\; x/[HC_3H_5O_3]_o \qquad so \; x \;=\; 3.7x10^{-3} \; M$$

20. Now we can calculate $K_a \;=\; (3.7x10^{-3})(3.7x10^{-3})/(0.10 - 3.7x10^{-3}) \;=\; 1.4x10^{-4}$

● **Bases**

The hydroxides of all the group I and II metals except Be are strong bases which correspond to both the Arrhenius and Brønsted-Lowry definitions. The Group II hydroxides ionize to supply two OH^- groups and are not very soluble.

NaOH and KOH are common lab bases, and "slaked lime", $Ca(OH)_2$ is an important industrial reagent used, among other things for removing SO_2 from stack gases. It is also used in combination with "soda ash", Na_2CO_3 to remove Ca^{2+} and Mg^{2+} from "hard" water:
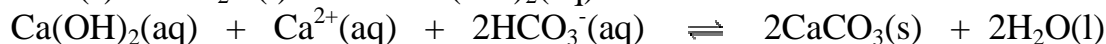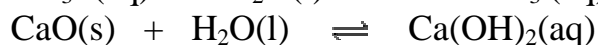
$CO_3^{2-}(aq) \;+\; H_2O(l) \;\rightleftharpoons\; HCO_3^-(aq) \;+\; OH^-(aq)$
$CaO(s) \;+\; H_2O(l) \;\rightleftharpoons\; Ca(OH)_2(aq)$
$Ca(OH)_2(aq) \;+\; Ca^{2+}(aq) \;+\; 2HCO_3^-(aq) \;\rightleftharpoons\; 2CaCO_3(s) \;+\; 2H_2O(l)$
The calculation of the pH of strong bases is trivial:

Example: (14.12)

Calculate the pH of 0.05 M NaOH solution. Answer:

The major species are Na^+, OH^- and H_2O.

The OH^- coming from the auto-ionization of water can be neglected, so:

$[OH^-] \;=\; 5.0x10^{-2} \; M$ and

$K_w \;=\; [H^+][OH^-] \;=\; [H^+](5.0x10^{-2})1.0x10^{-14}$

$[H^+] \;=\; 2x10^{-13} \qquad so \; pH \;=\; 12.70$

There are a number of substances which are able to accept a proton from water because they have lone pairs:
$B:(aq) \;+\; H_2O(l) \;\rightleftharpoons\; B:H^+(aq) \;+\; OH^-(aq)$
They include ammonia and alkyl amines, and pyridine, carbonate, phosphate and many others:
$K_b \;=\; [BH^+][OH^-]/[B]$

(Table 14.3)	Values of K_b for Some Common Weak Bases)		
Name	**Formula**	**Conjugate Acid**	**K_b**
Ammonia	NH_3	NH_4^+	1.8×10^{-5}
Methylamine	CH_3NH_2	$CH_3NH_3^+$	4.4×10^{-4}
Dimethylamine	$(CH_3)_2NH$	$(CH_3)_2NH_2^+$	5.1×10^{-4}
Trimethylamine	$(CH_3)_3N$	$(CH_3)_3NH^+$	5.3×10^{-4}
Ethylamine	$C_2H_5NH_2$	$C_2H_5NH_3^+$	5.6×10^{-4}
Aniline	$C_6H_5NH_2$	$C_6H_5NH_3^+$	3.8×10^{-10}
Pyridine	C_6H_5N	$C_6H_5NH^+$	1.7×10^{-9}

Example: (14.13)

Calculate the pH of a 15.0 M solution of ammonia in water.

Answer:

The major species in solution will be NH_3 and H_2O.

There are two sources of OH⁻ but much more will come from NH_3:

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

$K_b = 1.8 \times 10^{-5} = [NH_4^+][OH^-]/[NH_3]$

The starting concentration of NH_3 is 15.0 m, and at equilibrium the concentrations are:

$[NH_3] = 15.0 - A \sim 15.0$ M

$[NH_4^+] = A$

$[OH^-] = A$

Therefore:

$A^2/15.0 = 1.5 \times 10^{-5}$ so $A = 1.6 \times 10^{-2} = [OH^-]$

We are OK on the 5% rule

$pOH = \log(1.6 \times 10^{-2}) = 1.8$ so $pH = 14 - pOH = 12.2$

Notice that only about 0.11% of the NH_3 has reacted with water: bottles labelled "ammonium hydroxide" are not really what they say they are!

- **Polyprotic Acids**

There are many acids that have more than one ionizable H. They are called *polyprotic*. The examples given are phosphoric acid whch is triprotic and sulphuric and carbonic acids which are diprotic. (Carbonic acid is virtually non-existant because it dissociates to CO_2 and water - not an acid/base reaction. Nevertheless, it is convenient to pretend that solutions of CO_2 in water are H_2CO_3)

$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$
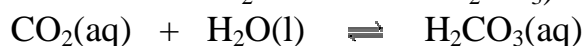
They are characterized by successive K_a's which get progressively smaller. (Table 14.4) It naturally becomes more difficult to remove positively charged protons from acid *anions*

TABLE 14.4 Stepwise Dissociation Constants for Several Common Polyprotic Acids

Name	Formula	K_{a_1}	K_{a_2}	K_{a_3}
Phosphoric acid	H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.8×10^{-13}
Arsenic acid	H_3AsO_4	5×10^{-3}	8×10^{-8}	6×10^{-10}
Carbonic acid	H_2CO_3	4.3×10^{-7}	5.6×10^{-11}	
Sulfuric acid	H_2SO_4	Large	1.2×10^{-2}	
Sulfurous acid	H_2SO_3	1.5×10^{-2}	1.0×10^{-7}	
Hydrosulfuric acid*	H_2S	1.0×10^{-7}	$\sim 10^{-19}$	
Oxalic acid	$H_2C_2O_4$	6.5×10^{-2}	6.1×10^{-5}	
Ascorbic acid (vitamin C)	$H_2C_6H_6O_6$	7.9×10^{-5}	1.6×10^{-12}	

*The K_{a_2} value for H_2S is very uncertain. Because it is so small, the K_{a_2} value is very difficult to measure accurately.

(Table 14.4) Stepwise Dissociation Constants for several Common Polyprotic Acids				
Name	**Formula**	**K_{a1}**	**K_{a2}**	**K_{a3}**
Phosphoric Acid	H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.8×10^{-13}
Arsenic Acid	H_3AsO_4	5×10^{-3}	8×10^{-8}	6×10^{-10}

"Carbonic acid"*	H_2CO_3	4.3×10^{-7}	5.6×10^{-11}	
Sulphuric acid	H_2SO_4	large	1.2×10^{-2}	
Sulphurous acid	H_2SO_3	1.5×10^{-2}	1.0×10^{-7}	
"Hydrosulphuric acid"*	H_2S	1.0×10^{-7}	$\sim 10^{-19}$	
Oxalic acid	$H_2C_2O_4$	6.5×10^{-2}	6.1×10^{-5}	
Ascorbic Acid	$H_2C_6H_6O_6$	7.9×10^{-5}	1.6×10^{-12}	
* These acids are CO_2 and H_2S dissolved in water.				

Phosphoric Acid

This polyprotic acid is typical in that its K_a's differ by several (5) orders of magnitude. The result is that only the first ionization in water makes a contribution to the hydrogen ion concentration, and calculating the pH presents no new problems.

Example: (14.15)

Calculate th pH of 5.0 M H_3PO_4 and the concentrations of $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-}.

Answer: The calculation of $[H^+]$ in the usual way gives 0.19 M, thus a pH of 0.72. (The usual approximation is just OK.)

This yields $[H_3PO_4]$ = 5.0 - 0.19 = 4.8 M and a "starting" concentration of $[H_2PO_4^-]$ = 0.19.

For the concentration of HPO_4^{2-} use:

K_{a2} = 6.2×10^{-8} = $[H^+][HPO_4^{2-}]/[H_2PO_4^-]$
6.2×10^{-8} = $(0.19)[HPO_4^{2-}]/(0.19)$ so $[HPO_4^{2-}]$ = 6.2×10^{-8} M
For the concentration of PO_4^{3-} use:
K_{a3} = 4.8×10^{-13} = $[H^+][PO_4^{3-}]/[HPO_4^{2-}]$
4.8×10^{-13} = $(0.19)[HPO_4^{2-}]/(6.2 \times 10^{-8})$ so $[HPO_4^{2-}]$ = 1.6×10^{-19} M

Sulphuric Acid

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This acid is unique among the polyprotic acids listed in that *its first dissociation step is complete* - it is a strong acid. Two cases are illustrated by the following examples: a rather strong (1.0 M) solution of H_2SO_4 and a weaker one (1.0×10^{-2} M) where the "usual" approximation is *not* valid.

Example: (14.16)

Calculate the pH of a 1.0 M solution of sulphuric acid.

Answer:

The major solution species are H^+, HSO_4^- and H_2O

The "starting" concentrations, since the sulphuric acid is completely dissociated are:

$[H^+] = 1.0$ M
$[HSO_4^-] = 1.0$
At equilibrium for the *second* dissociation step they are:
$[H^+] = 1.0 + A$
$[HSO_4^-] = 1.0 - A$
$[SO_4^{2-}] = A$
$K_{a2} = 1.2 \times 10^{-2} = [H^+][SO_4^{2-}]/[HSO_4^-] = (1.0 + A)(A)/(1.0 - A)$
$1.2 \times 10^{-2} \sim (1.0)(A)/1.0)$ so $A = 1.2 \times 10^{-2}$ M, which is 1.2% of 1.0 thus acceptable.
Strictly, $[H^+] = 1.0 + 1.2 \times 10^{-2}$, but, of course, only 2 significant figures are appropriate, so $[H^+] = 1.0$ and the pH = 0.00.

Example: (14.17)
Calculate the pH of a 1.00×10^{-2} M solution of sulphuric acid.

Answer:

The major solution species are H^+, HSO_4^- and H_2O

The "starting" concentrations, since the sulphuric acid is completely dissociated are:

$[H^+] = 0.0100$ M
$[HSO_4^-] = 0.0100$
At equilibrium for the *second* dissociation step they are:
$[H^+] = 0.0100 + A$
$[HSO_4^-] = 0.0100 - A$
$[SO_4^{2-}] = A$
$K_{a2} = 1.2 \times 10^{-2} = [H^+][SO_4^{2-}]/[HSO_4^-] = (0.0100 + A)(A)/(0.0100 - A)$
Attempt the usual approximation:
$1.2 \times 10^{-2} \sim (0.0100)(A)/0.0100)$ so $A = 1.2 \times 10^{-2}$ M.

This is way over 5% of 0.0100, thus unacceptable. We are obliged to go back and use the full quadratic form:
$$A^2 + (2.2 \times 10^{-2})A - (1.2 \times 10^{-4}) = 0$$
The positive root is $A = 4.5 \times 10^{-3}$, so $[H^+] = 0.0145$ M, and the pH = 1.84

● **Acid-Base Properties of Salts**

Salts are ionic compounds which dissociate into ions in solution. Such solutions are not always neutral for a variety of reasons:

Salts that Produce Neutral Solutions

The conjugate ions derived from strong acids or bases are weak, and therefore have no effect on the acidity or basicity of solutions. Solutions of salts of Na^+ or K^+ with any of the strong acid anions: Cl^-, HSO_4^-, NO_3^-, etc have pH's of about 7.0.

Salts that Produce Basic Solutions

Consider a solution of sodium acetate. The major species present are Na^+, CH_3COO^- and H_2O. Sodium ions will not affect the acidity, but acetate is a ion derived fron a weak acid, so it has significant base strength, and water itself is weakly amphoteric, so we have the reaction:.
$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$$
$$K_b = [CH_3COOH][OH^-]/[CH_3COO^-]$$
Now we know $K_a = 1.8 \times 10^{-5}$. We also know that $K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$. Therefore $[OH^-] = K_w/[H^+]$. Substituting:
$$K_b = [CH_3COOH]K_w/[CH3COO^-][H^+] = K_w/K_a$$
$$K_a.K_b = K_w$$
Example: (14.18)

Calculate the pH of 0.30 M NaF solution. K_a for HF = 7.2×10^{-4}.

Answer: The major species in solution will be Na^+, F^- and H_2O

$$F^-(aq) + H_2O(l) \rightleftharpoons HF(aq) + OH^-(aq)$$

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$K_b = [HF][OH^-]/[F^-] = K_w/K_a = 1.0x10^{-14}/7.2x10^{-4} = 1.4x10^{-11}$

"Starting" concentrations are:

$[HF] = 0$
$[F-] = 0$
$[F-] = 0.30$
Equilibrium concentrations are:
$[HF] = A$
$[F-] = A$
$[F-] = 0.30 - A$
$K_b = 1.4x10^{-11} = (A)(A)/(0.30 - A) \sim A^2/(0.30)$ Therefore: $A \sim 2x10^{-6}$
$[OH^-] = A = 2.00x10^{-6} M$
$pOH = 5.69$
$pH = 14.00 - 5.69 = 8.31$, which is just on the basic side of neutral.

Base Strength in Aqueous Solution

HCN is a weak acid, $K_a = 6.2x10^{-10}$ and, so CN⁻ might be expected to be a strong base. It really is not, $K_b = 1.6x10^{-5}$. Why? Compare the two reactions defining these quantities:
$HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$
$CN^-(aq) + H_2O(l) \rightleftharpoons HCN(aq) + OH^-(aq)$
In the first, CN⁻ competes with H_2O for the proton from H_3O^+; in the second CN⁻ competes with OH⁻ for the proton from H_2O. These observations lead to the order of base strength:

$$OH^- > CN^- > H_2O$$

Salts that Produce Acid Solutions

There are two types of salt that produce acidic solutions:

Consider a solution of ammonium chloride which yields NH_4^+, Cl⁻ and H_2O as the major solution species. Chloride is neutral, but NH_4^+ is the cation of a weak base and leads to acidity in the resulting solution:

$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$

Example: (14.19)
Calculate the pH of 0.10 M NH₄Cl solution. K_b for $NH_3 = 1.8x10^{-5}$.

Answer: Major species in solution are NH_4^+, Cl⁻ and H_2O. Both NH_4^+ and H_2O can produce H⁺ and, because NH_4^+ is the stronger acid of the two, we must consider the reaction:

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$NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq)$

$K_a = [NH_3][H^+]/[NH_4^+]$

We start with $[NH_4^+] = 0.10$ M. At equilibrium the concentrations are:

$[NH_4^+] = 0.10 - A$ M

$[NH_3] = A$
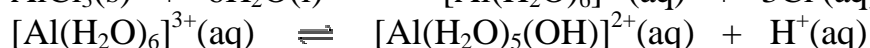
$[H^+] = A$

$K_a = K_w/K_b = 1.0 \times 10^{-14}/1.8 \times 10^{-5} = 5.6 \times 10^{-10}$

$5.6 \times 10^{-10} = (A)(A)/(0.10 - A)$ so $A = 7.5 \times 10^{-6}$ M (OK by 5% test)

Therefore the pH = 5.13, just a little on the acid side

The second situation where acidic solutions are produced occurs when a solution of a highly charged or particularly small ion is involved. An example of this is a solution of $AlCl_3$. This dissociates in water and the Al^{3+} ion is strongly coordinated by six water molecules. The polarizing effect of the Al^{3+} makes thes water molecules more acidic than uncoordinated water:

$AlCl_3(s) + 6H_2O(l) \longrightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$

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

Given that $K_a = 1.4 \times 10^{-5}$ for this process, the pH can be calculated in the usual way.

(Exercise 14.20)

Finally, there are, of course, salts which are made from a combination of a weak acid and a weak base. Examples given in the book are ammonium acetate, Ammonium cyanide and aluminum sulphate. The calcualtion of the pH is rather more complicated than the preceding cases, but a qualitative answer can be obtained by comparing the K_a of the acidic ion with the K_b of the basic ion. If K_a is greater than K_b, the solution will be on the acid side:

For example, consider aluminum sulphate: (from 14.21) K_a for $[Al(H_2O)_6]^{3+} = 1.4 \times 10^{-5}$

K_a for hydrogensulphate is 1.2×10^{-2} enabling us to calculate K_b for sulphate as:

$K_b = K_w/K_a = 1.0 \times 10^{-14}/1.2 \times 10^{-2} = 8.3 \times 10^{-13}$

K_a for hydrated Al^{3+} is greater than K_b for sulphate the solution will be appreciably acidic.

- **The Effect of Structure on Acid-Base Properties**

There are perhaps three basic factors to consider:

- Bond polarity - the greater the % ionic character, the stronger the acid.

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- Bond strength - the weaker the bond, the stronger the acid.
- Stabilization of the conjugate base anion - the bigger the ion, the stronger the acid because the negative charge can be delocalized over a larger volume.

These factors are not truly independent of each other, but provide a way of looking at trends among similar molecules such as:

Hydrohalic acids

Acid	Bond Enthalpy $(kJ\ mol^{-1})$	$\chi_X - \chi_H$	% Ionic Character*	Anion Radius (Å)
HF	565	1.9	59%	1.36
HCl	427	0.9	18%	1.81
HBr	363	0.7	12%	1.95
HI	295	0.4	4%	2.16

Calculated using the Pauling formula: % Ionic Character = $(1 - \exp(-0.25(\chi_A - \chi_B)^2)) \times 100\%$

([Table](#))

Acid strength is in the order:
$$H\text{-}F \ < \ H\text{-}Cl \ < \ H\text{-}Br \ < \ H\text{-}I$$
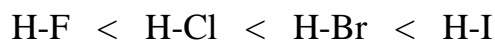
HF is the only weak acid in the series. The others are all essentially 100% ionized in water, but can be placed in the above order by measuring their acid dissociation constants in a non-aqueous solvent which is itself an acid, for example pure (glacial) acetic acid.

The explanation of the order depends on the balance of the three factors listed above. The bond strength and anion size criteria correspond to the observed order, while the bond polarity criterion runs counter to the observed order.

(Table 14.8) Some Oxyacids

Name	Formula	K_a
Sulphuric acid	$(HO)_2SO_2$	Large
Perchloric acid	$HOClO_3$	Strong
Sulphurous acid	$(HO)_2SO$	1.5×10^{-2}
Chloric acid	$HOClO_2$	~1
Nitric acid	$HONO_2$	Large
Chlorous acid	$HOClO$	1.2×10^{-2}
Hypochlorous acid	$HOCl$	3.5×10^{-8}
Nitrous acid	$HONO$	1.2×10^{-2}

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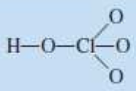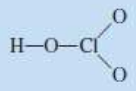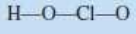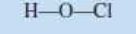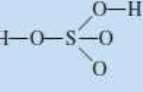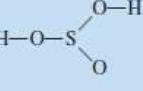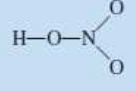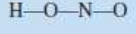
Oxyacids

Nitrous acid	HONO	4.0×10^{-4}

TABLE 14.8   Several Series of Oxyacids and Their K_a Values

Oxyacid	Structure	K_a Value
$HClO_4$	H—O—Cl(—O)(—O)(=O)	Large ($\sim 10^7$)
$HClO_3$	H—O—Cl(—O)(=O)	~ 1
$HClO_2$	H—O—Cl—O	1.2×10^{-2}
HClO	H—O—Cl	3.5×10^{-8}
H_2SO_4	H—O—S(—O—H)(—O)(=O)	Large
H_2SO_3	H—O—S(—O—H)(=O)	1.5×10^{-2}
HNO_3	H—O—N(—O)(=O)	Large
HNO_2	H—O—N—O	4.0×10^{-4}

The other oxygens increase the effective electronegativity of the one carrying the hydrogen thus increasing the bond polarity (and weakening the bond).

For a related series, e.g. HOCl to $HOClO_3$, the more oxygens that there are, the more the negative charge on the anion will be delocalized (spread out), so the stronger the acid. Thus, for perchlorate ion, it is possible to draw structural (Lewis) formulae placing the formal negative charge on any one of the four oxygens. The weaker acids have fewer oxygens on which this charge can be placed.

(Table 14.9)	Electronegativity and Acid Strength		
Name	**Acid (HOX)**	**χ_X**	**K_a**
Hypochlorous acid	HOCl	3.0	4×10^{-8}
Hypobromous acid	HOBr	2.8	2×10^{-9}
Hypoiodous acid	HOI	2.5	2×10^{-11}
Methanol	HOCH$_3$	2.3 (C)	$\sim 10^{-15}$

Comparing a series of similar oxyacids with differing halogens shows the effect of electronegativity in isolation:

● **Acid-Base Properties of Oxides**

In the previous section, the HOX containing compounds all featured an electronegative X. When X is a metal, the metal-oxygen bon is more likely to break *heterolytically* to give the metal cation plus an OH⁻ group.

When a non-metal oxide (often called an acid anhydride) dissolves in water, the product is an acid. Examples are CO_2, SO_2, SO_3, NO_2 etc).

When an electropositive metal oxide dissolves in water, it is effectively the O^{2-} ion reacting with the water to produce OH⁻. Examples are CaO and K_2O

● **The Lewis Acid-Base Model**

There is one other important acid-base definition in common use: the Lewis definition. An acid is an electron pair acceptor and a base is an electron pair donor. The Lewis definition includes Brønsted-Lowry acids and bases, for example a proton (acid) and ammonia or hydroxide (base), but extends the range of molecules covered to include many containing no acidic hydrogen. Examples include acids BF_3, BeH_2, which contains hydridic ($H^{\delta-}$) hydrogen.

- **<u>Strategy for Solving Acid-Base Problems : a Summary</u>**

This is a review and will be left to the student to study.