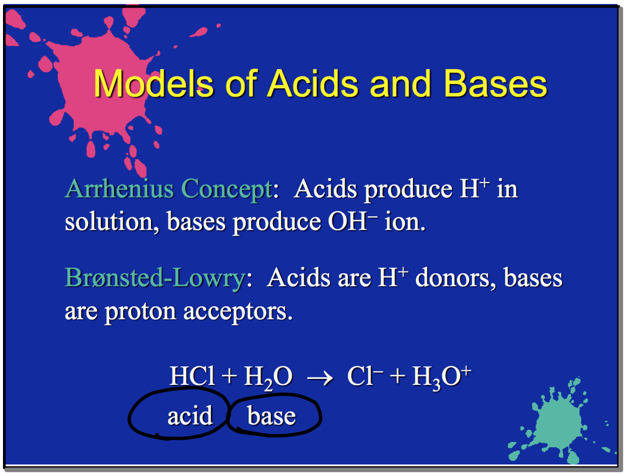
Acid/Base Equilibria



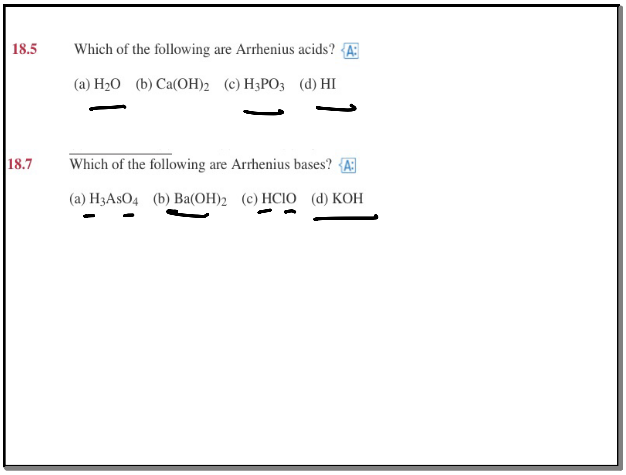
Models of Acids and Bases

Arrhenius Concept: Acids produce H^+ in solution, bases produce OH^- ion.

Brønsted-Lowry: Acids are H^+ donors, bases are proton acceptors.

$$HCl + H_2O \rightarrow Cl^- + H_3O^+$$

acid base



18.5 Which of the following are Arrhenius acids?

(a) H_2O (b) $Ca(OH)_2$ (c) H_3PO_3 (d) HI

18.7 Which of the following are Arrhenius bases?

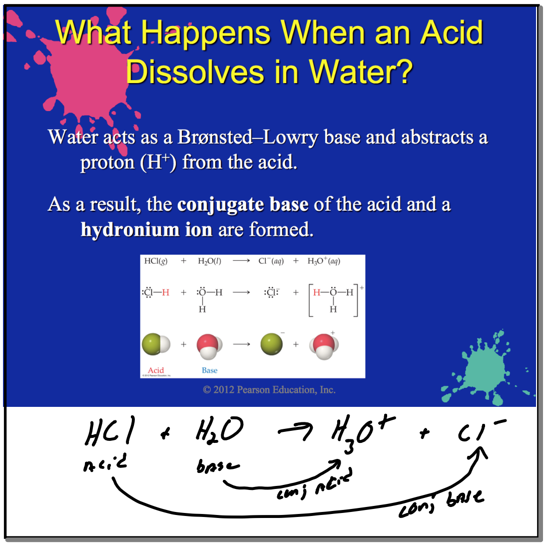
(a) H_3AsO_4 (b) $Ba(OH)_2$ (c) HClO (d) KOH

A Brønsted–Lowry acid…

…must have a removable (acidic) proton.

A Brønsted–Lowry base…

…must have a pair of nonbonding electrons.



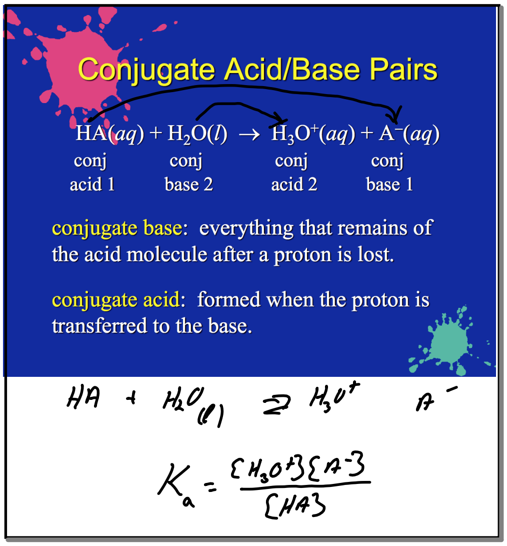
What Happens When an Acid Dissolves in Water?

Water acts as a Brønsted–Lowry base and abstracts a proton (H^+) from the acid.

As a result, the **conjugate base** of the acid and a **hydronium ion** are formed.

$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$

acid base conj acid conj base



Conjugate Acid/Base Pairs

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

conj acid 1	conj base 2	conj acid 2	conj base 1

conjugate base: everything that remains of the acid molecule after a proton is lost.

conjugate acid: formed when the proton is transferred to the base.

$$HA + H_2O_{(l)} \rightleftharpoons H_3O^+ \quad A^-$$

$$K_a = \frac{\{H_3O^+\}\{A^-\}}{\{HA\}}$$

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Acid Dissociation Constant (K_a)

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

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{[H^+][A^-]}{[HA]}$$

K_a ↑

$$HA + H_2O_{(l)} \rightleftharpoons H_3O^+ + A^-$$

$$HA \rightleftharpoons H^+ + A^-$$

18.11 Write the K_a expression for each of the following in water:

(a) HNO_2 (b) CH_3COOH (c) $HBrO_2$

18.12 Write the K_a expression for each of the following in water:

(a) $H_2PO_4^-$ (b) H_3PO_2 (c) HSO_4^-

11. a. $HNO_2 + H_2O_{(l)} \rightleftharpoons H_3O^+ + NO_2^-$

acid base acid base

$$K_a = \frac{\{H_3O^+\}\{NO_2^-\}}{\{HNO_2\}}$$

11. b. $CH_3COOH + H_2O_{(l)} \rightleftharpoons H_3O^+ + CH_3COO^-$

12. c $HSO_4^- + H_2O_{(l)} \rightleftharpoons H_3O^+ + SO_4^{2-}$

acid base

Acid Strength

Strong Acid:

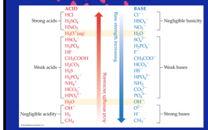
- Its equilibrium position lies far to the right. (HNO_3)
- Yields a weak conjugate base. (NO_3^-)

$$HA \rightarrow H^+ + A^-$$

1M 0 0

0 1M 1M

Acid and Base Strength



Strong acids are completely dissociated in water.

- Their conjugate bases are quite weak.

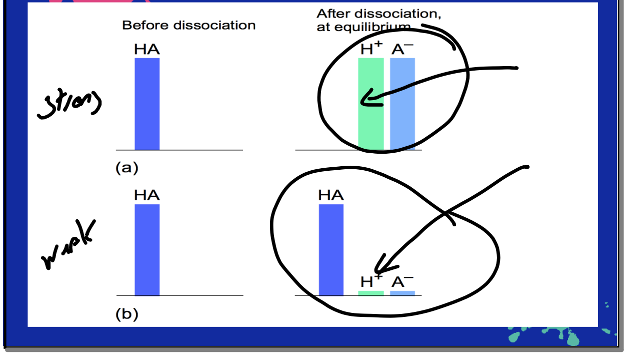
Weak acids only dissociate partially in water.

- Their conjugate bases are weak bases.

strong $HA + H_2O_{(l)} \rightarrow H_3O^+ + A^-$

weak $HA + H_2O_{(l)} \rightleftharpoons H_3O^+ + A^-$

Strong Acid - Weak Acid



Strong Acids

You will recall that the seven strong acids are HCl, HBr, HI, HNO_3, H_2SO_4, $HClO_3$, and $HClO_4$.

These are, by definition, strong electrolytes and exist totally as ions in aqueous solution.

For the monoprotic strong acids,

$$[H_3O^+] = [acid].$$

$$HCl \rightarrow H^+ + Cl^-$$

0.1M 0 0

0 0.1M 0.1M

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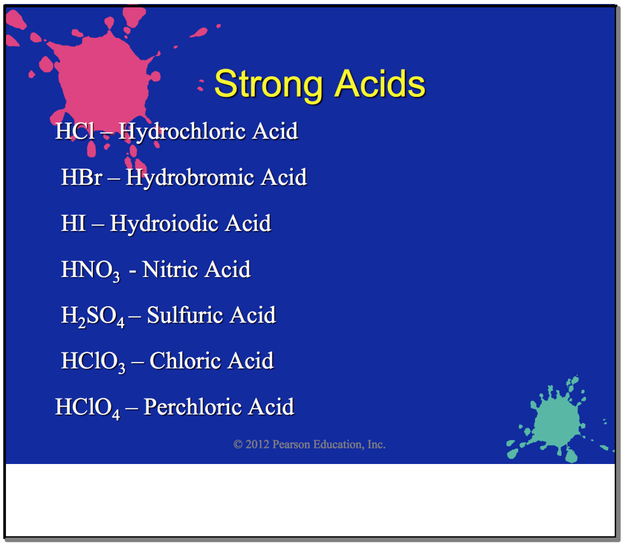


Strong Acids

HCl – Hydrochloric Acid

HBr – Hydrobromic Acid

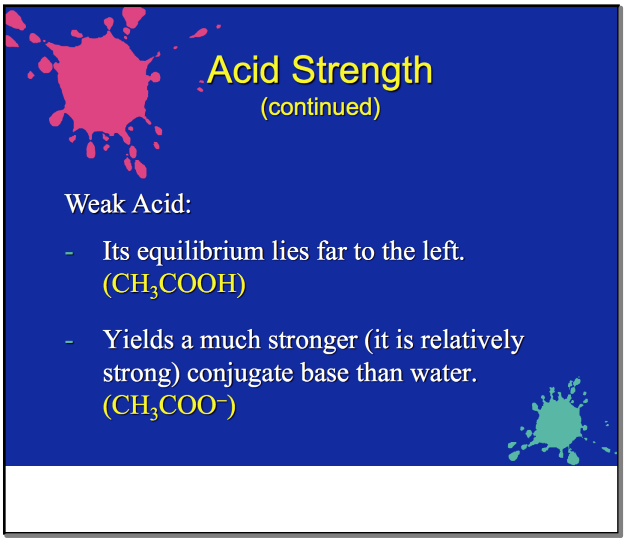
HI – Hydroiodic Acid

HNO_3 - Nitric Acid

H_2SO_4 – Sulfuric Acid

$HClO_3$ – Chloric Acid

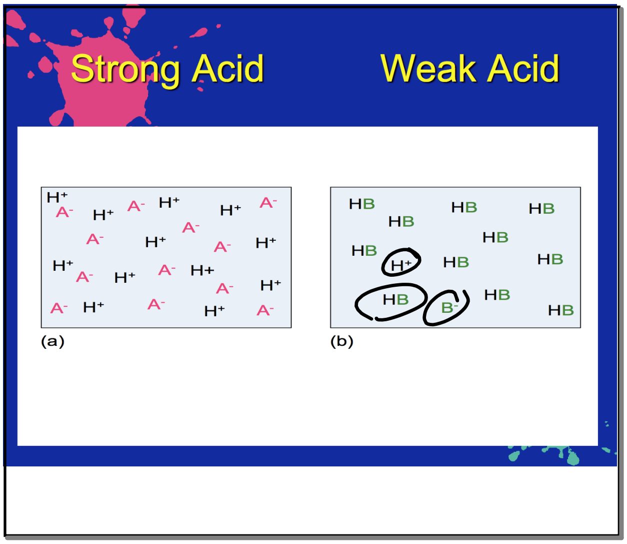
$HClO_4$ – Perchloric Acid



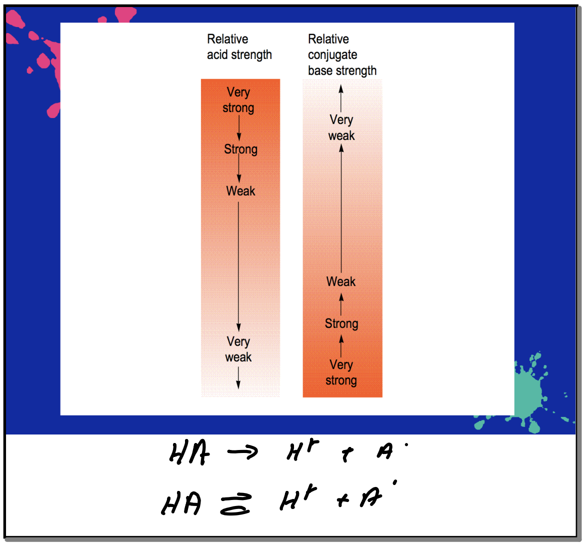
Acid Strength
(continued)

Weak Acid:

- Its equilibrium lies far to the left. (CH_3COOH)
- Yields a much stronger (it is relatively strong) conjugate base than water. (CH_3COO^-)



Strong Acid Weak Acid



$HA \rightarrow H^+ + A^-$

$HA \rightleftharpoons H^+ + A^-$

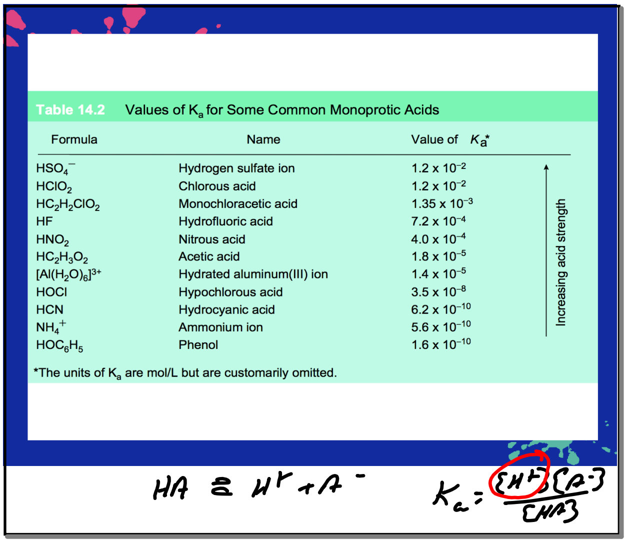


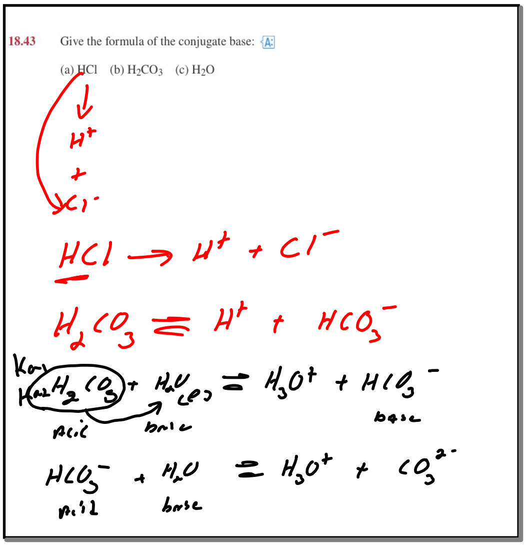
Table 14.2 Values of K_a for Some Common Monoprotic Acids

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}

*The units of K_a are mol/L but are customarily omitted.

$HA \rightleftharpoons H^+ + A^-$

$K_a = \frac{\{H^+\}\{A^-\}}{\{HA\}}$



18.43 Give the formula of the conjugate base:

(a) HCl (b) H_2CO_3 (c) H_2O

H^+
+
Cl^-

$HCl \rightarrow H^+ + Cl^-$

$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$

K_a

K_{a1} $H_2CO_3 + H_2O_{(l)} \rightleftharpoons H_3O^+ + HCO_3^-$

Acid base base

$HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{2-}$

Acid base

18.47 In each equation, label the acids, bases, and conjugate pairs: A:

(a) $HCl + H_2O \rightleftharpoons Cl^- + H_3O^+$

(b) $HClO_4 + H_2SO_4 \rightleftharpoons ClO_4^- + H_3SO_4^+$

(c) $HPO_4^{2-} + H_2SO_4 \rightleftharpoons H_2PO_4^- + HSO_4^-$

base acid

Water as an Acid and a Base

Water is amphoteric (it can behave either as an acid or a base).

$$H_2O + H_2O \rightarrow H_3O^+ + OH^-$$

acid 1 base 2 conj acid 2 conj base 1

$K_w = 1 \times 10^{-14}$ at 25° C

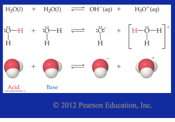
$$K_w = [H_3O^+][OH^-] = 1\times10^{-14}$$

Autoionization of Water

As we have seen, water is amphoteric.

In pure water, a few molecules act as bases and a few act as acids.

This is referred to as **autoionization**.



$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

0 0

+x +x

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

$$K_w = [H_3O^+][OH^-] = 10^{-14}$$

$$(x)(x) = 10^{-14}$$

$$x = 10^{-7} M$$

Ion Product Constant

The equilibrium expression for this process is

$$K_c = [H_3O^+]\,[OH^-]$$

This special equilibrium constant is referred to as the **ion product constant** for water, K_w.

At 25°C, $K_w = 1.0 \times 10^{-14}$

The pH Scale

$$\boxed{pH \approx -\log[H^+]}$$ $pH = -\log[H_3O^+]$

pH in water ranges from 0 to 14.

$$K_w = 1.00 \times 10^{-14} = [H^+]\,[OH^-]$$

$$pK_w = 14.00 = pH + pOH$$

As pH rises, pOH falls (sum = 14.00).

18.22 Which solution has the higher pH? Explain. A:

(a) A 0.1 *M* solution of an acid with $K_a = 1\times10^{-4}$ or one with $K_a = 4\times10^{-5}$

(b) A 0.1 *M* solution of an acid with $pK_a = 3.0$ or one with $pK_a = 3.5$

$K_a = 0.001$ $K_a = 3.16\times10^{-4}$

(c) A 0.1 *M* solution or a 0.01 *M* solution of a weak acid

(d) A 0.1 *M* solution of a weak acid or a 0.1 *M* solution of a strong acid

(e) A 0.1 *M* solution of an acid or a 0.01 *M* solution of a base

(f) A solution of pOH 6.0 or one of pOH 8.0

$pH = -\log[H^+]$ $pK_a = -\log K_a$

$K_a = 10^{-pK_a}$

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

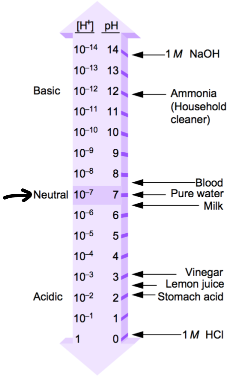
$$\log(10^{-14}) = \log([H^+][OH^-])$$

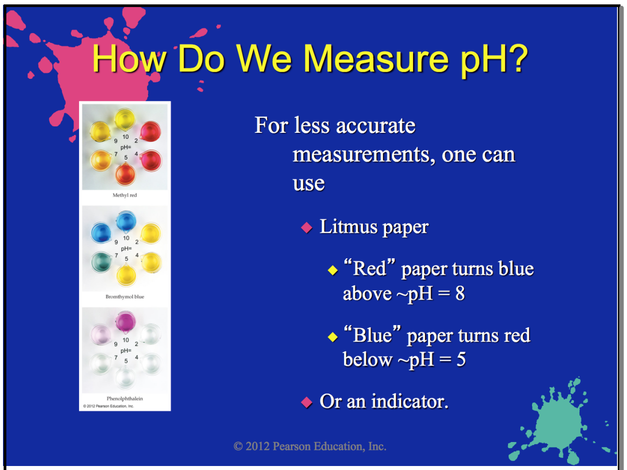
$$-\log(10^{-14} = -\log[H^+] + -\log[OH^-]$$

$$pK_w = pH + pOH = 14$$

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

$$pH + pOH = 14$$

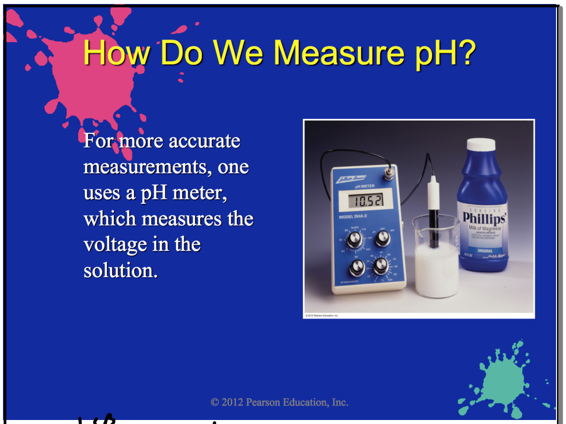




How Do We Measure pH?

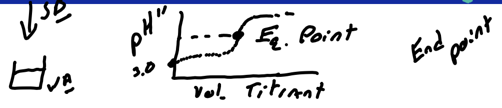
For less accurate measurements, one can use

- Litmus paper
  - "Red" paper turns blue above ~pH = 8
  - "Blue" paper turns red below ~pH = 5
- Or an indicator.



How Do We Measure pH?

For more accurate measurements, one uses a pH meter, which measures the voltage in the solution.



18.27 (a) What are $[H_3O^+]$, $[OH^-]$, and pOH in a solution with a pH of 9.85?

$pOH = ?$

$= 4.15$

$pH + pOH = 14$

$[OH^-] = 7.08 \times 10^{-5}$

$pOH = -\log [OH^-]$

$pH = 9.85$

$[H^+] = 1.41 \times 10^{-10}$

$pH = -\log [H^+]$

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

$K_w = [H^+][OH^-]$

$= (1.41 \times 10^{-10})(7.08 \times 10^{-5}) = 1 \times 10^{-14}$

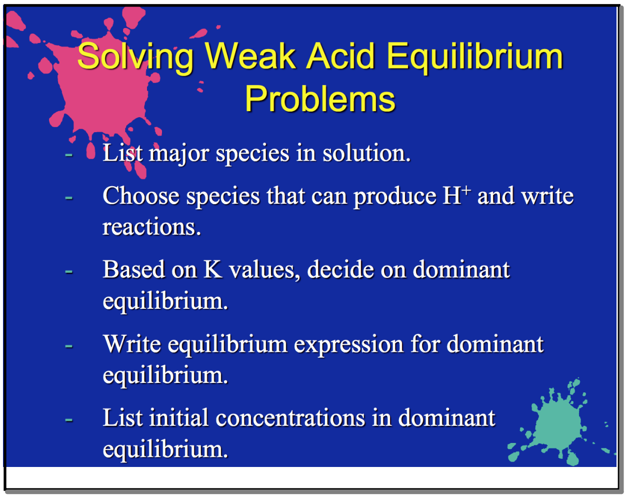
18.24 (a) What is the pH of 0.0333 *M* HNO_3? Is the solution neutral, acidic, or basic? (

$HNO_3 \rightarrow H^+ + NO_3^-$

$0.0333 \quad 0 \quad 0$

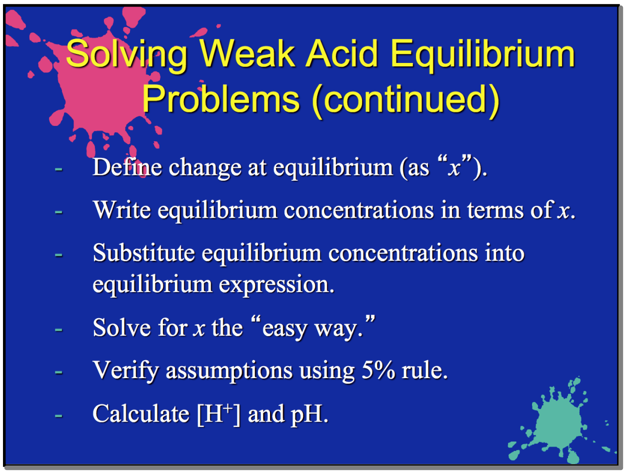
$0 \quad 0.0333 \quad 0.0333$

$pH = 1.48$



Solving Weak Acid Equilibrium Problems

- List major species in solution.
- Choose species that can produce H^+ and write reactions.
- Based on K values, decide on dominant equilibrium.
- Write equilibrium expression for dominant equilibrium.
- List initial concentrations in dominant equilibrium.



Solving Weak Acid Equilibrium Problems (continued)

- Define change at equilibrium (as "*x*").
- Write equilibrium concentrations in terms of *x*.
- Substitute equilibrium concentrations into equilibrium expression.
- Solve for *x* the "easy way."
- Verify assumptions using 5% rule.
- Calculate $[H^+]$ and pH.

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18.64 A 0.15 M solution of butanoic acid, $CH_3CH_2CH_2COOH$, contains 1.51×10^{-3} M H_3O^+. What is the K_a of butanoic acid? {A:

$HA \rightleftharpoons H^+ + A^-$ $K_a = \frac{[H^+][A^-]}{[HA]}$

$HA + H_2O \rightleftharpoons H_3O^+ + A^-$

I	0.15	0	0
Δ	−x	+x	+x
E	0.15−x	$\boxed{x}$	x

1.51×10^{-3} M

$$K = \frac{(x)(x)}{(0.15-x)} = \frac{(1.51\times10^{-3})^2}{(0.15-1.51\times10^{-3})} = 1.54\times10^{-5}$$

18.66 Nitrous acid, HNO_2, has a K_a of 7.1×10^{-4}. What are $[H_3O^+]$, $[NO_2^-]$, and $[OH^-]$ in 0.60 M HNO_2? {A:

$HNO_2 + H_2O_{(l)} \rightleftharpoons H_3O^+ + NO_2^-$

I	0.60 M	0	0
Δ	−x	+x	+x
E	0.60−x	x	x

$$K_a = \frac{[H_3O^+][NO_2^-]}{[HNO_2]} = 7.1\times10^{-4}$$

$$\frac{(x)(x)}{(0.60\cancel{-x})} = 7.1\times10^{-4}$$

$x = 2.06\times10^{-2} = [H_3O^+]$
$= NO_2^-$

$$\frac{(2.06\times10^{-2})^2}{(0.60-2.06\times10^{-2})} = 7.3\times10^{-4}$$

$K_w = [H_3O^+][OH^-] = 10^{-14}$

$$[OH^-] = \frac{10^{-14}}{2.06\times10^{-2}} = 4.85\times10^{-13}$$

easy
5% rule

$$\frac{2.06\times10^{-2}}{0.60}\times100 = 3.44$$

18.68 Chloroacetic acid, $ClCH_2COOH$, has a pK_a of 2.87. What are $[H_3O^+]$, pH, $[ClCH_2COO^-]$, and $[ClCH_2COOH]$ in 1.25 M $ClCH_2COOH$? {A:

HA

A⁻

$HA + H_2O \rightleftharpoons H_3O^+ + A^-$

I	1.25	0	0
Δ	−x	+x	+x
E	1.25−x	x	x

$$K_a = \frac{(x)(x)}{(1.25\cancel{-x})} = 1.35\times10^{-3}$$

$x = 0.041 = [H_3O^+]$

$pK_a = -\log K_a$

$pH = -\log(0.041) = 1.39$

Percent Dissociation (Ionization)

$$\%\ \text{dissociation} = \frac{\text{amount dissociated}(M)}{\text{initial concentration}(M)} \times 100\%$$

18.70 In a 0.20 M solution, a weak acid is 3.0% dissociated. {A:

(a) Calculate the $[H_3O^+]$, pH, $[OH^-]$, and pOH of the solution.

(b) Calculate K_a of the acid.

$HA + H_2O \rightleftharpoons \boxed{H_3O^+} + A^-$

0.20 M	0	0
−x	+x	+x
0.20−x	$\boxed{x}$	x

$$K_a = \frac{(x)(x)}{(0.20-x)} = 1.9\times10^{-4}$$

$$\frac{x}{0.20}\times100 = 3.0$$

$x = 0.0060$
$= [H_3O^+] = [A^-]$

$pH = -\log(0.0060) = 2.22$

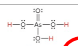
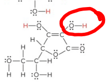
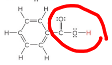
$pOH = 11.78$

$pH + pOH = 14$

$[OH^-] = 1.67\times10^{-12}$

$pOH = -\log(OH^-)$

18.78 Use **Appendix C** to calculate the percent dissociation of 0.55 M benzoic acid, C_6H_5COOH. {A:

Name and Formula	Lewis Structure†	K_{a1}	K_{a2}	K_{a3}
Arsenic acid H_3AsO_4		6×10^{-3}	1.1×10^{-7}	3×10^{-12}
Ascorbic acid $H_2C_6H_6O_6$		1.0×10^{-5}	5×10^{-12}	
Benzoic acid C_6H_5COOH		6.3×10^{-5}		

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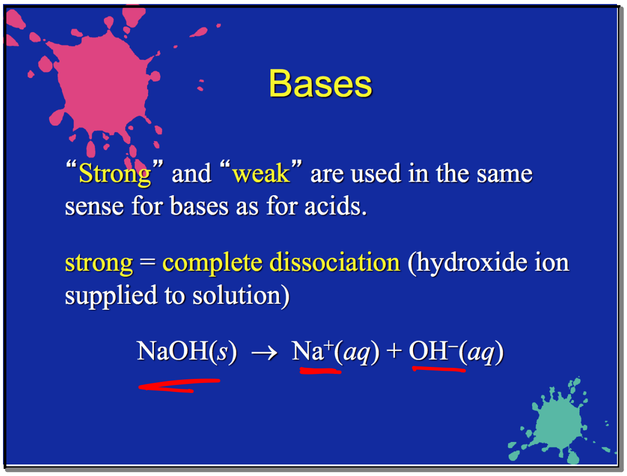
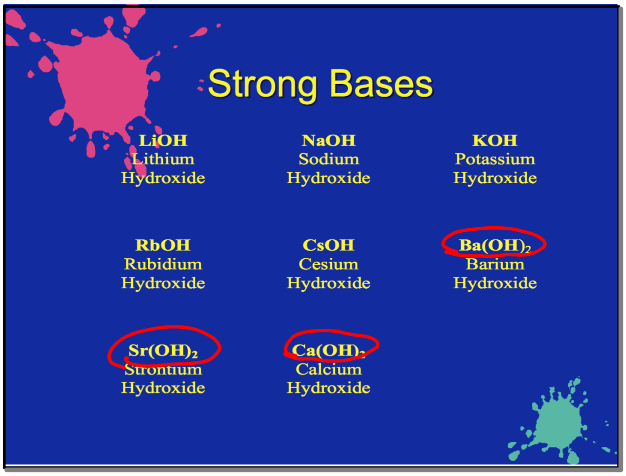


Bases

"Strong" and "weak" are used in the same sense for bases as for acids.

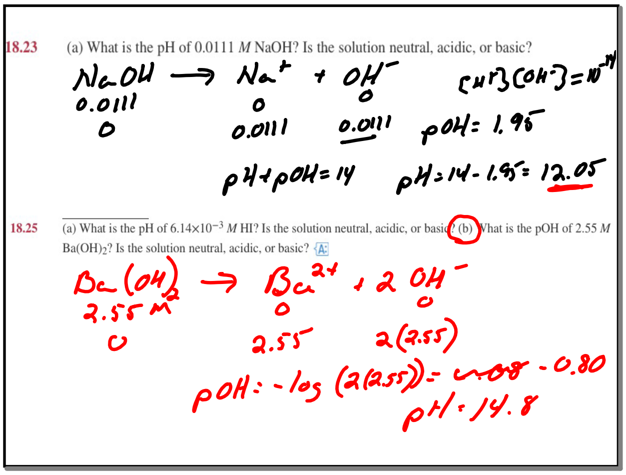
strong = complete dissociation (hydroxide ion supplied to solution)

$NaOH(s) \rightarrow Na^+(aq) + OH^-(aq)$



Strong Bases

LiOH Lithium Hydroxide	**NaOH** Sodium Hydroxide	**KOH** Potassium Hydroxide
RbOH Rubidium Hydroxide	**CsOH** Cesium Hydroxide	**$Ba(OH)_2$** Barium Hydroxide
$Sr(OH)_2$ Strontium Hydroxide	**$Ca(OH)_2$** Calcium Hydroxide	



18.23 (a) What is the pH of 0.0111 *M* NaOH? Is the solution neutral, acidic, or basic?

$$NaOH \rightarrow Na^+ + OH^- \qquad [H^+][OH^-]=10^{-14}$$

0.0111   0   0

0   0.0111   0.0111   pOH = 1.95

$pH + pOH = 14 \qquad pH = 14 - 1.95 = \underline{12.05}$

18.25 (a) What is the pH of 6.14×10^{-3} *M* HI? Is the solution neutral, acidic, or basic? (b) What is the pOH of 2.55 *M* $Ba(OH)_2$? Is the solution neutral, acidic, or basic? A:

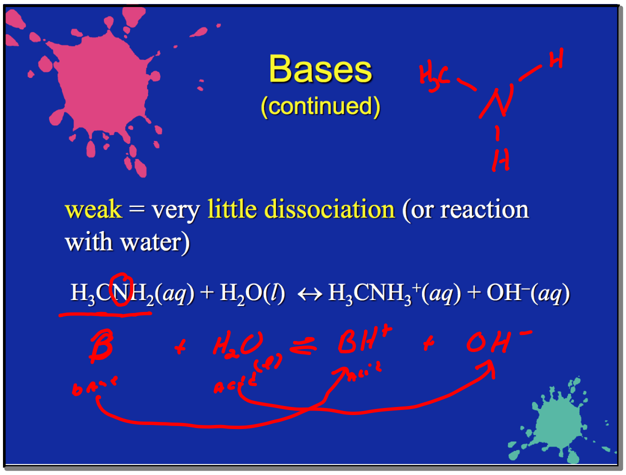
$$Ba(OH)_2 \rightarrow Ba^{2+} + 2\,OH^-$$

2.55 M   0   0

0   2.55   2(2.55)

$pOH = -\log(2(2.55)) =$ ~~-.08~~ -0.80

$pH = 14.8$



Bases

(continued)

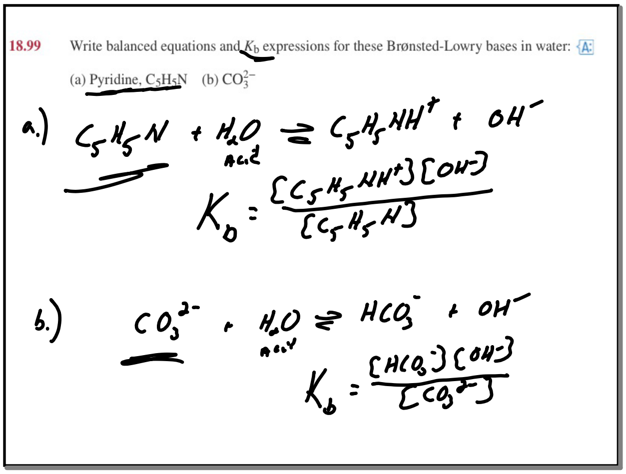
H3C — N — H, H

weak = very little dissociation (or reaction with water)

$H_3CNH_2(aq) + H_2O(l) \leftrightarrow H_3CNH_3^+(aq) + OH^-(aq)$

$$B + H_2O_{(l)} \rightleftharpoons BH^+ + OH^-$$

base   acid   acid



18.99 Write balanced equations and K_b expressions for these Brønsted-Lowry bases in water: A:

(a) Pyridine, C_5H_5N (b) CO_3^{2-}

a.) $C_5H_5N + H_2O \rightleftharpoons C_5H_5NH^+ + OH^-$

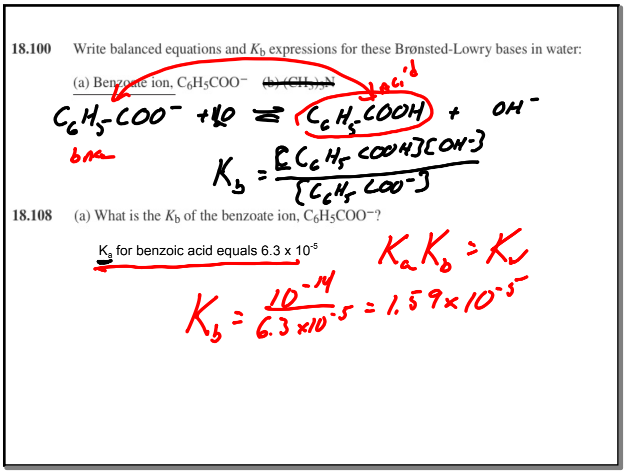
acid

$$K_b = \frac{[C_5H_5NH^+][OH^-]}{[C_5H_5N]}$$

b.) $CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$

acid

$$K_b = \frac{[HCO_3^-][OH^-]}{[CO_3^{2-}]}$$



18.100 Write balanced equations and K_b expressions for these Brønsted-Lowry bases in water:

(a) Benzoate ion, $C_6H_5COO^-$ ~~(b) $(CH_3)_3N$~~

$$C_6H_5\text{-}COO^- + H_2O \rightleftharpoons C_6H_5\text{-}COOH + OH^-$$

base   acid

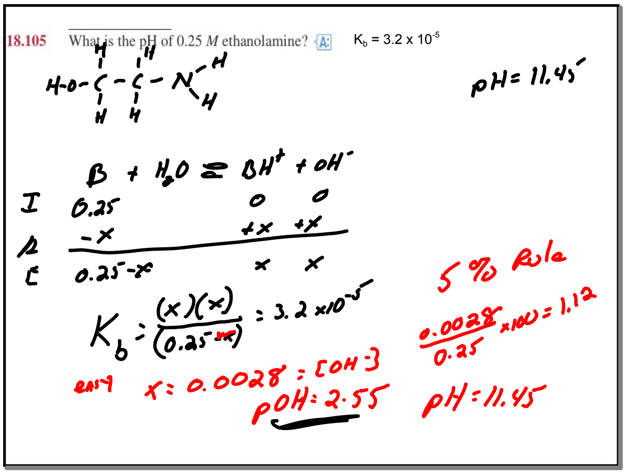
$$K_b = \frac{[C_6H_5COOH][OH^-]}{[C_6H_5COO^-]}$$

18.108 (a) What is the K_b of the benzoate ion, $C_6H_5COO^-$?

K_a for benzoic acid equals 6.3 x 10^{-5}

$$K_aK_b = K_w$$

$$K_b = \frac{10^{-14}}{6.3\times10^{-5}} = 1.59\times10^{-5}$$



18.105 What is the pH of 0.25 *M* ethanolamine? A: $K_b = 3.2 \times 10^{-5}$

pH= 11.45

$B + H_2O \rightleftharpoons BH^+ + OH^-$

I 0.25 0 0

Δ −x +x +x

E 0.25−x x x

$K_b = \frac{(x)(x)}{(0.25-\cancel{x})} = 3.2 \times 10^{-5}$

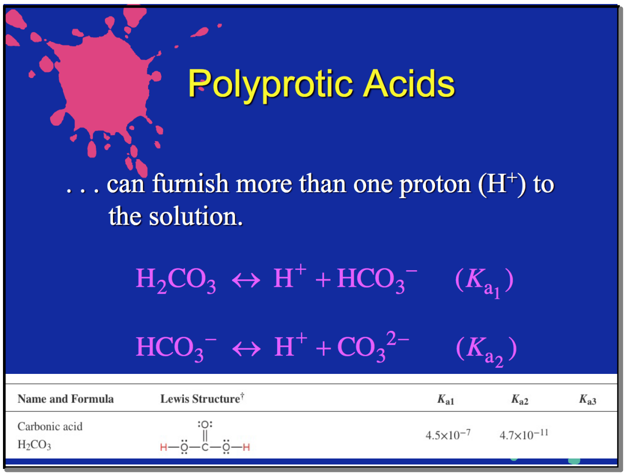
easy $x = 0.0028 = [OH^-]$

pOH = 2.55

5 % Rule

$\frac{0.0028}{0.25} \times 100 = 1.12$

pH = 11.45



Polyprotic Acids

. . . can furnish more than one proton (H^+) to the solution.

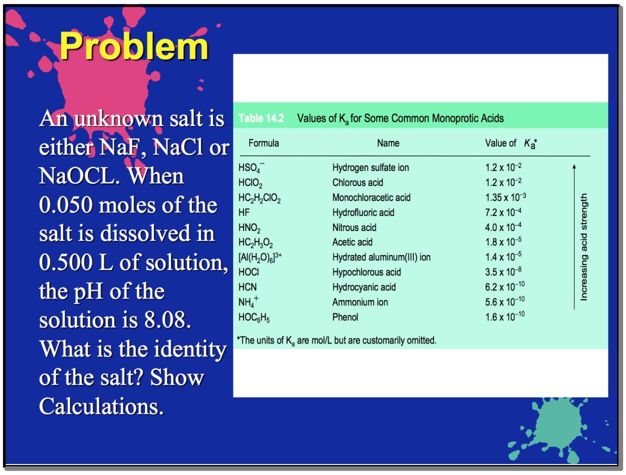
$$H_2CO_3 \leftrightarrow H^+ + HCO_3^- \quad (K_{a_1})$$

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-} \quad (K_{a_2})$$

Name and Formula	Lewis Structure†	K_{a1}	K_{a2}	K_{a3}
Carbonic acid H_2CO_3	H—Ö—C(=O)—Ö—H	4.5×10^{-7}	4.7×10^{-11}	

Acid-Base Properties of Salts

Cation	**Anion**	**Acidic or Basic**	**Example**
neutral	neutral	neutral	NaCl
neutral	conj base of weak acid	basic	NaF
conj acid of weak base	neutral	acidic	NH_4Cl
conj acid of weak base	conj base of weak acid	depends on K_a & K_b values	$Al_2(SO_4)_3$



Problem

An unknown salt is either NaF, NaCl or NaOCL. When 0.050 moles of the salt is dissolved in 0.500 L of solution, the pH of the solution is 8.08. What is the identity of the salt? Show Calculations.

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 mol/L but are customarily omitted.

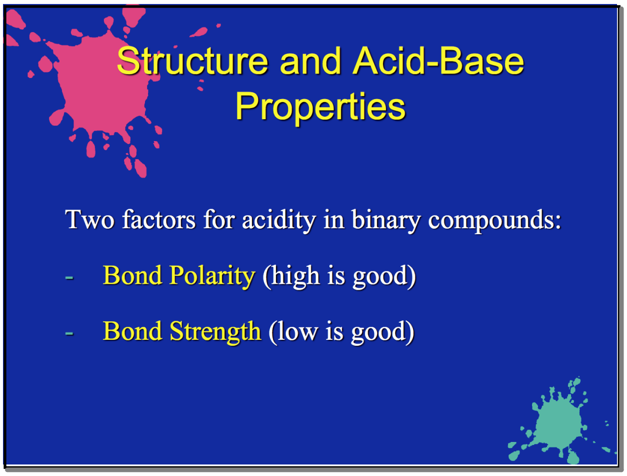
Problem

Sorbic acid (C_5H_7COOH) is a weak monoprotic acid with $K_a = 1.7 \times 10^{-5}$. Its salt (potassium sorbate) is added to cheese to inhibit the formation of mold.

What is the pH of a solution containing 9.50 g of potassium sorbate in 2.00 L of solution?

Problem

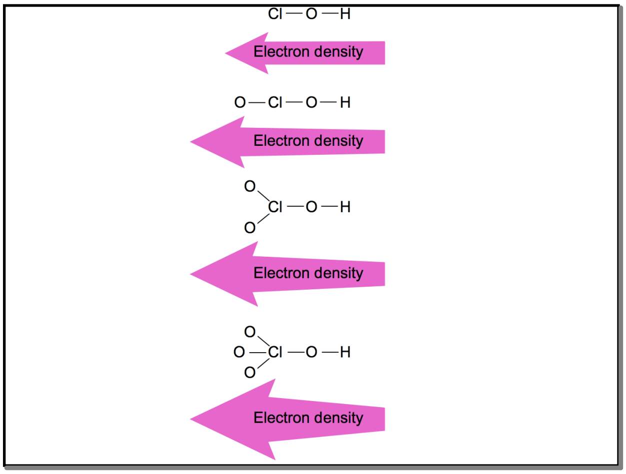
Trisodium phosphate (Na_3PO_4) is available in hardware stores as TSP and is used as a cleaning agent. The label on a box of TSP warns that the substance is very basic (caustic or alkaline). What is the pH of a solution containing 35.0 g of TSP in a liter of solution?

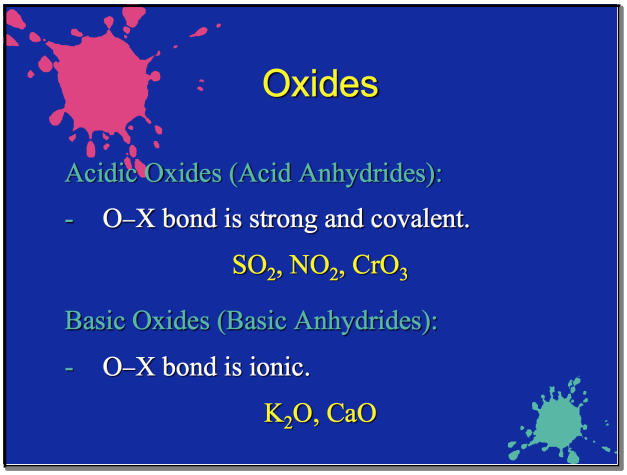


Structure and Acid-Base Properties

Two factors for acidity in binary compounds:

- Bond Polarity (high is good)
- Bond Strength (low is good)





Oxides

Acidic Oxides (Acid Anhydrides):

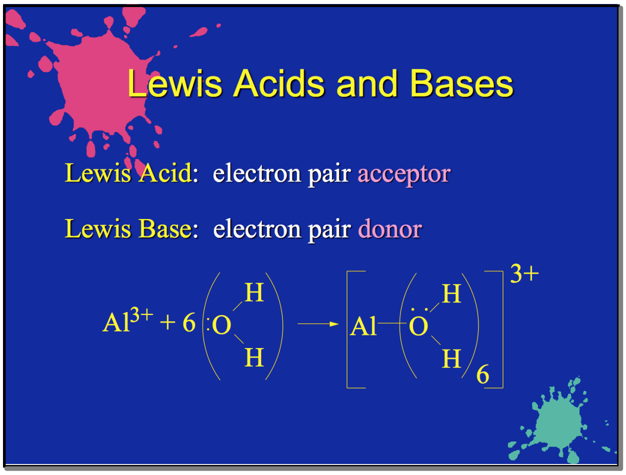
- O–X bond is strong and covalent.

SO_2, NO_2, CrO_3

Basic Oxides (Basic Anhydrides):

- O–X bond is ionic.

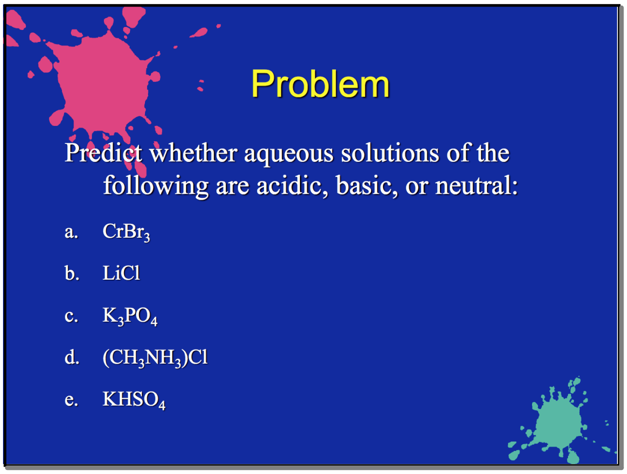
K_2O, CaO



Lewis Acids and Bases

Lewis Acid: electron pair acceptor

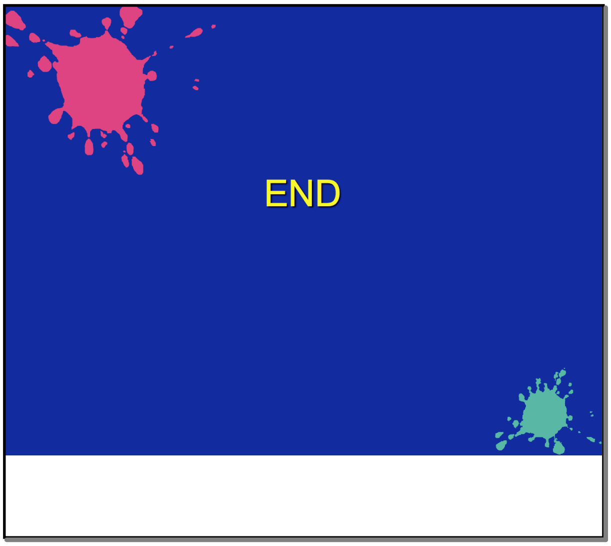
Lewis Base: electron pair donor



Problem

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

a. $CrBr_3$
b. LiCl
c. K_3PO_4
d. $(CH_3NH_3)Cl$
e. $KHSO_4$



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