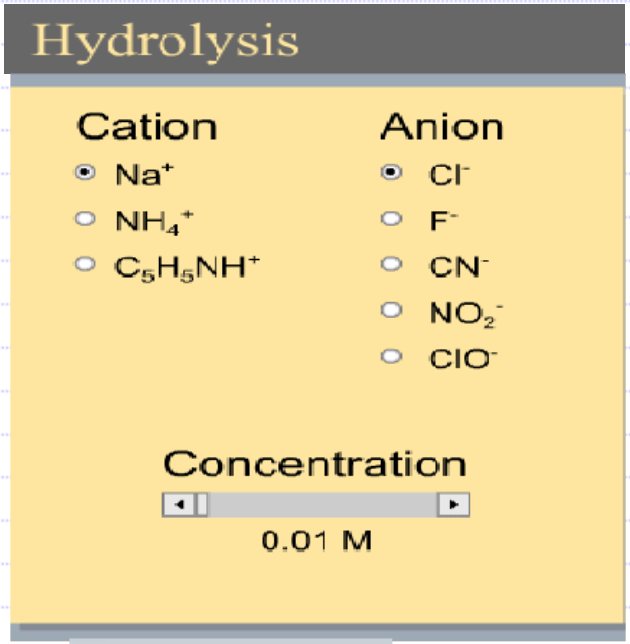
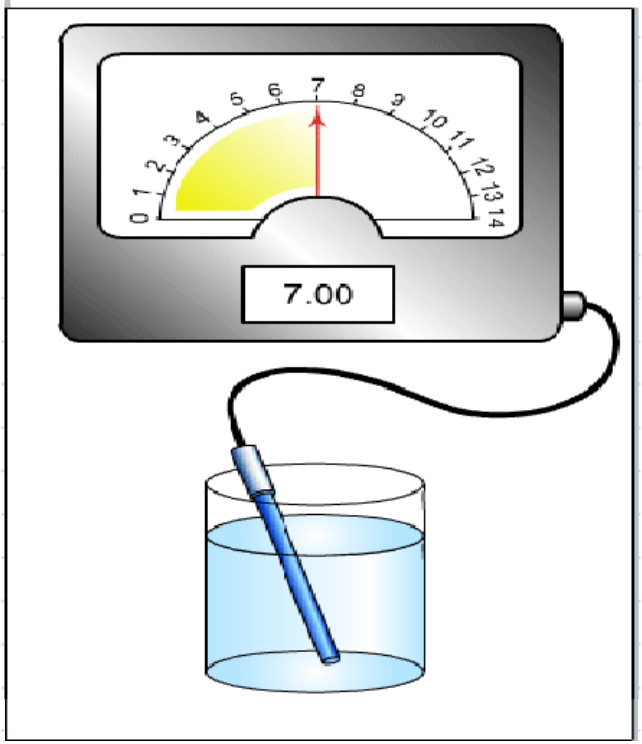
16.5 Acid-Base Properties of Salts

Hydrolysis – Neutral Cations and Anions



See Class Web Site



Neutral Cations

The 6 cations associated with the six strong bases:

Li^+	$LiOH$
Na^+	$NaOH$
K^+	KOH
Ca^{2+}	$Ca(OH)_2$
Ba^{2+}	$Ba(OH)_2$
Sr^{2+}	$Sr(OH)_2$

Non neutral cations are all potential weak acids ... ie NH_4^+

Neutral Anions

The 6 anions associated with the six strong acids.

Cl^-	HCl
Br^-	HBr
I^-	HI
NO_3^-	HNO_3
SO_4^{2-}	H_2SO_4
ClO_4^-	$HClO_4$

Non neutral anions are all potential weak bases ... ie F^-

16.5 Acid-Base Properties of Salts

Acid–Base Properties of Salts

An aqueous solution of **NaClO** is expected to be:

a) Acidic
b) Basic ✓
c) Neutral

$NaClO(aq) = Na^+ + ClO^-$

- Na^+ → Neutral cation
- ClO^- → Non neutral anion … weak base
  - $ClO^- + H_2O(l) \rightleftharpoons HClO(aq) + OH^-$

16.5 Acid-Base Properties of Salts

Acid–Base Properties of Salts

An aqueous solution of **ammonium nitrite** is expected to be:

Ka HNO_2 = 4.5×10^{-4} Kb NH_3 = 1.8×10^{-5}

a) Acidic ✓
b) Basic
c) Neutral

$NH_4NO_2(aq) \rightarrow NH_4^+ + NO_2^-$

NH_4^+ → Non neutral cation ... weak acid

NO_2^- → Non neutral anion ... weak base

$NH_4^+ + H_2O(l) \Leftrightarrow NH_3(aq) + H_3O^+$; $K_a = ?$

Acid — Conjugate Base

$K_a K_b = 1 \times 10^{-14}$ @ 25°C

$K_a = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$

$NO_2^- + H_2O(l) \Leftrightarrow HNO_2(aq) + OH^-$; $K_b = ?$

Base — Conjugate acid

$K_b K_a = 1 \times 10^{-14}$ @ 25°C

$K_b = \frac{1 \times 10^{-14}}{4.5 \times 10^{-4}} = 2.2 \times 10^{-11}$

K_a for NH_4^+ > K_b for NO_2^-

NH_4^+ wins hence solution acidic

16.5 Acid-Base Properties of Salts

Determining pH of a Salt Solution

What is the pH of an 0.432M aqueous solution of NaCN
Ka HCN = 4.0×10^{-10}.

$NaCN(aq) \rightarrow Na^+ + CN^-$

	CN^-	+	$H_2O(l)$	=	HCN	+	OH^-
I	0.432				0		0
C	-x				x		x
E	0.432 - x				x		x

CN^- (Weak base) $\xrightarrow{+H^+}$ HCN (its conjugate acid)

$K_a K_b = 1 \times 10^{-14}$ @ 25°C

$$K_b = \frac{1 \times 10^{-14}}{4.0 \times 10^{-10}} = 2.5 \times 10^{-5}$$

$[CN^-] > 100(2.5 \times 10^{-5})$
Thus $0.432 - x \approx 0.432$

$$K_b = \frac{[HCN][OH^-]}{[CN^-]}$$

$$2.5 \times 10^{-5} = \frac{x \cdot x}{0.432}$$

$$x^2 = 0.432(2.5 \times 10^{-5})$$

$$x = \sqrt{0.432(2.5 \times 10^{-5}}$$

$$= 3.29 \times 10^{-3} = [OH^-]$$

$$pOH = -\log_{10}(3.29 \times 10^{-3}) = 2.48$$

$pH + pOH = 14$ @ 25°C

$$pH = 14 - 2.48$$

$$= 11.52$$

17.1 Acid-Base Reactions

Types of Reactions

	Reaction	Example	pH at Eq	Extent
1	Strong acid + strong base	$HCl(aq) + NaOH(aq) \rightarrow H_2O(\ell) + NaCl(aq)$	7	100%
2	Strong acid + weak base	$HCl(aq) + NH_3(aq) \rightarrow NH_4Cl(aq)$	< 7	100%
3	Strong base + weak acid	$NaOH(aq) + HClO(aq) \rightarrow H_2O(\ell) + NaClO(aq)$	> 7	~100%
4	Weak acid + weak base	$HClO(aq) + NH_3(aq) \rightleftarrows NH_4ClO(aq)$	Depends on Ka Vs Kb	?

SA : Strong Acid. SB : Strong Base WA : Weak Acid WB : Weak Base

	Reaction	Salt Produced		pH
1	SA + SB	$NaCl(aq) = Na^+ + Cl^-$	Cation & Anion neutral	7
2.	SA + WB	$NH_4Cl(aq) = NH_4^+ + Cl^-$	NH_4^+ is a weak acidic cation. $NH_4^+ + H_2O(l) \Leftrightarrow NH_3(aq) + H_3O^+$	< 7
3.	WA + SB	$NaClO(aq) = Na^+ + ClO^-$	ClO^- is a weak basic anion. $ClO^- + H_2O(l) \Leftrightarrow HClO(aq) + OH^-$	> 7
4.	WA + WB	$NH_4ClO(aq) = NH_4^+ + ClO^-$	NH_4^+ is a weak acidic cation. $NH_4^+ + H_2O(l) \Leftrightarrow NH_3(aq) + H_3O^+$ ClO^- is a weak basic anion $ClO^- + H_2O(l) \Leftrightarrow HClO(aq) + OH^-$	?*

* pH depends on which K is larger, Ka or Kb

17.1 Acid-Base Reactions

Strong Acid/Strong Base Reactions

$$HCl(aq) + NaOH(aq) \overset{?}{=} NaCl(aq) + H_2O(l)$$

Net Ionic Equation:

$$HCl(aq) + NaOH(aq) = NaCl(aq) + H_2O(l)$$

$$H_3O^+ + Cl^- + Na^+ + OH^- = Na^+ + Cl^- + H_2O(l) + H_2O(l)^*$$

$$H_3O^+ + OH^- = 2\,H_2O(l)$$

* As we wrote H_3O^+ on reactant side, had to add $H_2O(l)$ to product side so as to keep the chemical equation balanced.

$$H_2O(l) + H_2O(l) \Leftrightarrow H_3O^+ + OH^- \;;\; K = K_w$$

$$H_3O^+ + OH^- = 2\,H_2O(l) \;;\; K = \frac{1}{K_w}$$

$$= \frac{1}{1 \times 10^{-14}}$$

$$= 1 \times 10^{14}$$

$K \ggg 1$: Very product favored, goes 100%. Thus = rather than $\Leftrightarrow$

17.1 Acid-Base Reactions

Strong Acid/Weak Base Reactions

$$HCl(aq) + NH_3(aq) \overset{?}{=} NH_4Cl(aq)$$

NET IONIC EQUATION:

$HCl(aq) + NH_3(aq) = NH_4Cl(aq)$

$H_3O^+ + Cl^- + NH_3(aq) = NH_4^+ + Cl^- + H_2O(l)$ *

$H_3O^+ + NH_3(aq) = NH_4^+ + H_2O(l)$

* See previous slide as to why we had to add $H_2O(l)$ to the product side.

$NH_4^+ + H_2O(l) \Leftrightarrow NH_3(aq) + H_3O^+ \quad K_a = 5.6 \times 10^{-10}$

$H_3O^+ + NH_3(aq) \Leftrightarrow NH_4^+ + H_2O(l) \quad K = \frac{1}{5.6 \times 10^{-10}} = 1.8 \times 10^9$

$K >>> 1$, very product favored, essentially 100%

17.1 Acid-Base Reactions

Weak Acid/Weak Base

$$HClO(aq) + NH_3(aq) \overset{?}{\Leftrightarrow} NH_4ClO(aq)$$

Net Ionic Equation:

$$HClO(aq) + NH_3(aq) \Leftrightarrow NH_4^+ + ClO^-$$

$HClO(aq) + H_2O(l) \Leftrightarrow H_3O^+ + ClO^-$	$K = 3.5 \times 10^{-8}$
$NH_3(aq) + H_2O(l) \Leftrightarrow NH_4^+ + OH^-$	$K = 1.8 \times 10^{-5}$
$HClO(aq) + NH_3(aq) + 2H_2O(l) \Leftrightarrow NH_4^+ + ClO^- + H_3O^+ + OH^-$	$K = 6.3 \times 10^{-13}$
$H_3O^+ + OH^- \Leftrightarrow 2\,H_2O(l)$	$K^* = 1.0 \times 10^{14}$
$HClO(aq) + NH_3(aq) \Leftrightarrow NH_4^+ + ClO^-$	$K = 63$

$K^* = 1/Kw$

$K \approx 1$: Significant quantities of reactants and products present at equilibrium.

Curious about the pH at the equivalance point?

Hydrolsis of NH_4ClO

$$NH_4ClO(aq) = NH_4^+ + ClO^-$$

a) NH_4^+ is an acidic cation.

b) ClO^- is a basic anion.

a) $NH_4^+ + H_2O(l) \Leftrightarrow NH_3(aq) + H_3O^+ \quad K_a = 5.6 \times 10^{-10}$

b) $ClO^- + H_2O(l) \Leftrightarrow HClO(aq) + OH^- \quad K_b = 2.9 \times 10^{-7}$

$K_b > K_a$

$pH > 7.$