POLYPROTIC ACIDS AND BASES: Very important!

-- acids that can lose, and bases that can pick up, more than one H^+ (e.g. diprotic H_2A and triprotic H_3A acids).

Ionization occurs stepwise, and each step has its own K_a.

$H_3PO_4\,(aq) \rightleftharpoons H^+\,(aq) + H_2PO_4^-\,(aq)$ $K_{a1} = 7.2 \times 10^{-3}$
$H_2PO_4^-\,(aq) \rightleftharpoons H^+\,(aq) + HPO_4^{2-}\,(aq)$ $K_{a2} = 6.3 \times 10^{-8}$
$HPO_4^{2-}\,(aq) \rightleftharpoons H^+\,(aq) + PO_4^{3-}\,(aq)$ $K_{a3} = 4.2 \times 10^{-13}$

↑ increasing acid strength

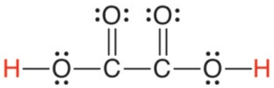
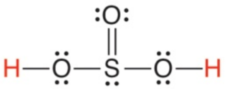
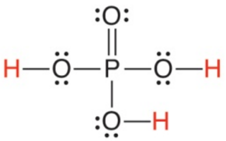
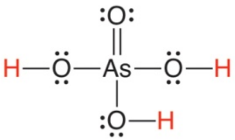
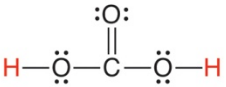
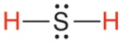
<u>Note</u>: (i) $K_{a1} > K_{a2} > K_{a3}$ <u>Always</u> true for polyprotic acids, *i.e.,* each ionization step is more difficult because it is more difficult to remove H^+ from a molecule as its negative charge increases.

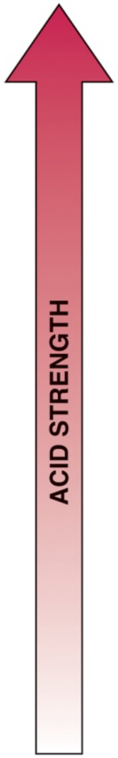
<u>BUT</u> this does <u>not</u> apply for ionic salts of these acids, *e.g.,* Na_3PO_4, Na_2SO_4, etc. They dissociate 100% in one step.

$$Na_3PO_4\,(aq) \rightarrow 3\,Na^+\,(aq) + PO_4^{3-}\,(aq)$$

(ii) The conjugate bases are polyprotic bases, i.e., PO_4^{3-} is a triprotic base – it can pick up 3 H^+.

Table 18.5 Successive K_a values for Some Polyprotic Acids at 25°C

Name (Formula)	**Lewis Structure***	K_{a1}	K_{a2}	K_{a3}
Oxalic acid ($H_2C_2O_4$)		5.6×10^{-2}	5.4×10^{-5}	
Sulfurous acid (H_2SO_3)		1.4×10^{-2}	6.5×10^{-8}	
Phosphoric acid (H_3PO_4)		7.2×10^{-3}	6.3×10^{-8}	4.2×10^{-13}
Arsenic acid (H_3AsO_4)		6×10^{-3}	1.1×10^{-7}	3×10^{-12}
Carbonic acid (H_2CO_3)		4.5×10^{-7}	4.7×10^{-11}	
Hydrosulfuric acid (H_2S)		9×10^{-8}	1×10^{-17}	



*Red type indicates the ionizable protons.

Example Problem: Calculate the pH and concentration of each species in a 5.0 M H_3PO_4 solution.

(a) First dissociation:

$$H_3PO_4\,(aq) \rightleftharpoons H^+\,(aq) + H_2PO_4^-\,(aq)$$

$K_{a1} = 7.2 \times 10^{-3}$

	H_3PO_4	H^+	$H_2PO_4^-$
[init]	5.0 M	0	0
[change]	-x	+x	+x
[equil]	(5.0-x)	x	x

$$K_a = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} = \frac{x^2}{(5.0-x)} = 7.2 \times 10^{-3} \approx \frac{x^2}{5.0} \qquad \text{(assume } x \ll 5.0\text{)}$$

$\therefore\ x^2 = (5.0)(7.2 \times 10^{-3})\quad \therefore\ x = 0.19\ M$

(Check assumption: % ionization = $\left(\frac{x}{5.0 - x}\right)100\% = 4\%$.

Also, $\frac{[H_3PO_4]\text{init}}{K_{a1}} = 694 > 400$. Okay.)

At equilibrium, $[H_3PO_4] = (5.0 - 0.19) = 4.81\ M = 4.8\ M$

$[H^+] = 0.19\ M$ and $[H_2PO_4^-] = 0.19\ M$

(b) Second dissociation: $H_2PO_4^-(aq) \rightleftharpoons H^+(aq) + HPO_4^{2-}(aq)$

$K_{a2} = 6.3 \times 10^{-8}$

[init]	0.19 M	0.19	0
[change]	-y	+y	+y
[equil]	(0.19-y)	(0.19+y)	y

$$K_{a2} = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]} = \frac{y(0.19+y)}{(0.19-y} = 6.3 \times 10^{-8} = y$$ (assume y << 0.19)

$y = 6.3 \times 10^{-8}$ (very small - assumption definitely okay !!)

Note: (1) **$[H^+]$ from second dissociation = K_{a2} = $[HPO_4^{2-}]$**
(2) **$[H^+]$ from second dissociation is negligible!**

(c) Third dissociation: $HPO_4^{2-}(aq) \rightleftharpoons H^+(aq) + PO_4^{3-}(aq)$

$K_{a3} = 4.2 \times 10^{-13}$

[init]	6.3×10^{-8} M	0.19	0
[change]	-z	+z	+z
[equil]	(6.3×10^{-8})-z	(0.19+z)	z

$$K_{a3} = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]} = \frac{(0.19+z)z}{(6.3\text{x}10^{-8})-z} \approx = 4.2 \times 10^{-13}$$

$\therefore z = = 1.4 \times 10^{-19}$ M (assumption okay !!)

$[H^+]$ from third dissociation completely negligible – almost nothing.

(d) Calculate $[OH^-]$, pH and pOH

pH = $-\log[H^+] = -\log(0.19) = 0.72$ pOH = $-\log[OH^-]$ and pOH = 14.00 – pH

via $[OH^-]$ $[H^+][OH^-] = K_w = 1.0 \times 10^{-14}$ (at 25 °C)

$$\therefore [OH^-] = \frac{1.0 \times 10^{-14}}{[H^+]} = \frac{1.0 \times 10^{-14}}{0.19} = 5.3 \times 10^{-14}$$

pOH = $-\log[OH^-] = -\log(5.3 \times 10^{-14}) = 13.28$

(via pH pH + pOH = 14.00 ∴ pOH = 14.00 – pH = 14.00 = 0.72 = 13.28

Summary: In a 5.0 M H_3PO_4 solution:

$[H_3PO_4] = 4.8$ M	$[H^+] = [H_3O^+] = 0.19$ M
$[H_2PO_4^-] = 0.19$ M	$[OH^-] = 5.3 \times 10^{-14}$ M
$[HPO_4^{2-}] = 6.3 \times 10^{-8}$ M	pH = 0.72
$[PO_4^{3-}] = 1.4 \times 10^{-19}$ M	pOH = 13.28

** **Remember**: (1) The $[H_3O^+]$ is determined by K_{a1}. $[H_3O^+]$ from other dissociations (K_{a2}, K_{a3}) is negligible, and is ignored.

(2) $[HPO_4^{2-}]$ from second dissociation = K_{a2} **

$$\begin{tikzcd}
H_3O^+ \arrow[r, leftrightarrow, "K_w = {[H^+][OH^-]}"] \arrow[d, leftrightarrow, "pH = -\log{[H_3O^+]}"'] & OH^- \arrow[d, leftrightarrow, "pOH = -\log{[OH^-]}"] \\
pH \arrow[r, leftrightarrow, "pH + pOH = 14.00"'] & pOH
\end{tikzcd}$$

Section 18.5: Weak Base Equilibria

We will consider weak bases that are molecules containing a N with a lone pair: NH_3, RNH_2, etc. (Other weak bases also known, however.)

General equilibrium for a weak base in water

conjugate pair

$$B_{(aq)} + H_2O_{(aq)} \rightleftharpoons BH^+_{(aq)} + OH^-_{(aq)}$$

(base) (acid) (acid) (base)

conjugate pair

This is a "base-dissociation reaction" or "base-ionization reaction" (**NOTE:** The base doesn't actually dissociate!)

K_b = base-dissociation (ionization) constant

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

($[H_2O]$ is a constant and contained within K_b)

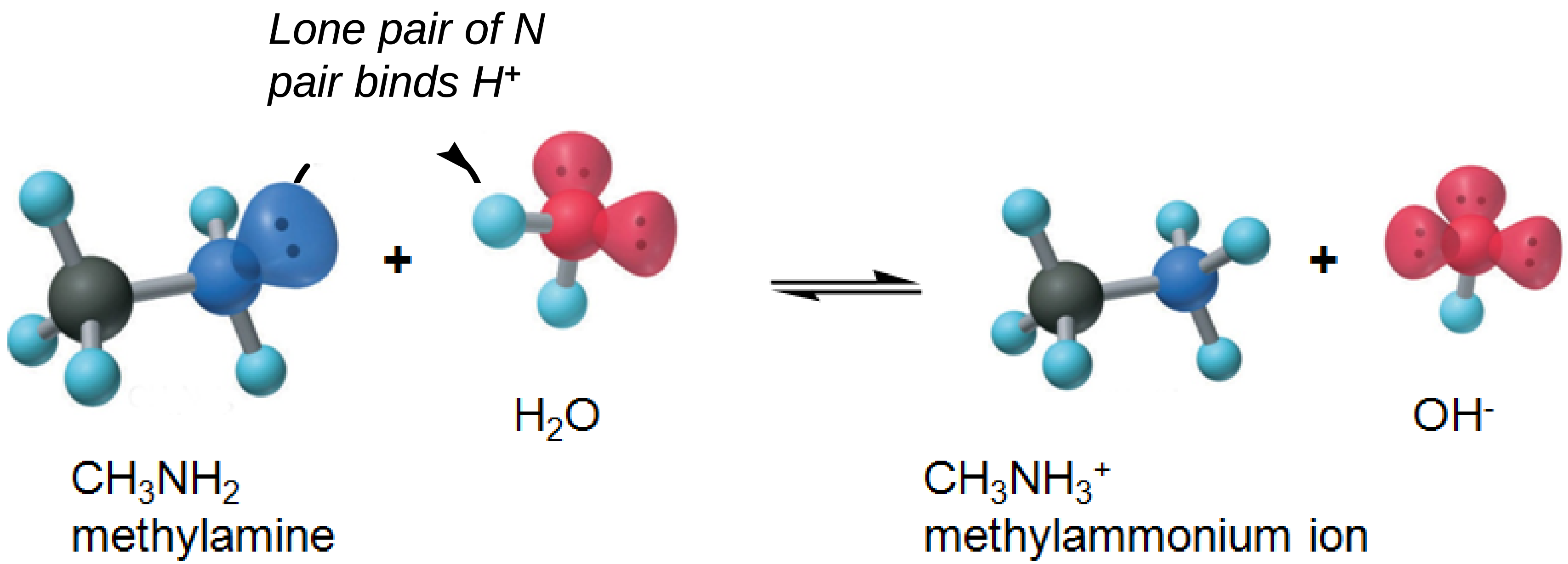
Question. Write the base-ionization and K_b eqns for ammonia (NH_3)

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

$$K_b = \ = 1.8 \times 10^{-5}$$

** Solve calculations similarly to weak acids! **

Figure 18.9 Abstraction of a proton from water by the base methylamine.



Example 1. What is K_b for quinine (anti-malarial drug) if the pH of a 1.5×10^{-3} M solution is 9.84? (**NOTE:** pH > 7.00 ∴ quinine is a base)

	Qui (aq)	+	H_2O (aq)	⇌	$HQui^+$ (aq)	+	OH^- (aq)
[init]	1.5×10^{-3} M				0		0
[change]	-x				+x		+x
[equil]	(1.5×10^{-3})-x				x		x

$$K_b = \frac{[HQui^+][OH^-]}{[Qui]} = \frac{x^2}{(1.5 \times 10^{-3}) - x} \approx \frac{x^2}{1.5 \times 10^{-3}}$$

pH = 9.84 ∴ pOH = 4.16 ∴ $[OH^-] = x = 6.9 \times 10^{-5}$ M

(check: $x = [OH^-] \ll 1.5 \times 10^{-3}$ (4.6%) ∴ assumption okay)

$$\therefore K_b = \frac{(6.9 \times 10^{-5})^2}{1.5 \times 10^{-3}} = \mathbf{3.1 \times 10^{-6}}$$

Example 2. Calculate the pH of a 15.0 M solution of NH_3 ($K_b = 1.8 \times 10^{-5}$)

	NH_3 (aq)	+	H_2O (aq)	⇌	NH_4^+ (aq)	+	OH^- (aq)
[init]	15.0 M				0		0
[change]	-x				+x		+x
[equil]	15.0-x				x		x

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{x^2}{(15.0 - x)} \approx \frac{x^2}{15.0} = 1.8 \times 10^{-5}$$

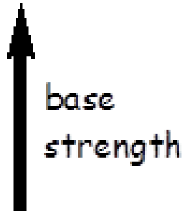
∴ $x^2 = 2.7 \times 10^{-4}$ ∴ $x = 1.6 \times 10^{-2}$ (<< 15.0 ∴ assumption okay)

∴ $[OH^-] = 1.6 \times 10^{-2}$ M ∴ pOH = 1.80 ∴ pH = 14.00 - 1.80 = **12.20**

NOTE: (i) $pK_b = -\log K_b$
(ii) just like pK_a, strength of base increases with decreasing pK_b
(See **Table 18.6**)

The bigger is K_b, the more OH^- is generated.
The smaller is pK_b, the more OH^- is generated.

base	**formula**	**K_b**	**pK_b**
Diethylamine	$NHEt_2$	8.6×10^{-4}	3.07
Methylamine	NH_2Me	4.4×10^{-4}	3.36
Ammonia	NH_3	1.8×10^{-5}	4.74
Pyridine	C_5H_5N	1.7×10^{-9}	8.77



Relationship Between K_a and K_b of a conjugate acid/base

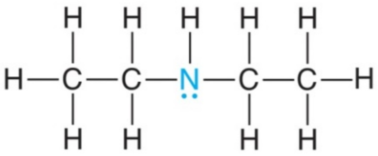
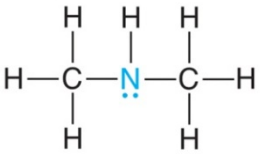
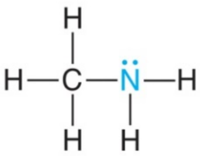
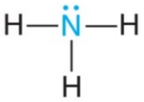
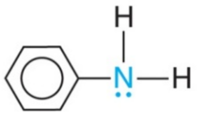
K_a = acid dissociation constant (*e.g.* for NH_4^+)
K_b = base dissociation constant (*e.g.* for NH_3)

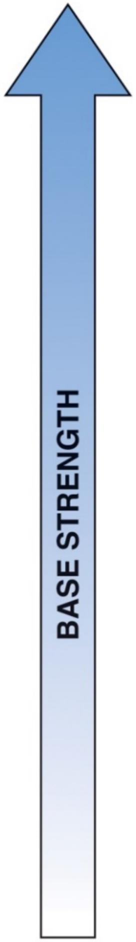
Since NH_3 and NH_4^+ are a conjugate acid/base pair, it is not surprising that K_a for NH_4^+ and K_b for NH_3 are related.

$$\boxed{K_aK_b = K_w} \quad = 1.0 \times 10^{-14} \qquad \text{(at 25 °C)}$$

(K_a for a weak acid)(K_b for its conjugate base) = K_w
same as (K_b for a weak base)(K_a for its conjugate acid) = K_w

Table 18.6 K_b Values for Some Molecular (Amine) Bases at 25°C

Name (Formula)	**Lewis Structure***	K_b
Diethylamine $[(CH_3CH_2)_2NH]$	 $\begin{array}{ccccccccccc} & & H & & H & & H & & H & & H \\ & & \vert & & \vert & & \vert & & \vert & & \vert \\ H & — & C & — & C & — & \underset{\cdot\cdot}{N} & — & C & — & C & — & H \\ & & \vert & & \vert & & & & \vert & & \vert \\ & & H & & H & & & & H & & H \end{array}$	8.6×10^{-4}
Dimethylamine $[(CH_3)_2NH]$	 $\begin{array}{ccccccc} & & H & & H & & H \\ & & \vert & & \vert & & \vert \\ H & — & C & — & \underset{\cdot\cdot}{N} & — & C & — & H \\ & & \vert & & & & \vert \\ & & H & & & & H \end{array}$	5.9×10^{-4}
Methylamine (CH_3NH_2)	 $\begin{array}{ccccccc} & & H & & & & \\ & & \vert & & & & \\ H & — & C & — & \overset{\cdot\cdot}{N} & — & H \\ & & \vert & & \vert & & \\ & & H & & H & & \end{array}$	4.4×10^{-4}
Ammonia (NH_3)	 $\begin{array}{ccccc} H & — & \overset{\cdot\cdot}{N} & — & H \\ & & \vert & & \\ & & H & & \end{array}$	1.76×10^{-5}
Pyridine (C_5H_5N)		1.7×10^{-9}
Aniline $(C_6H_5NH_2)$		4.0×10^{-10}



*Blue type indicates the basic nitrogen and its lone pair.

Example 1: K_a for HF is 6.8×10^{-4}. What is K_b for F^-?

F^- is the conjugate base of HF, therefore its K_b is related to the K_a of HF by

$$K_aK_b = K_w \qquad \therefore K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.8 \times 10^{-4}} = 1.5 \times 10^{-11}$$

Note: K_b very small $\therefore$ do not get much $[OH^-]$ in a solution of e.g. NaF.

Example 2: What is the pH of a 2.5 M solution of sodium acetate (NaAc)? K_a for acetic acid (HAc) is 1.8×10^{-5}.

Acetate ($Ac^- = CH_3COO^-$) is the conjugate base of acetic acid ($HAc = CH_3COOH$).

	$Ac^-(aq)$	$+\ H_2O(l)\ \rightleftharpoons$	$HAc(aq)$	$+\ OH^-(aq)$
[init]	2.5 M		0	0
[change]	-x		+x	+x
[equil]	(2.5-x)		x	x

$$K_b = \frac{[HAc][OH^-]}{[Ac^-]} = \frac{x^2}{(2.5-x)} \approx \frac{x^2}{2.5} \quad \text{(assume } x \ll 2.5\text{)}$$

We need K_b. We were given K_a. ** be careful not to use the wrong K! **

$$\therefore K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.55 \times 10^{-10}$$

$$\therefore \frac{x^2}{2.5} = 5.55 \times 10^{-10} \quad \therefore x = 3.72 \times 10^{-5} = 3.7 \times 10^{-5}\text{ M}$$ (small! - assumption okay)

$\therefore [OH^-] = 3.7 \times 10^{-5}$ $\therefore$ pOH = -log $[OH^-]$ = 4.43 $\therefore$ pH = 14.00 – pOH = **9.57**

Sections 18.6 and 18.8. Not covering in class - read for yourselves. TA's will also cover in discussion periods.

Section 18.7. Salt Solutions

Salts contain cations (C^+) and anions (A^-), *e.g.,* Na^+ and Cl^- in NaCl; K^+ and OH^- in KOH. Some salts, when dissolved in water, give neutral solutions (pH = 7.00), some give acidic solutions (pH < 7.00) and some give basic solutions (pH > 7.00). We must understand why, and be able to do calculations.

Answer: If the cation is a weak acid or the anion is a weak base, then there will be an acid dissociation or a base ionization when the salt is dissolved in water, giving H_3O^+ or OH^- and changing the pH from 7.00.

FOUR POSSIBILITIES

A. **Neutral solutions**: (Only one way to get this.) The anion of a strong acid (Cl^-, Br^-, I^-, NO_3^-, ClO_4^-) and the cation of a strong base (Na^+, K^+, Li^+, Rb^+, Cs^+, Ca^{2+}, Sr^{2+}, Ba^{2+}). Such a salt = NaCl, $KClO_4$, RbI, CsBr, $LiNO_3$, etc. Neither the cation nor anion can react with H_2O to give H^+ or OH^-.

Thus, $NaCl\ (s) + H_2O\ (l) \rightarrow Na^+\ (aq) + Cl^-\ (aq)$

Nothing else happens! $\therefore$ pH = 7.00 (neutral)

B. Acidic solutions: (Three ways to get this.)

(i) The anion of a strong acid (Cl^-, Br^-, I^-, NO_3^-, ClO_4^-) and the cation (conjugate acid) of a weak base (*e.g.,* NH_4^+).
The anion does not react with water, but the cation is a weak acid and will form H_3O^+.

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

As with any weak acid, this makes the solution acidic (pH <7.00). Same for other cations such as NH_3Me^+, $NH_2Et_2^+$, etc.

(ii) $[Fe(H_2O)_6]^{3+}\,(aq) + H_2O\,(l) \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+}\,(aq) + H_3O^+(aq)$

This is an example of a "complex ion" – the Fe atom is attached to six H_2O molecules to give $[Fe(H_2O)_6]^{3+}$. H_2O molecules attached to M^{n+} ions become more acidic than a free H_2O molecule—therefore, they behave as weak acids.

(iii) Certain salts such as $NaHSO_4$ (containing Na^+ and HSO_4^- ions) also give acidic solutions because the HSO_4^- is a weak acid.

$$HSO_4^-\,(aq) + H_2O(l) \rightleftharpoons H_3O^+\,(aq) + SO_4^{2-}\,(aq)$$

This is the second dissociation of the diprotic acid H_2SO_4. We do not see the first dissociation because we are <u>not</u> starting with H_2SO_4, but $NaHSO_4$.

C. Basic Solutions (Only one way.)

The anion (*i.e.,* the conjugate base) of a weak acid (F^-, NO_2^-, ClO^-, acetate$^-$, PO_4^{3-}, etc.) and the cation of a strong base (Na^+, K^+, Ca^{2+}, etc.). The cation does not react with water, but the anion is a weak base and thus gives OH^-, *e.g.,* NaCN, KF, sodium acetate (CH_3COONa), Na_2CO_3, $Ca(HCO_3)_2$, Na_2SO_3, etc., etc., etc. (lots !!).

Example: NaCN dissolves in H_2O to give Na^+ (aq) and CN^- (aq) ions. Then:

$$CN^- (aq) + H_2O (l) \rightleftharpoons HCN (aq) + OH^- (aq)$$

This is a typical base-ionization reaction $\therefore$ pH > 7.00

D. Either Acidic or Basic Solutions

If both the cation and the anion can react with water, then the solution will be either acidic or basic, depending on the K_a and K_b of the ions.

The anion is the conjugate base of a weak acid and the cation is the conjugate acid of a weak base, *i.e.*, a mix of types B and C above.

e.g., NH_4F, NH_4ClO, $NHMe_3CN$, etc.

Example: NH_4SH dissolves to give NH_4^+ (aq) and HS^- (aq) ions.

$$NH_4^+ (aq) + H_2O (l) \rightleftharpoons NH_3 (aq) + H_3O^+ (aq)$$
$$HS^- (aq) + H_2O (l) \rightleftharpoons H_2S (aq) + OH^- (aq)$$

The cation produces H_3O^+, the anion produces OH^-. Who wins?? Whichever reaction produces more will determine the pH.

The reaction with the bigger K (K_a vs K_b) will win.

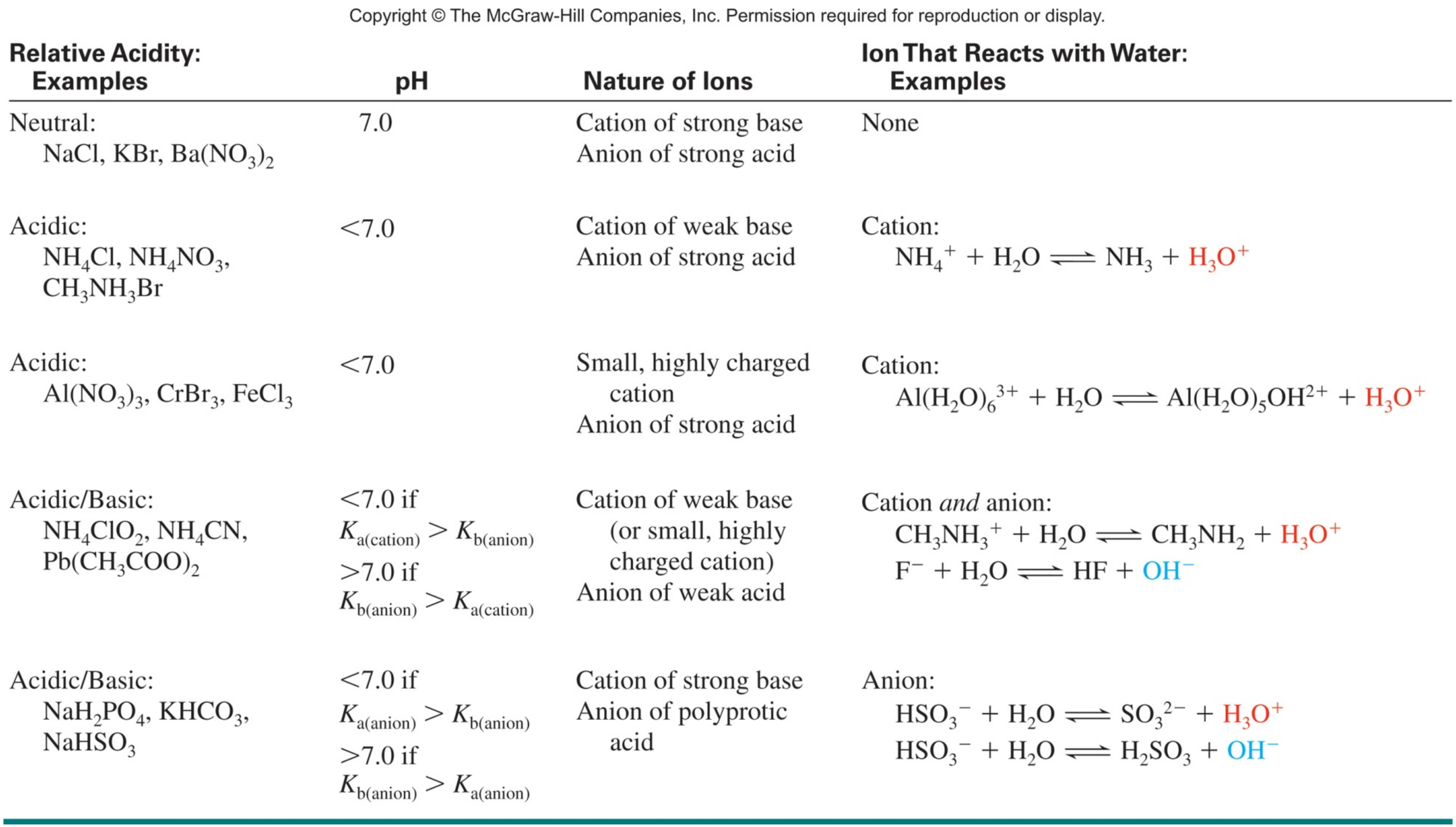
$$K_a (NH_4^+) = \frac{K_w}{K_b(NH_3)} = \frac{1.0 \times 10^{-14}}{1.76 \times 10^{-5}} = 5.7 \times 10^{-10}$$

$$K_b (HS^-) = \frac{K_w}{K_a(H_2S)} = \frac{1.0 \times 10^{-14}}{9 \times 10^{-8}} = 1 \times 10^{-7}$$

RULE: IF $K_a > K_b$, solution is acidic
IF $K_a < K_b$, solution is basic

∴ a solution of NH_4SH is basic

Table 18.7 The Acid-Base Behavior of Salts in Water



Relative Acidity: Examples	pH	Nature of Ions	Ion That Reacts with Water: Examples
Neutral: NaCl, KBr, $Ba(NO_3)_2$	7.0	Cation of strong base Anion of strong acid	None
Acidic: NH_4Cl, NH_4NO_3, CH_3NH_3Br	<7.0	Cation of weak base Anion of strong acid	Cation: $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$
Acidic: $Al(NO_3)_3$, $CrBr_3$, $FeCl_3$	<7.0	Small, highly charged cation Anion of strong acid	Cation: $Al(H_2O)_6^{3+} + H_2O \rightleftharpoons Al(H_2O)_5OH^{2+} + H_3O^+$
Acidic/Basic: NH_4ClO_2, NH_4CN, $Pb(CH_3COO)_2$	<7.0 if $K_{a(cation)} > K_{b(anion)}$ >7.0 if $K_{b(anion)} > K_{a(cation)}$	Cation of weak base (or small, highly charged cation) Anion of weak acid	Cation *and* anion: $CH_3NH_3^+ + H_2O \rightleftharpoons CH_3NH_2 + H_3O^+$ $F^- + H_2O \rightleftharpoons HF + OH^-$
Acidic/Basic: NaH_2PO_4, $KHCO_3$, $NaHSO_3$	<7.0 if $K_{a(anion)} > K_{b(anion)}$ >7.0 if $K_{b(anion)} > K_{a(anion)}$	Cation of strong base Anion of polyprotic acid	Anion: $HSO_3^- + H_2O \rightleftharpoons SO_3^{2-} + H_3O^+$ $HSO_3^- + H_2O \rightleftharpoons H_2SO_3 + OH^-$

Sample Problem 18.13

Predicting Relative Acidity of Salt Solutions from Reactions of the Ions with Water

PROBLEM: Predict whether aqueous solutions of the following are acidic, basic, or neutral.

(a) Potassium perchlorate, $KClO_4$

(b) Sodium benzoate, C_6H_5COONa

(c) Chromium(III) nitrate, $Cr(NO_3)_3$

(a) This solution will be neutral.

(b) This solution will be basic.

(c) This solution will be acidic.

Section 18.9: The Lewis Definition of Acids and Bases

The third and most recent definition of acids and bases. It is very different from the Arrhenius and Bronsted definitions - the Lewis definition does not involve or mention H^+. Instead, the definition is based on electron pairs:

a base is a species that can donate an electron pair
an acid is a species that can accept an electron pair

A Bronsted base also needs to have an electron pair, to bind the H^+. However, for the first time, an acid is defined without mentioning H^+ - thus, many things are Lewis acids that were not included in the other definitions, e.g. CO_2 and Fe^{2+} are not Arrhenius or Bronsted acids, but they are Lewis acids since they can accept an electron pair in their reactions.

The Lewis definition is much more useful than the others because it can be applied to all species and reactions. The other definitions are only useful for species and reactions involving H^+.

Note: 1) A Lewis acid must have a vacant orbital into which it can accept the electron pair 2) H^+ is a Lewis acid.

A Lewis acid/Lewis base reaction gives a Lewis adduct:

$$\begin{array}{ccccc} B: & + & A & \rightleftharpoons & B\text{-}A \\ \text{base} & & \text{acid} & & \text{adduct} \end{array}$$

e.g.

$$NH_3 + H^+ \rightleftharpoons NH_4^+$$

$$OH^- + H^+ \rightleftharpoons H_2O$$

**** These examples do involve H^+, but Lewis acid/base reactions in general do not have to involve H^+ ****

Molecules as Lewis Acids

Many neutral molecules function as Lewis acids, if they contain an atom that can accept an electron pair (for example, an atom that is electron deficient with less than 8 valence electrons).

e.g. BF_3 + $:NH_3$ $\rightleftharpoons$ $BF_3\text{-}NH_3$
acid base adduct
also $AlCl_3$ + $:Cl^-$ $\rightleftharpoons$ $AlCl_4^-$

(See the textbook for the structures of these adducts)

Lewis Acids with Polar Multiple Bonds

Molecules that contain polar multiple bonds can function as Lewis acids e.g. CO_2, SO_2, etc. In such cases, the central atom is electron deficient with a vacant orbital that can accept an electron pair.

e.g. when CO_2 dissolves in water, it forms the weak diprotic acid H_2CO_3 (carbonic acid) from a Lewis acid/Lewis base reaction:

$O{=}C{=}O$ + $H_2O:$ $\rightleftharpoons$ H_2CO_3
acid base adduct

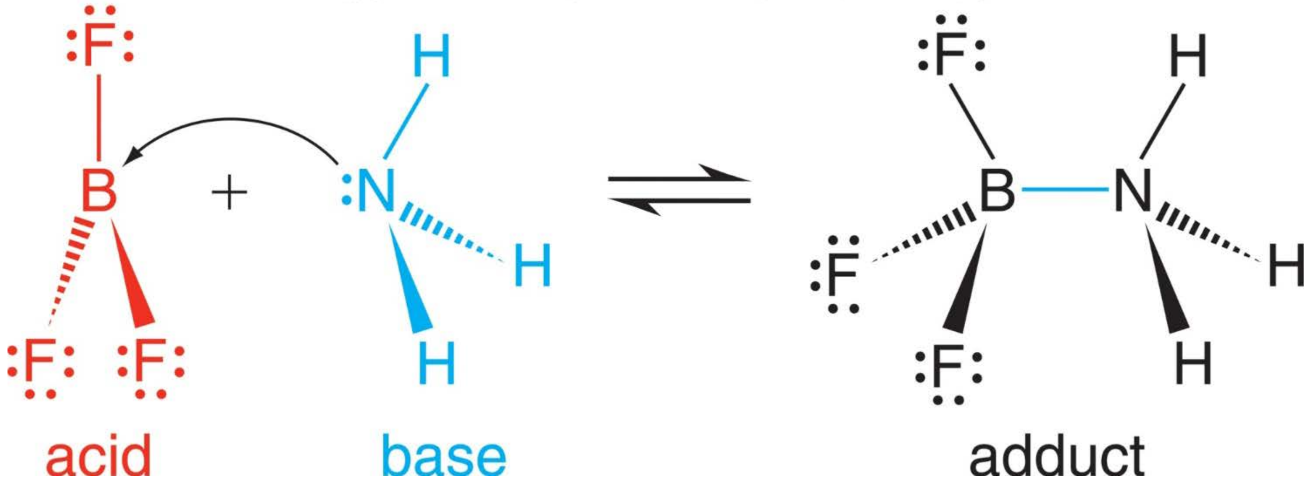
Metal Cations as Lewis Acids

We saw earlier that a "complex ion" such as $Fe(H_2O)_6^{3+}$ is a weak acid. Such a complex ion is the adduct from a Lewis acid/base reaction.

Fe^{3+} + $6\ H_2O:$ $\rightleftharpoons$ $Fe(H_2O)_6^{3+}$
acid base adduct
Cr^{3+} + $6\ :NH_3$ $\rightleftharpoons$ $Cr(NH_3)_6^{3+}$
Fe^{2+} + $6\ :CN^-$ $\rightleftharpoons$ $Fe(CN)_6^{4-}$

Electron-Deficient Molecules as Lewis Acids

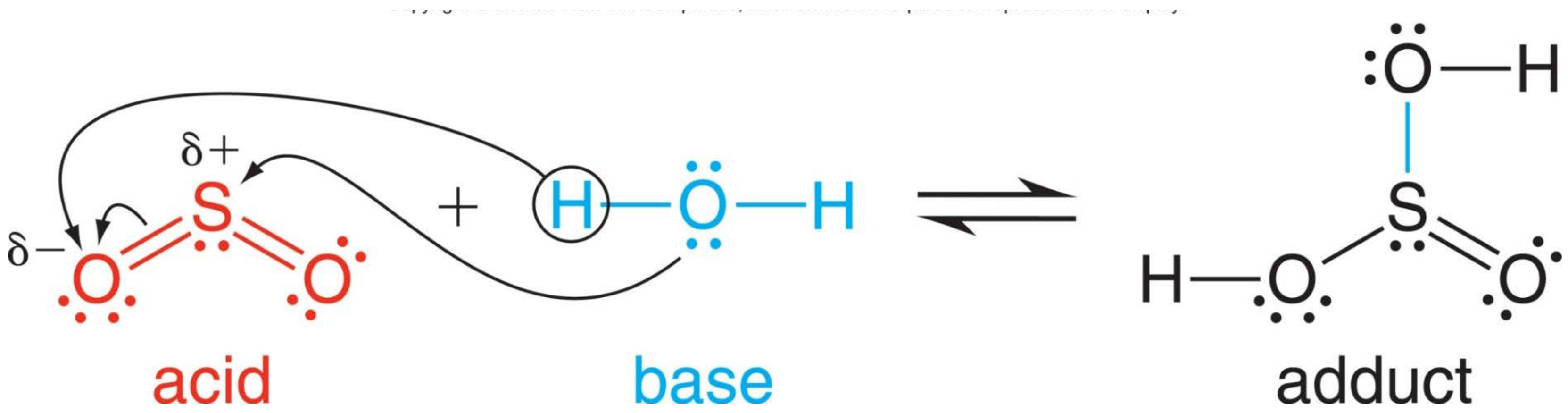
B and Al often form electron-deficient molecules, and these atoms have an unoccupied *p* orbital that can accept a pair of electrons:



BF_3 accepts an electron pair from ammonia to form a covalent bond.

Lewis Acids with Polar Multiple Bonds

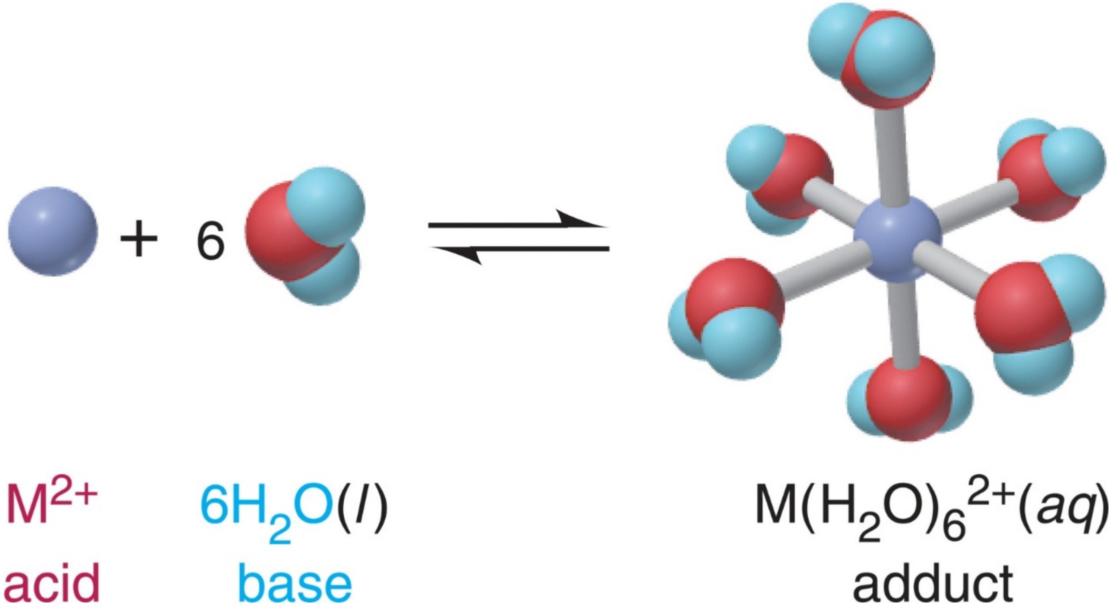
Molecules that contain a polar multiple bond often function as Lewis acids:



The O atom of an H_2O molecule donates a lone pair to the S of SO_2, forming a new S–O σ bond and breaking one of the S–O π bonds.

Metal Cations as Lewis Acids

A metal cation acts as a Lewis acid when it dissolves in water to form a hydrated ion:



The O atom of an H_2O molecule donates a lone pair to an available orbital on the metal cation.

Also, since many metal ions M^{n+} dissolved in water exist as the complex ion $M(H_2O)_x{}^{n+}$ (x = 6 usually), the reactions of these ions are the exchange of one Lewis base for another one.

$$\underset{\text{adduct}}{Ni(H_2O)_6{}^{2+}(aq)} + \underset{\text{base}}{6\ {:}NH_3(aq)} \rightleftharpoons \underset{\text{adduct}}{Ni(NH_3)_6{}^{2+}(aq)} + \underset{\text{base}}{6\ H_2O(l)}$$

The value of K_c depends on the relative strength of the two Lewis bases competing to bind to the Lewis acid Ni^{2+} i.e. on the relative Lewis base strength.
In the above case, NH_3 is a much stronger Lewis base than H_2O, so the reaction lies far to the right ($K_c >> 1$).

Sample Problem 18.15. Identify the Lewis acids and bases:

a) $\underset{\text{acid}}{H^+} + \underset{\text{base}}{OH^-} \rightleftharpoons \underset{\text{adduct}}{H_2O}$ (OH^- has electron pairs on the O atom that can be donated; H^+ has an empty orbital to accept them.)

b) $\underset{\text{base}}{Cl^-} + \underset{\text{acid}}{BCl_3} \rightleftharpoons \underset{\text{adduct}}{BCl_4{}^-}$ (Cl^- has electron pairs; BCl_3 is electron deficient with an empty orbital on the B atom)

c) $\underset{\text{acid}}{K^+} + \underset{\text{base}}{6H_2O} \rightleftharpoons \underset{\text{adduct}}{K(H_2O)_6{}^+}$ (The H_2O is the Lewis base because the O atom still has electron pairs, even after it used one of them to donate to the H^+ in reaction a))

Question: Which of the following are Lewis acids, and which are Lewis bases? PH_3 BH_3 H_2S $AlCl_3$ HS^-

Answer: For PH_3, H_2S , HS^- : the central atom has lone pairs (and a full outer shell of 8 electrons) ∴ they are electron-pair donors i.e. Lewis bases.
For BH_3 and AlH_3 : the B and Al atoms have only 6 outer electrons and no lone pair ∴ they are electron deficient and are an electron-pair acceptors i.e. a Lewis acids.