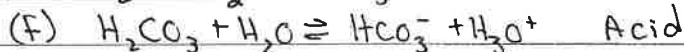
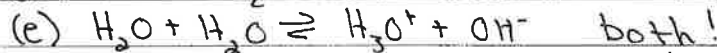
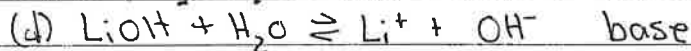
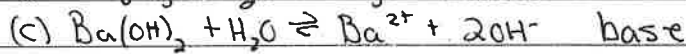
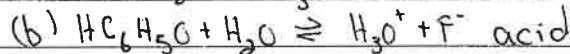
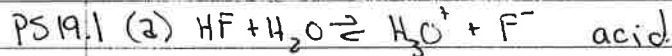


Problem set # 1



PS19.2

(a) $[\text{H}^+] = 1.4 \times 10^{-3} \text{M}$ $\text{pH} = -\log(1.4 \times 10^{-3}) = 2.85$ } acidic!
 $[\text{OH}^-] = 7.14 \times 10^{-12} \text{M}$ $\text{pOH} = 14 - 2.85 = 11.15$ }

(b) $[\text{OH}^-] = 2.08 \times 10^{-7} \text{M}$ $\text{pOH} = -\log(2.08 \times 10^{-7}) = 6.68$ } basic
 $\text{pH} = 14 - 6.68 = 7.32$ }

(c) $\text{pOH} = -\log(6.44 \times 10^{-14}) = 13.19$ } acidic
 $\text{pH} = 14 - 13.19 = 0.81$ }

(d) $\text{pH} = -\log(7.11 \times 10^{-11}) = 10.14$ } basic
 $\text{pOH} = 14 - 10.14 = 3.86$ }

(e) $\text{pH} = -\log(4) = -0.602$ } acidic
 $\text{pOH} = 14 - (-0.602) = 14.602$ }

(f) $\text{pOH} = -\log(10.1) = -1.00$ } basic
 $\text{pH} = 14 - (-1.00) = 15$ }

PS19.3 (a) $[H^+] \text{ antilog}(-7.41) = 3.89 \times 10^{-8}$ $[H^+][OH^-] = 1 \times 10^{-14}$
 $[OH^-] = 1 \times 10^{-14} / 3.89 \times 10^{-8} = 2.57 \times 10^{-7}$

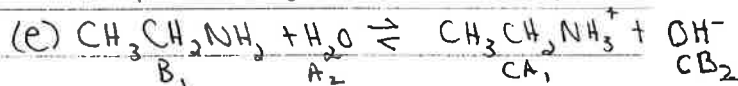
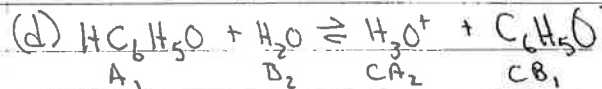
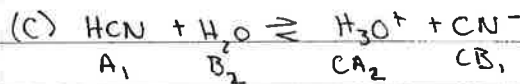
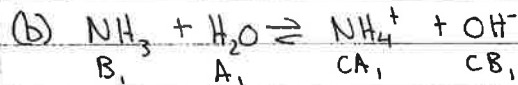
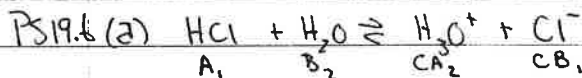
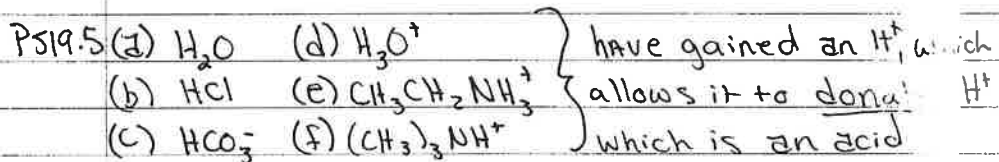
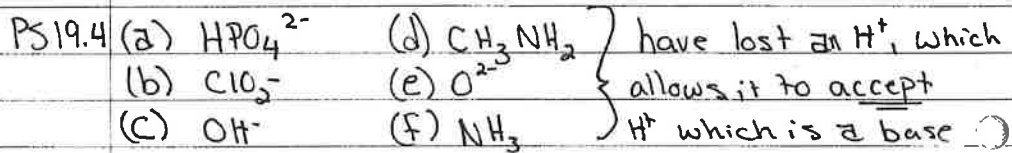
(b) $[H^+] = 1 \times 10^{-11}$ $[OH^-] = 1 \times 10^{-3}$

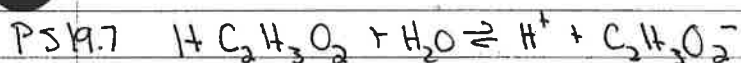
(c) $[H^+] = 1.7 \times 10^{-14}$ $[OH^-] = 5.89 \times 10^{-1}$

(d) $[H^+] = 1 \times 10^{-7}$ $[OH^-] = 1 \times 10^{-7}$

(e) $[H^+] = 1.26 \times 10^{-15}$ $[OH^-] = 7.94$

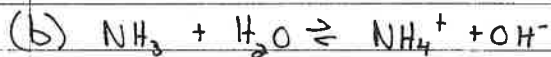
(f) $[H^+] = .286$ $[OH^-] = 3.50$





$$(a) \quad .100 \text{ M} \quad 1.34 \times 10^{-3} \quad 1.34 \times 10^{-3}$$

$$[\text{H}^+] = \text{antilog}(-\text{pH}) \quad K_A = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = \frac{(1.34 \times 10^{-3})^2}{.100} = 1.82 \times 10^{-5}$$



$$.812 \quad 3.8 \times 10^{-3} \quad 3.8 \times 10^{-3} \quad K_B = \frac{(3.8 \times 10^{-3})^2}{.812}$$

$$\text{pOH} = 14 - 11.58 = 2.42$$

$$[\text{OH}^-] = \text{antilog}(-\text{pOH})$$

$$= 1.78 \times 10^{-5}$$

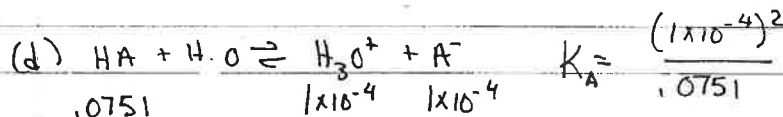


$$.500 \quad 4.68 \times 10^{-4} \quad 4.68 \times 10^{-4} \quad K_B = \frac{(4.68 \times 10^{-4})^2}{.500}$$

$$\text{pOH} = 14 - 10.67 = 3.33$$

$$[\text{OH}^-] = \text{antilog}(-3.33)$$

$$= 4.38 \times 10^{-7}$$



$$.0751$$

$$1 \times 10^{-4}$$

$$1 \times 10^{-4}$$

$$.0751$$

$$[\text{H}^+] = \text{antilog}(-4.00)$$

$$= 1 \times 10^{-4}$$

$$= 1.33 \times 10^{-7}$$

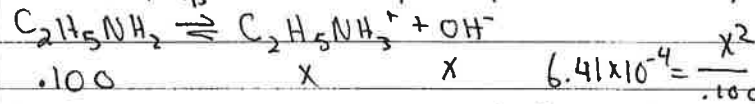
* These K values make sense as these are all weak acids & bases

PS 19.8 (a) HNO_3 - acid, $K_a \uparrow \uparrow$, strong, $[\text{H}^+] = .100 \text{ M}$ pH = 1

(B) H_2O - neutral, $K_w = 1 \times 10^{-14}$, weak, $[\text{H}^+] = 1 \times 10^{-7}$ pH = 7

(c) NaOH - base, $K_B \uparrow \uparrow$, strong, $[\text{H}^+] = 1 \times 10^{-13}$ pH = 13

(d) Base, $K_B = 6.41 \times 10^{-4}$, weak, $[\text{H}^+] = 1.25 \times 10^{-12}$ pH = 11.90



$$x = [\text{OH}^-] = .008$$

(e) weak acid, $K_a = 3.53 \times 10^{-4}$, $[\text{H}^+] = 5.9 \times 10^{-3}$ pH = 2.22

$$3.53 \times 10^{-4} = \frac{x^2}{.100} \quad x = [\text{H}^+] = 5.9 \times 10^{-3}$$

(f) weak acid, $K_a = 4.6 \times 10^{-4}$, $[\text{H}^+] = 6.78 \times 10^{-3}$ pH = 2.17

$$4.6 \times 10^{-4} = \frac{x^2}{.1} \quad x = [\text{H}^+] = 6.78 \times 10^{-3}$$

(g) weak base, $K_b = 3.7 \times 10^{-4}$, $[\text{H}^+] = 1.64 \times 10^{-12}$ pH = 11.79

$$3.7 \times 10^{-4} = \frac{x^2}{.1} \quad x = [\text{OH}^-] = .0061$$

$$[\text{H}^+] = 1.64 \times 10^{-12}$$

(h) weak base, $K_b = 1.78 \times 10^{-9}$, $[\text{H}^+] = 7.52 \times 10^{-10}$ pH = 9.12

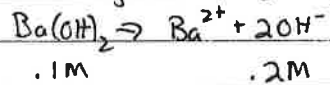
$$1.78 \times 10^{-9} = \frac{x^2}{.1} \quad x = [\text{OH}^-] = 1.33 \times 10^{-5}$$

$$[\text{H}^+] = 7.52 \times 10^{-10}$$

(i) weak acid, $K_a = 1.28 \times 10^{-10}$, $[\text{H}^+] = 3.58 \times 10^{-6}$ pH = 5.44

$$1.28 \times 10^{-10} = \frac{x^2}{.1} \quad x = [\text{H}^+] = 3.58 \times 10^{-6}$$

j) Strong base, $K_D \uparrow \uparrow$, $[H^+] = 5 \times 10^{-14}$, $pH = 13.3$



k) weak acid, $K_a = 3.53 \times 10^{-4}$, $[H^+] = .0013$, $pH = 2.88$

$$3.53 \times 10^{-4} = \frac{x^2}{.00491} \quad x = [H^+] = .0013$$

l) weak acid, $K_a = 2.95 \times 10^{-5}$, $[H^+] = .0017$, $pH = 2.76$

$$2.95 \times 10^{-5} = \frac{x^2}{.1} \quad x = [H^+] = .0017$$

(A) HNO_3 $pH = 1$

(F) HNO_2 $pH = 2.17$

(E) .16M HF $pH = 2.22$

(L) HOCl $pH = 2.76$

(K) .00491M HF $pH = 2.88$

(I) $\text{HC}_6\text{H}_5\text{O}$ $pH = 5.44$

(B) H_2O $pH = 7.00$

(H) $\text{C}_5\text{H}_5\text{N}$ $pH = 9.12$

(G) CH_3NH_2 $pH = 11.79$

(D) $\text{C}_2\text{H}_5\text{NH}_2$ $pH = 11.90$

(C) NaOH $pH = 13.0$

(J) Ba(OH)_2 $pH = 13.3$

Problem Set # 2

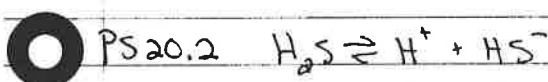
PS20.1



I	.100	0	0	
C	-x	+x	+x	$8.0 \times 10^{-5} = \frac{x^2}{.1}$
E	.100-x	x	x	$[x] = [H^+] = 2.8 \times 10^{-3}$



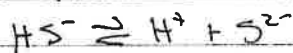
I	2.8×10^{-3}	2.8×10^{-3}	0	$1.6 \times 10^{-12} = \frac{2.8 \times 10^{-3} x}{2.8 \times 10^{-3}}$
C	-x	+x	+x	
E	$2.8 \times 10^{-3} - x$	$2.8 \times 10^{-3} + x$	x	$[H^+] = 2.8 \times 10^{-3}$



I	.100	0	0
C	-x	+x	+x

$K_{a1} = 9.1 \times 10^{-8}$
 $K_{a2} = 1.0 \times 10^{-19}$

E	.100-x	x	x	$9.1 \times 10^{-8} = \frac{x^2}{.100}$	$x = [H^+] = 9.54 \times 10^{-5}$
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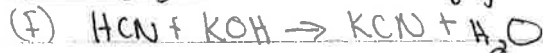
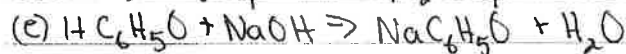
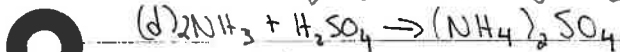


I	9.54×10^{-5}	9.54×10^{-5}	0
C	-x	+x	+x
E	$9.54 \times 10^{-5} - x$	$9.54 \times 10^{-5} + x$	x

$1.0 \times 10^{-19} = \frac{9.54 \times 10^{-5} x}{9.54 \times 10^{-5}}$

pH = 4.02

$[S^{2-}] = 1 \times 10^{-19}$



- PS20.4
- (a) $F^- + H_2O \rightleftharpoons HF + OH^-$ (Base)
 - (b) $ClO_2^- + H_2O \rightleftharpoons HClO_2 + OH^-$ (Base)
 - (c) $NO_2^- + H_2O \rightleftharpoons HNO_2 + OH^-$ (Base)
 - (d) $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$ (acid)
 - (e) $CH_3NH_3^+ + H_2O \rightleftharpoons CH_3NH_2 + H_3O^+$ (acid)
 - (f) $C_2H_5NH_3^+ + H_2O \rightleftharpoons C_2H_5NH_2 + H_3O^+$ (acid)

PS20.5 It appears anions are basic and cations are acidic. They are all conjugates of weak acids & bases

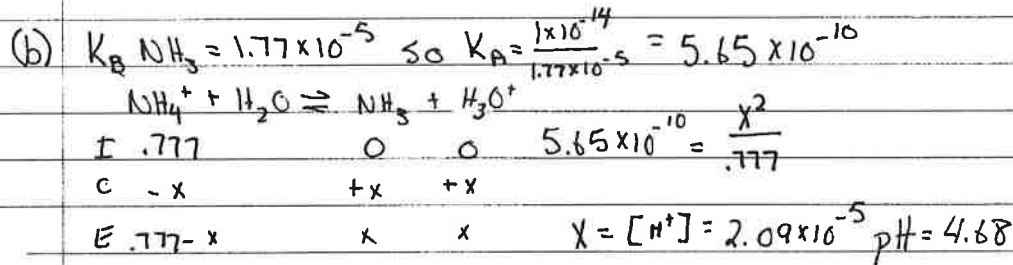
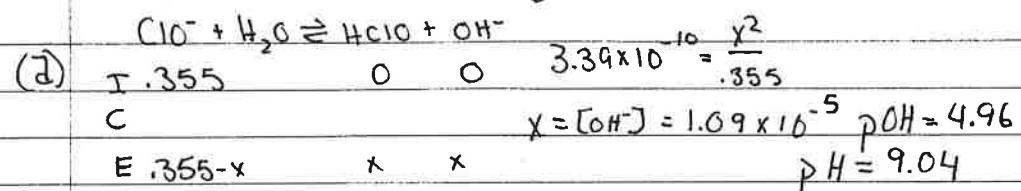
PS20.6

- (a) KOH & $H_2C_2O_4$
- (b) KOH & $HClO$
- (c) $C_2H_5NH_2$ & HNO_3
- (d) NH_3 & HCl
- (e) KOH & HCl
- (f) NH_3 & H_2SO_4

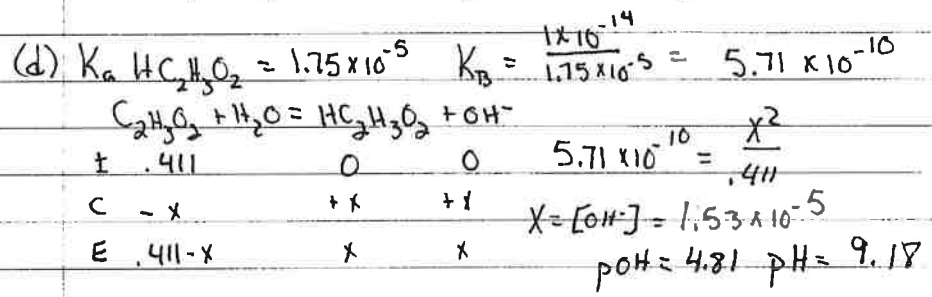
PS20.7

- (a) basic
- (b) basic
- (c) acidic
- (d) acidic
- (e) neutral
- (f) acidic

PS20.8 $K_a \text{ HClO} = 2.95 \times 10^{-5}$ so $K_B = \frac{1 \times 10^{-14}}{2.95 \times 10^{-5}} = 3.39 \times 10^{-10}$



(c) no hydrolysis (strong acid - strong base)



(e) no hydrolysis (strong acid / base)

PS20.9 $\text{XO}_4^- < \text{OXO}_3^- < \text{O}_2\text{XOH}$

the more Oxygen the more you pull electron density away from H^+ , thus allowing it to be easier to jump ship!

16 Acid-Base Equilibria

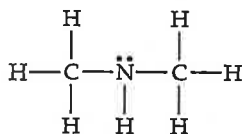
Visualizing Concepts

- 16.1 *Analyze.* From the structures decide which reactant fits the description of a Brønsted-Lowry (B-L) acid, a B-L base, a Lewis acid, and a Lewis base. *Plan.* A B-L acid is an H^+ donor, and a B-L base is an H^+ acceptor. A Lewis acid is an electron pair acceptor and a Lewis base is an electron pair donor. *Solve.*
- $H-X$ is a B-L acid, because it loses H^+ during reaction. NH_3 is a B-L base, because it gains H^+ during reaction.
 - By virtue of its unshared electron pair, NH_3 is the electron pair donor and Lewis base. HX is the electron pair acceptor and Lewis acid.
- 16.2 *Plan.* The stronger the acid, the greater the extent of ionization. The stronger the acid, the weaker its conjugate base. In an acid-base reaction, equilibrium will favor the side with the weaker acid and base. *Solve.*
- HY is stronger than HX . Starting with six HY molecules, four are dissociated; of six HX molecules, only two are dissociated. Because it is dissociated to a greater extent, HY is the stronger acid.
 - If HY is the stronger acid, Y^- is the weaker base and X^- is the stronger base.
 - HX and Y^- , the reactants, are the weaker acid and base. Equilibrium lies to the left, and $K_c < 1$.
- 16.3 *Plan.* Strong acids are completely ionized. The acid that is least ionized is weakest, and has the smallest K_a value. At equal concentrations, the weakest acid has the smallest $[H^+]$ and highest pH. *Solve.*
- HY is a strong acid. There are no neutral HY molecules in solution, only H^+ cations and Y^- anions.
 - HX has the smallest K_a value. It has most neutral acid molecules and fewest ions.
 - HX has the fewest H^+ and highest pH.
- 16.4 *Analyze/Plan.* Consider how K_a and $[HA]$ influence extent of ionization (or percent ionization).
- Solve.* The greater the extent of ionization, the less valid the approximation that x is small relative to $[HA]$. The greater the value of K_a , the stronger the acid and the greater the extent of ionization. On the other hand, the smaller the $[HA]$, the greater the percent ionization. The approximation is then most valid for small K_a and large $[HA]$. All three cases have the same $[HA]$, and case (a) has the smallest K_a . The approximation is most valid for case (a).

- 16.5 *Plan.* The definition of percent ionization is $\frac{[\text{H}^+]}{[\text{HA}]_{\text{initial}}} \times 100$. *Solve.*
- (a) Curve C shows the effect of initial concentration on percent ionization of a weak acid.
- (b) The percent ionization is inversely related to initial acid concentration; only curve C shows a decrease in percent ionization as acid concentration increases.

- 16.6 *Plan.* The stronger the acid, the greater the extent of ionization. The stronger the acid, the weaker its conjugate base. *Solve.*
- (a) HY has most H^+ and is strongest; HX has the fewest H^+ and is weakest. The order of base strength is the reverse of the order of acid strength. $\text{Y}^- < \text{Z}^- < \text{X}^-$
- (b) The strongest base, X^- , has the largest K_b value.

- 16.7 *Plan.* Write the molecular formula so we can count the correct number of valence electrons. Use the atom connectivity shown to draw the Lewis structure. *Solve.*
- (a) The molecular formula is $(\text{CH}_3)_2\text{NH}$, or $\text{C}_2\text{H}_7\text{N}$. The number of valence electrons is $2(4) + 7 + 5 = 20 e^-$, $10 e^-$ pr.

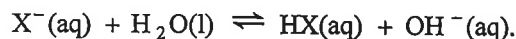


- (b) The compound is an amine. It is an ammonia molecule where two H atoms have been replaced by CH_3 groups.

- 16.8 *Plan.* Evaluate the interactions of Na^+ and X^- with H_2O .

Solve. Na^+ does not affect the $[\text{H}^+]$ or $[\text{OH}^-]$ of an aqueous solution. It is a "negligible" acid in water (which can be thought of as the conjugate acid of the strong base NaOH).

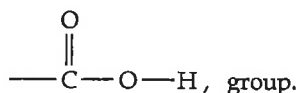
X^- is the conjugate base of HX . It is not a negligible base in water, because we see from the diagram that one X^- has gained an H^+ to form HX . In this solution, H_2O acts as the Brønsted-Lowry acid, according to the hydrolysis equilibrium:



The missing ion is $\text{OH}^-(\text{aq})$. According to the equilibrium reaction, the number of HX molecules and OH^- ions are equal. Since there is 1 HX molecule in the diagram, 1 OH^- should be shown.

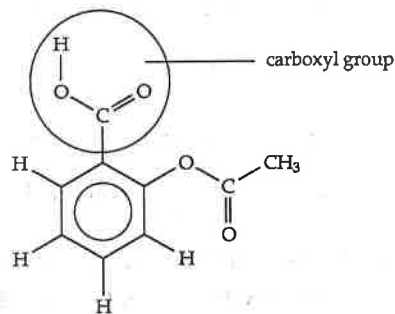
- 16.9 *Plan.* Evaluate the molecular structures to determine if the acids are binary acids or oxyacids. Consider the trends in acid strength for both classes of acids. *Solve.*

- (a) The molecules are oxyacids; in both cases, the ionizable H atom is attached to O. The right molecule is a carboxylic acid; the ionizable H is part of a carboxyl,



- (b) Increasing the electronegativity of X increases the strength of both acids. As X becomes more electronegative and attracts more electron density, the O-H bond becomes weaker and more polar. This increases the likelihood of ionization and increases acid strength. An electronegative X group also stabilizes the anionic conjugate bases by delocalizing the negative charge. This causes the ionization equilibrium to favor products, and the values of K_a to increase.

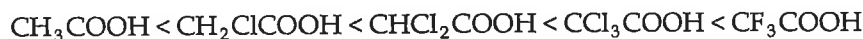
16.10 The carboxyl group is the H-atom group at the "top" of the molecule.



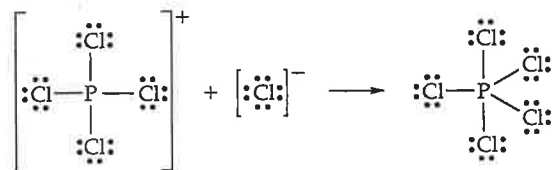
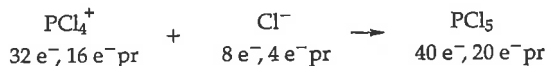
The group on the right of the molecule is not a carboxyl group because it contains no ionizable H.

16.11 *Analyze/Plan.* The acids listed are all carboxylic acids with two carbon atoms. They vary by having different substituents attached to the terminal (non-carbonyl) carbon atom. Consider how these substituents affect acidity, or acid strength.

Solve. The acids have different numbers and kinds of electronegative substituents on the terminal C atoms. Electronegative substituents affect acid strength in two ways. They withdraw electron density from the carbonyl group, making the O-H bond more polar and more likely to ionize. And, they stabilize the conjugate base, the carboxylate anion, by delocalizing negative charge. The more electronegative substituents, and the greater their electronegativity, the stronger the acid. Acetic acid, CH_3COOH , has 3 H atoms bonded to the terminal C. As we replace H with Cl, acid strength increases going from CH_2ClCOOH to CHCl_2COOH to CCl_3COOH to CF_3COOH . Finally, F is more electronegative than Cl; so CF_3COOH is the most acidic. The order listed in the exercise is the order of increasing acidity.



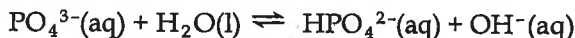
16.12 (a) *Plan.* Count valence electrons and draw the correct Lewis structures. Consider The definition of Lewis acids and bases. *Solve.*



PCl_4^+ accepts an electron pair from Cl^- ; PCl_4^+ is the Lewis acid and Cl^- is the Lewis base.

16.90 The solution is basic because of the hydrolysis of PO_4^{3-} . The molarity of PO_4^{3-} is

$$\frac{35.0 \text{ g Na}_3\text{PO}_4}{1.00 \text{ L soln}} \times \frac{1 \text{ mol Na}_3\text{PO}_4}{163.9 \text{ g Na}_3\text{PO}_4} = 0.2135 = 0.214 \text{ M PO}_4^{3-}$$



$$K_b = \frac{[\text{HPO}_4^{2-}][\text{OH}^-]}{[\text{PO}_4^{3-}]} = \frac{K_w}{K_a \text{ for HPO}_4^{2-}} = \frac{1.0 \times 10^{-14}}{4.2 \times 10^{-13}} = 0.0238 = 2.4 \times 10^{-2}$$

Ignoring the further hydrolysis of HPO_4^{2-} ,

$$[\text{OH}^-] = [\text{HPO}_4^{2-}] = x, [\text{PO}_4^{3-}] = 0.214 - x$$

$$2.4 \times 10^{-2} = \frac{x^2}{(0.214 - x)}; x^2 + 2.4 \times 10^{-2}x - 0.0051 = 0$$

Since K_b is relatively large, we will not assume x is small compared to 0.275.

$$x = \frac{-0.024 \pm \sqrt{(0.024)^2 - 4(1)(-0.0051)}}{2(1)} = \frac{-0.024 \pm \sqrt{0.0210}}{2(1)}$$

$$x = 0.060 \text{ M OH}^-; \text{pH} = 14 + \log(0.060) = 12.78$$

Acid-Base Character and Chemical Structure

- 16.91 (a) As the electronegativity of the central atom (X) increases, more electron density is withdrawn from the X-O and O-H bonds, respectively. In water, the O-H bond is ionized to a greater extent and the strength of the oxyacid increases.
- (b) As the number of nonprotonated oxygen atoms in the molecule increases, they withdraw electron density from the other bonds in the molecule and the strength of the oxyacid increases.
- 16.92 (a) Acid strength increases as the polarity of the X-H bond increases and decreases as the strength of the X-H bond increases.
- (b) Assuming the element, X, is more electronegative than H, as the electronegativity of X increases, the X-H bond becomes more polar and the strength of the acid increases. This trend holds true as electronegativity increases across a row of the periodic chart. However, as electronegativity decreases going down a family, acid strength increases because the strength of the H-X bond decreases, even though the H-X bond becomes less polar.
- 16.93 (a) HNO_3 is a stronger acid than HNO_2 because it has one more nonprotonated oxygen atom, and thus a higher oxidation number on N.
- (b) For binary hydrides, acid strength increases going down a family, so H_2S is a stronger acid than H_2O .
- (c) H_2SO_4 is a stronger acid because H^+ is much more tightly held by the anion HSO_4^- .
- (d) For oxyacids, the greater the electronegativity of the central atom, the stronger the acid, so H_2SO_4 is a stronger acid than H_2SeO_4 .

- (e) CCl_3COOH is stronger because the electronegative Cl atoms withdraw electron density from other parts of the molecule, which weakens the O-H bond and makes H^+ easier to remove. Also, the electronegative Cl delocalizes negative charge on the carboxylate anion. This stabilizes the conjugate base, favoring products in the ionization equilibrium and increasing K_a .
- 16.94 (a) For binary hydrides, acid strength increases going across a row, so HCl is a stronger acid than H_2S .
- (b) For oxyacids, the more electronegative the central atom, the stronger the acid, so H_3PO_4 is a stronger acid than H_3AsO_4 .
- (c) HBrO_3 has one more nonprotonated oxygen and a higher oxidation number on Br, so it is a stronger acid than HBrO_2 .
- (d) The first dissociation of a polyprotic acid is always stronger because H^+ is more tightly held by an anion, so $\text{H}_2\text{C}_2\text{O}_4$ is a stronger acid than HC_2O_4^- .
- (e) The conjugate base of benzoic acid, $\text{C}_6\text{H}_5\text{COO}^-$, is stabilized by resonance, while the conjugate base of phenol, $\text{C}_6\text{H}_5\text{O}^-$, is not. $\text{C}_6\text{H}_5\text{COOH}$ has greater tendency to form its conjugate base and is the stronger acid.
- 16.95 (a) BrO^- (HClO is the stronger acid due to a more electronegative central atom, so BrO^- is the stronger base.)
- (b) BrO^- (HBrO_2 has more nonprotonated O atoms and is the stronger acid, so BrO^- is the stronger base.)
- (c) HPO_4^{2-} (larger negative charge, greater attraction for H^+)
- 16.96 (a) NO_2^- (HNO_3 is the stronger acid because it has more nonprotonated O atoms, so NO_2^- is the stronger base.)
- (b) PO_4^{3-} (K_a for HAsO_4^{2-} is greater than K_a for HPO_4^{2-} , so K_b for PO_4^{3-} is greater and PO_4^{3-} is the stronger base. Note that P is more electronegative than As and H_3PO_4 is a stronger acid than H_3AsO_4 , which could lead to the conclusion that AsO_4^{3-} is the stronger base. As in all cases, the measurement of base strength, K_b , supercedes the prediction. Chemistry is an experimental science.)
- (c) CO_3^{2-} (The more negative the anion, the stronger the attraction for H^+ .)
- 16.97 (a) True.
- (b) False. In a series of acids that have the same central atom, acid strength increases with the number of nonprotonated oxygen atoms bonded to the central atom.
- (c) False. H_2Te is a stronger acid than H_2S because the H-Te bond is longer, weaker, and more easily dissociated than the H-S bond.
- 16.98 (a) True.
- (b) False. For oxyacids with the same structure but different central atom, the acid strength increases as the electronegativity of the central atom increases.
- (c) False. HF is a weak acid, weaker than the other hydrogen halides, primarily because the H-F bond energy is exceptionally high.