Ch. 16 Acids + Bases

- acid/base character (pH) of solution has enormous impact
  a) lake biosystem (acid rain)
  b) farming/gardening (soil pH, alkalinity, etc
  c) rusting/corrosion
  d) biology
  - cells, proteins, blood, enzymes, hormones need very tight pH control

Most bio reaction mechs involve H^+ transfer

$\Rightarrow [H^+]$ huge impact on rates

16.1 Bronsted-Lowry Concept of Acids/Bases

$\boxed{\begin{array}{l}\text{acid: } H^{\oplus} \text{ donor} \\ \text{base: } H^+ \text{ acceptor}\end{array}}$

water + acid: $HCl + H_2O \longrightarrow H_3O^+ + Cl^-$

donor acceptor
"acid" "base"

water + base: $NH_3 + H_2O \longrightarrow HO^{\ominus} + NH_4^{\oplus}$

acceptor donor
"base" "acid"

- a "base" needs a lone pair
- a base gets more $\oplus$
- an acid $\ominus$

- water can give (acid) or take (base) (depends on what other thing wants)

<u>Conjugate Acid-Base Pairs</u>

- differ by one $H^{\oplus}$

<u>ex</u>

HF $\quad F^{\ominus}$

H_2O $\quad {}^{\ominus}OH$

$NH_4^{\oplus}$ $\quad NH_3$

conj

$$\begin{array}{ccccccc} HF & + & H_2O & \rightleftharpoons & H_3O^{\oplus} & + & F^{\ominus} \\ A & & B & & A & & B \end{array}$$

conj

① every acid/base rxn has 2 conjugate pairs

② each <u>side</u> has one acid (H^+ donor) and one base

③ conjugate of an acid functions as base
   base   acid

1. Draw the conjugate bases

a. HCN

b. HCl

c. CH_4

2. Draw the conjugate acids

a. SO_4^{2-}

b. NH_3

c. $Cl^{\ominus}$

3. Identify each as an acid or base

$$NH_3 + HClO \rightleftharpoons NH_4^{\oplus} + ClO^{\ominus}$$

1. Draw the conjugate bases

a. HCN $\quad$ $^{\ominus}CN$

b. HCl $\quad$ $Cl^{\ominus}$

c. CH_4 $\quad$ $^{\ominus}CH_3$

2. Draw the conjugate acids

a. SO_4^{2-} $\quad$ HSO_4^{-}

b. NH_3 $\quad$ $NH_4^{\oplus}$

c. $Cl^{\ominus}$ $\quad$ HCl

3. Identify each as an acid or base

$$\underset{\text{base}}{NH_3} + \underset{\text{acid}}{HClO} \rightleftharpoons \underset{\text{acid}}{NH_4^{\oplus}} + \underset{\text{base}}{ClO^{\ominus}}$$

Acid/Base Strength

① – strong acids are better $H^{\oplus}$ donors than weaker acids
– strong base H^{+} acceptors

② depends on love for $H^{\oplus}$

HA $A^{\ominus}$

– if $A^{\ominus}$ loves $H^{\oplus}$, $A^{\ominus}$ strong base (grab)
HA weak/non acid (hold $H^{\oplus}$)

– " " doesn't love $H^{\oplus}$ ⇒ $A^{\ominus}$ weak/non base (won't grab H^{+})
⇒ HA strong acid (release H

③

Acid Strength	Strength of Conjugate Base
strong	nonbasic
weak	weak
nonacid	strong base

weaker — stronger
stronger — weaker

④ Strong acid: ionizes fully in water
~~Memorize 6: HCl, HBr, HI, HNO_3, H_2SO_4~~, $HClO_4$

$$\underbrace{HCl}_{\text{none left}} + H_2O \longrightarrow H_3O^{\oplus} + Cl^{\ominus}$$

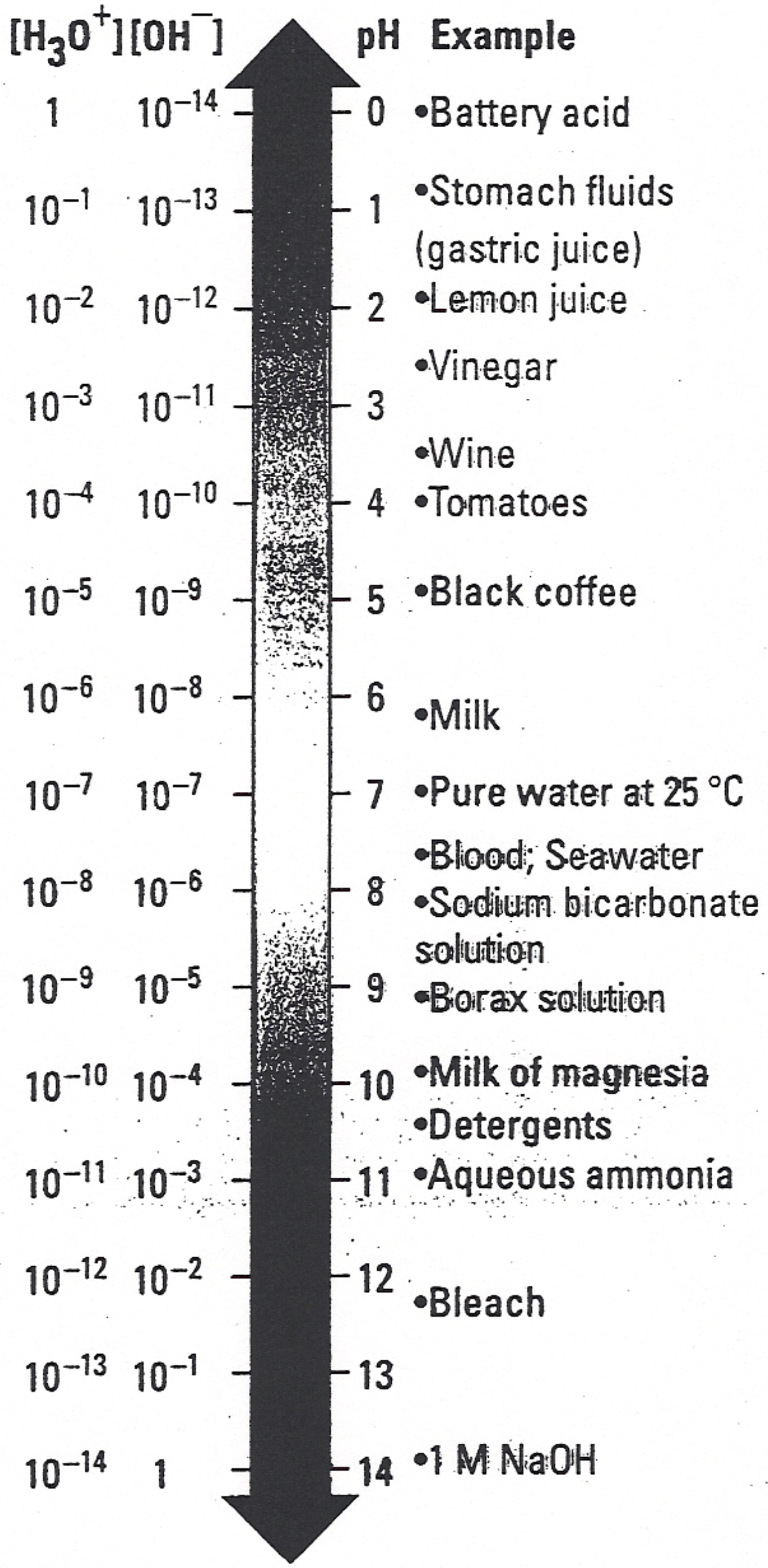

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Figure 16.2

Ionization Constants for Some Acids and Their Conjugate Bases at 25 °C

Increasing Acid Strength

Increasing Base Strength

Acid name	Acid	$K_a = \dfrac{[H_3O^+]\begin{bmatrix}\text{conj}\\ \text{base}\end{bmatrix}}{[\text{conj acid}]}$	Base name	Base	$K_b = \dfrac{\begin{bmatrix}\text{conj}\\ \text{base}\end{bmatrix}[OH^-]}{[\text{conj base}]}$
Perchloric acid	$HClO_4$	Large	Perchlorate ion	ClO_4^-	Very small
Sulfuric acid	H_2SO_4	Large	Hydrogen sulfate ion	HSO_4^-	Very small
Hydrochloric acid	HCl	Large	Chloride ion	Cl^-	Very small
Nitric acid	HNO_3	≈ 20	Nitrate ion	NO_3^-	$\approx 5 \times 10^{-16}$
Hydronium ion	H_3O^+	1.0	Water	H_2O	1.0×10^{-14}
Sulfurous acid	H_2SO_3	1.2×10^{-2}	Hydrogen sulfite ion	HSO_3^-	8.3×10^{-13}
Hydrogen sulfate ion	HSO_4^-	1.2×10^{-2}	Sulfate ion	SO_4^{2-}	8.3×10^{-13}
Phosphoric acid	H_3PO_4	7.5×10^{-3}	Dihydrogen phosphate ion	$H_2PO_4^-$	1.3×10^{-12}
Hexaaquairon(III) ion	$Fe(H_2O)_6^{3+}$	6.3×10^{-3}	Pentaaquahydroxoiron(III) ion	$Fe(H_2O)_5OH^{2+}$	1.6×10^{-12}
Hydrofluoric acid	HF	7.2×10^{-4}	Fluoride ion	F^-	1.4×10^{-11}
Nitrous acid	HNO_2	4.5×10^{-4}	Nitrite ion	NO_2^-	2.2×10^{-11}
Formic acid	$HCOOH$	1.8×10^{-4}	Formate ion	$HCOO^-$	5.6×10^{-11}
Benzoic acid	C_6H_5COOH	6.3×10^{-5}	Benzoate ion	$C_6H_5COO^-$	1.6×10^{-10}
Acetic acid	CH_3COOH	1.8×10^{-5}	Acetate ion	CH_3COO^-	5.6×10^{-10}
Propanoic acid	CH_3CH_2COOH	1.4×10^{-5}	Propanoate ion	$CH_3CH_2COO^-$	7.1×10^{-10}
Hexaaquaaluminum ion	$Al(H_2O)_6^{3+}$	7.9×10^{-6}	Pentaaquahydroxoaluminum ion	$Al(H_2O)_5OH^{2+}$	1.3×10^{-9}
Carbonic acid	H_2CO_3	4.2×10^{-7}	Hydrogen carbonate ion	HCO_3^-	2.4×10^{-8}
Hexaaquacopper(II) ion	$Cu(H_2O)_6^{2+}$	1.6×10^{-7}	Pentaaquahydroxocopper(II) ion	$Cu(H_2O)_5OH^+$	6.25×10^{-8}
Hydrogen sulfide	H_2S	1×10^{-7}	Hydrogen sulfide ion	HS^-	1×10^{-7}
Dihydrogen phosphate ion	$H_2PO_4^-$	6.2×10^{-8}	Hydrogen phosphate ion	HPO_4^{2-}	1.6×10^{-7}
Hydrogen sulfite ion	HSO_3^-	6.2×10^{-8}	Sulfite ion	SO_3^{2-}	1.6×10^{-7}
Hypochlorous acid	$HClO$	3.5×10^{-8}	Hypochlorite ion	ClO^-	2.9×10^{-7}
Hexaaqualead(II) ion	$Pb(H_2O)_6^{2+}$	1.5×10^{-8}	Pentaaquahydroxolead(II) ion	$Pb(H_2O)_5OH^+$	6.7×10^{-7}
Hexaaquacobalt(II) ion	$Co(H_2O)_6^{2+}$	1.3×10^{-9}	Pentaaquahydroxocobalt(II) ion	$Co(H_2O)_5OH^+$	7.7×10^{-6}
Boric acid	$B(OH)_3(H_2O)$	7.3×10^{-10}	Tetrahydroxoborate ion	$B(OH)_4^-$	1.4×10^{-5}
Ammonium ion	NH_4^+	5.6×10^{-10}	Ammonia	NH_3	1.8×10^{-5}
Hydrocyanic acid	HCN	4.0×10^{-10}	Cyanide ion	CN^-	2.5×10^{-5}
Hexaaquairon(II) ion	$Fe(H_2O)_6^{2+}$	3.2×10^{-10}	Pentaaquahydroxoiron(II) ion	$Fe(H_2O)_5OH^+$	3.1×10^{-5}
Hydrogen carbonate ion	HCO_3^-	4.8×10^{-11}	Carbonate ion	CO_3^{2-}	2.1×10^{-4}
Hexaaquanickel(II) ion	$Ni(H_2O)_6^{2+}$	2.5×10^{-11}	Pentaaquahydroxonickel(II) ion	$Ni(H_2O)_5OH^+$	4.0×10^{-4}
Hydrogen phosphate	HPO_4^{2-}	3.6×10^{-13}	Phosphate ion	PO_4^{3-}	2.8×10^{-2}
Water	H_2O	1.0×10^{-14}	Hydroxide ion	OH^-	1.0
Hydrogen sulfide ion	HS^-	1×10^{-19}	Sulfide ion	S^{2-}	1×10^5
Ethanol	C_2H_5OH	Very small	Ethoxide ion	$C_2H_5O^-$	Large
Ammonia	NH_3	Very small	Amide ion	NH_2^-	Large
Hydrogen	H_2	Very small	Hydride ion	H^-	Large
Methane	CH_4	Very small	Methide ion	CH_3^-	Large

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Table 16.2

Weak Acid: ionizes incompletely in water; equilibrium (usually very little)

$$HF + H_2O \rightleftarrows H_3O^{\oplus} + F^{\ominus}$$

- a wide range of strengths; some "weak" acids are "weaker" than others

Non Acid: doesn't ionize at all in water

$$CH_4 + H_2O \longleftarrow \underbrace{H_3O^{\oplus} + CH_3^{\ominus}}_{\text{none}}$$

Direction + Strength

* acid/base reactions $\boxed{\text{always}}$ go from stronger acid/base to weaker acid + base

$\boxed{\text{K favors weaker}}$

$$\underset{\text{stronger acid}}{HCl} + \underset{\text{stronger base}}{NaOH} \longrightarrow \underset{\text{weaker acid}}{H_2O} + \underset{\text{weaker base}}{Na^{\oplus}Cl^{\ominus}} \quad K \text{ large! } (K \gg 1)$$

$$\underset{\text{weaker acid}}{H_2S} + \underset{\text{weaker base}}{F^{\ominus}} \rightleftarrows \underset{\text{stronger acid}}{HF} + \underset{\text{stronger base}}{HS^{\ominus}} \quad K \text{ small } (K<1)$$

a. stronger acid + base always on same side
b. if you know any of relative strengths, can predict sense, K
c. if given K info, can identify weaker/stronger

① HF is stronger than HNO_2.
Predict the "direction" of the reaction, and say whether K will be greater or less than 1. (ID each as Acid or base)

$HF + Na^{\oplus}NO_2^{\ominus}$ $\quad\quad$ $Na^{\oplus}F^{\ominus} + HNO_2$ $\quad$ K 1

② $HF + Cl^{\ominus}$ $\quad\quad$ $HCl + F^{\ominus}$ $\quad$ K 1

③ $HA + B^{\ominus} \rightleftharpoons A^{\ominus} + HB$ $\quad$ $K > 1$

Classify each as the weaker or stronger acid or base.

④ Ditto for

$HCN + SO_4^{2-} \rightleftharpoons HSO_4^{-} + {}^{\ominus}CN$ $\quad$ $K < 1$

1. HF is stronger than HNO_2. Predict the "direction" of the reaction, and say whether K will be greater or less than 1. (ID each as Acid or base)

$$\underset{\text{stronger acid}}{HF} + \underset{\text{stronger base}}{Na^{\oplus}NO_2^{\ominus}} \rightleftarrows \underset{\text{weaker base}}{Na^{\oplus}F^{\ominus}} + \underset{\text{weaker acid}}{HNO_2} \qquad K > 1$$

2. $$\underset{\text{weaker acid}}{HF} + \underset{\text{weaker base}}{Cl^{\ominus}} \longleftarrow \underset{\text{stronger acid}}{HCl} + \underset{\text{stronger base}}{F^{\ominus}} \qquad K < 1$$

3. $$\underset{\text{stronger acid}}{HA} + \underset{\text{stronger base}}{B^{\ominus}} \rightleftharpoons \underset{\text{weaker base}}{A^{\ominus}} + \underset{\text{weaker acid}}{HB} \qquad K > 1$$

Classify each as the weaker or stronger acid or base.

4. Ditto for

$$\underset{\text{weaker acid}}{HCN} + \underset{\text{weaker base}}{SO_4^{2-}} \rightleftharpoons \underset{\text{stronger acid}}{HSO_4^{-}} + \underset{\text{stronger base}}{{}^{\ominus}CN} \qquad K < 1$$

16.1,2 Recognizing Acids

① Memorize 6 Strong

HCl $\quad HNO_3 \quad H_2SO_4 \quad HClO_4$
HBr
HI

– all other acids assume weak

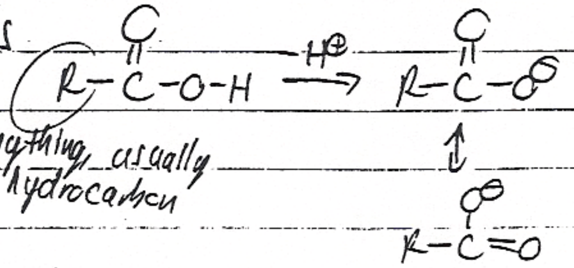
② Weak acids

a. usually formula written with H in front

$HF \quad HCN \quad H_2S \quad H_2CO_3$ --- acids

$CH_4 \quad NH_3 \quad SiH_4$ ··· nonacids

b. carboxylic acids



– written as CH_3COOH, C_2H_5COOH, etc.

not acidic — acidic

anion stabilized by resonance

★ Note: NOT ALL H's are acidic!!

C. T-metal Cations: in water they are "hydrated" and weak acids (16.5, p. 743)

General: $M^{+}(H_2O)_x + H_2O \rightleftharpoons H_3O^{+} + M(H_2O)_{x-1}(OH)$

ex: $Fe^{3+}(H_2O)_6 + H_2O \rightleftharpoons [Fe(H_2O)_5OH]^{2+} + H_3O^{\oplus}$

$Cu^{2+}(H_2O)_4 + H_2O \rightleftharpoons [Cu(H_2O)_3(OH)]^{\oplus} + H_3O^{\oplus}$

Recognizing Bases

① Soluble metal hydroxides ⇒ strong bases

- all Group 1 metal hydroxides, many G2 ...

$LiOH,\ NaOH,\ KOH \cdots\ Ca(OH)_2,\ Ba(OH)_2 \cdots$

$\underset{1\ mol}{NaOH(aq)} \xrightarrow{H_2O} Na^{\oplus}(aq) + \underset{1\ mol}{OH^{-}(aq)}$ (Complete)

- most T-metal hydroxides have limited solubility

$\underset{1\ mol}{CuOH(s)} \overset{H_2O}{\rightleftharpoons} Cu^{+}(aq) + \underset{<1\ mol}{OH^{-}(aq)}$ (Incomplete)

② Amines: Neutral N Compounds ⇒ Weak Bases

Parent: $\underset{\text{weak base}}{H_3N:} + H_2O \rightleftharpoons OH^{-} + \underset{\text{weak acid}}{NH_4^{\oplus}}$

- N lone pair accepts $H^{\oplus}$

- puts formal ⊕ charge on N

Amine base: $\underbrace{CH_3NH_2 \quad (CH_3)_2NH \quad C_6H_5NH_2}_{\text{weak bases}}$ etc.

Conj Acids: $CH_3\overset{\oplus}{N}H_3 \quad (CH_3)_2\overset{\oplus}{N}H_2 \quad C_6H_5\overset{\oplus}{N}H_3$ } weak acids

③ $\boxed{\text{Any conjugate base of a weak acid is \underline{weak} \underline{base}}}$

— for any anion, write its conj acid:
if acid strong anion nonbase
" weak weak base

$\boxed{\text{Key: write conj. acid and decide indirectly from that!}}$

		Conj	
weak	$F^{\ominus}$	HF	weak
	$^{\ominus}CN$	HCN	
	$H_2PO_4^{\ominus}$	H_3PO_4	
non	$Cl^{\ominus}$	HCl	strong
strong	$H^{\ominus}$	H_2	Non-acids
	$^{\ominus}CH_3$	CH_4	

④ Any anion whose "conjugate acid" is a non-acid is a strong base

16-8

① Classify as Strong Acid, Weak Acid, Strong Base, Weak Base, or Non-acid/base

a. HBr

b. HF

c. $CH_3CH_2NH_2$

d. CH_3CH_2COOH

e. H_2SO_4

f. H_3PO_4

g. $HClO$

h. $ClO^{\ominus}$

i. $Cl^{\ominus}$

j. $NO_3^{\ominus}$

k. O^{2-}

l. CH_4

m. $NaOH$

① Classify as Strong Acid, Weak Acid, Strong Base, Weak Base, or Non-acid/base

a. HBr SA

b. HF WA

c. $CH_3CH_2NH_2$ WB

d. CH_3CH_2COOH WA

e. H_2SO_4 SA

f. H_3PO_4 WA

g. $HClO$ WA

h. $ClO^{\ominus}$ WB

i. $Cl^{\ominus}$ non base

f. $NO_3^{\ominus}$ non base

~~g~~k. O^{2-} strong base

l. CH_4 non base

m. $NaOH$ strong base

16.3 Autoionization of water

$$\underset{B}{H_2O_{(l)}} + \underset{a}{H_2O_{(l)}} \rightleftharpoons \underset{A}{H_3O^+_{(aq)}} + \underset{b}{OH^-_{(aq)}}$$

new!!

$\boxed{K_w = [H_3O^+][OH^-] = 1\times10^{-14}}$

note: H^+ vs. H_3O^+. $H^{\oplus}$ (proton) in water exists as H_3O^+, but H^+ shorter to write!!

① water both weakly acidic + basic!

② amount of ion is teeny but important!!

③ $K_w = 10^{-14}$ always true

neutral: $[H_3O^+] = [OH^-] = 10^{-7}$

acidic: $[H_3O^+] > 1\times10^{-7}$ $[OH^-] < 10^{-7}$

basic: $[H_3O^+] < 10^{-7}$ $[OH^-] > 10^{-7}$

④ If either $[H_3O^+]$ or $[OH^-]$ known, can calculate other

16.4 The pH Scale

$\boxed{pH = -\log[H_3O^+]}$ - nicer numbers

$\boxed{[H_3O^+] = 10^{-pH}}$

① higher pH ⟹ less H^+
lower pH ⟹ more H^+

pH 3.0 4.6 10.2

← more acidic

→ less acidic

② $pH = 7$ neutral
$pH < 7$ acidic
$pH > 7$ basic

③ pH change of 1 = tenfold change in $[H^+]$
2 = 100

④ ~~sig figs~~: # sig figs in $[H^+]$ = # digits after decimal in pH

$[H^+] = \underbrace{3.6}_{\text{2 sig fig}} \times 10^{-6} \Rightarrow pH = 5.\underbrace{44}_{\text{2 after decimal}}$

⑤ Small pH changes ⇒ dead
$7.35 < \text{blood} < 7.45$
– bio rates often H^+ catalyzed, with 2nd or 3rd order rate dependence on $[H^+]$

☆ ⑥ $\boxed{pOH = -\log[OH^-]}$ $\boxed{[OH^-] = 10^{-pOH}}$

7. Since $10^{-14} = [H^+][OH^-]$
"p"

$$\boxed{14.00 = pH + pOH}$$

☆ 8. Skills: interconvert among

$$\boxed{\begin{array}{ccc} [H^+] & \rightleftarrows & [OH^-] \\ \downarrow\uparrow & & \uparrow\downarrow \\ pH & \rightleftarrows & pOH \end{array}}$$

To know any allows you to find any of others!

1. Find pH for following

a. $[H_3O^+] = 1.0 \times 10^{-4}$

b. $[H^+] = 1.0 \times 10^{-11}$

c. $[H^+] = 3.2 \times 10^{-4}$

d. $[OH^-] = 1.0 \times 10^{-8}$

e. $[OH^-] = 5.8 \times 10^{-4}$

g. $pOH = 8.30$

2. Find pOH.

a. $[H^+] = 3.9 \times 10^{-5}$

b. $[OH^-] = 3.9 \times 10^{-5}$

c. $pH = 3.95$

3. Find both $[H^+]$ $[OH^-]$

a. $pH = 3.72$

b. $pH = 9.81$

c. $[H^+] = 3.5 \times 10^{-8}$

d. $[OH^-] = 4.1 \times 10^{-3}$

1. Find pH for following

a. $[H_3O^+] = 1.0 \times 10^{-4}$ 4.00

b. $[H^+] = 1.0 \times 10^{-11}$ 11.00

c. $[H^+] = 3.2 \times 10^{-4}$ 3.49 (notice: lower than 4, not above 4)

d. $[OH^-] = 1.0 \times 10^{-8} \rightarrow pOH = 8.00 \rightarrow pH = 6.00$
$\rightarrow [H^+] = 1.0 \times 10^{-6} \rightarrow$

e. $[OH^-] = 5.8 \times 10^{-4} \rightarrow pOH = 3.24 \rightarrow pH = 10.76$
$\rightarrow [H^+] = 1.72 \times 10^{-11} \rightarrow$

g. $pOH = 8.30$ $pH = 5.70$

2. Find pOH.

a. $[H^+] = 3.9 \times 10^{-5} \rightarrow pH = 4.41 \rightarrow pOH = 9.59$
$\rightarrow OH^- = 2.56e^{-10} \rightarrow$

b. $[OH^-] = 3.9 \times 10^{-5} \rightarrow pOH = 4.41$

c. $pH = 3.95 \rightarrow 10.05$

3. Find both

	$[H^+]$	$[OH^-]$
a. $pH = 3.72$ ($pOH = 10.28$)	1.91×10^{-4}	5.25×10^{-11}
b. $pH = 9.81$ $pOH = 4.19$	1.55×10^{-10}	6.46×10^{-5}
c. $[H^+] = 3.5 \times 10^{-8}$	—	2.86×10^{-7}
d. $[OH^-] = 4.1 \times 10^{-3}$	2.44×10^{-12}	—

C. Polyprotic Acids: More than One H^+ Available

H_2SO_4, H_3PO_4, H_2CO_3 ...

1. Each H^+ gets successively <u>less</u> acidic (by >1000)

less acidic ↓				more basic ↓
	H_3PO_4	$K_{a1} = 10^{-3}$	$H_2PO_4^-$	
	$H_2PO_4^-$	$K_{a2} = 10^{-8}$	HPO_4^{2-}	
	HPO_4^{2-}	$K_{a3} = 10^{-13}$	PO_4^{3-}	

2. As acids in water, only consider one ionization

3. When <u>base</u> is added, however, all $H^{\oplus}$'s come off (stoich permitting)

$$H_3PO_4 + H_2O \rightleftharpoons H_3O^{\oplus} + H_2PO_4^-$$

but $$H_3PO_4 + 3\,OH^- \longrightarrow 3H_2O + PO_4^{3-}$$

4. H_2SO_4: 1st strong, 2nd weak

$$\underset{\text{none}}{H_2SO_4} \xrightarrow[\boxed{\text{complete}}]{\text{water}} H^{\oplus} + \underset{\text{lot}}{HSO_4^{\ominus}} \underset{\boxed{\text{weak}}}{\overset{\text{water}}{\rightleftharpoons}} 2H^{\oplus} + \underset{\text{little}}{SO_4^{2-}}$$

5. Some anions are complex: both acidic + basic!!

$$HCO_3^{\ominus} \rightleftharpoons H^{\oplus} + CO_3^{2-}$$

$$HCO_3^{\ominus} \xrightarrow{H_2O} OH^{\ominus} + H_2CO_3$$

① What is pH of 1.36×10^{-3} M H_2SO_4?

$[H^+] = 1.36\times10^{-3} \xrightarrow{-\log} \boxed{pH = 2.87}$

② An HCl solution has pH = 2.16. What is [HCl]?

$\boxed{[H^+] = 10^{-2.16} = 6.92\times10^{-3}}$

③ What is pH for 0.013 M KOH solution?

$OH^- = 0.013 \rightarrow pOH = 1.89 \rightarrow pH = 12.11$

$OH^- = 0.013 \rightarrow H^+ = 7.69\times10^{-13} \rightarrow pH = 12.11$

④ What is pH for a solution that is 0.013 M in $Ca(OH)_2$?

$\rightarrow 0.026\ M\ [OH^-] \longrightarrow pOH = 1.59 \rightarrow \boxed{pH = 12.41}$

⑤ What is pH if 22 g of $Ba(OH)_2$ (90 g/mol) is dissolved in 760 mL of water?

$$x \text{ mol } OH^- = \frac{22g}{} \cdot \frac{1 \text{ mol } Ba(OH)_2}{90g\ Ba(OH)_2} \cdot \frac{2 \text{ mol } OH^-}{1 \text{ mol } Ba(OH)_2} = 0.489 \text{ mol } OH \qquad [OH^-] = \frac{0.489 \text{ mol } OH^-}{.760 L}$$

$[OH^-] = 0.643$ M

$\boxed{pH = 13.81} \leftarrow pOH = 0.192 \leftarrow [OH^-] = 0.643\ M$

1. pH → K_a What is K_a for an acid if an 0.15 M solution is prepared and found to have pH = 4.86?

$[H^+] = 10^{-4.86} = 1.38\times10^{-5}$

	$HA \rightleftharpoons$	H^+	$+ A^-$
	.15	0	0
	−x	+x	+x
	.15−x	x	x

$K_a = \frac{(1.38\times10^{-5})^2}{(.15-1.38\times10^{-5})} = \boxed{1.27\times10^{-9}}$

$\boxed{pH \to [H^+] \to K_a}$

2. K_a → pH What is pH for a 0.15 M solution of an acid with $K_a = 2.2\times10^{-6}$?

$\boxed{K_a \to [H^+] \to pH}$

	$HA \rightleftharpoons$	H^+	$+ A^-$
I	.15	0	0
C	−x	+x	+x
E	.15−x	x	x
G ~~E~~	.15	x	x

$K_a = \frac{x^2}{.15} = 2.2\times10^{-6}$

$x^2 = 3.3\times10^{-7}$

$x = [H^+] = 5.74\times10^{-4}$

$\boxed{pH = 3.24}$

3. If an 0.23 M solution of an acid gives pH = 3.82, what is K_a for acid?

$\to [H^+] = 1.51\times10^{-4}$

$\boxed{pH \to [H^+] \to K_a}$

$K_a = \frac{(1.51\times10^{-4})^2}{.23-(1.51\times10^{-4})} = \cancel{9.96\times10^{-8}}$ (without substract) $\boxed{9.92\times10^{-8}}$

4. If a 0.11 M solution has a $K_a = 1.3\times10^{-8}$ acid, what is pH?

$\boxed{K_a \to [H^+] \to pH}$

$[H^+] = \sqrt{(0.11)(1.3\times10^{-8})}$

$= 3.78\times10^{-5}$

$\boxed{pH = 4.42}$

D. Weak Bases

$$A^- + H_2O \rightleftharpoons OH^- + HA$$

	A^-	OH^-	HA
I	$[A^-]_i$	0	0
C	$-x$	$+x$	x
E	$[A^-]_i - x$	x	x
E*	$[A^-]_i$	x	x

$$\boxed{K_b = \frac{[OH^-]^2}{[A^-]_i}}$$

$$\boxed{[OH^-] = \sqrt{K_b \cdot [A^-]_i}}$$

Applications

① $pH \rightarrow K_b$: $pH \rightarrow pOH \rightarrow [OH]^- \rightarrow K_b$

② $K_b \rightarrow pH$ $K_b \rightarrow [OH^-] \rightarrow pOH \rightarrow pH$

E. Relationship Between K_a + K_b for Conjugate acids/Bases

Review: stronger the acid, weaker the conjugate base (and vice versa)

Look at Table 16.2: $\boxed{K_a \times K_b = 1.0 \times 10^{-14}}$ (see book for derivation)

① Given one, can solve for other
② tables routinely provide only one; expect you to solve for other
③ Can rank relative strengths of acids (or bases) given info about conjugates
④ Tough problem: given K_a for conjugate acid, calculate pH for a solution of weak base
logic: $K_a \rightarrow K_b \longrightarrow [OH^-] \rightarrow pOH \rightarrow pH$

① $pH \rightarrow K_b$ what is K_b if an 0.123 M solution of a weak base gives $pH = 10.62$?

② $K_b \rightarrow pH$ If K_b for a weak base is 1.6×10^{-5}, what is the pH of an 0.222 M solution of the base?

① $pH \rightarrow K_b$ What is K_b if an 0.123 M solution of a weak base gives $pH = 10.62$?

↳ $pOH = 3.38 \rightarrow [OH^-] = 4.17 \times 10^{-4}$

$B + H_2O \rightleftharpoons {}^{\ominus}OH + BH^{\oplus}$

I	.123	0	0
C	−x	+x	+x
E	.123−x	x	x
↳E*	.123	4.17×10^{-4} ...	

$K_b = \frac{(4.17 \times 10^{-4})^2}{(.123 - 4.17 \times 10^{-4})} = \boxed{1.42 \times 10^{-6}}$

$\boxed{pH \rightarrow pOH \rightarrow [OH^-] \rightarrow K_b}$

② $K_b \rightarrow pH$ If K_b for a weak base is 1.6×10^{-5}, what is the pH of an 0.222 M solution of the base?

$B + H_2O \rightleftharpoons {}^{\ominus}OH + HB$

I	.222	0	0	0
C	−x		+x	+x
E	.222−x		x	x
↳E*	.222		x	x

$\boxed{K_b \rightarrow [OH^-] \rightarrow pOH \rightarrow pH}$

$[OH^-] = \sqrt{(.222)(1.6 \times 10^{-5})}$

$= \sqrt{3.55 \times 10^{-6}}$

$\boxed{[OH^-] = 1.88 \times 10^{-3}}$

↓

$pOH = 2.72$

↓

$\boxed{pH = 11.28}$

	K_a
HCN	4.9×10^{-10}
HF	6.8×10^{-4}
HN_3	1.9×10^{-5}

1. What is K_b for N_3^-?

2. Rank the basicity, 1 being highest.

$^{\ominus}CN$ $\qquad$ $F^{\ominus}$ $\qquad$ $N_3^{\ominus}$

3. What is pH for a solution that is 0.12 M in NaF?

4. What is pH for a solution that is 0.20 in NaCN?

Acidity		K_a	Basicity	
3	HCN	4.9×10^{-10}	$CN^{\ominus}$	1
1	HF	6.8×10^{-4}	$F^{\ominus}$	3
2	HN_3	1.9×10^{-5}	$N_3^{\ominus}$	2

1. What is K_b for N_3^-?

$$K_a K_b = 10^{-14}$$

$$\boxed{K_b = \frac{10^{-14}}{1.9 \times 10^{-5}} = 5.26 \times 10^{-10}}$$

2. Rank the basicity, 1 being highest.

$^{\ominus}CN$	$F^{\ominus}$	$N_3^{\ominus}$	Opposite acidity strength
1	3	2	

3. What is pH for a solution that is 0.12 M in NaF? $NaF \equiv F^{\ominus}$ weak base

$\boxed{K_a \rightarrow K_b \rightarrow [OH^-] \rightarrow pOH \rightarrow pH}$ $K_b =$

$$K_b = \frac{10^{-14}}{6.8 \times 10^{-4}} = 1.47 \times 10^{-11}$$

$$[OH^-] = \sqrt{(0.12)(1.47 \times 10^{-11})}$$

$$= 1.33 \times 10^{-6} \rightarrow pOH = 5.88 \rightarrow \boxed{pH = 8.12}$$

4. What is pH for a solution that is 0.20 in NaCN? Same logic. $K_a \rightarrow K_b \rightarrow OH^- \rightarrow pOH \rightarrow pH$

$$K_b = \frac{10^{-14}}{4.9 \times 10^{-10}} = 2.04 \times 10^{-5}$$

$$OH^- = \sqrt{0.20 \times 2.04 \times 10^{-5}}$$

$$= 2.02 \times 10^{-3} \rightarrow pOH = 2.69 \rightarrow \boxed{pH = 11.31}$$

Derivation of $K_a K_b = 10^{-14}$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \qquad K_b = \frac{[OH^-][HA]}{[A^-]}$$

so $$K_a K_b = \left(\frac{[H_3O^+][A^-]}{[HA]}\right) \frac{[OH^-][HA]}{[A^-]} = [H_3O^+][OH^-]$$
$$= 1.0 \times 10^{-14}$$

Thus $\boxed{K_a K_b = K_w = 10^{-14}}$

① For Strong Acid ($K_a > 1$) get Nonbase ($K_b < 10^{-14}$)

② For Non Acid ($K_a < 10^{-14}$) get strong base ($K_b > 1$)

③ For weak Acid ($10^{-14} < K_a < 1$) get weak Base ($10^{-14} < K_b < 1$)

TABLE 16.5 **Some Conjugate Acid–Base Pairs**

Acid	K_a	Base	K_b
HNO_3	(Strong acid)	NO_3^-	(Negligible basicity)
HF	6.8×10^{-4}	F^-	1.5×10^{-11}
$HC_2H_3O_2$	1.8×10^{-5}	$C_2H_3O_2^-$	5.6×10^{-10}
H_2CO_3	4.3×10^{-7}	HCO_3^-	2.3×10^{-8}
NH_4^+	5.6×10^{-10}	NH_3	1.8×10^{-5}
HCO_3^-	5.6×10^{-11}	CO_3^{2-}	1.8×10^{-4}
OH^-	(Negligible acidity)	O^{2-}	(Strong base)

acid strength

base strength

16.8 Acid-Base Properties of Salts (Ionic Compounds)

$FeCl_2$	$MgBr_2$	$NaCN$
pH < 7	pH = 7	pH > 7
acidic	neutral	basic

Recall: "salts" formed by acid/base reaction
"salt" = ionic

ex: SA/SB $HCl + NaOH \rightarrow H_2O + NaCl$ neutral
WA/SB $HF + NaOH \rightarrow H_2O + NaF$ basic
SA/WB $HCl + NH_3 \rightarrow NH_4^{\oplus} Cl^{\ominus}$ acidic
WA/WB $HF + NH_3 \rightarrow NH_4^{\oplus} F^{\ominus}$ can't tell

Observations:
① salts can be acidic, basic, or neutral
② depends on strengths of acids/bases from which they form
③ the "ions" in the salts are conjugates; may be acidic or basic!!

A. General Logic to Predict: Identify Ions Individually
1. Cations: acidic or neutral
a. Group I or II cations are neutral
$Li^{\oplus}$, $Na^{\oplus}$, $K^{\oplus}$, Mg^{2+}, Ba^{2+} ...
– no impact on pH

b. Al^{3+}, T-metal cations are <u>acidic</u>
(see 16.5, p. 743)

$$Al^{3+} \xrightarrow{\text{water}} \underset{\text{weak acid}}{[Al(H_2O)_6]^{3+}} \rightleftharpoons H^{\oplus} + [Al(OH)(H_2O)_5]^{2+}$$

- due to hydrates

c. Ammoniums are acidic
$NH_4^{\oplus}$, $CH_3NH_3^{\oplus}$ ...

2. Anions: basic or neutral
a. neutral: conjugates of strong acids
$Cl^{\ominus}$, $Br^{\ominus}$, $I^{\ominus}$, NO_3^-, ClO_4^-,

b. basic: conjugates of weak acids (or nonacids)
ex $F^{\ominus}$, $ClO^{\ominus}$, ...

3. "Amphoteric" anions derived from polyprotic acids: can be acidic or basic
- not test responsible
HCO_3^-, $H_2PO_4^-$, HSO_3^- ...

B. Predicting acidic/neutral/basic (Qualitatively)

cation	anion	salt solution	ex
neutral	neutral	neutral	$NaCl$, KNO_3
acidic	neutral	acidic	NH_4Cl, $Fe(NO_3)_3$
neutral	basic	basic	NaF, $K(ClO)$
acidic	basic	can't predict (without K's)	NH_4F, $Fe(N_3)_3$

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1. Predict as Acidic, Basic, Neutral, or Can't Tell.

a. Na_2SO_3

b. $MgCl_2$

c. NH_4CN

d. $CoCl_2$

e. $NaNO_3$

f. KN_3

g. $AlCl_3$

h. CH_3NH_3Br

2. Rank the following in terms of increasing pH, 1 being lowest. (ID as strong/weak acid, strong/weak base, or neutral first!)

$NaCl$ CaF_2 $ZnBr_2$ HNO_3 KOH

1. Predict as Acidic, Basic, Neutral, or Can't Tell.

a. Na_2SO_3 HSO_3^-
N WB WA
$\boxed{\text{basic}}$

e. $NaNO_3$
neut neut
$\boxed{\text{Neutral}}$

b. $MgCl_2$ HCl
N non B SA
$\boxed{\text{neutral}}$

f. KN_3
neut WB
$\boxed{\text{basic}}$

c. NH_4CN
WA WB
$\boxed{\text{can't tell}}$

g. $AlCl_3$
$\boxed{\text{acidic}}$

d. $CoCl_2$
A neut
$\boxed{\text{acidic}}$

h. CH_3NH_3Br
$\boxed{\text{acidic}}$

2. Rank the following in terms of increasing pH, 1 being lowest. (ID as strong/weak acid, strong/weak base, or neutral first!)

NaCl	CaF_2	$ZnBr_2$	HNO_3	KOH
neut	weak base	weak acid	strong acid	strong base
3	4	2	5	1

16.7 Molecular Structure and Acid/Base Strength
Why is something strong or weak?
Acidic or basic? Can we predict
from structure, without K's?

A. 3 Factors on Acid Strength
1. H-A bond strength: stronger
$\rightarrow$ less acidic
- why H-F (strong bond) weak,
but H-Cl, H-Br, H-I strong
- row 2 bonds (H-F, O-H, N-H, C-H)
usually stronger than row 3,4 analogs

related by e^- love

2. $\overset{\delta+}{H}$-A polarity
↳ based on electroneg
CH_4 nonpolar   H-Br polar

3. Stability of conjugate $A^{\ominus}$
- electron love again a factor

$CH_4 \not\rightarrow H^{\oplus} + {}^{\ominus}CH_3$

$HF \rightarrow H^{\oplus} + F^{\ominus}$ ← more love

more acidic

B. Practical Patterns

$\boxed{\text{Horizontal}}$

1. Acidity increases left → right

	CH_4	NH_3	H_2O	HF
K_a	10^{-50}	10^{-32}	10^{-14}	10^{-4}

$\underbrace{10^{-50} \quad 10^{-32}}_{\text{nonacids}}$

→ e^- love, electronegativity / bond polarity, anion stability

$SiH_4 < PH_3 < SH_2 < HCl$

2. $\boxed{\text{Vertical}}$ Acidity increases down
- due to decreasing H-A bond strength (even though contrary to e^- love)

$HF < HCl$ $\quad$ $H_2O < H_2S < H_2Se$

$K_a = 10^{-14} \quad 10^{-9} \quad 10^{-6}$

Note: basicity of conjugates linked!!

$^{\ominus}NH_2 > F^{\ominus}$

$F^{\ominus} > Cl^{\ominus}$

c. "Oxoacids" (Nonmetal hydroxides)
– many structures have -OH
$Z(OH)_y(O)_x$

KOH base $H_2CO_3 \equiv C(OH)_2O$ weak acid $H_2SO_4 = S(OH)_2O_2$ strong acid

1. metal-OH's are basic $Na^{\oplus}$ $^{\ominus}OH$ $^{\ominus}OH$ dc.
nonmetal-OH's are acidic $F-O-H^{\delta+}$ $H^{\oplus}$ dcu
$F O^{\ominus} + H^{\oplus}$

2. Oxoacid acidity increases L → R

ex Row 3: $Si(OH)_4 < P(OH)_3 < S(OH)_2 < Cl(OH)$
– electron love increases polarity of O-H bond

3. "Extra" O's increase acidity
$\underbrace{HClO_4 > HClO_3}_{\text{strong}} > \underbrace{HClO_2 > HClO}_{\text{weak}}$

why? Extra ē loving O:
① weakens O-H
② polarizes O-H
③ stabilizes anion (resonance)

$H_2SO_4 > H_2SO_3$
strong   weak

$\boxed{\text{* Any neutral oxoacid with} \geq 2 \text{ extra O's is a strong acid}}$

strong: H_2SO_4, $HClO_3$ weak: H_2CO_3, H_3PO_4, H_2SO_3 ...

(10-26)

D. Carboxylic Acids: RCOOH ≡ $R\overset{O}{\overset{\|}{C}}{-}O{-}H$
oxoacid

$RCOOH \longrightarrow H^{\oplus} + R\overset{O}{\overset{\|}{C}}{-}O^{\ominus}$

$\updownarrow$

$R{-}\overset{O^{\ominus}}{\overset{|}{C}}{=}O$

resonance stabilized

$R\overset{O}{\overset{\|}{C}}OH > RCH_2OH$ (alcohol)

10^{-5} 10^{-20} $\longrightarrow RCH_2O^{\ominus} + H^{\oplus}$

weak   non

no resonance stabilization

E. "Hydrides"

M–H metal hydride ⇒ basic

$Na^{\oplus}H^{\ominus} + H_2O \longrightarrow H_2 + Na^{\oplus}\,{}^{\ominus}OH$

nonmetal "hydrides:" neutral or acidic

CH_4 neutral

$\overset{\delta+}{H}{-}\overset{\delta-}{Cl}$ acidic

$\boxed{\text{Polarity reversal}}$

(16-27)

① Which are acidic vs. basic vs. neutral in water?

$HClO_3$ CH_3COOH CH_3NH_2 $Ca(OH)_2$

② Rank Acidity (1 strongest)

HF H_2O H_2SO_4 CH_4

③ Rank Acidity

$HClO_4$ $HClO_3$ H_2SO_4 H_2SO_3

④ Rank Acidity H_2O H_2S H_2Se

⑤ " " HBr H_2Se H_3As H_4Ge

⑥ Which would be strong? $HBrO_3$ $HBrO$

H_2CO_3 H_3PO_3

⑦ Rank basicity $^{\ominus}CH_3$ $^{\ominus}NH_2$ $^{\ominus}OH$ $F^{\ominus}$

⑧ " " HPO_4^{2-} $H_2PO_4^-$ HSO_4^-

(16-27)

① Which are acidic vs. basic vs. neutral in water?

$HClO_3$ A CH_3COOH A CH_3NH_2 B $Ca(OH)_2$ B

② Rank Acidity (1 strongest)

HF ② H_2O ③ H_2SO_4 ① CH_4 ④

③ Rank Acidity

$HClO_4$ ① $HClO_3$ ② H_2SO_4 ③ H_2SO_3 ④

$\boxed{\text{Left-right, \# of extra Oxygens}}$

④ Rank Acidity H_2O ③ H_2S ② H_2Se ①

$\boxed{\text{Up-down}}$

⑤ " " HBr ① H_2Se ② H_3As ③ H_4Ge ④

$\boxed{\text{Left-right}}$

⑥ Which would be strong? $HBrO_3$ HBrO H_2CO_3 H_3PO_3

$\boxed{\text{\# of Ox's}}$

2 extra

⑦ Rank basicity ① $^{\ominus}CH_3$ ② $^{\ominus}NH_2$ ③ $^{\ominus}OH$ ④ $F^{\ominus}$

⑧ " " HPO_4^{2-} ① $H_2PO_4^-$ ② HSO_4^- ③ nonbase

$\boxed{\text{\#ox's, conjugates}}$

16.10 Lewis Acids + Bases: focus on electron pairs, not $H^{\oplus}$ movement

$\boxed{\begin{array}{l}\text{Lewis acid: } e^- \text{ pair acceptor} \\ \text{'' base: } e^- \text{ pair donor}\end{array}}$

Covers "acid-base" that doesn't involve $H^{\oplus}$

$H^{\oplus} \leftarrow :\ddot{O}H^{\ominus} \rightarrow H-\ddot{O}H$

$H^{\oplus} \leftarrow :NH_3 \rightarrow H-\overset{\oplus}{N}H_3$

$F_3B \leftarrow :F^{\ominus} \rightarrow BF_4^{\ominus}$

$Al^{3+} \leftarrow :\ddot{O}H_2 \rightarrow [Al-\ddot{O}H_2]^{3+}$ how metal hydrates form!

$Zn^{2+} + :NH_3 \rightarrow [Zn-NH_3]^{2+}$

Note: ① "base" must have lone pair ($F^{\ominus}$, $:\ddot{O}H_2$, $:NH_3$ ...)

② all anions have lone pairs, LB potential

③ "acid" must be able to accept

- all cations can!!
- some neutrals: BF_3, SO_2, ...

① Identify the Lewis acid + Lewis base

a. $Fe^{3+} + 6\,H_2O \rightarrow [Fe(H_2O)_6]^{3+}$

b. $H^{\oplus} + CH_3NH_2 \rightarrow CH_3\overset{\oplus}{N}H_3$

c. $Br-CH_3 + I^{\ominus} \rightarrow Br^{\ominus} + CH_3-I$

d. $Ni^{2+} + 4\,N_3^- \rightarrow [Ni(N_3)_4]^{2-}$

② Which would not be a Lewis acid?

$AlCl_3$ Ti^{4+} NO_3^- $ZnSO_4$

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① Identify the Lewis acid + Lewis base

a. Fe^{3+} + $6\ H_2O \rightarrow [Fe(H_2O)_6]^{3+}$
LA LB

b. $H^{\oplus}$ + $CH_3NH_2 \rightarrow CH_3\overset{\oplus}{N}H_3$
LA LB

c. $Br-CH_3$ + $I^{\ominus} \rightarrow Br^{\ominus} + CH_3-I$
LA LB

d. Ni^{2+} + $4\ N_3^- \rightarrow [Ni(N_3)_4]^{2-}$
LA LB

② Which would not be a Lewis acid?

$AlCl_3$ Ti^{4+} NO_3^- $ZnSO_4$