Mass and charge balance

When you have complex eqv., do:
1. Write down all the unknowns
2. Create # of equations = # of unknowns from K value and mass/charge balance.
3. Back substitute and solve

Example. HA in H₂O makes H⁺, OH⁻, HA, A⁻ so need 4 equations.

1. \[ K_w = [H^+] [OH^-] \]
2. \[ K_a = \frac{[H^+] [A^-]}{[HA]} \]

From these:

Plus 3. charge balance:

\[ [H^+] = [A^-] + [OH^-] \]

4. Mass balance (take from known mass of starting materials)

Here:

\[ C_{HA} = \frac{[HA] + [A^-]}{\text{all the forms at equilibrium}} \]

Equilibria Calculations: dilute solutions

If a solution is dilute the approximations don't hold. Typically 10⁻⁵ M or less. Why? \( K_w \) produces 10⁻⁷ M H⁺ and OH⁻.

What to do with dilute solutions?

- Solve the complex case as above.
- Dilute strong acid \( \equiv \text{make quadratic} \) stick Ca in and solve.
- Dilute weak acid \( \equiv \text{make cubic} \) for exact answer.

OK recognize that dilute acid or base makes pH close to neutral H₂O (around 7)

so 10⁻⁹ M HA \( \approx 7 \) (actually a little less)

10⁻⁸ M Na⁺H \( \approx 7 \) (actually a little more)
Equilibrium Calculations: weak polyprotic acids (amphiprotic case)

There are two forms of polyprotic acids:

Diprotic ($H_2A$) \[ H_2A \rightleftharpoons HA^- \rightleftharpoons A^- \]

Tripotonic ($H_3A$) \[ H_3A \rightleftharpoons H_2A^- \rightleftharpoons HA^- \rightleftharpoons A^- \]

You can make buckets showing the possible calculations for each in which protons are removed by pH adding off:

Diprotic: weak acid, buffer, amphiprotic buffer, weak base
Tripotonic: weak acid, buffer, amphiprotic buffer, weak base

So if you know the kind of solution, you can crank out a pH.

Amphiprotic is easy. \[ H^+ = \sqrt{\frac{K_a_1 K_a_2}{K_b}} \]

Equilibrium Calculations: weak polyprotic acids (non-amphiprotic case)

Note that if the $K_a$s are far apart, polyprotic acid calculations become simple $A/B$ calculation just like monoprotic case.

So if $pK_a = 3$ and 9

Then:

- $H_2A$ is a weak acid: \[ H^+ = \sqrt{K_a_1 C_A} \]
- $H_2A$ is a buffer: \[ H^+ = K_a_1 \frac{C_A}{C_B} \]
- $HA^-$ is amphiprotic
- $HA^-$ is a buffer: \[ H^+ = K_a_2 \frac{C_A}{C_B} \]
- $A^-$ is a weak base: \[ H^+ = \sqrt{K_b C_A} \]

What is pH if $pK_b = 3, 9$?

Answer:

- $H_2A$ buffer, $pH = 6$
Polyprotic acid calculations (estimates using alpha diagrams)

Diagrams make it possible to quickly order the relative concentrations of species at equilibrium in solution. This is especially true of polyprotic acids, creating a diagram:

1. Create pH scale
2. Make dots where pH = pK
3. Swoop

Example: Draw the pH diagram for H₃A where pKₐ = 3, 7, 11

What is the relative concentration of H₃A species at pH 4?
H₃A⁻ > H₃A > HA⁻ > A⁻³

Equilibrium Calculations: sulfuric acid case.

H₂SO₄ is a special case because

1. It is strong
Ka₁ ≈ ∞

2. The second K is large
so the weak acid approximation doesn't work
Ka₂ = 1.1 × 10⁻²

Need to work step-wise to solve.

What is [SO₄²⁻] concentration for 0.2 M H₂SO₄?

Step 1:
H₂SO₄ ⇌ H⁺ + SO₄²⁻

Step 2:
HSO₄⁻ ⇌ H⁺ + SO₄²⁻
Common ion calculation (Ksp)

\[ \text{AgCl} \rightleftharpoons \text{Ag}^+ + \text{Cl}^- \]

Simple molal solubility problem

\[ \text{NaCl} \text{ and NaCl} \rightleftharpoons \text{Na}^+ + \text{Cl}^- \]

0.1 M Cl\(^-\)

What is the [Ag\(^+\)] in solution formed from saturation of AgCl in H\(_2\)O if K\(_{\text{sp}}\) = 1 \times 10\(^{-10}\)?

Answer:

\[ K_{\text{sp}} = 1 \times 10^{-10} = [\text{Ag}^+][\text{Cl}^-] = (1 \times 10^{-9})(1 \times 10^{-9}) = x^2 \]

Now add 0.1 M NaCl to that saturated solution. What is the new [Ag\(^+\)] in saturated AgCl?

Selectively precipitating (Ksp)

Magic anion: \(\text{Cl}^-\)

Ag\(^+\) Ag\(^+\)

Ca\(^+\) Ca\(^+\)

Na\(^+\) Na\(^+\)

Can I selectively remove Ag\(^+\) because its solubility with a magic anion is really small?

Give:

\[ [\text{Ag}^+] [\text{anion}] = 10^{-12} \text{ fn Ag}^+ \]
\[ [\text{Ca}^+] [\text{anion}] = 10^{-9} \text{ fn Ca}^+ \]
\[ [\text{Na}^+] [\text{anion}] = 10^{-1} \text{ fn Na}^+ \]

This says that if I add 0.1 M anion, then at 10\(^{-11}\) M the Ag\(^+\) comes out first. Then at 10\(^{-3}\) M the Ca\(^+\) comes out, etc. An 8 order of magnitude separation. 5) Ag\(^+\) and Ca\(^+\)