Chem 103 lecture 3a

Pop quiz
pH and pH calculations
Polyprotic acids
Lewis acids/bases

Summary

$[H_3O^+]$ $[OH^-] = 1.0 \times 10^{-14}$; pH + pOH = 14.00

$pH = -\log[H_3O^+]$ and $pOH = -\log[OH^-]$

$K_a = [H^+][A^-]/[HA]$ $K_b = [HA][OH^-]/[A^-]$

$\mathbf{K_aK_b = 1.0 \times 10^{-14}}$ => $pK_a + pK_b = 14.00$

$[H^+] = 10^{-pH}$ $[OH^-] = 10^{-pOH}$

$pK_a = -\log K_a$ and $pK_b = -\log K_b$

Recall the 5 scenarios:

There are at least 5 scenarios we'll encounter involving pH calculations. You are expected to **MASTER** these calculations.

1) Strong acid solutions
2) Strong base solutions
3) Pure Weak acid solutions
4) Pure weak base solutions
5) Buffer solutions

pH of a strong acid solution

As mentioned earlier, there are at least 5 "scenarios" involving pH calculations. Most simple : pH of a strong acid solution.

For example: What is the pH of a 0.020 M HCl solution?

Answer:

Since HCl is a strong acid, it dissociates completely:

$[HCl]_F = 0.020\ M = [H_3O^+]$

So, $pH = -\log [H_3O^+] = -\log [HCl]_F = -\log(.020) = 1.70$

pH of a strong base solution

2nd scenario:

What is the pH of a 5.2×10^{-4}M NaOH solution?

Answer: Since NaOH is a strong base, we can write:

$[NaOH] = [OH^-] = 5.2 \times 10^{-4}M$

It is easier to determine pOH first:

$pOH = -\log[OH^-] = -\log(5.2 \times 10^{-4}) = 3.28$

$pH = 14.00 - 3.28 = 10.72$ (makes sense?)

Yes because it is a basic pH

Net ionic equations and ICE

You are also expected to know how to write and recognize *net ionic equations*.

e.g. What is the K_a equilibrium for a NH_4Cl solution?

$NH_4^+ + H_2O$ <==> $NH_3 + H_3O^+$

Or even, NH_4^+ <===> $NH_3 + H^+$

You are supposed to master ICE type calculations involving K_a and K_b equilibria.

I=initial, C=change, E= equilibrium

pH of a weak acid solution

What is the pH of a $2.5x10^{-3}$M acetic acid (HA, $K_a=1.8x10^{-5}$)

Answer: **Acetic acid (HA)** is a **WEAK ACID**,

Use the K_a equilibrium: $HA <===> H^+ + A^-$

initial	0.025	0	0
change	-x	+x	+x
equilibrium	0.025-x	x	x

$x^2/(.025-x) = 1.8x10^{-5} \Rightarrow x^2 + 1.8x10^{-5}x - 4.5x10^{-7} = 0$

Solve for x by the quadratic equation. $x = 6.6x10^{-4}$

$pH = -\log(6.6 \times 10^{-4}) = 3.18$

pH of a weak acid solution..,

$HA <===> H^+ + A^-$

0.025-x x x

$K_a = [H^+][A^-] / [HA] = x^2/(.025-x) = 1.8x10^{-5}$

$x^2/(.025-x) = 1.8x10^{-5} \Rightarrow x^2 + 1.8x10^{-5}x - 4.5x10^{-7} = 0$

Solve for x by quadratic formula. $x=(-b\pm\sqrt{(b^2-4ac)})/2a$

$x = \{-(1.8x10^{-5})\pm\sqrt{((1.8x10^{-5})^2-4(1)(-4.5x10^{-7}))}\}/2(1)$

$\Rightarrow$ **$x = 6.6x10^{-4}$** M or $x = -6.8x10^{-4}$ (choose positive value)

$pH = -\log(6.6 \times 10^{-4}) = 3.18$

pH of a weak acid (5% rule)

Redo same problem using approximation (5% rule):

What's pH of $2.5x10^{-2}$M acetic acid (HA, $K_a=1.8x10^{-5}$)

Answer:Use K_a equilibrium: $HA <===> H^+ + A^-$

0.025-x x x

$x^2/(.025-x) = 1.8x10^{-5} \Rightarrow x^2/(.025) \approx 1.8x10^{-5}$

Solve for x: $x = \{(0.025)(1.8x10^{-5})\}^{1/2} = 6.7 \times 10^{-4}$

$pH = -\log(6.7x10^{-4}) = 3.17$ (compare with 3.18)

Note: $6.7x10^{-4}(100\%)/.025 = 3\% < 5\%$

pH of a weak base solution

What is the pH of 0.10 M ammonia? ($K_b = 1.8x10^{-5}$M)

Answer: Use the K_b equilibrium. $NH_3 + H_2O <===> NH_4^+ + OH^-$

0.10-x x x

$x^2/(0.10-x) = 1.8x10^{-5}$. Using 5% rule:

$x^2 \approx (1.8x10^{-5})(0.10) \Rightarrow x = 1.3x10^{-3} = [OH^-]$

pOH = 2.87 $\Rightarrow$ pH = 14.00-2.87 = 11.13 (makes sense?)

Neutralization reactions

When an acid encounters a base, neutralization occurs:

Example: $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$

Net ionic eq: $H^+ + OH^- \rightarrow H_2O$

Example: $HA(aq) + NaOH(aq) \rightarrow NaA(aq) + H_2O$

Net ionic eq: $HA(aq) + OH^-(aq) \rightarrow A^-(aq) + H_2O(l)$

Strong acid + strong base ---> 100% completion

Strong + weak ---> 100% completion

Weak + weak ---> not 100% completion

Strong Acid + strong base. pH = ?

Problem:20.0 mLs of 1M HCl + 21.0 mLs of 1M NaOH. pH =?

$HCl + NaOH \rightarrow NaCl + H_2O$ (easiest: "follow the moles"):

mmol $HCl = M_{HCl}V_{HCl} = (1M)(20.0mL) = 20.0$ mmol HCl

mmol $NaOH = M_{NaOH}V_{NaOH} = (1M)(21.0mL) = 21.0$mmol NaOH

Limitg reagt is HCl: mmol NaOH excess=21.0-20.0=1.0mmol

So $[OH^-]$ = mole OH^-/total Vol(L) = mmol OH^-/total mLs

$[OH^-] = 1.0mmol/(20.0+21.0)mL = 1.0/41.0$ M = 0.0244M

$pOH = -\log(0.0244) = 1.613$; $pH = 14.00-1.653 = 12.387$

Strong Acid + weak base. pH = ?

Problem:20.0 mLs of 1M HCl + 21.0 mLs of 1M NH_3. pH =?

$HCl(aq) + NH_3(aq) \rightarrow NH_4Cl(aq)$ (easiest: "follow the moles"):

mmol HCl=$M_{HCl}V_{HCl}$ =(1M)(20.0mL)=20.0 mmol HCl

mmol NH_3=$M_{NH3}V_{NH3}$ = (1M)(21.0mL)=21.0mmol NH_3

Limitg reagt is HCl: mmol NH_3 excess=21.0-20.0=1.0mmol

$[NH_3]$ = 1.0mmol/41.0mL = 0.0244M

Weak base: K_b equil: $NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-$

$0.0244-x \qquad x \qquad x$

Strong Acid + weak base. pH = ? (continuation)

Problem:20.0 mLs of 1M HCl + 21.0 mLs of 1M NH_3. pH =?

In previous slide: (note: $K_b = 1.8x10^{-5}$ for NH_3)

Weak base: K_b equil: $NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-$

$0.0244-x \qquad x \qquad x$

$1.8x10^{-5} = x^2/(0.0244-x) \approx x^2/(0.0244)$ (by 5% rule)

$x \approx \sqrt{\{(1.8x10^{-5})(0.0244)\}} = 6.72x10^{-4} = [OH^-]$

pOH = 3.173 ; pH = 14.000 - 3.173 = 10.827

Continuation…

Previous 2 examples show need to determine what final solution contains. Treat the solution as being one of the various scenarios. Remember that if after neutralization, there is a mixture of strong and weak, the strong dominates the pH.

Polyprotic acids

*Poly*protic acids can donate more than 1 proton.

Examples: H_2CO_3 (carbonic acid); H_3PO_4 (phosphoric acid).

H_2CO_3 in water has following K_a equilibria:

$H_2CO_3 + H_2O \leftrightarrows H_3O^+ + HCO_3^- \qquad K_{a1} = 4.2x10^{-7}$

$NaHCO_3$ in water has following K_a equilibria :

$HCO_3^- + H_2O \leftrightarrows H_3O^+ + CO_3^{2-} \qquad K_{a2} = 4.8x10^{-11}$

There are 2 K_a's and deprotonation is *stepwise*

pH of pure polyprotic weak acid.

pH=? for 0.100 M H_2CO_3? ($K_{a1}=4.2x10^{-7}$,$K_{a2}=4.7x10^{-11}$)

Solution: there are 2 equilibria simultaneously occuring:

$\overset{Ka1}{H_2CO_3 \leftrightarrows HCO_3^-} \quad \overset{Ka2}{HCO_3^- \leftrightarrows CO_3^{2-}}$

In this problem, what is the major species?

H_2CO_3 , a weak acid!

Treat it as a *monoprotic weak acid* HA, using only K_{a1}

pH of pure weak polyprotic base

pH =? for 0.100M Na_2CO_3. ($K_{a1}=4.2x10^{-7}$, $K_{a2}=4.7x10^{-11}$)

We have the same 2 equilibria as in the previous example:

$\overset{Ka1}{H_2CO_3 \leftrightarrows HCO_3^-} \quad \overset{Ka2}{HCO_3^- \leftrightarrows CO_3^{2-}}$

$Kb2=Kw/Ka1 \qquad Kb1=Kw/Ka2$

In this problem, what is the major species?

CO_3^{2-}, a weak base!

Treat it as a monoprotic weak base, using $K_{b1} = 10^{-14.00}/K_{a2}$

pH of pure intermediate form

pH =? for 0.100M $NaHCO_3$. ($K_{a1}=4.2x10^{-7}$, $K_{a2}=4.7x10^{-11}$)

We have the same 2 equilibria as in the previous example:

Ka1 Ka2

$H_2CO_3 <===> HCO_3^- <===> CO_3^{2-}$

Express K_a's as pK_a's: $pK_{a1}=-\log(4.2x10^{-7})=6.38$;$pK_{a2}=10.33$

What is the major species in this problem?

It's the intermediate species: HCO_3^-. (without proof)

$pH = (1/2)(pK_{a1} + pK_{a2}) = (1/2)(6.38+10.33)= 8.36$

Lewis Acids

Lewis acids = electron pair acceptors

Lews bases = electron pair donors

Consider ammonia, NH_3 and a boron trichloride, BCl_3

Do the Lewis structures of both of them.

NH_3 has a lone pair; BCl_3 has an empty orbital

NH_3 can "donate" it's lone pair to BCl_3 to form a coordinate covalent bond or "dative" bond:

$NH_3 + BCl_3$ ---> NH_3-BCl_3

Which is the base? Which is the acid?

Answers to the pop quiz 1

1) Because water can act as a Bronsted-Lowry acid or base, it is said to be _____.

a. amphiphilic
b. amphihydrous
c. amphiphobic
d. amphiprotic
e. amphoteric

D: amphiprotic

Answers to the pop quiz 2

2) Organic compounds classified as bases often have the formula

a. R-CHO.
b. CH_3-$(CH_2)_n$-CH_3.
c. R-COOH.
d. R-NH_2.
e. R-OH.

D: R-NH_2

Answers to the pop quiz 3

3) The product of the reaction between methylamine, CH_3NH_2, and hydrochloric acid is

a. $CH_4NH_2^+ Cl^-$
b. $CH_3NH^- H_2Cl^+$
c. $CH_3NH_3^+ Cl^-$
d. $CH_3NH_3^- Cl^+$
e. $CH_3NH_4^{2+} (Cl^-)_2$

C: $CH_3NH_3^+ Cl^-$

Answers to the pop quiz 4

4) A solution is not neutral. Which one of these statements is true?

a. $[H_3O^+] = 1.0 \times 10^{-7}$ M
b. $[H_3O^+] = [OH^-]$
c. $[H_3O^+][OH^-] = 1.0 \times 10^{-7}$
d. $[OH^-] = 1.0 \times 10^{-7}$ M
e. $[H_3O^+][OH^-] = 1.0 \times 10^{-14}$

E: $[H_3O^+][OH^-] = 1.0 \times 10^{-14}$

Answers to the pop quiz 5

5) In a neutral polyprotic acid, the value of K_{a2} will be _____ the value of K_{a1} because _____.
a. smaller than; it is more difficult to remove a hydrogen ion from a cation than from a neutral molecule
b. larger than; it is more difficult to remove a hydrogen ion from an anion than from a neutral molecule
c. larger than; it is more difficult to remove a hydrogen ion from a cation than from a neutral molecule
d. smaller than; it is more difficult to remove a hydrogen ion from an anion than from a neutral molecule
e. the same as; both hydrogen ions are bonded to the same anion

D