## Acids and Bases

Paper- CC-V

Unit-I

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## MODELS OF ACIDS AND BASES

- ARRHENIUS: ACIDS PRODUCE H<sup>+</sup> IONS IN SOLUTION,
   BASES PRODUCE OH<sup>-</sup> IONS.
- BRØNSTED-LOWRY: ACIDS ARE PROTON (H+)
   DONORS, BASES ARE PROTON ACCEPTORS.

$$HCL + H_2O \rightleftharpoons CL^- + H_3O^+$$

ACID BASE

## **ACID IN WATER**

$$HA(AQ)$$
 +  $H_2O(L)$   $H_3O^+(AQ)$  +  $A^-(AQ)$ 
+  $A^-(AQ)$ 

Acid Base Conjugate acid Conjugate base

- CONJUGATE BASE IS EVERYTHING THAT REMAINS OF THE ACID MOLECULE AFTER A PROTON IS LOST.
- CONJUGATE ACID IS FORMED WHEN THE PROTON IS TRANSFERRED TO THE BASE.



## **ACID STRENGTH**

#### STRONG ACID:

- IONIZATION EQUILIBRIUM LIES FAR TO THE RIGHT.
- YIELDS A WEAK CONJUGATE BASE.

#### WEAK ACID:

- IONIZATION EQUILIBRIUM LIES FAR TO THE LEFT.
- WEAKER THE ACID, STRONGER ITS CONJUGATE BASE.

# Acid Strength HA $H^+$ HB H<sup>+</sup> B<sup>-</sup> $H^+A^-$ HA HB Weak acid Strong acid © Cengage Learning. All Rights Reserved.

## VARIOUS WAYS TO DESCRIBE ACID STRENGTH

Property	Strong Acid	Weak Acid
<ul> <li>K<sub>a</sub> value</li> <li>Position of the dissociation</li> <li>(ionization) equilibrium</li> </ul>	$K_a$ is large Far to the right	$K_a$ is small Far to the left
Equilibrium concentration of [H <sup>+</sup> ] compared with original concentration of HA	$[H^+] \approx [HA]_0$	$[H^+] \ll [HA]_0$
Strength of conjugate base compared with that of water	A <sup>–</sup> much weaker base than H <sub>2</sub> O	A <sup>−</sup> much stronger base than H <sub>2</sub> O

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#### WATER AS AN ACID AND A BASE

- WATER IS AMPHOTERIC:
  - BEHAVES EITHER AS AN ACID OR AS A BASE.
- AT 25° C:

$$K_W = [H^+][OH^-] = 1.0 \times 10^{-14}$$

• NO MATTER WHAT THE SOLUTION CONTAINS, THE PRODUCT OF [H $^+$ ] AND [OH $^-$ ] MUST ALWAYS EQUAL 1.0  $\times$  10 $^{-14}$  AT 25 $^\circ$  C.

## THREE POSSIBLE SITUATIONS

- $[H^+] = [OH^-]$ ; NEUTRAL SOLUTION
- [H<sup>+</sup>] > [OH<sup>-</sup>]; ACIDIC SOLUTION
- $[OH^-] > [H^+]$ ; BASIC SOLUTION



### **SELF-IONIZATION OF WATER**

$$HA(AQ) + H2O(L)$$
  $H3O+(AQ) + A-(AQ)$ 

ACID BASE

WHAT IS THE EQUILIBRIUM CONSTANT

EXPRESSION FOR AN ACID ACTING IN WATER?

IF THE EQUILIBRIUM LIES TO THE RIGHT, THE VALUE FOR  $K_A$  IS \_\_\_\_\_\_.

LARGE (OR >1)

IF THE EQUILIBRIUM LIES TO THE LEFT, THE VALUE FOR  $K_A$  IS \_\_\_\_\_\_.

SMALL (OR <1)

$$HA(AQ) + H_2O(L) \longrightarrow H_3O^+(AQ) + A^-(AQ)$$

IF WATER IS A BETTER BASE THAN A-, DO PRODUCTS OR REACTANTS DOMINATE AT EQUILIBRIUM?

DOES THIS MEAN HA IS A STRONG OR WEAK ACID?

IS THE VALUE FOR  $K_A$  GREATER OR LESS THAN 1?

CONSIDER A 1.0 M SOLUTION OF HCL.

ORDER THE FOLLOWING FROM STRONGEST TO WEAKEST BASE AND EXPLAIN:

 $H_2O(L)$ 

A-(AQ) (FROM WEAK ACID HA)

 $CL^{-}(AQ)$ 

- HOW GOOD IS CL-(AQ) AS A BASE?
- IS A-(AQ) A GOOD BASE?

THE BASES FROM STRONGEST TO WEAKEST ARE:

A-, H<sub>2</sub>O, CL-

#### CONSIDER A SOLUTION OF NAA WHERE A- IS THE ANION FROM WEAK ACID HA:

$$A^{-}(AQ) + H_{2}O(L) \longrightarrow HA(AQ) + OH^{-}(AQ)$$

BASE ACID CONJUGATE CONJUGATE

ACID BASE

a) WHICH WAY WILL EQUILIBRIUM LIE?

LEFT

CONSIDER A SOLUTION OF NAA WHERE A- IS THE ANION FROM WEAK ACID HA:

$$A^{-}(AQ) + H_{2}O(L) \Longrightarrow HA(AQ) + OH^{-}(AQ)$$

BASE ACID CONJUGATE CONJUGATE

ACID BASE

B) IS THE VALUE FOR  $K_B$  GREATER THAN OR LESS THAN 1? LESS THAN 1

#### CONSIDER A SOLUTION OF NAA WHERE A- IS THE ANION FROM WEAK ACID HA:

$$A^{-}(AQ) + H_{2}O(L) \longrightarrow HA(AQ) + OH^{-}(AQ)$$

BASE ACID CONJUGATE CONJUGATE

ACID BASE

C) DOES THIS MEAN A<sup>-</sup> IS A STRONG OR WEAK BASE?

WEAK BASE

ACETIC ACID (HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>) AND HCN ARE BOTH WEAK ACIDS. ACETIC ACID IS A STRONGER ACID THAN HCN.

ARRANGE THESE BASES FROM WEAKEST TO STRONGEST AND EXPLAIN YOUR ANSWER:

 $H_2O$   $CL^ CN^ C_2H_3O_2^-$ 

• 
$$H_2O(L) + H_2O(L)$$
  $H_3O^{+}(AO) + OH^{-}(AQ)$ 

ACID BASE CONJUGATE CONJUGATE

ACID BASE

• AT 25° C,  $K_W = 1.0 \times 10^{-14}$ 

THE BASES FROM WEAKEST TO STRONGEST ARE:

 $CL^{-}$ ,  $H_2O$ ,  $C_2H_3O_2^{-}$ ,  $CN^{-}$ 

#### DISCUSS WHETHER THE VALUE OF K FOR THE REACTION:

$$HCN(AQ) + F^{-}(AQ) \rightleftharpoons CN^{-}(AQ) + HF(AQ)$$

<1

=1

 $(K_A \text{ FOR HCN IS } 6.2 \times 10^{-10}; K_A \text{ FOR HF IS } 7.2 \times 10^{-4}.)$ 

**EXPLAIN YOUR ANSWER.** 

#### CALCULATE THE VALUE FOR K FOR THE REACTION:

$$HCN(AQ) + F^{-}(AQ) \longrightarrow CN^{-}(AQ) + HF(AQ)$$

 $(K_A \text{ FOR HCN IS } 6.2 \times 10^{-10}; K_A \text{ FOR HF IS } 7.2 \times 10^{-4}.)$ 

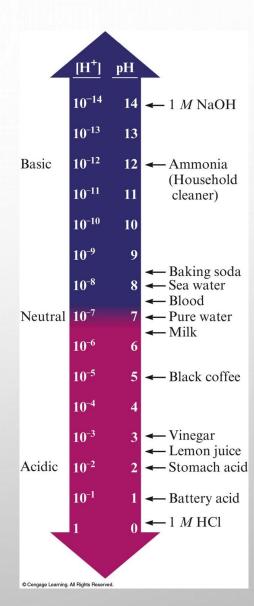
$$K = 8.6 \times 10^{-7}$$

- PH = -LOG[H<sup>+</sup>]
- PH CHANGES BY 1 FOR EVERY POWER OF 10 CHANGE IN [H<sup>+</sup>].
- A COMPACT WAY TO REPRESENT SOLUTION ACIDITY.
- PH DECREASES AS [H+] INCREASES.
- SIGNIFICANT FIGURES:
  - THE NUMBER OF DECIMAL PLACES IN THE LOG IS EQUAL TO THE NUMBER OF SIGNIFICANT FIGURES IN THE ORIGINAL NUMBER.

## PH RANGE

- PH = 7; *NEUTRAL*
- PH > 7; *BASIC* 
  - HIGHER THE PH, MORE BASIC.
- PH < 7; *ACIDIC* 
  - LOWER THE PH, MORE ACIDIC.

# THE PH SCALE AND PH VALUES OF SOME COMMON SUBSTANCES



#### **EXERCISE!**

#### CALCULATE THE PH FOR EACH OF THE FOLLOWING SOLUTIONS.

a) 
$$1.0 \times 10^{-4} M H^{+}$$

$$PH = 4.00$$

B) 0.040 M OH-

PH = 12.60

#### **EXERCISE!**

## THE PH OF A SOLUTION IS 5.85. WHAT IS THE [H+] FOR THIS SOLUTION?

$$[H^+] = 1.4 \times 10^{-6} M$$

## PH AND POH

#### • RECALL:

$$K_{W} = [H^{+}][OH^{-}]$$

$$-LOG K_W = -LOG[H^+] - LOG[OH^-]$$

$$PK_W = PH + POH$$

$$14.00 = PH + POH$$

#### **EXERCISE!**

#### CALCULATE THE POH FOR EACH OF THE FOLLOWING SOLUTIONS.

a)  $1.0 \times 10^{-4} M H^{+}$ 

POH = 10.00

B) 0.040 M OH-

POH = 1.40

#### **EXERCISE!**

## THE PH OF A SOLUTION IS 5.85. WHAT IS THE [OH-] FOR THIS SOLUTION?

 $[OH^{-}] = 7.1 \times 10^{-9} M$ 

#### THINKING ABOUT ACID—BASE PROBLEMS

- WHAT ARE THE MAJOR SPECIES IN SOLUTION?
- WHAT IS THE DOMINANT REACTION THAT WILL TAKE PLACE?
  - IS IT AN EQUILIBRIUM REACTION OR A REACTION THAT WILL GO ESSENTIALLY TO COMPLETION?
  - REACT ALL MAJOR SPECIES UNTIL YOU ARE LEFT WITH AN EQUILIBRIUM REACTION.
- SOLVE FOR THE PH IF NEEDED.

CONSIDER AN AQUEOUS SOLUTION OF 2.0  $\times$  10<sup>-3</sup> M HCL.

WHAT ARE THE MAJOR SPECIES IN SOLUTION?

WHAT IS THE PH?

PH = 2.70

CALCULATE THE PH OF A 1.5  $\times$  10<sup>-11</sup> M SOLUTION OF HCL.

PH = 7.00

CALCULATE THE PH OF A 1.5  $\times$  10<sup>-2</sup> M SOLUTION OF HNO<sub>3</sub>.

• WHEN HNO<sub>3</sub> IS ADDED TO WATER, A REACTION TAKES PLACE IMMEDIATELY:

$$HNO_3 + H_2O \longrightarrow H_3O^+ + NO_3^-$$

• WHY IS THIS REACTION NOT LIKELY?

$$NO_3^-(AQ) + H_2O(L)$$
 HNO<sub>3</sub>(AQ) + OH<sup>-</sup>(AQ)

- WHAT REACTION CONTROLS THE PH?
- $H_2O(L) + H_2O(L) \longrightarrow H_3O^+(AQ) + OH^-(AQ)$
- IN AQUEOUS SOLUTIONS, THIS REACTION IS ALWAYS TAKING PLACE.
- BUT IS WATER THE MAJOR CONTRIBUTOR OF H+ (H<sub>3</sub>O+)?

PH = 1.82

## SOLVING WEAK ACID EQUILIBRIUM PROBLEMS

- 1. LIST THE MAJOR SPECIES IN THE SOLUTION.
- 2. CHOOSE THE SPECIES THAT CAN PRODUCE H<sup>+</sup>, AND WRITE BALANCED EQUATIONS FOR THE REACTIONS PRODUCING H<sup>+</sup>.
- 3. USING THE VALUES OF THE EQUILIBRIUM CONSTANTS FOR THE REACTIONS YOU HAVE WRITTEN, DECIDE WHICH EQUILIBRIUM WILL DOMINATE IN PRODUCING H<sup>+</sup>.
- 4. WRITE THE EQUILIBRIUM EXPRESSION FOR THE DOMINANT EQUILIBRIUM.

# SOLVING WEAK ACID EQUILIBRIUM PROBLEMS

- 5. LIST THE INITIAL CONCENTRATIONS OF THE SPECIES PARTICIPATING IN THE DOMINANT EQUILIBRIUM.
- 6. DEFINE THE CHANGE NEEDED TO ACHIEVE EQUILIBRIUM; THAT IS, DEFINE X.
- 7. WRITE THE EQUILIBRIUM CONCENTRATIONS IN TERMS OF X.
- 8. SUBSTITUTE THE EQUILIBRIUM CONCENTRATIONS INTO THE EQUILIBRIUM EXPRESSION.

# SOLVING WEAK ACID EQUILIBRIUM PROBLEMS

- 9. SOLVE FOR X THE "EASY" WAY, THAT IS, BY ASSUMING THAT  $[HA]_0 X$  ABOUT EQUALS  $[HA]_0$ .
- 10.USE THE 5% RULE TO VERIFY WHETHER THE APPROXIMATION IS VALID.
- 11.CALCULATE [H<sup>+</sup>] AND PH.

CONSIDER A 0.80 M AQUEOUS SOLUTION OF THE WEAK ACID HCN ( $K_A = 6.2 \times 10^{-10}$ ).

WHAT ARE THE MAJOR SPECIES IN SOLUTION?

HCN, H<sub>2</sub>O

# LET'S THINK ABOUT IT...

WHY AREN' T H+ OR CN- MAJOR SPECIES?

### **CONSIDER THIS**

$$HCN(AQ) + H_2O(L) \longrightarrow H_3O^+(AQ) + CN^-(AQ)$$

$$K_A = 6.2 \times 10^{-10}$$

$$H_2O(L) + H_2O(L) \qquad H_3O^+(AQ) + OH^-(AQ)$$

$$K_W = 1.0 \times 10^{-14}$$

WHICH REACTION CONTROLS THE PH? EXPLAIN.

## CALCULATE THE PH OF A 0.50 M AQUEOUS SOLUTION OF THE WEAK ACID HF.

$$(K_A = 7.2 \times 10^{-4})$$

# LET'S THINK ABOUT IT...

WHAT ARE THE MAJOR SPECIES IN SOLUTION?

HF, H<sub>2</sub>O

WHY AREN' T H+ AND F- MAJOR SPECIES?

# LET'S THINK ABOUT IT...

WHAT ARE THE POSSIBILITIES FOR THE DOMINANT REACTION?

$$HF(AQ) + H_2O(L) \qquad \qquad H_3O^+(AQ) + F^-(AQ)$$

$$K_A = 7.2 \times 10^{-4}$$

$$H_2O(L) + H_2O(L) \qquad \qquad H_3O^+(AQ) + OH^-(AQ)$$

$$K_W = 1.0 \times 10^{-14}$$

WHICH REACTION CONTROLS THE PH? WHY?

## STEPS TOWARD SOLVING FOR PH

$$HF(aq) + H_2O \qquad \qquad H_3O^+(aq) + F^-(aq)$$
Initial 0.50 M  $\sim 0 \sim 0$ 
Change  $-x + x + x$ 
Equilibrium 0.50-x x x

$$K_{\rm A} = 7.2 \times 10^{-4}$$

$$PH = 1.72$$

# PERCENT DISSOCIATION (IONIZATION)

Percent dissociation = 
$$\frac{\text{amount dissociated (mol/L)}}{\text{initial concentration (mol/L)}} \times 100\%$$

 FOR A GIVEN WEAK ACID, THE PERCENT DISSOCIATION INCREASES AS THE ACID BECOMES MORE DILUTE.

A SOLUTION OF 8.00 M FORMIC ACID (HCHO<sub>2</sub>) IS 0.47% IONIZED IN WATER.

CALCULATE THE  $K_A$  VALUE FOR FORMIC ACID.

$$K_A = 1.8 \times 10^{-4}$$

CALCULATE THE PH OF AN 8.00 M SOLUTION OF FORMIC ACID. USE THE DATA FROM THE PREVIOUS SLIDE TO HELP YOU SOLVE THIS PROBLEM.

PH = 1.42

THE VALUE OF  $K_{\Delta}$  FOR A 4.00 M FORMIC ACID SOLUTION SHOULD BE:

**HIGHER THAN** 

LOWER THAN THE SAME AS

THE VALUE OF  $K_{\Delta}$  OF AN 8.00 M FORMIC ACID SOLUTION.

#### **EXPLAIN.**

THE PERCENT IONIZATION OF A 4.00 M FORMIC ACID SOLUTION SHOULD BE:

HIGHER THAN LOWER THAN THE SAME AS

THE PERCENT IONIZATION OF AN 8.00 M FORMIC ACID SOLUTION.

#### **EXPLAIN.**

THE PH OF A 4.00 M FORMIC ACID SOLUTION SHOULD BE:

**HIGHER THAN** 

LOWER THAN THE SAME AS

THE PH OF AN 8.00 M FORMIC ACID SOLUTION.

#### EXPLAIN.

# CALCULATE THE PERCENT IONIZATION OF A 4.00 *M* FORMIC ACID SOLUTION IN WATER.

% IONIZATION = 0.67%

CALCULATE THE PH OF A 4.00 *M* SOLUTION OF FORMIC ACID.

PH = 1.57

- ARRHENIUS: BASES PRODUCE OH<sup>-</sup> IONS.
- BRØNSTED-LOWRY: BASES ARE PROTON ACCEPTORS.
- IN A BASIC SOLUTION AT 25° C, PH > 7.
- IONIC COMPOUNDS CONTAINING OH ARE GENERALLY CONSIDERED STRONG BASES.
  - LIOH, NAOH, KOH, CA(OH)<sub>2</sub>
- POH = -LOG[OH<sup>-</sup>]
- PH = 14.00 POH

CALCULATE THE PH OF A 1.0  $\times$  10<sup>-3</sup> M SOLUTION OF SODIUM HYDROXIDE.

PH = 11.00

CALCULATE THE PH OF A 1.0  $\times$  10<sup>-3</sup> M SOLUTION OF CALCIUM HYDROXIDE.

PH = 11.30

• EQUILIBRIUM EXPRESSION FOR WEAK BASES USES  $K_{\rm B}$ .

$$CN^{-}(AQ) + H_{2}O(L) \rightleftharpoons HCN(AQ) + OH^{-}(AQ)$$

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

 PH CALCULATIONS FOR SOLUTIONS OF WEAK BASES ARE VERY SIMILAR TO THOSE FOR WEAK ACIDS.

• 
$$K_W = [H^+][OH^-] = 1.0 \times 10^{-14}$$

- POH = -LOG[OH<sup>-</sup>]
- PH = 14.00 POH

## CALCULATE THE PH OF A 2.0 M SOLUTION OF AMMONIA (NH<sub>3</sub>).

$$(K_{\rm B} = 1.8 \times 10^{-5})$$

$$PH = 11.78$$

# Polyprotic acids

- ACIDS THAT CAN FURNISH MORE THAN ONE PROTON.
- ALWAYS DISSOCIATES IN A STEPWISE MANNER, ONE PROTON AT A TIME.
- THE CONJUGATE BASE OF THE FIRST DISSOCIATION EQUILIBRIUM BECOMES THE ACID IN THE SECOND STEP.
- FOR A TYPICAL WEAK POLYPROTIC ACID:

$$K_{A1} > K_{A2} > K_{A3}$$

 FOR A TYPICAL POLYPROTIC ACID IN WATER, ONLY THE FIRST DISSOCIATION STEP IS IMPORTANT TO PH.

# CALCULATE THE PH OF A 1.00 M SOLUTION OF $H_3PO_4$ .

$$K_{A1} = 7.5 \times 10^{-3}$$

$$K_{A2} = 6.2 \times 10^{-8}$$

$$K_{A3} = 4.8 \times 10^{-13}$$

PH = 1.08

# CALCULATE THE EQUILIBRIUM CONCENTRATION OF $PO_4^{3-}$ IN A 1.00 M SOLUTION OF $H_3PO_4$ .

$$K_{A1} = 7.5 \times 10^{-3}$$

$$K_{A2} = 6.2 \times 10^{-8}$$

$$K_{A3} = 4.8 \times 10^{-13}$$

$$[PO_4^{3-}] = 3.6 \times 10^{-19} M$$

- IONIC COMPOUNDS.
- WHEN DISSOLVED IN WATER, BREAK UP INTO ITS IONS (WHICH CAN BEHAVE AS ACIDS OR BASES).

- THE SALT OF A STRONG ACID AND A STRONG BASE GIVES A NEUTRAL SOLUTION.
  - KCL, NANO<sub>3</sub>

- A BASIC SOLUTION IS FORMED IF THE ANION OF THE SALT IS THE CONJUGATE BASE OF A WEAK ACID.
  - NAF, KC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>
  - $K_{W} = K_{A} \times K_{B}$ 
    - $\triangleright$  USE  $K_{\rm B}$  WHEN STARTING WITH BASE.

- AN ACIDIC SOLUTION IS FORMED IF THE CATION OF THE SALT IS THE CONJUGATE ACID OF A WEAK BASE.
  - NH<sub>4</sub>CL
  - $K_{W} = K_{A} \times K_{B}$ 
    - $\triangleright$  USE  $K_A$  WHEN STARTING WITH ACID.

## Acid base properties of salt

		Acidic	
Cation	Anion	or Basic	Example
neutral	neutral	neutral	NaCl
neutral	conjugate base of weak acid	basic	NaF
conjugate acid of weak base	neutral	acidic	NH <sub>4</sub> CI
conjugate acid of weak base	conjugate base of weak acid	depends on $K_a$ & $K_b$ values	$Al_2(SO_4)_3$

## QUALITATIVE PREDICTION OF PH OF SALT SOLUTIONS (FROM WEAK PARENTS)

Qualitative Prediction of pH for Solutions of Salts for Which Both Cation and Anion Have Acidic or Basic Properties

$$K_a > K_b$$
 pH < 7 (acidic)  
 $K_b > K_a$  pH > 7 (basic)  
 $K_a = K_b$  pH = 7 (neutral)

$$HC_2H_3O_2$$
  $K_A = 1.8 \times 10^{-5}$ 

HCN 
$$K_A = 6.2 \times 10^{-10}$$

CALCULATE THE K<sub>B</sub> VALUES FOR: C<sub>2</sub>H<sub>3</sub>O<sub>2</sub><sup>-</sup> AND CN<sup>-</sup>

$$K_{\rm B} (C_2 H_3 O_2^{-}) = 5.6 \times 10^{-10}$$

$$K_{\rm B}$$
 (CN<sup>-</sup>) = 1.6 × 10<sup>-5</sup>

ARRANGE THE FOLLOWING 1.0 M SOLUTIONS FROM LOWEST TO HIGHEST PH.

HBR NAOH NH<sub>4</sub>CL

NACN NH<sub>3</sub> HCN

NACL HF

JUSTIFY YOUR ANSWER.

HBR, HF, HCN, NH<sub>4</sub>CL, NACL, NACN, NH<sub>3</sub>, NAOH

CONSIDER A 0.30 M SOLUTION OF NAF.

THE  $K_A$  FOR HF IS 7.2 × 10<sup>-4</sup>.

WHAT ARE THE MAJOR SPECIES?

NA<sup>+</sup>, F<sup>-</sup>, H<sub>2</sub>O

# LET'S THINK ABOUT IT...

- WHY ISN' T NAF CONSIDERED A MAJOR SPECIES?
- WHAT ARE THE POSSIBILITIES FOR THE DOMINANT REACTIONS?

#### THE POSSIBILITIES FOR THE DOMINANT REACTIONS ARE:

1. 
$$F^{-}(AQ) + H_{2}O(L) \rightleftharpoons HF(AQ) + OH^{-}(AQ)$$

2. 
$$H_2O(L) + H_2O(L) \implies H_3O^+(AQ) + OH^-(AQ)$$

3. 
$$NA^+(AQ) + H_2O(L) \longrightarrow NAOH + H^+(AQ)$$

4. 
$$NA^+(AQ) + F^-(AQ) \rightleftharpoons NAF$$

HOW DO WE DECIDE WHICH REACTION CONTROLS THE PH?

$$F^-(AQ) + H_2O(L)$$
  $HF(AQ) + OH^-(AQ)$ 

$$H_2O(L) + H_2O(L)$$
  $H_3O^+(AQ) + OH^-(AQ)$ 

DETERMINE THE EQUILIBRIUM CONSTANT FOR EACH REACTION.

#### **EXERCISE!**

# CALCULATE THE PH OF A 0.75 M AQUEOUS SOLUTION OF NACN. $K_A$ FOR HCN IS 6.2 $\times$ 10<sup>-10</sup>.

WHAT ARE THE MAJOR SPECIES IN SOLUTION?

NA<sup>+</sup>, CN<sup>-</sup>, H<sub>2</sub>O

WHY ISN'T NACN CONSIDERED A MAJOR SPECIES?

- WHAT ARE ALL POSSIBILITIES FOR THE DOMINANT REACTION?
- THE POSSIBILITIES FOR THE DOMINANT REACTION ARE:
  - 1.  $CN^-(AQ) + H_2O(L) \longrightarrow HCN(AQ) + OH^-(AQ)$
  - 2.  $H_2O(L) + H_2O(L) \longrightarrow H_3O^+(AQ) + OH^-(AQ)$
  - 3.  $NA^+(AQ) + H_2O(L) \longrightarrow NAOH + H^+(AQ)$
  - 4.  $NA^+(AQ) + CN^-(AQ) \longrightarrow NACN$
- WHICH OF THESE REACTIONS REALLY OCCUR?

HOW DO WE DECIDE WHICH REACTION CONTROLS THE PH?

$$CN^{-}(AQ) + H_2O(L) \longrightarrow HCN(AQ) + OH^{-}(AQ)$$
  
 $H_2O(L) + H_2O(L) \longrightarrow H_3O^{+}(AQ) + OH^{-}(AQ)$ 

## STEPS TOWARD SOLVING FOR PH

$$CN^{-}(aq) + H_{2}O \rightleftharpoons HCN(aq) + OH^{-}(aq)$$
Initial  $0.75 M$   $0 \sim 0$ 

$$Change -x +x +x$$
Equilibrium  $0.75-x$   $x$   $x$ 

$$K_B = 1.6 \times 10^{-5}$$

PH = 11.54

## MODELS OF ACIDS AND BASES

- TWO FACTORS FOR ACIDITY IN BINARY COMPOUNDS:
  - BOND POLARITY (HIGH IS GOOD)
  - BOND STRENGTH (LOW IS GOOD)

#### BOND STRENGTHS AND ACID STRENGTHS FOR HYDROGEN HALIDES

Bond Strengths and Acid Strengths for Hydrogen Halides

H—X Bond	Bond Strength (kJ/mol)	Acid Strength in Water
H—F	565	Weak
H—Cl	427	Strong
H—Br	363	Strong
H—I	295	Strong

## **OXYACIDS**

- CONTAINS THE GROUP H—O—X.
- FOR A GIVEN SERIES THE ACID STRENGTH INCREASES WITH AN INCREASE IN THE NUMBER OF OXYGEN ATOMS ATTACHED TO THE CENTRAL ATOM.
- THE GREATER THE ABILITY OF X TO DRAW ELECTRONS TOWARD ITSELF, THE GREATER THE ACIDITY OF THE MOLECULE.

# SEVERAL SERIES OF OXYACIDS AND THEIR K<sub>A</sub> VALUES

**Table 14.8** | Several Series of Oxyacids and Their  $K_a$  Values

Oxyacid	Structure	K <sub>a</sub> Value
HClO₄	O	Large (∼10 <sup>7</sup> )
	H-O-Cl-O	
HClO₃	0	~1
110103	H—O—Cl	-
	O	
HClO <sub>2</sub>	H—O—CI—O	$1.2 \times 10^{-2}$
HCIO	H—O—CI	$3.5 \times 10^{-8}$
H <sub>2</sub> SO <sub>4</sub>	О—Н	Large
	H-O-S-O	
	O	
H <sub>2</sub> SO <sub>3</sub>	О—Н	$1.5 \times 10^{-2}$
	H-O-S	
	O	
HNO <sub>3</sub>	O	Large
	H-O-N	
	O	
HNO <sub>2</sub> © Cengage Learning, All Rights Reserved.	H—O—N—O	$4.0 \times 10^{-4}$

# COMPARISON OF ELECTRONEGATIVITY OF X AND $K_A$ VALUE

Comparison of Electronegativity of X and  $K_a$  Value for a Series of Oxyacids

Acid	X	Electronegativity of X	K <sub>a</sub> for Acid
HOCI	Cl	3.0	$4  imes 10^{-8}$
HOBr	Br	2.8	$2 \times 10^{-9}$
HOI	1	2.5	$2 \times 10^{-11}$
HOCH <sub>3</sub>	CH <sub>3</sub>	2.3 (for carbon in CH <sub>3</sub> )	$\sim \! 10^{-15}$

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## **OXIDES**

- ACIDIC OXIDES (ACID ANHYDRIDES):
  - O—X BOND IS STRONG AND COVALENT.

SO<sub>2</sub>, NO<sub>2</sub>, CO<sub>2</sub>

WHEN H—O—X GROUPING IS DISSOLVED IN WATER, THE O—X BOND WILL
REMAIN INTACT. IT WILL BE THE POLAR AND RELATIVELY WEAK H—O BOND
THAT WILL TEND TO BREAK, RELEASING A PROTON.

### **OXIDES**

- BASIC OXIDES (BASIC ANHYDRIDES):
  - O—X BOND IS IONIC.

 $K_2O$ , CAO

 IF X HAS A VERY LOW ELECTRONEGATIVITY, THE O—X BOND WILL BE IONIC AND SUBJECT TO BEING BROKEN IN POLAR WATER, PRODUCING A BASIC SOLUTION.

## LEWIS ACIDS AND BASES

- LEWIS ACID: ELECTRON PAIR ACCEPTOR
- LEWIS BASE: ELECTRON PAIR DONOR

$$Al^{3+} + 6 \left( \begin{matrix} H \\ O \\ H \end{matrix} \right) \longrightarrow \left[ Al - \begin{matrix} H \\ O \\ H \end{matrix} \right]^{3+}$$

LEWIS ACID LEWIS BASE

## THREE MODELS FOR ACIDS AND BASES

#### Three Models for Acids and Bases

Model	Definition of Acid	Definition of Base
Arrhenius	H <sup>+</sup> producer	OH <sup>–</sup> producer
Brønsted–Lowry	H <sup>+</sup> donor	H <sup>+</sup> acceptor
Lewis	Electron-pair acceptor	Electron-pair donor

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## WHEN ANALYZING AN ACID-BASE EQUILIBRIUM PROBLEM:

- ASK THIS QUESTION: WHAT ARE THE MAJOR SPECIES IN THE SOLUTION AND WHAT IS THEIR CHEMICAL BEHAVIOR?
  - WHAT MAJOR SPECIES ARE PRESENT?
  - DOES A REACTION OCCUR THAT CAN BE ASSUMED TO GO TO COMPLETION?
  - WHAT EQUILIBRIUM DOMINATES THE SOLUTION?
  - LET THE PROBLEM GUIDE YOU. BE PATIENT.