Lecture 4

Salts, Polyprotic Acids, Oxides

Lecture Room for Next Week

There is a conference in Noyes Lab next week, so we have been kicked out of 100 Noyes Lab for the 1 pm lecture. The room for lecture next week is 144 Loomis.

Figure 14.6: The pH Scale and pH Values of Some Common Substances (p. 84)

 $H_2O(I) \leftrightarrow H^+(aq) + OH^-(aq)$

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

 $pH = -log[H^+]$

 $pOH = -log[OH^{-}]$

```
pH + pOH = 14.00
```

Acids add H⁺ to water. An acidic solution has: large [H⁺], so small [OH⁻] low pH, so high pOH



Bases add OH⁻ to water. A basic solution has: large [OH⁻], so small [H⁺] low pOH, so high pH

Values for K_b for Some Common Weak Bases (p. 81)

Table 14.3 Values of K _b for Some Common Weak Bases				
Name	Formula	Conjugate Acid	K _b	
Ammonia Methylamine Ethylamine Aniline Pyridine	$\begin{array}{c} \mathrm{NH}_3\\ \mathrm{CH}_3\mathrm{NH}_2\\ \mathrm{C}_2\mathrm{H}_5\mathrm{NH}_2\\ \mathrm{C}_6\mathrm{H}_5\mathrm{NH}_2\\ \mathrm{C}_5\mathrm{H}_5\mathrm{N}\end{array}$	${ m NH_4}^+ { m CH_3NH_3}^+ { m C_2H_5NH_3}^+ { m C_6H_5NH_3}^+ { m C_5H_5NH^+}$	$\begin{array}{c} 1.8 \times 10^{-5} \\ 4.38 \times 10^{-4} \\ 5.6 \times 10^{-4} \\ 3.8 \times 10^{-10} \\ 1.7 \times 10^{-9} \end{array}$	

Example K_b reaction for C_5H_5N , $K_b = 1.7 \times 10^{-9}$: $C_5H_5N(aq) + H_2O(I) \leftrightarrow OH^-(aq) + C_5H_5NH^+(aq)$

Values for K_a for Some Common Monoprotic Acids (p. 81)

Table 14.2Values of K_a for Some Common Monoprotic Acids			
Formula	Name	Value of K _a *	
$\begin{array}{l} HSO_4^{-} \\ HClO_2 \\ HC_2H_2ClO_2 \\ HF \\ HNO_2 \\ HC_2H_3O_2 \\ [Al(H_2O)_6]^{3+} \\ HOCl \\ HCN \\ NH_4^{+} \\ HOC_6H_5 \end{array}$	Hydrogen sulfate ion Chlorous acid Monochloracetic acid Hydrofluoric acid Nitrous acid Acetic acid Hydrated aluminum(III) ion Hypochlorous acid Hydrocyanic acid Ammonium ion Phenol	$ \begin{array}{c} 1.2 \times 10^{-2} \\ 1.2 \times 10^{-2} \\ 1.35 \times 10^{-3} \\ 7.2 \times 10^{-4} \\ 4.0 \times 10^{-4} \\ 1.8 \times 10^{-5} \\ 1.4 \times 10^{-5} \\ 3.5 \times 10^{-8} \\ 6.2 \times 10^{-10} \\ 5.6 \times 10^{-10} \\ 1.6 \times 10^{-10} \end{array} \right) \ \ \begin{array}{c} \text{fugure} \\ \text{gray by a constraint} \\ gray by a $	

Example K_a reaction for HNO_2 , $K_a = 4.0 \times 10^{-4}$: $HNO_2(aq) + H_2O(I) \leftrightarrow H_3O^+(aq) + NO_2^-(aq)$ or: $HNO_2(aq) \leftrightarrow H^+(aq) + NO_2^-(aq)$

Calculating the pH of Salt Solutions (p. 92)

Calculate the pH of the following solutions:

A.0.20 M NaF

B. 0.15 M NH₄NO₃

C. 0.78 M CaCl₂

Given:

$$K_a$$
 for HF = 7.2 x 10⁻⁴
 K_b for NH₃ = 1.8 x 10⁻⁵

pH of Salt Solutions – pH of Conjugate Acids and Conjugate Bases

Conjugate acid-base pairs: pairs of substances that only differ by a proton (H⁺) in their formulas, e.g., HCl and Cl⁻ or NH₄⁺ and NH₃.

For all conjugate acid-base pairs:

 $K_a \times K_b = K_w$ (At 25°C, $K_w = 1.0 \times 10^{-14}$)

Acids and Conjugate Bases (p. 84)

K _a	Acid	Conjugate Base	К _ь
~10 ⁻³	HF		
~10 ⁻⁵	HC ₂ H ₃ O ₂		
~10 ⁻¹¹	HOI		

For all conjugate acid-base pairs, $K_a \times K_b = K_w = 1.0 \times 10^{-14}$. Use it to fill in the table.

Bases and Conjugate Acids (p. 84)

К _ь	Base	Conjugate Acid	K _a
~10 ⁻⁵	NH ₃		
~10 ⁻⁸	HONH ₂		
~10 ⁻¹⁰	C ₆ H ₅ NH ₂		

For all conjugate acid-base pairs, $K_a \times K_b = K_w = 1.0 \times 10^{-14}$. Use it to fill in the table.

Acids and Conjugate Bases

K _a	Acid	Conjugate Base	$K_{b} = K_{w}/K_{a}$ $K_{b} = 10^{-14}/K_{a}$
~10 ⁻³	HF	F⁻	~10 ⁻¹¹
~10 ⁻⁵	HC ₂ H ₃ O ₂	$C_2H_3O_2^-$	~10 -9
~10 ⁻¹¹	HOI	OI	~10 ⁻³

The conjugate base of a weak acid is a weak base. The weaker the acid, the stronger the conjugate base.

Values for K_a for Some Common Monoprotic Acids (p. 81)

Table 14.2Values of K_a for Some Common Monoprotic Acids			
Formula	Name	Value of K _a *	
$\begin{array}{l} HSO_4^{-} \\ HClO_2 \\ HC_2H_2ClO_2 \\ HF \\ HNO_2 \\ HC_2H_3O_2 \\ [Al(H_2O)_6]^{3+} \\ HOCl \\ HCN \\ NH_4^{+} \\ HOC_6H_5 \end{array}$	Hydrogen sulfate ion Chlorous acid Monochloracetic acid Hydrofluoric acid Nitrous acid Acetic acid Hydrated aluminum(III) ion Hypochlorous acid Hydrocyanic acid Ammonium ion Phenol	$ \begin{array}{c} 1.2 \times 10^{-2} \\ 1.2 \times 10^{-2} \\ 1.35 \times 10^{-3} \\ 7.2 \times 10^{-4} \\ 4.0 \times 10^{-4} \\ 1.8 \times 10^{-5} \\ 1.4 \times 10^{-5} \\ 3.5 \times 10^{-8} \\ 6.2 \times 10^{-10} \\ 5.6 \times 10^{-10} \\ 1.6 \times 10^{-10} \end{array} \right) \ \ \begin{array}{c} \text{fugure} \\ \text{gray by a constraint} \\ gray by a $	

Example K_a reaction for HNO_2 , $K_a = 4.0 \times 10^{-4}$: $HNO_2(aq) + H_2O(I) \leftrightarrow H_3O^+(aq) + NO_2^-(aq)$ or: $HNO_2(aq) \leftrightarrow H^+(aq) + NO_2^-(aq)$

Bases and Conjugate Acids

К _ь	Base	Conjugate Acid	$K_{a} = K_{w}/K_{b}$ $K_{a} = 10^{-14}/K_{b}$
~10 ⁻⁵	NH ₃	NH ₄ +	~10 ⁻⁹
~10 ⁻⁸	HONH ₂	HONH ₃ ⁺	~10 ⁻⁶
~10 ⁻¹⁰	C ₆ H ₅ NH ₂	C ₆ H ₅ NH ₃ ⁺	~10-4

The conjugate acid of a weak base is a weak acid. The weaker the base, the stronger the conjugate acid.

Values for K_b for Some Common Weak Bases (p. 81)

Table 14.3 Values of K _b for Some Common Weak Bases				
Name	Formula	Conjugate Acid	K _b	
Ammonia Methylamine Ethylamine Aniline Pyridine	$\begin{array}{c} \mathrm{NH}_3\\ \mathrm{CH}_3\mathrm{NH}_2\\ \mathrm{C}_2\mathrm{H}_5\mathrm{NH}_2\\ \mathrm{C}_6\mathrm{H}_5\mathrm{NH}_2\\ \mathrm{C}_5\mathrm{H}_5\mathrm{N}\end{array}$	${ m NH_4}^+ { m CH_3NH_3}^+ { m C_2H_5NH_3}^+ { m C_6H_5NH_3}^+ { m C_5H_5NH^+}$	$\begin{array}{c} 1.8 \times 10^{-5} \\ 4.38 \times 10^{-4} \\ 5.6 \times 10^{-4} \\ 3.8 \times 10^{-10} \\ 1.7 \times 10^{-9} \end{array}$	

Example K_b reaction for C_5H_5N , $K_b = 1.7 \times 10^{-9}$: $C_5H_5N(aq) + H_2O(I) \leftrightarrow OH^-(aq) + C_5H_5NH^+(aq)$

Lecture Question (p. 94a)

Consider the following solutions:

0.20 M NaF, 0.15 M NH₄NO₃, 0.78 M CaCl₂ Place these solutions in order of increasing pH. a. NaF < NH_4NO_3 < $CaCl_2$ b. NaF < CaCl₂ < NH₄NO₃ c. $NH_4NO_3 < CaCl_2 < NaF$ d. $NH_4NO_3 < NaF < CaCl_2$ e. $CaCl_2 < NaF < NH_4NO_3$ Hint: Weak gives you weak and strong gives you garbage.

Lecture Question

Consider the following solutions:

0.20 M NaF, 0.15 M NH₄NO₃, 0.78 M CaCl₂ Place these solutions in order of increasing pH. a. NaF < NH₄NO₃ < CaCl₂ b. NaF < CaCl₂ < NH₄NO₃ c. $NH_4NO_3 < CaCl_2 < NaF$ acidic neutral basic d. $NH_4NO_3 < NaF < CaCl_2$ e. CaCl₂ < NaF < NH₄NO₃ Hint: Weak gives you weak and strong gives you garbage.

Question (p. 94a)

Are the following salts acidic, basic, or neutral?

 $\mathsf{NH}_4\mathsf{C}_2\mathsf{H}_3\mathsf{O}_2$

HONH₃OI

 $C_6H_5NH_3F$

Values for K_b for Some Common Weak Bases (p. 81)

Table 14.3 Values of K _b for Some Common Weak Bases				
Name	Formula	Conjugate Acid	K _b	
Ammonia Methylamine Ethylamine Aniline Pyridine	$\begin{array}{c} \mathrm{NH}_3\\ \mathrm{CH}_3\mathrm{NH}_2\\ \mathrm{C}_2\mathrm{H}_5\mathrm{NH}_2\\ \mathrm{C}_6\mathrm{H}_5\mathrm{NH}_2\\ \mathrm{C}_5\mathrm{H}_5\mathrm{N}\end{array}$	${ m NH_4}^+ { m CH_3NH_3}^+ { m C_2H_5NH_3}^+ { m C_6H_5NH_3}^+ { m C_5H_5NH^+}$	$\begin{array}{c} 1.8 \times 10^{-5} \\ 4.38 \times 10^{-4} \\ 5.6 \times 10^{-4} \\ 3.8 \times 10^{-10} \\ 1.7 \times 10^{-9} \end{array}$	

Example K_b reaction for C_5H_5N , $K_b = 1.7 \times 10^{-9}$: $C_5H_5N(aq) + H_2O(I) \leftrightarrow OH^-(aq) + C_5H_5NH^+(aq)$

From Appendix A5.3, HONH₂ has $K_b = 1.1 \times 10^{-8}$.

Values for K_a for Some Common Monoprotic Acids (p. 81)

Table 14.2Values of K_a for Some Common Monoprotic Acids			
Formula	Name	Value of K _a *	
$\begin{array}{l} HSO_4^{-} \\ HClO_2 \\ HC_2H_2ClO_2 \\ HF \\ HNO_2 \\ HC_2H_3O_2 \\ [Al(H_2O)_6]^{3+} \\ HOCl \\ HCN \\ NH_4^{+} \\ HOC_6H_5 \end{array}$	Hydrogen sulfate ion Chlorous acid Monochloracetic acid Hydrofluoric acid Nitrous acid Acetic acid Hydrated aluminum(III) ion Hypochlorous acid Hydrocyanic acid Ammonium ion Phenol	$ \begin{array}{c} 1.2 \times 10^{-2} \\ 1.2 \times 10^{-2} \\ 1.35 \times 10^{-3} \\ 7.2 \times 10^{-4} \\ 4.0 \times 10^{-4} \\ 1.8 \times 10^{-5} \\ 1.4 \times 10^{-5} \\ 3.5 \times 10^{-8} \\ 6.2 \times 10^{-10} \\ 5.6 \times 10^{-10} \\ 1.6 \times 10^{-10} \end{array} \right) \begin{array}{c} full full for a state of the second state of the$	

Example K_a reaction for HNO₂, $K_a = 4.0 \times 10^{-4}$:

 $HNO_{2}(aq) + H_{2}O(I) \leftrightarrow H_{3}O^{+}(aq) + NO_{2}^{-}(aq)$ or: $HNO_{2}(aq) \leftrightarrow H^{+}(aq) + NO_{2}^{-}(aq)$

From Appendix A5.2, HOI has $K_{b} = 2 \times 10^{-11}$.

Question

Are the following salts acidic, basic, or neutral?

```
\begin{aligned} \mathsf{NH}_4\mathsf{C}_2\mathsf{H}_3\mathsf{O}_2 &\to \mathsf{NH}_4^+ + \mathsf{C}_2\mathsf{H}_3\mathsf{O}_2^- \\ & \mathsf{wk} \operatorname{acid} + \mathsf{wk} \operatorname{base} \\ \mathsf{HONH}_3\mathsf{OI} &\to \mathsf{HONH}_3^+ + \mathsf{OI}^- \\ & \mathsf{wk} \operatorname{acid} + \mathsf{wk} \operatorname{base} \\ \mathsf{C}_6\mathsf{H}_5\mathsf{NH}_3\mathsf{F} &\to \mathsf{C}_6\mathsf{H}_5\mathsf{NH}_3^+ + \mathsf{F}^- \\ & \mathsf{wk} \operatorname{acid} + \mathsf{wk} \operatorname{base} \end{aligned}
```

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

Table 14.5 🕨	Qualitative Prediction of pH for Solutions of Salts for Which Both Cation and Anion Have Acidic or Basic Properties
$K_{a} > K_{b}$ $K_{b} > K_{a}$ $K_{a} = K_{b}$	pH < 7 (acidic) pH > 7 (basic) pH = 7 (neutral)

Question

Are the following salts acidic, basic, or neutral?

```
\begin{aligned} \mathsf{NH}_4\mathsf{C}_2\mathsf{H}_3\mathsf{O}_2 &\to \mathsf{NH}_4^+ + \mathsf{C}_2\mathsf{H}_3\mathsf{O}_2^- \\ & \mathsf{wk} \operatorname{acid} + \mathsf{wk} \operatorname{base} \\ \mathsf{HONH}_3\mathsf{OI} &\to \mathsf{HONH}_3^+ + \mathsf{OI}^- \\ & \mathsf{wk} \operatorname{acid} + \mathsf{wk} \operatorname{base} \\ \mathsf{C}_6\mathsf{H}_5\mathsf{NH}_3\mathsf{F} &\to \mathsf{C}_6\mathsf{H}_5\mathsf{NH}_3^+ + \mathsf{F}^- \\ & \mathsf{wk} \operatorname{acid} + \mathsf{wk} \operatorname{base} \end{aligned}
```

Bases and Conjugate Acids

К _ь	Base	Conjugate Acid	$K_{a} = K_{w}/K_{b}$ $K_{a} = 10^{-14}/K_{b}$
~10 ⁻⁵	NH ₃	NH ₄ +	~10 ⁻⁹
~10 ⁻⁸	HONH ₂	HONH ₃ ⁺	~10 ⁻⁶
~10 ⁻¹⁰	C ₆ H ₅ NH ₂	C ₆ H ₅ NH ₃ ⁺	~10-4

The conjugate acid of a weak base is a weak acid. The weaker the base, the stronger the conjugate acid.

Acids and Conjugate Bases

K _a	Acid	Conjugate Base	$K_{b} = K_{w}/K_{a}$ $K_{b} = 10^{-14}/K_{a}$
~10 ⁻³	HF	F⁻	~10 ⁻¹¹
~10 ⁻⁵	HC ₂ H ₃ O ₂	$C_2H_3O_2^-$	~10 -9
~10 ⁻¹¹	HOI	OI	~10 ⁻³

The conjugate base of a weak acid is a weak base. The weaker the acid, the stronger the conjugate base.

Question (p. 94a)

Are the following salts acidic, basic, or neutral?

$$\begin{split} \mathsf{NH}_{4}\mathsf{C}_{2}\mathsf{H}_{3}\mathsf{O}_{2} &\to \mathsf{NH}_{4}^{+} + \mathsf{C}_{2}\mathsf{H}_{3}\mathsf{O}_{2}^{-} \ \mathsf{pH}=7.0 \ (\mathsf{K}_{a}=\mathsf{K}_{b}) \\ & \mathsf{K}_{a}^{\sim}10^{-10} \ \mathsf{K}_{b}^{\sim}10^{-10} \\ \mathsf{HONH}_{3}\mathsf{OI} &\to \mathsf{HONH}_{3}^{+} + \mathsf{OI}^{-} \ \mathsf{pH}>7.0 \ (\mathsf{K}_{b}>\mathsf{K}_{a}) \\ & \mathsf{K}_{a}^{\sim}10^{-6} \ \mathsf{K}_{b}^{\sim}10^{-3} \\ \mathsf{C}_{6}\mathsf{H}_{5}\mathsf{NH}_{3}\mathsf{F} &\to \mathsf{C}_{6}\mathsf{H}_{5}\mathsf{NH}_{3}^{+} + \mathsf{F}^{-} \ \mathsf{pH}<7.0 \ (\mathsf{K}_{a}>\mathsf{K}_{b}) \\ & \mathsf{K}_{a}^{\sim}10^{-4} \ \mathsf{K}_{b}^{\sim}10^{-11} \end{split}$$

Calculating the pH of Salt Solutions (p. 92)

Calculate the pH of the following solutions:

A.0.20 M NaF

B. 0.15 M NH₄NO₃

C. 0.78 M CaCl₂

Given:

$$K_a$$
 for HF = 7.2 x 10⁻⁴
 K_b for NH₃ = 1.8 x 10⁻⁵

Lecture Question on Conjugate Acids and Conjugate Bases-p. 87.5

- Consider the K_a and K_b values given at the bottom of p. 87.5. Which of the following statements is false?
- a. The pH of a 1.0 *M* NaCl solution will be 7.00.
- b. CN⁻ is a weak base.
- c. $C_6H_5NH_3^+$ is a weak acid.
- d. A 1.0 *M* solution of NO₂⁻ will have a higher pH than a 1.0 *M* solution of CN⁻.
- e. A 1.0 M solution of $C_6H_5NH_3^+$ will have a lower pH than a 1.0 M solution of NH_4^+ .

Lecture Question on Conjugate Acids and Conjugate Bases

- Consider the K_a and K_b values given on the board. Which of the following statements is false?
- a. The pH of a 1.0 *M* NaCl solution will be 7.00.
- b. CN⁻ is a weak base.
- c. $C_6H_5NH_3^+$ is a weak acid.
- d. A 1.0 *M* solution of NO₂⁻ will have a higher pH than a 1.0 *M* solution of CN⁻.
- e. A 1.0 *M* solution of $C_6H_5NH_3^+$ will have a lower pH than a 1.0 *M* solution of NH_4^+ .

Stepwise Dissociation Constants for Several Common Polyprotic Acids

Table 14.4 🕨 Stepwise Dissociation Constants for Several Common Polyprotic Acids					
Name	Formula	K _{a1}	K _{a2}	K _{a³}	
Phosphoric acid	H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.8×10^{-13}	
Arsenic acid	H_3AsO_4	5×10^{-3}	8×10^{-8}	6×10^{-10}	
Carbonic acid	H_2CO_3	4.3×10^{-7}	5.6×10^{-11}		
Sulfuric acid	H_2SO_4	Large	1.2×10^{-2}		
Sulfurous acid	H_2SO_3	$1.5 imes 10^{-2}$	1.0×10^{-7}		
Hydrosulfuric acid [*]	H_2S	1.0×10^{-7}	$\sim 10^{-19}$		
Oxalic acid	$H_2C_2O_4$	$6.5 imes 10^{-2}$	6.1×10^{-5}		
Ascorbic acid (vitamin C)	$H_2C_6H_6O_6$	7.9×10^{-5}	1.6×10^{-12}		

Lecture Question (p. 94a)

- Consider a 0.10 M H₂SO₄ solution. What is the correct ordering of species present in this solution from largest to smallest concentration?
- a. $H^+ > HSO_4^- > SO_4^{2-}$ b. $HSO_4^- > SO_4^{2-} > H^+$ c. $H^+ > SO_4^{2-} > HSO_4^$ d. $HSO_4^- > H^+ > SO_4^{2-}$ e. $SO_4^{2-} > H^+ > HSO_4^-$

Lecture Question

Consider a 0.10 M H₂SO₄ solution. What is the correct ordering of species present in this solution from largest to smallest concentration?

a. $H^+ > HSO_4^- > SO_4^{2-}$ b. $HSO_4^- > SO_4^{2-} > H^+$ c. $H^+ > SO_4^{2-} > HSO_4^$ d. $HSO_4^- > H^+ > SO_4^{2-}$ e. $SO_4^{2-} > H^+ > HSO_4^{2-}$