Weekly Review

10/15-10/19

Grace 10/22/18

Buffers

- Definition

  A solution that ***resists*** pH change
- Composition (2 species)

Acid buffer: Weak acid and its conjugate base (HA and A^-)

Base buffer: weak base and its conjugate acid (B and BH^+)

- Create a buffer:

1. Mix a weak acid/base conjugate pair
2. Start with a weak acid and add a strong base (Not complete neutralization)
3. Start with a weak base and add a strong acid (Not complete neutralization)

Example: recognize a buffer

- Which of the following mixtures will be a buffer when dissolved in a liter of water?

1. 0.1 mol $Ba(OH)_2$ and 0.2 mol HI
2. 0.2 mol NH_3 and 0.2 mole HCl
3. 0.2 mol KCl and 0.3 mol HCl
4. 0.2 mol CH_3COOH and 0.1 mol NaOH
5. 0.2 mol HBr and 0.1 NaOH

- ***Key: 4.*** *First eliminate those options with only strong species. $Ba(OH)_2$ and HI in option #1, NaOH and HBr in option #5 are combinations of strong bases and strong acids. Option #3 consists of spectator ions from KCl and strong acid HCl. So only #2 and #4 have weak acid/base. Work neutralization reaction and we figured that #4 will end up with 0.1 M weak acid CH_3COOH leftover and 0.1M its conjugate base CH_3COONa* (**Pair!2 species**).

Common strong/weak acid/base

- Common weak acids

Acid Name	Formula	K_a
Hydrofluoric	HF	3.5×10^{-4}
Formic	HCOOH	1.8×10^{-4}
Acetic	CH_3COOH	1.8×10^{-5}
Hypochlorous	HClO	3.0×10^{-8}
Hydrocyanic	HCN	4.9×10^{-10}
lactic acid	$CH_3CH(OH)COOH$	1.38×10^{-4}
nitrous acid	HNO_2	4.0×10^{-4}
benzoic acid	C_6H_5COOH	6.4×10^{-5}

- Common strong acids

Strong Acids
Hydrochloric acid (HCl)
Hydrobromic acid (HBr)
Hydroiodic acid (HI)
Perchloric acid ($HClO_4$)
Chloric acid ($HClO_3$)
Sulfuric acid (H_2SO_4) (Only the first proton is strong)
Nitric acid (HNO_3)

- Common strong bases: NaOH, KOH, $Mg(OH)_2$, $Ba(OH)_2$
- Common weak base: Keep NH_3 in mind! Almost this guy every time!

Buffers

- Why is buffer important?

Human blood pH(7.4), otherwise you will be sick; maintain ocean pH to support aquatic life

- How does a buffer work?

A buffer has both acid and base species

when H^+ added, the base species in buffer will react to make conjugate acid, thus slowing down the increase of free H^+ in solution, resisting dramatic pH drop

When OH^- added, the acid species in buffer will react to make conjugate base, thus slowing down the increase of free OH^- in solution, resisting dramatic pH increase

- How could I design a buffer @ desired pH?

1. Pick up the conjugate pairs based on pH

   How: pKa is closest to the target pH

2. Calculate the amount of conjugate species using H-H equation

H-H equation

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

- Used to calculate pH of a buffer
- **Initial concentrations used:** '*the ratio of the conjugates*=$[A^-]/[HA]$' should be calculated from equilibria numbers, but as the weak acid/base dissociation is **small**, we can use the initial concentrations when mixing as equilibrium numbers.

$$pH \approx pK_a + \log\left(\frac{[A^-]_0}{[HA]_0}\right)$$

$$pOH \approx pK_b + \log\left(\frac{[BH^+]_0}{[B]_0}\right)$$

- **Note: Initial concentrations need to be calculated** if reaction with strong acid/base is used to make the buffer
- Use K_a for an acid buffer
- Use K_b for a base buffer

Calculate pH of a buffer

- **Example 1: Direct mix of a conjugate pair**
- If 200 mL of 0.5 M HF and 800 mL of 1.25 M NaF are mixed, what is the pH of the resulting solution? Assume pKa of HF is 2.5.

First identify this is acid buffer, use H-H equation in pKa form. Assume initial concentrations as equilibrium concentrations.

$$pH = pKa + log\frac{[\mathrm{A}^-]}{[HA]} = 2.5 + log\frac{1.25\ M*800mL/(200mL+800mL)}{0.5M*200mL/(200mL+800mL)}$$

$$= 2.5 + log10 = 3.5$$

Calculate pH of a buffer

- **Example 2: Reaction of strong acid/base to make a buffer**
- Calculate the pH of the solution resulting from mixing of 500mL 0.2 mol HCOOH and 500mL 0.1 mol NaOH. Assume formic acid pKa=3.7.

Find limiting reagent in neutralization: NaOH

Find resulting solution components and amounts and plug into H-H equation

$$pH = pKa + log\frac{[\mathrm{A}^-]}{[HA]} = 3.7 + log\frac{0.1\ M*500mL/(500mL+500mL)}{(0.2M*500mL-0.1\ M*500mL)/(500mL+500mL)}$$

$$= 3.7 + log1 = 3.7$$

When $\frac{[\mathrm{A}^-]}{[HA]}$=1 → perfect buffer, as it maximizes the buffer capacity.

Exam 2 Problems review

- Class average lowest ones

004 4.0 points

For the reaction

$$Br_2(g) \rightleftharpoons 2\,Br(g)$$

$\Delta G^\circ = +161.69$ kJ/mol at 25 °C. What is the value of K_p for this reaction?

$$\Delta G^\circ = -RT\ln K$$
$$K = \exp(-\Delta G^\circ/RT)$$
$$K = \exp(-161690/(8.314 \cdot 298.15))$$
$$K = 4.69 \times 10^{-29}$$

- Memorize this equation. Which constant R number should I use? Check the unit. Which one will cancel out all the unit to give the unitless K

Exam 2 Problems review

- Class average below 45% correctness ones: #4, #11, #18, #22

Which of the following produces the STRONGEST conjugate base?

1. HIO (pK_a = 10.64)

2. HClO (pK_a = 7.53)

3. HCOOH (pK_a = 3.75)

4. CH_3COOH (pK_a = 4.75)

5. HF (pK_a = 3.45)

- Weakest acid will produce the strongest conjugate base; smaller Ka indicates weaker acid

Exam 2 Problems review

022 **4.0 points**

What is the concentration of hydroxide ion in a 0.10 M solution of NaCN? The ionization constant of the weak acid HCN is 4.0×10^{-10}.

1. 6.3×10^{-6} M

2. None of these

3. 2.5×10^{-6} M

4. 1.6×10^{-9} M

5. 1.6×10^{-3} M

- NaCN is a salt. And it is a salt from a strong base(NaOH) and weak acid(HCN), so the solution of NaCN should be basic. Use Kb to calculate [OH^-].
- Find Kb $K_b = \frac{K_W}{K_a} = \frac{1*10^{-14}}{4*10^{-10}} = 2.5 * 10^{-5}$
- Calculate [OH^-] $K_b = 2.5 * 10^{-5} = \frac{x^2}{0.1-x}$ $\frac{0.1}{K_b} = 4000 > 1000$
- [OH^-] $= x = \sqrt{K_b * 0.1} = 1.6*10^{-3}$

we can simplify quadratic calculation