Chem 103

Lecture 3c
Acids and Bases2

Last time

- Finished Colligative properties
- Started Acids and Bases

Today

- pH, pOH calculations
- Buffer solutions

Recall K_a and K_b equilibria

- K_a equilibrium

HA + H_2O < = = > H_3O^+ + A^-, K_a = $\frac{[H_3O^+][A^-]}{[HA]}$

- K_b equilibrium

B + H_2O < = = > BH^+ + OH^-, K_b = $\frac{[BH^+][OH^-]}{[B]}$

KNOW how to write the K_a and K_b equilibria.

$K_aK_b = K_w = 1.0\text{x}10^{-14}$

Be able to prove this:

Since $K_a = [H_3O^+][A^-]/[HA]$ for acid HA.

For it's conjugate base, A^-, it is: $K_b = [HA][OH^-] / [A^-]$

So if multiply K_a of weak acid by K_b of its conjugate, then :

$K_aK_b = ([H_3O^+]\cancel{[A^-]}/\cancel{[HA]})\ (\cancel{[HA]}[OH^-] / \cancel{[A^-]})$

$\mathbf{K_aK_b = [H_3O^+][\ OH^-] = K_w = 1.0 \times 10^{-14}}$

This refers to conjugate pairs.

pH

Due to wide range of $[H_3O^+]$, log scale is convenient: "pH ".

Define pH: $\mathbf{pH = -log_{10}[H^+] = -log[H_3O^+]}$

pH of pure water: since $[H_3O^+] = 1.0\text{x}10^{-7}M$

pH = -log $\{[H_3O^+]\}$ = -log(1.0x10^{-7}M) = 7.00

This is the *neutral* pH

(Rule of thumb: pH > 7.0 is *basic*. pH < 7.0 is *acidic*.)

pH of some common liquids

Stomach acid (gastric juice)	1.0
Lemon juice	2.0
Soda	3.0
Tomato	4.0
Black coffee	5.0
Cow's milk	6.0
Human saliva	7.0
Human blood	7.4
Sea water	8.4
Soap/detergent	10.0
Household ammonia	11.5
Oven cleaner	13.5

pH of acidic solutions

If a solution contains 2.0×10^{-4} M H_3O^+, what's its pH? Acidic or basic?

pH = $-\log(2.0 \times 10^{-4}M) = 3.70$ (use your calculators)

It is acidic since $3.70 < 7.0$

Note: for calculating $[H^+]$ given the pH, use: $\mathbf{[H^+] = 10^{-pH}}$

For a pH 4.70 solution, what is $[H_3O^+]$ =?

$[H^+] = 10^{-pH} = 10^{-4.70} = 2.0 \times 10^{-5}$ (use your calculators)

pOH; pH + pOH = 14.00

Definition: $pOH = -\log[OH^-]$

Since: $[H_3O^+][OH^-] = 1.0x10^{-14}$

$-\log\{[H_3O^+][OH^-]\} = -\log\{1.0x10^{-14}\}$

$-\log[H_3O^+] - \log[OH^-] = 14.00$

Or, pH + pOH = 14.00

(so if you know pH, you can know pOH)

Summary so far…

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

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

pH + pOH = 14.00

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

$K_aK_b = 1.0 \times 10^{-14}$

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

Calculating pH of a solution

There are at least 5 scenarios we'll encounter involving pH calculations. You are expected to **MASTER** these calculations. (simple monoprotic acids/bases)

1) Strong acid solutions -use: pH = - log[acid]
2) Strong base solutions -use: pH = 14.00- log[base]
3) Pure Weak acid solutions -use: K_a equilibrium, ICE calculation of $[H^+]$
4) Pure weak base solutions -use: K_b equilibrium, ICE calculation of $[OH^-]$
5) Buffer solutions: -use K_a equil. ICE calc'n of $[H^+]$
   OR, use buffer equation: pH = pK_a + log {[base]/[acid]}

Calculations of salt solutions

A "salt" is a soluble ionic compound.

E.g. $NaCH_3CO_2$ ---> $Na^+ + CH_3CO_2^-$; $CH_3CO_2^-$ is acetate, a base.

NH_4Cl ---> $NH_4^+ + Cl^-$; NH_4 is ammonium, an acid.

In above examples, Na^+ and Cl^- act like "spectator ions".

Remember: HCH_3CO_2 is acetic acid; NH_3 is ammonia.

Calculations of salt solutions

NH_3 is a weak base. It is NOT a salt.

NH_4Cl is a salt.

Is a solution of NH_4Cl an acidic or basic solution?

NH_4^+ is *conjugate acid* of NH_3 so NH_4^+ is weak acid.

Cl^- is conjugate base of HCl a *strong* acid. So, Cl^- is so weak it can be ignored.

Thus the solution is a weak acid solution.

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?

$NH_4^+ + H_2O \Longleftrightarrow NH_3 + H_3O^+$

Or sometimes, $NH_4^+ \Longleftrightarrow NH_3 + H^+$

Master ICE calculations involving K_a and K_b equilibria.

I=initial, C=change, E= equilibrium

(1) pH of a strong acid solution

1) Strong acid solutions -use: pH = - log[acid]

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

(2) pH of a strong base solution

2) Strong base solutions -use: pH = 14.00- log[base]

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

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

$[NaOH] = [OH^-] = 5.2\times10^{-4}M$

It is easier to determine pOH first:

$pOH = -\log[OH^-] = -\log(5.2\times10^{-4}) = 3.28$

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

Yes because it is a basic pH

(3) pH of a weak acid solution

3) Pure Weak acid solutions -use: K_a equilibrium, ICE calculation of $[H^+]$

What is the pH of a 2.5×10^{-3}M acetic acid (HA, $K_a=1.8\times10^{-5}$)

Answer:

Use the K_a equilibrium: $\underset{0.025-x}{HA} \Longleftrightarrow \underset{x}{H^+} + \underset{x}{A^-}$

$x^2/(.025-x) = 1.8\times10^{-5} \Rightarrow x^2 + 1.8\times10^{-5}x - 4.5\times10^{-7} = 0$

Solve for x by the quadratic equation. $x = 6.6\times10^{-4}$

$pH = -\log(6.6\times10^{-4}) = 3.18$

(If you use 5% rule: $x^2/0.025 = 1.8\times10^{-5} \Rightarrow x = 6.7\times10^{-4} \Rightarrow pH = 3.17$)

Note: $\frac{6.7\times10^{-4}\times100\%}{0.025} = 2.7\% < 5\%$)

(4) pH of a weak base solution

(4) Pure weak base solutions -use: K_b equilibrium, ICE calculation of $[OH^-]$

What is the pH of 0.10 M ammonia? ($K_b = 1.8\times10^{-5}$M)

Answer: Use K_b equil. $\underset{0.10-x}{NH_3} + H_2O \Longleftrightarrow \underset{x}{NH_4^+} + \underset{x}{OH^-}$

$x^2/(0.10-x) = 1.8\times10^{-5}$. Using 5% rule:

$x^2 \approx (1.8\times10^{-5})(0.10) \Rightarrow x = 1.3\times10^{-3} = [OH^-]$

pOH = 2.87 => pH = 14.00-2.87 = 11.13

(5) pH of a buffer solution

5) Buffer solutions: -use K_a equil. ICE calc'n of [H^+]

OR, use buffer equation: pH = pK_a + log {[base]/[acid]}

(note: $pK_a = -\log K_{aa}$)

What is the pH of a solution containing 0.10 M NH_3 and 0.50 M NH_4Cl ? (K_b of NH_3 is 1.8×10^{-5}M)

Answer: Get K_a : $K_a = 10^{-14.00}/K_b = 10^{-14.00}/ 1.8\times10^{-5} = 5.5_5\times10^{-10}$

Use K_a equil. $\underset{0.50-x}{NH_4^+} + H_2O \Longleftrightarrow \underset{x}{H_3O^+} + \underset{0.10+x}{NH_3}$

Using 5% rule: $K_a = 5.5_5\times10^{-10} \approx x(0.10)/(0.50) \Rightarrow x = 2.7_8\times10^{-9} = [H_3O^+]$

pH = $-\log(2.7_8\times10^{-9})$= 8.56

Or, use buffer equation: pH = $-\log(5.5_5\times10^{-10})$ +log{(.10)/(.50)} = 8.56

Polyprotic acids

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

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

If you place H_2CO_3 in water you will have the following K_a equilibrium:

$H_2CO_3 + H_2O \Longleftrightarrow H_3O^+ + HCO_3^-$ $K_{a1} = 4.2\times10^{-7}$

If you place $NaHCO_3$ in water you have:

$HCO_3^- + H_2O \Longleftrightarrow H_3O^+ + CO_3^{2-}$ $K_{a2} = 4.8\times10^{-11}$

There are 2 K_a's

Neutralization reactions

When an acid encounters a base, neutralization occurs:

Example: HCl(aq) + NaOH(aq) --> NaCl(aq) + H_2O(l)

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

Example: HA(aq) + NaOH(aq) --> NaA(aq) + H_2O

Net ionic eq: HA(aq) + OH^-(aq) --> 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 --> 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)=21.0mmol 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) --> 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: $\underset{0.0244-x}{NH_3} + H_2O \Longleftrightarrow \underset{x}{NH_4^+} + \underset{x}{OH^-}$

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: $K_b = 1.8\times10^{-5}$ for NH_3)

Weak base: K_b equil: $\underset{0.0244-x}{NH_3} + H_2O \Longleftrightarrow \underset{x}{NH_4^+} + \underset{x}{OH^-}$

$1.8\times10^{-5} = x^2/(0.0244-x) \approx x^2/(0.0244)$ (by 5% rule)

$x \approx \sqrt{(1.8\times10^{-5})(0.0244)} = 6.72\times10^{-4} = [OH^-]$

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:

$H_2CO_3 + H_2O$ < = = > $H_3O^+ + HCO_3^-$ $K_{a1} = 4.2x10^{-7}$

$NaHCO_3$ in water has following K_a equilibria :

$HCO_3^- + H_2O$ < = = > $H_3O^+ + CO_3^{2-}$ $K_{a2} = 4.8x10^{-11}$

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:

$H_2CO_3 \overset{Ka1}{<===>} HCO_3^- \overset{Ka2}{<===>} CO_3^{2-}$

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:

$H_2CO_3 \underset{Kb2=Kw/Ka1}{\overset{Ka1}{<===>}} HCO_3^- \underset{Kb1=Kw/Ka2}{\overset{Ka2}{<===>}} CO_3^{2-}$

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:

$H_2CO_3 \overset{Ka1}{<===>} HCO_3^- \overset{Ka2}{<===>} CO_3^{2-}$

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?