Chem 222

#20 Ch 23, Ch26, Ch11
Mar 29, 2005
Announcement

- Your midterm will be returned probably this week.
- Reports for Exp 13, 15 are due this W/R.
- Reports for KH 5-1 is due on next M/T.
- Today we will cover Ch 23(1-3) Analytical Separation and Ch 26 (1) Ion-exchange Chromatography and Ch 11.
Exp DU 10-5

- Ion exchange separation and spectrophotometric determination of Ni$^{2+}$ and Co$^{2+}$

Separation by strong-base anion exchanger

In 9M HCl
- Co$^{2+}$ + 4Cl$^-$ $\rightarrow$ CoCl$_4^{2-}$ Absorbed
- Ni$^{2+}$ $\rightarrow$ Ni$^{2+}$ Not Absorbed

In 4M HCl

CoCl$_4^{2-}$ $\rightarrow$ Co$^{2+}$ + 4Cl$^-$ Eluted
26-1 Ion-Exchange Chromatography

Ion Exchangers

Polystyrene resin

Cross-link between polymer chains

Monomers

Styrene  Divinylbenzene

Cross-linked styrene-divinylbenzene copolymer

Strongly acidic cation-exchange resin

Strongly basic anion-exchange resin

Attracts cations

\(-\text{SO}_3^-\text{H}^+\)

Attracts anions

\(-\text{CH}_2\text{N}^+(\text{CH}_3)_3\text{Cl}^-\)
Strongly acidic cation-exchange resin

Strongly basic anion-exchange resin
23-1 Solvent Extraction

• Extraction is the transfer of a solute from one phase to another.

  Ex. Extraction of an aqueous solution with organic solvent

• The objective of extraction
  → Isolate or concentrate the analyte

Partition Coefficient:

\[ K = \frac{A_{S2}}{A_{S1}} = \frac{[S]_2}{[S]_1} \]
**Partition Coefficient:**

\[
K = \frac{A_{S2}}{A_{S1}} = \frac{[S]_2}{[S]_1}
\]

\( q \): Fraction of S in the phase 1  
\( M \): moles of S  
\( V_1, V_2 \): volume of solvent 1 & 2

\( [S]_2 = (1 - q)m/V \)  
\( [S]_1 = qm/V \)

The fraction in Phase 1 after 1 extraction  
\( q = V_1/(V_1 + KV_2) \quad (K \sim 0 \rightarrow q \sim 1) \)  
\( (K >> V_1/V_2 \rightarrow q \sim 0) \)

The fraction in Phase 1 after 2 extraction  
\( q^2 = \{V_1/(V_1 + KV_2)\}^2 \)

The fraction in Phase 1 after N extraction  
\( q^N = \{V_1/(V_1 + KV_2)\}^N \)
Ex. (p550)

- Solute A has a partition coefficient of 3 between toluene and water. Suppose that 100 mL of a 0.010 M aqueous solution of A are extracted with toluene.

What fraction of A remains in the aqueous phase (a) if one extraction with 500 mL is performed?

\[ K = \frac{[A]_{\text{toluene}}}{[A]_{\text{H2O}}} \]

\[ q = \frac{100 \text{ mL}}{100 \text{ mL} + (3)(500 \text{ mL})} = 0.062. \]

→ Only 6.2%

(b) With five 100-mL extractions, how much fraction of A is remaining?

\[ q = \left(\frac{100 \text{ mL}}{100 \text{ mL} + (3)(100 \text{ mL})}\right)^5 \]

\[ = (0.25)^5 = 0.00098 = 0.1\% \]
**pH Effects**

- If a solute is an acid or base, its charge changes as the pH is changed.
- A neutral species is more soluble in an organic solvent

Ex.

B is soluble in aqueous (1) and organic (2) phase  \( K = \frac{[B]_2}{[B]_1} \)

\( BH^+ \) is soluble in aqueous phase.

Distribution coefficient

\[
D = \frac{[B]_2}{[B]_1 + [BH^+]_1}
\]

\[= \frac{KKa}{Ka + [H^+]}\]
11-1 Diprotic Acids and Bases

\[
H_3N^+ \quad \text{CH-R} \leftrightarrow \text{Substituent} \quad -O_2C
\]

where R is a different group for each amino acid.

<table>
<thead>
<tr>
<th>Amino acid\textsuperscript{a}</th>
<th>Substituent\textsuperscript{a}</th>
<th>Carboxylic acid\textsuperscript{b} pK\textsubscript{a}</th>
<th>Ammonium\textsuperscript{b} pK\textsubscript{a}</th>
<th>Substituent\textsuperscript{b} pK\textsubscript{a}</th>
<th>Formula mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alanine (A)</td>
<td>$\text{CH}_3$</td>
<td>2.348</td>
<td>9.867</td>
<td></td>
<td>89.09</td>
</tr>
<tr>
<td>Arginine (R)</td>
<td>$\text{CH}_2\text{CH}_2\text{CH}<em>2\text{NH}</em>{2}$</td>
<td>1.823</td>
<td>8.991</td>
<td>(12.48)</td>
<td>174.20</td>
</tr>
<tr>
<td>Asparagine (N)</td>
<td>$\text{CH}_2\text{CNH}_2$</td>
<td>2.14\textsuperscript{c}</td>
<td>8.72\textsuperscript{c}</td>
<td></td>
<td>132.12</td>
</tr>
<tr>
<td>Aspartic acid (D)</td>
<td>$\text{CH}_2\text{CO}_2\text{H}$</td>
<td>1.990</td>
<td>10.002</td>
<td>3.900</td>
<td>133.10</td>
</tr>
<tr>
<td>Cysteine (C)</td>
<td>$\text{CH}_2\text{SH}$</td>
<td>(1.71)</td>
<td>10.77</td>
<td>8.36</td>
<td>121.16</td>
</tr>
<tr>
<td>Glutamic acid (E)</td>
<td>$\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$</td>
<td>2.23</td>
<td>9.95</td>
<td>4.42</td>
<td>147.13</td>
</tr>
<tr>
<td>Glutamine (Q)</td>
<td>$\text{CH}_2\text{CH}_2\text{CNH}_2$</td>
<td>2.17\textsuperscript{c}</td>
<td>9.01\textsuperscript{c}</td>
<td></td>
<td>146.15</td>
</tr>
<tr>
<td>Glycine (G)</td>
<td>$\text{H}$</td>
<td>2.350</td>
<td>9.778</td>
<td></td>
<td>75.07</td>
</tr>
<tr>
<td>Histidine (H)</td>
<td>$\text{CH}_2$</td>
<td>1.7\textsuperscript{c}</td>
<td>9.08\textsuperscript{c}</td>
<td>6.02\textsuperscript{c}</td>
<td>155.16</td>
</tr>
<tr>
<td>Isoleucine (I)</td>
<td>$\text{CH}($CH\textsubscript{2}$)$\textsubscript{2}$</td>
<td>2.319</td>
<td>9.754</td>
<td></td>
<td>131.17</td>
</tr>
</tbody>
</table>


\[
pH = pK_a + \log[A^-]/[AH] \rightarrow [A^-]/[AH] = 10^{(pH-pK_a)}
\]
Diprotic systems

\[
\begin{array}{c|c|c}
R & pK_{a1} & R \\
\hline
H_3N^+CHCO_2H & \leftrightarrow H_3N^+CHCO_2^- & \leftrightarrow H_2NCHCO_2^- \\
H_2L^+ & \leftrightarrow HL & L^- \\
\end{array}
\]

Equilibrium in Diprotic Systems

\[
\begin{align*}
H_2L^+ & \leftrightarrow HL + H^+ & K_{a1} = K_1 \\
HL & \leftrightarrow L^- + H^+ & K_{a2} = K_2 \\
L^- + H_2O & \leftrightarrow HL + OH^- & K_{b1} = K_W / [Q1] \\
HL + H_2O & \leftrightarrow H_2L^- + OH^- & K_{b2} = [Q2] \\
\end{align*}
\]

How much is the pH of 0.05 M of L_2H solution for L of K_1 = ?
P206 pH & Compositions of 0.05 M H$_2$L$^+$, HL, L$^-$ Solution

The acidic form H$_2$L$^+$

Leucine hydrochloride contains protonated species. Because $K_1 = 4.69 \times 10^{-3}$, H$_2$L$^+$ is a weak acid. HL is an even weaker acid: $k_2 = 1.79 \times 10^{-10}$. It appears that the H$_2$L$^+$ will dissociate only partly, and the resulting HL will hardly dissociate.

\[
\begin{align*}
H_2L^+ & \rightarrow HL + H^+ \\
F - x & \leftarrow x \quad x \\
K_1 &= [Q1]/(F - x) \quad \Rightarrow \quad x = 1.31 \times 10^{-2} \text{ M}
\end{align*}
\]

\[K_{a2} = [H^+][L^-]/[HL]\]

Basic Form L$^-$

The species, L$^-$, is found in a salt such as sodium leucinate. In solution, the salt gives L$^-$.

\[
\begin{align*}
L^- + H_2O & \leftarrow HL + OH^- \\
K_{b1} &= K_w/K_{a2} = 5.59 \times 10^{-5} \\
HL + H_2O & \rightarrow H_2L^+ + OH^- \\
K_{b2} &= K_w/K_{a1} = 2.13 \times 10^{-12}
\end{align*}
\]

$K_{b1}$ shows that L$^-$ will not hydrolyze very much to give HL. $K_{b2}$ shows H$_2$L$^+$ is generated even less.

\[
\begin{align*}
L^- + H_2O & \rightarrow HL + OH^- \\
F-x & \leftarrow x \quad x \\
K_{b1} &= [Q1] \\
K_{b2} &= [H_2L^+][OH^-]/[HL]
\end{align*}
\]
\( K_1 = \frac{x^2}{(F - x)} \)

\( K_1 = 4.69 \times 10^{-3} \) & \( F = 0.050 \) M

\( x^2 + K_1 x - FK_1 = 0 \)

\( \Rightarrow x = \frac{-K_1 + (K_1^2 + 4FK_1)^{1/2}}{2} \)

\( = 1.31 \times 10^{-2} \)

\( \text{pH} = 1.89 \)

\( x \sim (K_1 F)^{1/2} = 1.53 \times 10^{-2} \)
Fractional Composition Diagram (p216)
The graph represents the fractional composition of a triprotic acid as a function of pH. The acid is denoted as $H_2A$ and it undergoes two dissociation reactions with pK$_1$ and pK$_2$.

- pK$_1$ = 3.053
- pK$_2$ = 4.494

The graph shows the concentration of each species (H$_2$A, HA$^-$, A$^{2-}$) as a function of pH, with maxima at pK$_1$ and pK$_2$. The fractional composition is given by $\alpha_{H_2A}$, $\alpha_{HA^-}$, and $\alpha_{A^{2-}}$. The graph also illustrates the transition from the monobasic form (H$_2$A) to the dibasic form (HA$^-$) and finally to the tribasic form (A$^{2-}$) as the pH increases.
A solution prepared from leucine, HL, is more complicated.

\[
\begin{align*}
\text{HL} & \rightarrow \text{H}^+ + \text{L}^-; \quad K_{a2} = 1.79 \times 10^{-10} & \quad (11-8) \\
\text{HL} + \text{H}_2\text{O} & \leftrightarrow \text{H}_2\text{L}^+ + \text{OH}^-; \quad K_{b2}=2.13 \times 10^{-12} \\
\end{align*}
\]

A molecule that can both donate and accept a proton is said to be **amphiprotic**.

To solve (11-8) & (11-9), we use charge [Q1]

\[
[\text{H}^+] + [\text{H}_2\text{L}^+] = [\text{L}^-] + [\text{OH}^-]
\]

\[
\begin{align*}
[\text{H}_2\text{L}^+] &= [\text{HL}][\text{H}^+]/K_{a1} \\
[\text{L}^-] &= [\text{HL}]K_{a2}/[\text{H}^+] \\
[\text{OH}^-] &= K_w/[\text{H}^+] \\
\rightarrow [\text{H}^+] + [\text{HL}][\text{H}^+]/K_{a1} &= [\text{HL}]K_{a2}/[\text{H}^+] + K_w/[\text{H}^+] \\
\{1+([\text{HL}]/K_{a1})\}[\text{H}^+]^2 &= ([\text{HL}]K_{a2} + K_w) \\
\end{align*}
\]

**Major species is** [HL] \( \rightarrow \) [HL] \( \sim F \)

\[
[\text{H}^+] = \left\{ \frac{FK_{a2} + K_w}{1+(F/K_{a1})} \right\}^{1/2}
\]

\[
= \left( \frac{FK_{a2}K_{a1} + K_{a1}K_w}{K_{a1} + F} \right)^{1/2}
\]  

(11-11)
Simplified Calculation for the Intermediate Form

\[ [H^+] = \left( \frac{FK_a K_a + K_a K_w}{K_a + F} \right)^{1/2} \]

Two additional assumptions

\[ K_{a2} F \gg K_w \]
\[ [H^+] = \left( \frac{FK_a K_a}{K_a + F} \right)^{1/2} \]

\[ K_{a1} \ll F \]

\[ [H^+] = \left( \frac{FK_a K_a}{F} \right)^{1/2} = \left( K_{a1} K_{a2} \right)^{1/2} \]

\[ \text{pH} = -\log[H^+] \]
\[ = -\log(K_{a1} K_{a2})^{1/2} \]
\[ = \left\{ -\log K_{a1} - \log K_{a2} \right\}/2 \]
\[ = [Q1] \]

(Remember This)

(11-12)
Ex. pH of the Intermediate Form of a Diprotic Acid (p210)

- KPH is a salt of the intermediate form of phathalic acid. Calculate the pH of both 0.10 M and 0.010 M KPH.

\[
\text{Phthalic acid} \quad \overset{pK_1 = 2.950}{\rightarrow} \quad \text{Monohydrogen phthalate} \quad \overset{pK_2 = 5.408}{\rightarrow} \quad \text{Phthalate}
\]

(Potassium hydrogen phthalate = $K^+\text{HP}^-$

\[F \gg K_1 = 10^{[Q1]} \quad \& \quad FK_2 \gg K_W = 10^{-14}\]

\[\text{pH} = [Q2] = 4.18\]

Check pH with the equation (11-11)

\[\text{pH} = \left(\frac{FK_{a2}K_{a1} + K_{a1}K_w}{K_{a1} + F}\right)^{1/2}\]

= 4.18 for $F = 0.10$ M

4.20 for $F = 0.010$ M
Intermediate Form, HA⁻ Summary

A solution prepared from the intermediate form HA⁻, is more complicated.

\[
\begin{align*}
HA^- & \rightleftharpoons H^+ + A^{2-} \quad K_{a2} \tag{11-8} \\
HA^- + H^+ & \rightleftharpoons H_2A ; 1/K_{a1} \tag{11-9}
\end{align*}
\]

\[
\text{pH} = \frac{\text{pK}_{a1} + \text{pK}_{a2}}{2} \Rightarrow [H^+] = 10^{-\text{pH}}
\]

\[
\begin{align*}
\checkmark [HA^-] &= F \\
\checkmark K_{a2} &= [H^+][A^{2-}]/[HA^-] \Rightarrow [A^{2-}] = K_{a2}[HA^-]/[H^+] \\
\checkmark 1/K_{a1} &= [H_2A]/[HA^-][H^+] \\
&\Rightarrow [H_2A] = [H^+][HA^-]/K_{a1}
\end{align*}
\]
Solution of H$_2$A
1. Treat H$_2$A as a monoprotic acid with $K_a = K_1$ to find [H$^+$], [HA$^-$], and [H$_2$A].

$$H_2A \overset{K_1}{\rightleftharpoons} H^+ + HA^- \quad \frac{x^2}{F-x} = K_1$$

2. Use the $K_2$ equilibrium to solve for [A$^{2-}$].

$$[A^{2-}] = \frac{K_2[HA^-]}{[H^+]} = K_2$$

Solution of HA$^-$
1. Use the approximation [HA$^-$] $\approx$ F and find the pH with Equation 11-11.

$$[H^+] = \sqrt{\frac{K_1K_2F + K_1K_w}{F + K_1}}$$

The pH should be close to $\frac{1}{2}(pK_1 + pK_2)$.

2. Using [H$^+$] from step 1 and [HA$^-$] $\approx$ F, solve for [H$_2$A] and [A$^{2-}$], using the $K_1$ and $K_2$ equilibria.

$$[H_2A] = \frac{[HA^-][H^+]}{K_1} \quad [A^{2-}] = \frac{K_2[HA^-]}{[H^+]$$

Solution of A$^{2-}$
1. Treat A$^{2-}$ as monobasic, with $K_b = K_{b1} = K_w/K_{a2}$ to find [A$^{2-}$], [HA$^-$], and [H$^+$].

$$A^{2-} + H_2O \overset{K_{a2}}{\rightleftharpoons} HA^- + OH^- \quad \frac{x^2}{F-x} = K_{b1} = \frac{K_w}{K_{a2}}$$

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{K_w}{x}$$

2. Use the $K_1$ equilibrium to solve for [H$_2$A].

$$[H_2A] = \frac{[HA^-][H^+]}{K_{a1}} = \frac{[HA^-](K_w/[OH^-])}{K_{a1}} = K_{b2}$$
The graph shows the fractional composition of a species as a function of pH, with two pKa values: $pK_1 = 3.053$ and $pK_2 = 4.494$. The formula $(pK_1 + pK_2)/2$ is also shown.
Exp KH 5-1 (due next M/R)

From Nernst’s equation

• \( E = K + m \log[I^-] \) \hspace{1cm} (5-1)
  \( m \sim -0.05916 \)

For \([I^-]\) of

\( 1.00 \times 10^{-2}, 10^{-3}, 10^{-4} \) M,

measure \( E \) and plot \( E \) vs \( \log[I^-] \)
  (or \( \log[KI] \))

\( \rightarrow \) \( K \) & \( m \) should be obtained by
  fitting a plot with \( y = K + mx \)
Concentration of Unknown

• \( E = K + m \log[I^-] \)

\[ E_2 = K + m \log[I^-]_{\text{added}} \]
\[ E_1 = K + m \log[I^-]_{\text{unknown}} \]

\( \Delta E \equiv E_2 - E_1 \)
\[ = m \log\left\{ \frac{[I^-]_{\text{added}}}{[I^-]_{\text{unknown}}} \right\} \]

\( A \equiv 10^{\Delta E/m} = \frac{[I^-]_{\text{added}}}{[I^-]_{\text{unknown}}} \)
\[ \Rightarrow \]
\( A = \frac{[I^-]_{\text{added}}}{X} \quad (X \equiv [I^-]_{\text{unknown}}) \)

\([I^-]_{\text{added}} = (50.0/55.0) \times X + S \quad (5.0/50.0)\)