Big K, Small k, and Buffers: Merging Equilibrium with Limiting Reactant

AACT AP Chemistry Review Webinar

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About Me:

- 19 year AP Chemistry and Physics Teacher
- AP Chemistry Reader, Table Leader, and Question Leader since 2006
- Co-Chair of the AP Test Development Committee (2015-17)

Advanced Placement Chemistry Laboratory Manual

An Inquiry and Forensic Approach Towards Chemical Experimentation
The Plan

- K and Buffer Discussion
- Q. vs. K
- Open Q&A
A Typical Progression

- Acid base definitions
- pH and strong acids / bases
- Weak acids and $K_a$
- Weak Bases and $K_b$
- Acid-Base properties of salts / hydrolysis
- Acid Base Reactions
- Buffers
- Titration
Understanding the "Equilibria" of the Acid-Base Reaction is the key step!

\[ \text{HCl(aq)} + \text{NaOH(aq)} \rightarrow \text{H}_2\text{O(l)} + \text{NaCl(aq)} \]

Why does this happen?

- It just does
- Desc. Chem
- Lab

Equilibrium vs. Stoichiometry
\[ \text{Ba}^{2+}(aq) + \text{EDTA}^{4-}(aq) \rightleftharpoons \text{Ba(EDTA)}^{2-}(aq) \quad K = 7.7 \times 10^7 \]

6. The polyatomic ion \( \text{C}_{10}\text{H}_{12}\text{N}_{2}\text{O}_{8}^{4-} \) is commonly abbreviated as \( \text{EDTA}^{4-} \). The ion can form complexes with metal ions in aqueous solutions. A complex of \( \text{EDTA}^{4-} \) with \( \text{Ba}^{2+} \) ion forms according to the equation above. A 50.0 mL volume of a solution that has an \( \text{EDTA}^{4-}(aq) \) concentration of 0.30 \( M \) is mixed with 50.0 mL of 0.20 \( M \) \( \text{Ba(NO}_3\text{)}_2 \) to produce 100.0 mL of solution.

(a) Considering the value of \( K \) for the reaction, determine the concentration of \( \text{Ba(EDTA)}^{2-}(aq) \) in the 100.0 mL of solution. Justify your answer.

(b) The solution is diluted with distilled water to a total volume of 1.00 L. After equilibrium has been reestablished, is the number of moles of \( \text{Ba}^{2+}(aq) \) present in the solution greater than, less than, or equal to the number of moles of \( \text{Ba}^{2+}(aq) \) present in the original solution before it was diluted? Justify your answer.

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**Learning objective 6.6** The student can, given a set of initial conditions (concentrations or partial pressures) and the equilibrium constant, \( K \), use stoichiometric relationships and the law of mass action (\( Q \) equals \( K \) at equilibrium) to determine qualitatively and/or quantitatively the conditions at equilibrium for a system involving a single reversible reaction. [See SP 2.2, 6.4; Essential knowledge 6.A.3]

**Learning objective 6.7** The student is able, for a reversible reaction that has a large or small \( K \), to determine which chemical species will have very large versus very small concentrations at equilibrium. [See SP 2.2, 2.3; Essential knowledge 6.A.4]

**Learning objective 6.17** The student can, given an arbitrary mixture of weak and strong acids and bases (including polyprotic systems), determine which species will react strongly with one another (i.e., with \( K > 1 \)) and what species will be present in large concentrations at equilibrium. [See SP 6.4; Essential knowledge 6.C.1]
A question

You Spill 100 ml of 3M NaOH on the floor. What should you neutralize it with?
The demo

A student needs to dissolve a sample of Milk of Magnesia (Mg(OH)₂). Which of the following would be best?

- Water
- HCl
- HC₂H₃O₂
Mg(OH)$_2$ $\rightleftharpoons$ Mg$^{2+}$ + 2OH$^-$
The demo
Equilibrium Constants

\[
\begin{align*}
\text{Mg(OH)}_2 & \rightleftharpoons \text{Mg}^{2+} + 2\text{OH}^- & K = 2 \times 10^{-11} \\
2\text{H}^+ + 2\text{OH}^- & \rightleftharpoons 2\text{H}_2\text{O} & K = 1 \times 10^{28} \\
\text{Mg(OH)}_2 + 2\text{H}^+ & \rightleftharpoons \text{Mg}^{2+} + 2\text{H}_2\text{O} & K = 2 \times 10^{17} \\
\text{Mg(OH)}_2 & \rightleftharpoons \text{Mg}^{2+} + 2\text{OH}^- & K = 2 \times 10^{-11} \\
2\text{HC}_2\text{H}_3\text{O}_2 & \rightleftharpoons 2\text{H}^+ + 2\text{C}_2\text{H}_3\text{O}_2^- & K = 4 \times 10^{-10} \\
2\text{H}^+ + 2\text{OH}^- & \rightleftharpoons 2\text{H}_2\text{O} & K = 1 \times 10^{28} \\
2\text{HC}_2\text{H}_3\text{O}_2 + \text{Mg(OH)}_2 & \rightleftharpoons \text{Mg}^{2+} + 2\text{H}_2\text{O} + 2\text{C}_2\text{H}_3\text{O}_2^- & K = 8 \times 10^{7}
\end{align*}
\]
Take Home for Students

1) Weak acids are only “weak” w.r.t. water. Other reactions go to completion

2) Limiting Reactant will occur in systems that can’t reach equil. or have large K

2) “Equilibrium” mathematics should only be used when K is moderate to small. DO NOT TREAT differently from “normal” stoichiometry! (all one continuum)
Examples

. Will a solution of hydrochloric acid completely react with sodium hydroxide?

\[ \text{H}_3\text{O}^+ + \text{OH}^- \leftrightarrow 2 \text{H}_2\text{O} \quad \text{K} = 1 \times 10^{14} \]

. Will a solution of nitrous acid completely react with potassium hydroxide?

\[ \text{HNO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{NO}_2^- \quad \text{K}_a = 5 \times 10^{-4} \]
\[ \text{H}_3\text{O}^+ + \text{OH}^- \leftrightarrow 2 \text{H}_2\text{O} \quad \text{K} = 1 \times 10^{14} \]
\[ \text{HNO}_2 + \text{OH}^- \leftrightarrow \text{H}_2\text{O} + \text{NO}_2^- \quad \text{K}_{\text{net}} = 5 \times 10^{10} \]
Examples

. Will a solution of hydrochloric acid completely react with potassium fluoride?

\[ F^- + H_2O \leftrightarrow HF + OH^- \quad K_b = 1 \times 10^{-11} \]
\[ H_3O^+ + OH^- \leftrightarrow 2 H_2O \quad K = 1 \times 10^{14} \]
\[ F^- + H_3O^+ \leftrightarrow HF + H_2O \quad K_{net} = 1 \times 10^3 \]

. Will a solution of nitrous acid completely react with potassium fluoride?

\[ HNO_2 + H_2O \leftrightarrow H_3O^+ + NO_2^- \quad K_a = 5 \times 10^{-4} \]
\[ F^- + H_2O \leftrightarrow HF + OH^- \]
\[ H_3O^+ + OH^- \leftrightarrow 2 H_2O \]
\[ HNO_2 + F^- \leftrightarrow HF + NO_2^- \quad K_{net} = 5 \times 10^{-1} \]
<table>
<thead>
<tr>
<th>Acid Name</th>
<th>Acid</th>
<th>$K_a$</th>
<th>Base</th>
<th>$K_b$</th>
<th>Base Name</th>
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<tbody>
<tr>
<td>Perchloric acid</td>
<td>HClO₄</td>
<td>large</td>
<td>ClO₄⁻</td>
<td>very small</td>
<td>perchlorate ion</td>
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<td>Sulfuric acid</td>
<td>H₂SO₄</td>
<td>large</td>
<td>HSO₄⁻</td>
<td>very small</td>
<td>hydrogen sulfate ion</td>
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<tr>
<td>Hydrochloric acid</td>
<td>HCl</td>
<td>large</td>
<td>Cl⁻</td>
<td>very small</td>
<td>chloride ion</td>
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<td>Nitric acid</td>
<td>HNO₃</td>
<td>large</td>
<td>NO₃⁻</td>
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<td>H₂O⁺</td>
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<td>H₂O</td>
<td>1.8 x 10⁻¹⁶</td>
<td>water</td>
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<td>Sulfurous acid</td>
<td>H₂SO₃</td>
<td>1.2 x 10⁻²</td>
<td>HSO₄⁻</td>
<td>8.3 x 10⁻¹⁵</td>
<td>hydrogen sulfite ion</td>
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<tr>
<td>Hydrogen sulfate ion</td>
<td>HSO₄⁻</td>
<td>1.2 x 10⁻²</td>
<td>SO₄²⁻</td>
<td>8.3 x 10⁻¹⁵</td>
<td>sulfate ion</td>
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<td>Phosphoric acid</td>
<td>H₃PO₄</td>
<td>7.5 x 10⁻³</td>
<td>H₂PO₄⁻</td>
<td>1.3 x 10⁻¹²</td>
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<tr>
<td>Hexaaquairon(III)  ion</td>
<td>Fe(H₂O)₆³⁺</td>
<td>6.3 x 10⁻³</td>
<td>Fe(H₂O)₅O₂H²⁺</td>
<td>1.6 x 10⁻¹²</td>
<td>pentaaquahydroxiron(III) ion</td>
</tr>
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<td>Hydrofluoric acid</td>
<td>HF</td>
<td>7.2 x 10⁻⁴</td>
<td>F⁻</td>
<td>1.4 x 10⁻¹¹</td>
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<td>4.5 x 10⁻⁴</td>
<td>NO₂⁻</td>
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<td>HCO₂H</td>
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<td>HCO₂⁻</td>
<td>5.6 x 10⁻¹</td>
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<td>C₆H₅CO₂H</td>
<td>6.3 x 10⁻⁵</td>
<td>C₆H₅CO₂⁻</td>
<td>1.6 x 10⁻⁶</td>
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<tr>
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<td>4.2 x 10⁻⁷</td>
<td>HCO₃⁻</td>
<td>2.4 x 10⁻⁴</td>
<td>hydrogen carbonate ion</td>
</tr>
<tr>
<td>Hexaaquacopper(II) ion</td>
<td>Cu(H₂O)₆²⁺</td>
<td>1.6 x 10⁻⁷</td>
<td>Cu(H₂O)₅O₂H⁺</td>
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<td>H₂S</td>
<td>1 x 10⁻⁷</td>
<td>HS⁻</td>
<td>1 x 10⁻⁷</td>
<td>hydrogen sulfide ion</td>
</tr>
<tr>
<td>Dihydrogen phosphate ion</td>
<td>H₂PO₄⁻</td>
<td>6.2 x 10⁻⁸</td>
<td>HPO₄²⁻</td>
<td>1.6 x 10⁻⁸</td>
<td>hydrogen phosphate ion</td>
</tr>
<tr>
<td>Hydrogen sulfite ion</td>
<td>HSO₄⁻</td>
<td>6.2 x 10⁻⁸</td>
<td>SO₄²⁻</td>
<td>1.6 x 10⁻⁷</td>
<td>sulfite ion</td>
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<td>Hypochlorous acid</td>
<td>HClO₂</td>
<td>3.5 x 10⁻⁵</td>
<td>ClO⁻</td>
<td>2.9 x 10⁻⁷</td>
<td>hypochlorite ion</td>
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<tr>
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<td>Pb(H₂O)₆²⁺</td>
<td>1.5 x 10⁻⁸</td>
<td>Pb(H₂O)₅O₂H⁺</td>
<td>6.7 x 10⁻⁷</td>
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<td>Co(H₂O)₆²⁺</td>
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<td>Co(H₂O)₅O₂H⁺</td>
<td>7.7 x 10⁻⁶</td>
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<tr>
<td>Boric acid</td>
<td>B(OH)₃(H₂O)</td>
<td>7.3 x 10⁻¹⁰</td>
<td>B(OH)₄⁻</td>
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<td>Fe(H₂O)₆²⁺</td>
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<td>Fe(H₂O)₅O₂H⁺</td>
<td>3.1 x 10⁻⁵</td>
<td>pentaaquahydroxiron(II) ion</td>
</tr>
<tr>
<td>Hydrogen carbonate ion</td>
<td>HCO₃⁻</td>
<td>4.8 x 10⁻¹¹</td>
<td>CO₃²⁻</td>
<td>2.1 x 10⁻⁴</td>
<td>carbonate ion</td>
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<tr>
<td>Hexaaquaniickel(II) ion</td>
<td>Ni(H₂O)₆²⁺</td>
<td>2.5 x 10⁻¹¹</td>
<td>Ni(H₂O)₅O₂H⁺</td>
<td>4.0 x 10⁻⁴</td>
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<td>Hydrogen phosphate ion</td>
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<td>3.6 x 10⁻¹⁴</td>
<td>PO₄³⁻</td>
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<td>Water</td>
<td>H₂O</td>
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<td>OH⁻</td>
<td>55.5</td>
<td>hydroxide ion</td>
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<tr>
<td>Hydrogen sulfide ion</td>
<td>H²S⁻</td>
<td>1 x 10⁻¹⁹</td>
<td>S²⁻</td>
<td>1 x 10⁻¹</td>
<td>sulfide ion</td>
</tr>
<tr>
<td>Ethanol</td>
<td>C₂H₅OH</td>
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<td>C₂H₅O⁻</td>
<td>large</td>
<td>ethoxide ion</td>
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<td>NH₃⁻</td>
<td>large</td>
<td>amide ion</td>
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<tr>
<td>Hydrogen</td>
<td>H₂</td>
<td>very small</td>
<td>H⁻</td>
<td>large</td>
<td>hydride ion</td>
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<tr>
<td>Methane</td>
<td>CH₄</td>
<td>very small</td>
<td>CH₄⁻</td>
<td>large</td>
<td>methide ion</td>
</tr>
</tbody>
</table>

The values of $K_a$ for HS⁻ and $K_b$ for HS⁻ are estimates.
Monitor the pH during titration of 10ml 0.1M HCl with 0.1 M NaOH

\[ \text{H}_3\text{O}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{H}_2\text{O} \]  
\[ K = 1 \times 10^{14} \]

\[ [\text{H}_3\text{O}^+] = 0.0009 / 0.011 = 0.082 \text{ M} \]

\[ \text{pH} = 1.00 \text{ (eqvH}_2\text{O} = 0.0001 \text{ mol.)} \]
Titration Curve

5.0 ml
\([H_3O^+] = 0.033 \text{ M}\)

pH = 1.48

12.0 ml
\([OH^-] = 0.0091 \text{ M}\)

pOH = 2.04

Volume: 1.0 mL
pH: 1.09

\[\text{H}_3\text{O}^+\]
\[\text{OH}^-\]
What about a weak acid?

\[
HA \leftrightarrow H^+ + A^- \quad K_a = 1 \times 10^{-5}
\]

\[
H^+ + OH^- \leftrightarrow H_2O \quad K = 1 \times 10^{14}
\]

\[
HA + OH^- \leftrightarrow H_2O + A^- \quad K_{net} = 1 \times 10^{11}
\]

\[
[H_3O^+] = 0.001
\]

\[pH = 3.00\]
How do you calculate pH?

\[ \text{HA} \leftrightarrow \text{H}^+ + \text{A}^- \]

\[
\begin{array}{c c c}
0.0006 & 0 & 0.0004 \\
0.014 & +x & 0.014 \\
-1 & +x & +x
\end{array}
\]

Before \( x = 0.001 \), what now?

\[
\begin{array}{c c c}
0.0006 & +x & 0.0004 \\
0.014 & +x & 0.014
\end{array}
\]

\[ K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \]
The buffer equation

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

- Combination of large \( K \) and \( K_a \) = LR
- \([H^+]\) depends on ratio of moles of HA to A

\[ [H^+] = 1 \times 10^{-5} \frac{0.0006}{0.0004} = 0.000015 \]

\( \text{pH} = 4.82 \)
At 5.0 ml added?

\[
\text{HA} + \text{OH}^- \rightleftharpoons \text{H}_2\text{O} + \text{A}^- \\
K_{\text{neq}}[\text{H}^+] = \frac{1}{K_a} \cdot \frac{[\text{HA}]}{[\text{A}^-]}
\]

\[\begin{align*}
&0.0006 \quad 0.0005 \\
&0.0005 \\
&0.0005
\end{align*}\]

\[
[H^+] = 1 \times 10^{-5} \cdot \frac{0.0005}{0.0005} = 1 \times 10^{-5}
\]

\[
\text{pH} = 5.00
\]
Buffers are Combination of Big K and Little K

- Have students draw particulate representations initially
- Move to mathematical once there is comfort
- Allows for quick writing of NIE
- Particulate also good for buffer capacity
- Do Titration Curves 1st and then discuss buffers.
- Mastery = All BI - 6
Ba^{2+}(aq) + EDTA^{4-}(aq) \rightleftharpoons Ba(EDTA)^{2-}(aq) \quad K = 7.7 \times 10^7

6. The polyatomic ion $C_{10}H_{12}N_2O_8^{4-}$ is commonly abbreviated as EDTA$^{4-}$. The ion can form complexes with metal ions in aqueous solutions. A complex of EDTA$^{4-}$ with Ba$^{2+}$ ion forms according to the equation above. A 50.0 mL volume of a solution that has an EDTA$^{4-}(aq)$ concentration of 0.30 $M$ is mixed with 50.0 mL of 0.20 $M$ Ba(NO$_3$)$_2$ to produce 100.0 mL of solution.

(a) Considering the value of $K$ for the reaction, determine the concentration of Ba(EDTA)$^{2-}(aq)$ in the 100.0 mL of solution. Justify your answer.

(b) The solution is diluted with distilled water to a total volume of 1.00 L. After equilibrium has been reestablished, is the number of moles of Ba$^{2+}(aq)$ present in the solution greater than, less than, or equal to the number of moles of Ba$^{2+}(aq)$ present in the original solution before it was diluted? Justify your answer.
If 0.10 mol of AgNO$_3$(s) is added to 1.00 L of a saturated Ag$_2$CrO$_4$(aq) solution, will [CrO$_4^{2-}$] increase, decrease, or remain the same? JYA. (Assume a negligible change in volume of solution occurs).

Possible Answer:

Decrease. The Ag$^+$ will bond to CrO$_4^{2-}$, and remove it from solution.

Credit Worthy?
1. **Kinetic argument**
Decrease. The AgNO$_3$(s) will dissolve and dissociate to produce additional Ag$^+(aq)$. The additional Ag$^+(aq)$ will increase the rate of precipitation of Ag$_2$CrO$_4$ over that of dissolution, decreasing [CrO$_4^{2-}$] until a new equilibrium is established.

2. **$Q$ vs $K$ argument**
Decrease. The AgNO$_3$(s) will dissolve and dissociate to produce additional Ag$^+(aq)$. The additional Ag$^+(aq)$ will increase $Q_{sp}$ making it greater than $K_{sp}$, shifting the solubility equilibrium of Ag$_2$CrO$_4$ toward reactants, thus decreasing [CrO$_4^{2-}$].
3. Le Châtelier’s principle argument
Decrease. The AgNO$_3$(s) will dissolve and dissociate to produce additional Ag$^+(aq)$. The additional Ag$^+(aq)$ is a stress in the Ag$_2$CrO$_4$ dissolution equilibrium. Adding product to an equilibrium reaction will shift the solubility equilibrium of Ag$_2$CrO$_4$ toward reactant to remove the stress of added product and thus decrease [CrO$_4^{2-}$].

Student Answer:
Decrease. The Ag$^+$ will bond to CrO$_4^{2-}$, and remove it from solution.
2016 AP® CHEMISTRY FREE-RESPONSE QUESTIONS

\[ \text{Ba}^{2+}(aq) + \text{EDTA}^{4−}(aq) ⇌ \text{Ba(EDTA)}^{2−}(aq) \quad K = 7.7 \times 10^7 \]

6. The polyatomic ion \( \text{C}_{10}\text{H}_{12}\text{N}_{2}\text{O}_{8}^{4−} \) is commonly abbreviated as \( \text{EDTA}^{4−} \). The ion can form complexes with metal ions in aqueous solutions. A complex of \( \text{EDTA}^{4−} \) with \( \text{Ba}^{2+} \) ion forms according to the equation above. A 50.0 mL volume of a solution that has an \( \text{EDTA}^{4−}(aq) \) concentration of 0.30 \( M \) is mixed with 50.0 mL of 0.20 \( M \) \( \text{Ba(NO}_3\text{)}_2 \) to produce 100.0 mL of solution.

(a) Considering the value of \( K \) for the reaction, determine the concentration of \( \text{Ba(EDTA)}^{2−}(aq) \) in the 100.0 mL of solution. Justify your answer.

(b) The solution is diluted with distilled water to a total volume of 1.00 L. After equilibrium has been reestablished, is the number of moles of \( \text{Ba}^{2+}(aq) \) present in the solution greater than, less than, or equal to the number of moles of \( \text{Ba}^{2+}(aq) \) present in the original solution before it was diluted? Justify your answer.

The number of moles of \( \text{Ba}^{2+}(aq) \) increases because the percent dissociation of \( \text{Ba(EDTA)}^{2−}(aq) \) increases as the solution is diluted.

OR

A mathematical justification such as the following:
The dilution from 100.0 mL to 1.00 L reduces the concentrations of all species to one tenth of their original values.

Immediately after the dilution, the reaction quotient, \( Q \), can be determined as shown below.

\[ Q = \frac{1}{10} \left[ \frac{\text{Ba(EDTA)}^{2−}}{\text{Ba}^{2+}} \right] \times \frac{1}{10} \left[ \frac{\text{EDTA}^{4−}}{} \right] = 10K \]

Because \( Q > K \), the net reaction will produce more reactants to move toward equilibrium, so the number of moles of \( \text{Ba}^{2+}(aq) \) will be greater than the number in the original solution.

1 point is earned for stating that the number of moles of \( \text{Ba}^{2+}(aq) \) will increase.

1 point is earned for a valid justification.
Thank you!

Resources
- PDF of Presentation
- Potent Acid Handout
- Quantitative Demo (Jesse Bernstein)
  - http://bit.ly/2mNHF7n

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