CH 302 Unit 2 Day 2

LE CHAT'S, INTRO THE ACID BASE

Le Chatelier's Principle

- Le Chatelier's Principle creates the guidelines for how a system responds to any disruption of equilibrium
- In other words, a system at equilibrium will respond to stress by directly opposing the stress.
- Factors that might disrupt equilibrium include:
  1. Adding or removing species involved in a reaction
  2. A change in the volume or pressure
  3. Dilution or concentration of the system
  4. Adding an inert gas at constant pressure
  5. Adding an inert gas at constant volume (doesn't actually impact eq)
  6. A change in temperature

Le Chatelier's Principle - Temperature

- To simplify the relationship between K and temperature, we can think of temperature like a product or a reactant of a chemical reaction depending on whether the reaction is exothermic or endothermic.
- Endothermic reactions are driven by an input of heat; therefore, heat is like a reactant. Increasing the heat is like adding a reactant. This shifts the equilibrium toward the products.

$$\text{Heat} + \text{Reactants} \rightleftharpoons \text{Products}$$

- Exothermic reactions have an output of heat; therefore, heat is like a product. Increasing the heat is like adding a product. This shifts the equilibrium toward the reactants.

$$\text{Reactants} \rightleftharpoons \text{Products} + \text{Heat}$$

Temperature Dependence of K

K's dependence on temperature depends on whether the reaction is endothermic or exothermic. The van't Hoff Equation is:

if $\Delta H > 0$, $T\uparrow$ $K\uparrow$

if $\Delta H < 0$, $T\uparrow$ $K\downarrow$

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta H_{rxn}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Le Chatelier's Principle - Questions

Consider the reaction below when it is at equilibrium:

$3NO_2(g) + H_2O(l) \rightleftharpoons 2HNO_3(aq) + NO(g)$ $\Delta H^\circ = -34 kJ/mol$ at 298 K

In which direction will the reaction shift when:

a. 3 moles of NO(g) are removed $Q < K$ $\rightarrow$
b. The temperature is raised to 320 K $T\uparrow K\downarrow$ $\leftarrow$
c. The total volume is decreased $V\downarrow P\uparrow$ $\rightarrow$
d. An inert gas is added at constant volume NOTHING
e. An inert gas is added at constant pressure (in a piston system) $V\uparrow P\downarrow$ $\leftarrow$
f. The temperature is lowered to 100 K $T\downarrow K\uparrow$ $\rightarrow$
g. 4 moles of HNO_3 are added $Q > K$ $\leftarrow$

Acids and Bases

IDENTIFYING ACIDS AND BASES, CALCULATING pH

Acid Base Equilibria Roadmap

1. Define and identify acids and bases
2. Solve for pH and pOH for strong and weak acids/bases

} Today

3. Identify and analyze the products of a full neutralization reaction (adding acid to base and vice versa)
4. Identify and analyze the products of a partial neutralization
5. Understand neutralization reactions in the context of titrations and indicators

} Hard Stuff

6. Understand the role of pH in regulating the dominant species of a polyprotic acid

Acids and Bases Fundamentals

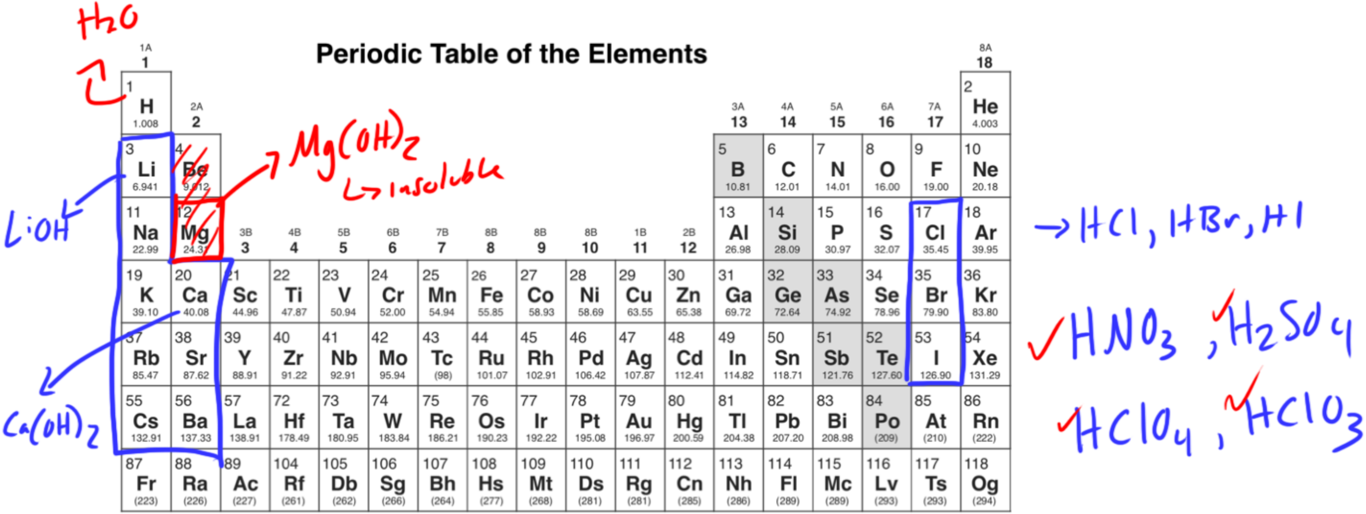
- The study of acids and bases revolves around understanding the chemical environment of aqueous solutions associated with proton (hydronium) and hydroxide concentrations.
  $\to H_3O^+ = H^+(aq)$
- The standard units of measurement for acids and bases are pH and pOH

"p" = -log

$$pH = -\log[H^+] \qquad pOH = -\log[OH^-]$$

- Some things to note about this relationship:
  - Because this relationship is based on the negative log, **a high value of [H⁺] will have a low pH value.**
  - By using a logarithmic scale, you should understand that a difference between pH = 2 and pH = 7 is not a difference of 5, **but 5 orders of magnitude**.

Identifying Strong Acids & Bases



What's actually happening in Acid/Base Equilibria

You place 0.15 moles of methylamine (weak base) into 1 L water. What happens?

$$CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$$

Weak base | weak acid | conjugate weak acid | conj. base

Conceptual Question:
What is the dominant species in solution for the reaction discussed above?

a. CH_3NH_2
b. $CH_3NH_3^+$
c. H^+
d. OH^-

A particularly important K value

K_w represents the auto-ionization of water; that is, it is the equilibrium constant for the following reaction at 298.15K:

1) $K_a \cdot K_b = K_w = [OH^-][H_3O^+]$

2) $14 = pOH + pH$

3) Conjugate of a weak base is NOT a strong acid

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$

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

- **K_w represents the standard for our pH scale at room temperature**
  - For a neutral solution, pH = 7
    - **Acidic solutions** have pH < 7
    - **Basic solutions** have pH > 7
- ✓ Therefore, the H^+ and OH^- concentrations are equal to 1.0×10^{-7} for a neutral solution at room temperature

Quantifying Acids and Bases

- The standard units of measurement for acids and bases are pH and pOH

$$\text{pH} = -\log[H^+] \qquad \text{pOH} = -\log[OH^-]$$

- In a strong acid or strong base solution, we can use this relationship:

$$\text{pH} = -\log[C_A] \qquad \text{pOH} = -\log[C_B]_*$$

$Ca(OH)_2$
$2 \cdot C_B$

- pH and pOH can be interconverted using the relationship based on pK_w (14):

$$\text{pH} = 14 - pOH \qquad \text{pOH} = 14 - pH$$

Quantifying Weak Acids and Bases

if $\frac{C_A}{K_a} \geq 1000$, ✓ ignore x

- For a weak acid, we are dealing with a more interesting equilibrium (additional steps). The approximation formulas are below:

$$[H^+] = \sqrt{C_{HA} \cdot K_a} \qquad [OH^-] = \sqrt{C_B \cdot K_b}$$

$K_a = \frac{x^2}{C_A}$

- Don't forget that at any time you can convert between different terms:

$$K_w = 1 \cdot 10^{-14} = [H^+][OH^-]$$

$$K_w = K_a K_b$$

$$\frac{K_w}{K_a} = K_b$$

$$\frac{K_w}{K_b} = K_a$$

R	HA	$\rightleftharpoons H^+$	$+ A^-$
I	C_A	ϕ	ϕ
C	$-x$	$+x$	$+x$
E	$C_A - x$	x	x

Quantifying Weak Acids and Bases

- Important Reminder: K_a will get you $[H^+]$, K_b will get you $[OH^-]$. Therefore, K_a corresponds to a weak acid reaction and K_b corresponds to a weak base reaction.

$HA \rightleftharpoons H^+ + A^-$ → $$K_a = \frac{[H^+][A^-]}{[HA]}$$ → $$pH = -\log[H^+]$$

$\frac{x^2}{C_A - x}$ → $[H^+] = \sqrt{C_A \cdot K_a}$

(Solve using approximation or quadratic)

$B \rightleftharpoons BH^+ + OH^-$ → $$K_b = \frac{[OH^-][BH^+]}{[B]}$$ → $$pOH = -\log[OH^-]$$

Acid Base Reactions Recap

1. Strong Acid

   $HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$ $pH = -\log(C_A)$

2. Strong Base

   $NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$ $pOH = -\log(C_B)$

   $Ca(OH)_2(aq) \rightarrow Ca^{2+}(aq) + 2OH^-$ $pOH = -\log(2 \times C_B)$

3. Weak Acid

   $HA(aq) \rightarrow H^+(aq) + A^-(aq)$ $K_a = \frac{x^2}{C_A - x}$ $pH = -\log[H^+]$

4. Weak Base

   $H_2O(l) + B(aq) \rightarrow BH^+ + OH^-(aq)$ $K_b = \frac{x^2}{C_B - x}$ $pOH = -\log[OH^-]$

Warm-Up Question

Classify each solution as acidic, basic, or neutral:

1. 0.5 M HF
2. 0.5 M CH_3COOH } Weak acids
3. 0.5 M $(CH_3)_2NH$ → weak base
4. 0.5 M NaOH → strong base
5. 0.5 M NaCl → salt, neutral

Conceptual Question K_w

Which of the following is/are true for a neutral pure water solution at any temperature?

Note: ΔH˚ for the auto-ionization of water is about 55.7 kJ/mol.

i. $K_w = 1.0 \times 10^{-14}$

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

iii. $[H^+]=[OH^-]$

iv. $[H^+]$ and $[OH^-]$ aren't always equal

v. pH = 14 – pOH

vi. pH decreases as temperature goes up

vii. pH = 7

Warm-Up Question

What is the pH of a 0.50 M HNO_3 solution?

$$pH = -\log[HNO_3]$$

$$0.30 = -\log(0.50)$$

Warm-Up Question

What is the hydrogen ion concentration of a 0.30 M calcium hydroxide solution?

$pOH = -\log(0.60)$

$= 0.2218...$

$pH = 14 - 0.2218...$

$= 13.778$

$[H^+] = 10^{-13.778} = 1.67 \times 10^{-14}$

$Ca(OH)_2 \rightarrow 2 \times 0.30\ M$

$= 0.60\ M$

$K_w = [H^+][OH^-]$

$\frac{1 \times 10^{-14}}{0.60} = \frac{[H^+](0.60\ M)}{0.60}$

1.67×10^{-14}

Challenge Question I

The hydrogen ion concentration in a 25˚C solution is 630 times the concentration of the hydroxide ion. What is the pH of this solution?

$$K_w = [H_3O^+][OH^-]$$

$$1\times10^{-14} = (x)\left(\frac{x}{630}\right)$$

$$6.30\times10^{-12} = x^2$$

$$x = 2.51\times10^{-6} = [H_3O^+]$$

$$pH = 5.60$$

Challenge Question II

Trichloroacetic acid is a harsh chemical, typically used for cosmetic treatments such as tattoo removal. What is the pH of a .0100 M trichloroacetic acid solution (CCl_3COOH)?

K_a = 2.1 x 10^{-1}

$HA \rightleftharpoons A^- + H^+$

R	$CCl_3COOH \rightleftharpoons$	CCl_3COO^- +	H^+
I	0.0100 M	∅	∅
C	−x	+x	+x
E	0.0100 − x	x	x

$$0.21 = \frac{x^2}{0.0100 - x}$$

$$0 = x^2 + 0.21x - 0.0021$$

$$x = \frac{-B \pm \sqrt{B^2 - 4AC}}{2A}$$

→ $x = 0.00956$ = $[H^+]$ → −log → **2.019**

→ $x = -0.21956$